

Feature Article

Poly(amidoamine), polypropylenimine, and related dendrimers and dendrons possessing different 1 → 2 branching motifs: An overview of the divergent procedures

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Abstract

This review presents an overview of 1 → 2 branched dendrimers and dendrons, created by a divergent procedure, from their synthesis to modern day applications. The first members of this branched class of fractal macromolecules were prepared through a cascade synthesis, which was later replaced by the iterative divergent synthetic approach. Most classes of this 1 → 2 *N*-, *Aryl*-, *C*-, *Si*-, and *P*-branched families are included and catalogued by their mode of connectivity. Dendritic macromolecules have had significant impact in the field of material sciences and are one of the major starting points for nanotechnology as a result of the numerous modifications that can be conducted, either on the surface or within their molecular infrastructure, thus taking advantage of their unimolecular micelle properties. These host cavities, maintained by the dendritic branches, allow for the incorporation of nanoparticles as well as metal particles, which make these attractive in catalysis and imaging studies. The solubility of these fractal constructs can be tailored depending on their surface modifications. Highly water-soluble, neutral dendrimers appended with, grown from, or acting as hosts to specific molecules give rise to a wide variety of biomedical applications such as drug delivery systems and MRI imaging agents. The inherent supramolecular or supramacromolecular chemistry has been exploited but the design and construction of uniquely tailored macrostructures have just begun. Laser dyes, as well as electron and energy donor and acceptor functionality, have also been paired with these fractal constructs in order to probe their uses in the field of molecular electronics. With their synthetic control, seemingly limitless modifications and wide variety of potential applications, as well as their now commercial availability, these 1 → 2 branched dendrimers have become an important nanostructured tools for diverse utilitarian applications. This review mainly covers 1 → 2 branched non-chiral dendrimers prepared by a divergent process but selected chiral surfaces are considered as well as metal encapsulation and a few hyperbranched routes to related imperfect dendrimers.

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Keywords: Dendrons; Dendrimers; Polyamidoamine (PAMAM) dendrimers; poly(propylene imine) dendrimers; divergent synthesis; P-dendrimers; Si-dendrimers; Aryl-dendrimers; review; 1 → 2 branching

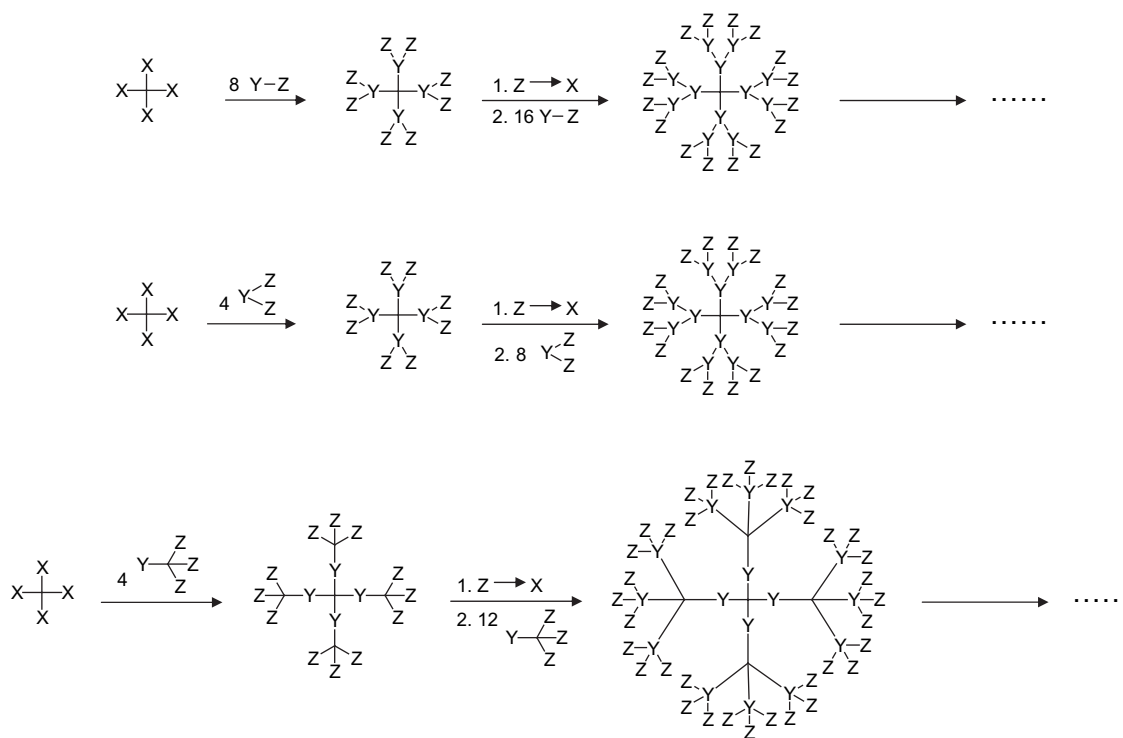
1. General concepts

The divergent route to dendrimer synthesis is based on the construction of a molecular superstructure starting with a focal point or core and progressing outward to the periphery, as

illustrated in [Scheme 1](#). Dendrimers are built in layers, or generations, upon a defined core that possesses a specific number of active sites, to which the successive tiers are, for the most part, covalently attached. The number of active sites on the core determines their *n*-directionality and limits the number of building blocks that can be added to form the next generation. This trend is repeated (iterative synthesis) as the reactive sites on the periphery of the previous generation are revealed for the assembly of the next generational growth layer. Assuming that the monomer's functional group(s), steric

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Scheme 1. Divergent procedures for macromolecular construction.

hindrance, and active site accessibility do not interfere with the construction of ideal dendrimers, the divergent process permits the exponential growth of free active sites per generation.

Perfect growth is only achieved when each active site is occupied by a building block (monomer) denoting the next tier; otherwise, imperfect structural assembly results leading to internal termini and variable internal void regions, which starts to resemble a hyperbranched motif normally derived by a random one-step procedure. If these imperfections or “branching defects” occur early in the generational growth, they can have serious repercussions on the overall micellar properties of the resulting dendrimer.

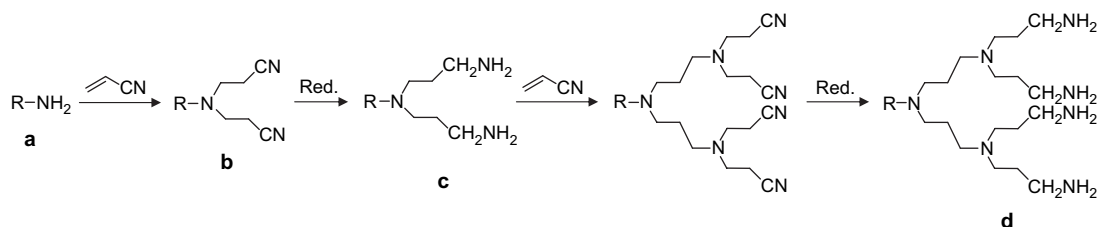
The number of branches in a dendritic structure is dependent on the branching valency of the monomeric building blocks, including the core. If the core is a primary amine, the amine nitrogen would then be divalent, leading to a $1 \rightarrow 2$ branching motif. If three building blocks were added to the primary amine generating an ammonium salt, a $1 \rightarrow 3$ branching motif would result. With a neutral divalent amine core, proceeding with a $1 \rightarrow 2$ fractal branching pattern with a simple commercial ($1 \rightarrow 1$) monomer leads to a $1 \rightarrow 2 \rightarrow 4 \rightarrow 8 \rightarrow 16 \rightarrow 32 \rightarrow \dots$ motif. If a tetravalent core is used [Scheme 1 (top)], the procession would follow a $4 \rightarrow 8 \rightarrow 16 \rightarrow 32 \rightarrow \dots$ branching pattern. Using the same tetravalent core with a $1 \rightarrow 2$ branched monomer [Scheme 1 (middle)] would lead to the same $4 \rightarrow 8 \rightarrow 16 \rightarrow 32 \rightarrow 64 \rightarrow 128 \rightarrow \dots$ branching series; whereas using the $1 \rightarrow 3$ branched monomer [Scheme 1 (bottom)] would lead to a $4 \rightarrow 12 \rightarrow 36 \rightarrow 108 \rightarrow 324 \rightarrow 972 \rightarrow \dots$ branched series with a notable increase in the number of peripheral groups,

this latter branching motif will be addressed in a forthcoming review.

2. Early procedures

The preparation and characterization of straightforward fractal-like structures constructed by an iterative approach were first reported in 1978 by Vögtle et al. [1], in the quest for multiarmed, supramolecular materials [2]. This “cascade synthesis” was defined as “reaction sequences which can be conducted repeatedly.” The prominent features of polyamine **2d** included the trigonal *N*-branched centers and the minimal distance imposed by the propyl linkage between branching centers and terminus in order to prevent diminished yields resulting from steric hindrance caused by the branching center. A Michael-type addition between amine **2a** and an activated olefin afforded the dinitrile **2b**, which was subsequently reduced to give the terminal diamine **2c**. This simple process was repeated to give the desired heptaamine **2d**. However, due to synthetic difficulties necessary to achieve high yield conversions, the iterative process was curtailed but the most important aspect of this original synthetic methodology [Scheme 1 (top)] was that it introduced the iterative “cascade” method to the chemist’s repertoire. Interestingly, Tomalia and Dewald [3] defined a “dendrimer” as a branched macromolecule, which had three or more tiers, and thus heptaamine **2d** is technically not a dendrimer; it is, however, an example of a multi-armed [2], meso- [4] or medio-molecule (Scheme 2).

In a series of patents from 1979–1983, Denkewalter et al. [5–7] reported the first divergent preparation of fractal-like polypeptides possessing an $1 \rightarrow 2$ C-branching pattern

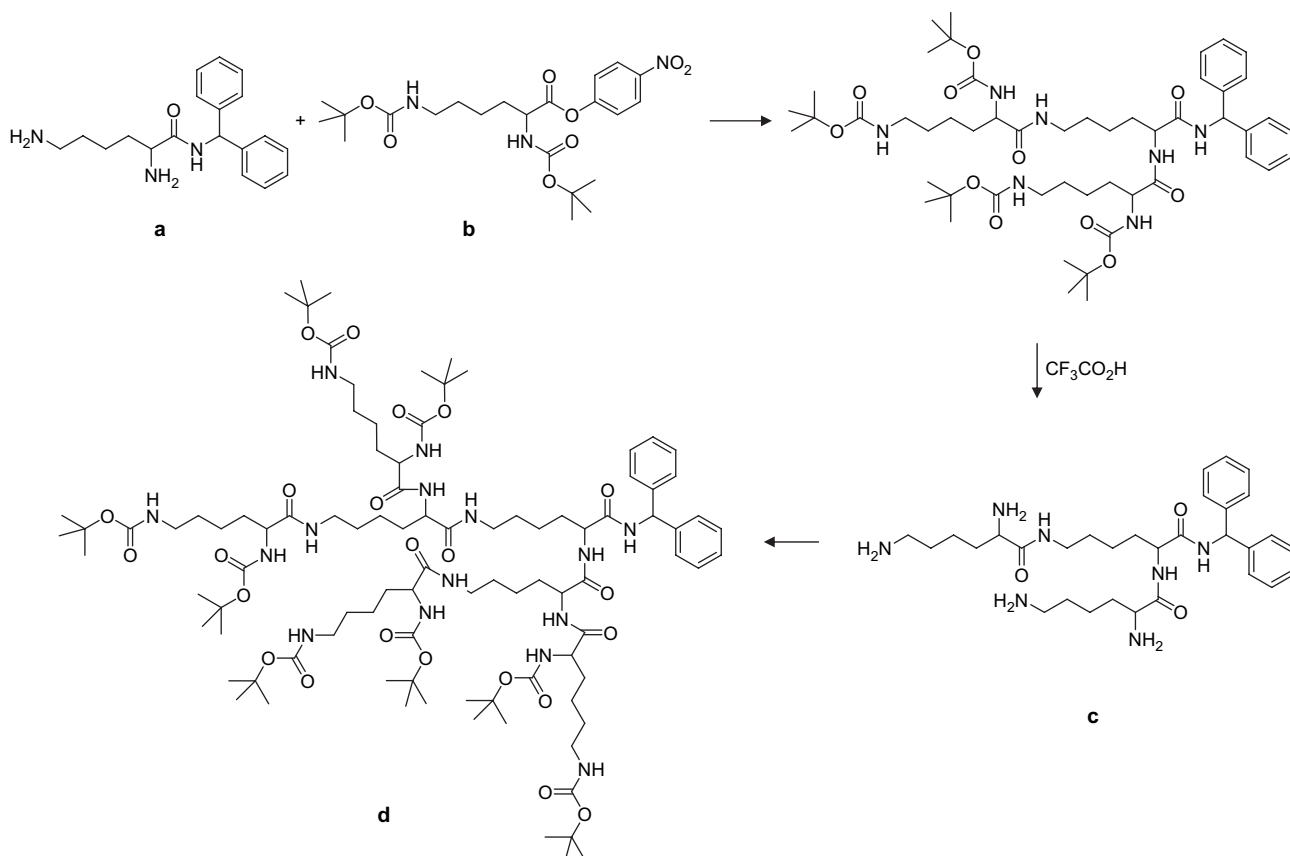


Scheme 2. Vögtle et al.'s [1] original repetitive synthesis.

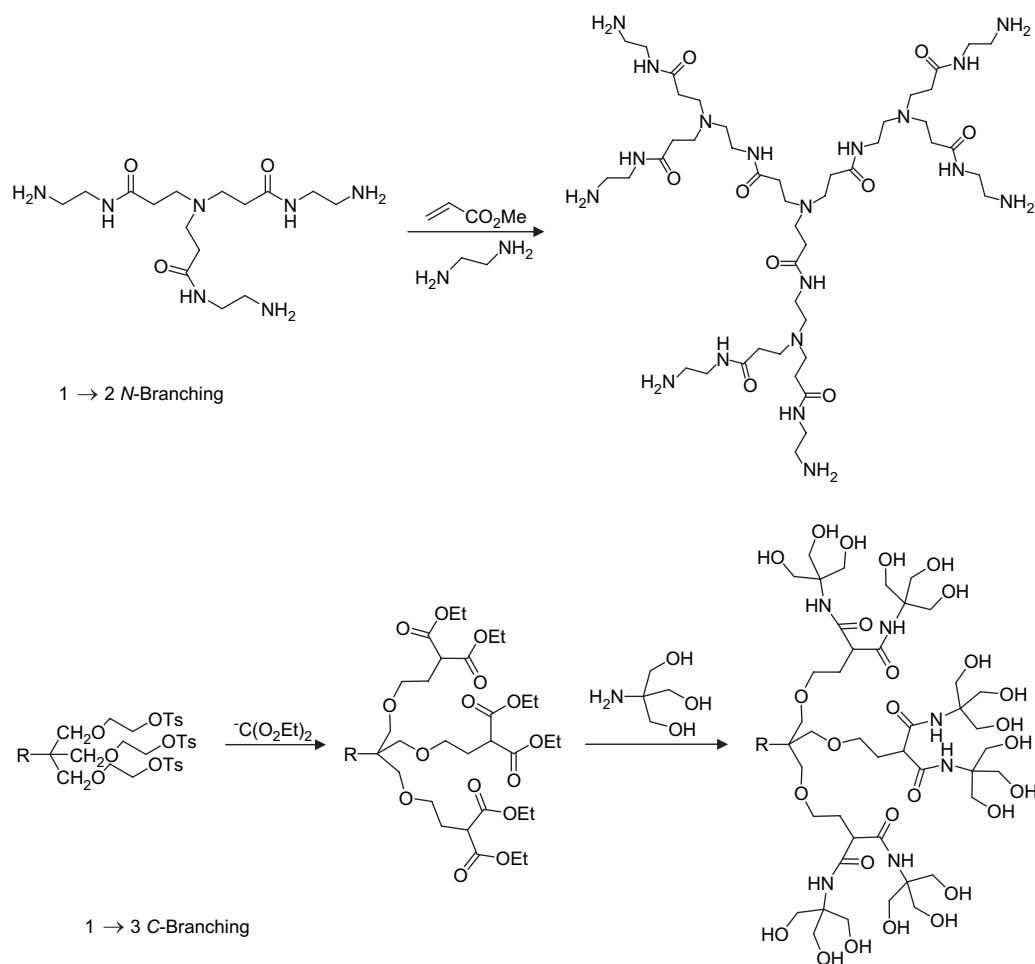
[Scheme 1 (middle)] and utilizing the protected chiral amino acid, *N,N'*-bis(*tert*-butoxycarbonyl)-L-lysine, as the key 1 → 2 branching monomer. A two-directional, asymmetric core **3a** was generated from L-lysine and benzhydrylamine. The coupling procedure used a simple peptide coupling methodology with an activated *p*-nitrophenyl ester **3b**, followed by removal of the *tert*-butoxycarbonyl (*t*-BOC) protecting groups. The terminal polyamines of **3c** were then available for constructing the next tier. Repetition of this easy iterative sequence led to lysine-branched biopolymers with up to 1023 (idealized number) terminal (*t*-BOC)-protected lysine groups resulting in an approximate generational doubling of the molecular weight through the 10th generation (G10; *ca.* 233,600 amu). Their original [5] and related patents [6,7], however, afforded little insight into their purification, characterization, physical or chiral properties. Over the years since their reported formation, many research groups have utilized these types of

dendrons and dendrimers possessing a lysine-infrastructure; a few references are cited [8–15] to afford entrance to these chiral macromolecules [16–21]. These and other dendrimers derived from a chiral infrastructure were previously reviewed [22] and will not be considered herein (Scheme 3).

In 1985, Newkome et al. [23] and Tomalia et al. [24] each published different divergent routes to branched fractal constructs possessing three or more generations: (1) 1 → 3 *C*-branching arborols [*Arbor*: Latin: tree; Scheme 1 (bottom)], which will be considered in detail in a forthcoming review, and (2) 1 → 2 *N*-branching dendrimers [*Dendro*:- Greek: tree-like; Scheme 1 (middle)], respectively, detailed in Scheme 4. These publications each described the synthetic procedures and spectral characterization supporting the structural assignments of the polyfunctional branched fractal macromolecules. There is another subtle but important difference between these two divergent processes: in the Vögtle–Tomalia routes



Scheme 3. Denkewalter et al.'s [5] preparation of dendritic polypeptides based on lysine.



Scheme 4. Tomalia et al.'s [24] (1 → 2 N-branching) and Newkome et al.'s [23] (1 → 3 C-branching) different divergent synthetic procedures.

[Scheme 1 (top)], the branching occurs at the surface substituent(s) and linear monomers were utilized; whereas the Denkwalter–Newkome approaches [Scheme 1 (middle, bottom)] have a *single* surface attachment utilizing monomers possessing 2- or 3-branching centers, respectively. These latter examples are divergent procedures but using simple 1 → 2 or 1 → 3 branched monomers but they can also be considered convergent processes depending on the monomer's branching complexity. This review describes these surface branching protocols under the appropriate branching pattern and mode of monomer connectivity and all subsequent divergent routes using the 1 → 2 branching motifs.

Several interesting comprehensive books [22,25–28], devoted journal issues [29–32], and recently, dendrimers in medicine [33] as well as numerous general reviews have appeared that predominately, but not exclusively, address different aspects of the commercially available PAMAM and PPI (denoting *polyaminoamine* and *polypropylenimine*, respectively) dendritic families, as related to selected topics such as: solubility enhancement of these polymeric nanoarchitectures [34], dendritic catalysis [35–44], dendritic gels [45], commercial aspects [46], general characterization [47], designing aspects for biomedical applications [48–64], ocular

drug delivery [65], drug and gene delivery systems [66], gene transfection [67], MRI agents [68–74], controllable nanomaterials and self-assembly [75–78], supramolecular chemistry thereof [79], the theory and simulation of dendrimers in solution [80], luminescence [81], dendritic biomimetics [82], dendronized polymers [83,84], dendritic polymers [85], dendrons on insoluble supports [86], optical excitation [87], the organometallic interface [88], dendrimers in molecular recognition [89], construction *via* cycloaddition reactions [90], dendrigraft materials [91], unimolecular micelle aspects [59,92–96], photonics and light harvesting [97–102], light-emitting diodes and solar cells [103], interior tailoring [104], capillary electrophoresis [105], dendrimers in anion recognition [106], cleavable dendrimers [107], metallo-dendrimers [40,41,108–111], from electronic to polymer-assisted therapeutics [112], and interdisciplinary vision [113].

In general, the theoretical aspects of the 1 → 2 branched dendrimers have been envisioned as a basic 1 → 2 fractal family and thus have not differentiated the diverse modes of chemical connectivity. If the dendrimer's structural composition was mentioned, the study will be referenced in the appropriate structural family; otherwise, they have been collected under a general section at the end of this review.

Because of the growth of this macromolecular field over the past two decades, coupled with the incredible expansion of new and specialized journals throughout the world, it is impossible to be rigorously comprehensive in this review. The intent of this review is to modernize our previous reviews in the specific topic of 1 → 2 branched dendrimers created by divergent processes.

3. 1 → 2 Branched

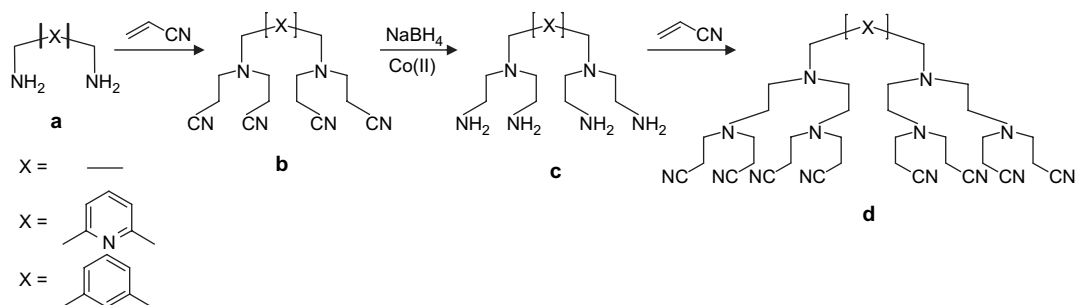
3.1. 1 → 2 *N*-branched, alkyl-connectivity

In their quest to expand the limits of supramolecular chemistry by the creation of new synthetic routes to mesomolecular polyfunctional constructs capable of host–guest chemistry, Vögtle et al. [1] synthesized a small group of non-macrocyclic, *N*-branched structures by a simple repetitive (iterative) process (Scheme 2 depicts the one-directional case). Using different two-directional cores, the treatment of ethylenediamine (**5a**), as well as either 2,6-bis(aminomethyl)pyridine or 1,3-bis(aminomethyl)benzene, *via* a Michael reaction [114] with CH₂=CHCN, gave the tetranitrile **5b**, which was reduced [Co(II)/NaBH₄] to produce hexamine **5c**. Repetition [115] of this reductive procedure, however, using diisobutylaluminum hydride *vs.* the Co(II)/NaBH₄ protocol to reduce the cyano groups, supported the original observations [1]. This terminal tetraamine was subsequently treated with excess CH₂=CHCN to generate the G2 octanitrile **5d**; because of difficulties associated with the removal of cobalt salts and the mass spectral characterization of the high molecular weight products, the cascade process was terminated at this stage, but the iterative mode of synthetic construction was established (Scheme 5).

Wörner and Mühlaupt [116] demonstrated an improved modification to circumvent the difficulties associated with using excess reagents and the complicated purification aspects with the one-step multiple conversion process. They improved the initial nitrile reduction step by using Raney nickel [117] at ambient temperature (8 bar H₂) with an added trace of NaOH in EtOH. They also found that when the cyanoethylation was conducted in MeOH, the formation of the troublesome mono-substituted side products was completely eliminated. Using these simple synthetic modifications [116], Vögtle's initial route, discovered 15 years earlier, could now be extended to

the G5 nitrile in very good overall yield. The increase in steric hindrance at the dendrimer periphery (*i.e.*, theoretically 64 cyano groups at G5) does, however, impede catalysis at surface, thus increasing the time required for complete reduction (*i.e.*, G1 and G5 required 7 and 96 h, respectively). The related four-directional dendrimers derived from pentaerythritol have also been prepared [118]. A two-directional dendrimer, based on a 4,7,10-trioxa-1,13-tridecanediamine (Jeffamine[®]) core, has been constructed by a similar two-step procedure, except that the reduction of the nitrile groups utilized an EtOH solution with PtO₂ and HCl (37%) under 45 psi of H₂ at 25 °C with variable times depending on generation [119]; other commercial Jeffamines[®] could also be used.

In back-to-back manuscripts with that of Wörner and Mühlaupt [116], de Brabander-van den Berg and Meijer [120] reported procedures for the large-scale preparation [98] of these PPI dendrimers with a 1,4-diaminobutane core using a sequence of reactions related to those originally employed [1]. Thus, the repetitive sequence – (1) addition of a primary amine to 2 equiv. of CH₂=CHCN, followed by (2) catalytic (Raney Cobalt) hydrogenation conducted in water – selectively afforded the desired polyamine in near quantitative conversion. As they noted “the process window for quantitative hydrogenation is small and side reactions easily occur;” nevertheless, this procedure has led to commercial production [121]. The critical ¹H NMR, ¹³C NMR, IR, MS, HPLC, GPC, DSM, TGA, and intrinsic viscosity (G2–4) [122] data are in total accord with the assigned structures [120]. The ¹⁵N NMR spectra of this PPI series confirmed their highly branched and well-defined structures [123,124]. The use of double-resonance 3D HMQC-TOCSY NMR on the G3 PPI has given greater insight to the overlapping ¹H resonances for the core, interior, and exterior methylene units, which were resolved and assigned [125]. The NOESY-HSQC 3D-NMR and NOESY 2D-NMR techniques (750 MHz) have also been used to get a better understanding of the chain's conformational mobility in this 1 → 2 *N*-branched family [126,127]; these techniques permitted proof-of-assignments and the NOE data derived from the internal proton interactions afforded information about the critical through-space chains and specific contacts. The VH-polarized Raman spectra (where VH refers to the signal obtained when the incident and scattered-light are polarized perpendicular to each other) of the G5 PPI possessing theoretically (CN)₆₄ moieties measured between 4 and 250 cm⁻¹ and at discrete temperatures (333–123 K) showed varying dynamic aspects depending



Scheme 5. Vögtle's [1] synthesis of a series of polyarmed mesomolecules.

on temperature and frequency range [128]. The viscosity of PPIs in MeOH has been shown to be Newtonian for every concentration and shear rate used; the value of Huggins coefficient indicated that these materials were soft spheres and do not interpenetrate [129]. The miscibility of G5 PPI and benzene has been investigated [130]; the miscibility of the amine-terminated PPI in benzene depends for the most part on the water content in the solvent.

Thus using the 1,4-diaminobutane (**6a**) core, the G5 polynitrile **6b** was initially produced in kilogram quantities [131] and then made commercially available [132–136]. The addition of ammonia and using MeOH, as solvent, during the hydrogenation facilitated an eight-fold increase in substrate concentration while allowing a 10-fold decrease in catalyst concentration, while the conversions of >99.5% were still observed [132]. Further, after 248 consecutive steps, the amino-terminated G5 PPIs possessed an approximate dendritic purity of 20% (ESI-MS); this relates to a monodispersity of *ca.* 1.002 [137]. The hydrodynamic radii of the G1–5 PPIs were determined to be 5.2, 7.3, 9.4, 11.7, and 14.0 Å, respectively, based on SAXS and SANS data [132,138]. This compares with molecular modeling values of 4.8, 6.2, 8.1, 9.8, and 11.9 Å, respectively, and equates well with the dense-core model. Ballauff et al. coated the G4 [139] or G5 [140] PPIs with biphenyl ether moieties by amide connectivity and evaluated the resultant structure by SANS concluding that the density distribution maximum occurs at the center of the molecule [141]. Other SANS studies in which the G4 PPI was coated with C₆H₅– [142–144] as well as C₆D₅– [145] termini have been reported; the enhanced contrast with the deuterated surface showed that the end groups were dispersed throughout the dendrimer [145]. Related SANS studies have been conducted [146] to determine the size changes of the G4 (radius-of-gyration = 12.4 ± 0.2 Å) and G5 (15.6 ± 0.2 Å) PPIs in concentrated solution; preliminary SAXS data support the hypothesis that these dendrimers can collapse at higher concentrations. Scherrenberg et al. [147] studied these amine- and nitrile-terminated PPIs with SANS, viscometry [148], and molecular dynamics, from which the dendrimer's dimensions were found to increase linearly with generation number as well as *ca.* $M^{1/3}$, where M is the dendrimer's molar mass. Fractal dimensionality of these compact structures was found to be *ca.* 3. The amine-termini were shown to exhibit substantial back-folding, which resulted in a monotonic density decrease on the way to the periphery and a homogeneous radial density distribution. SANS studies using the contrast variation technique permitted a radial distribution of the internal end-groups and further supported the dense-core model [145]. A model of charged PPIs that takes into account the osmotic pressure of the counter ions, its finite flexibility, and inhomogeneous radial distribution of the internal electric charge has been presented [149]. A box-counting method has also been applied [150] to the G5 PPI-(CN)₆₄. Intermolecular interactions have been examined [151,152] by means of SANS experiments; at high Q values, all data sets collapse to a single curve indicating that the internal structure is unaffected by neighboring molecules. Further at high concentrations, these dendrimers behave as soft spheres capable of molecular

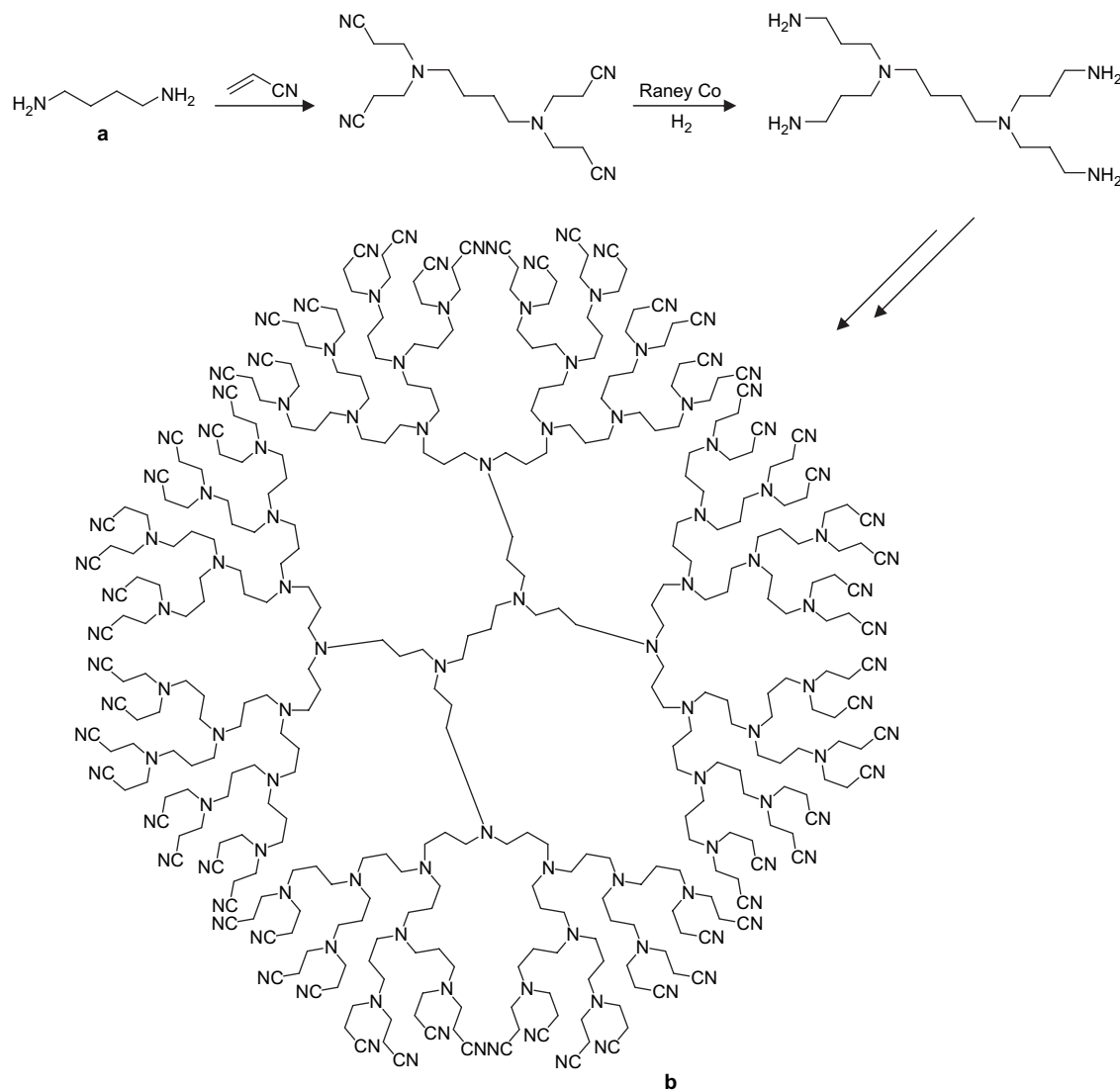
interpenetration. The G3–5 nitrile-terminated PPIs were analyzed by MALDI-TOF mass spectra, size exclusion chromatography (SEC), and dilute solution viscosity; the resultant data support their degree-of-imperfection, general types of impurities (missing arms), and compact spherical composition [153]. The mid-frequency Raman scattering data of the neat G5 PPI-(CN)₆₄, derived from the band profile analysis of its fundamental C≡N mode near 2246 cm⁻¹ at different temperatures, showed that the lattice relaxation processes were controlled by a stretched exponential modulation function with a dispersion parameter $\alpha = 0.90 \pm 0.05$ at 300 K and corresponding time constant $\tau_0 = 0.78$ ps [154] (Scheme 6).

Using a modified procedure, Astruc et al. [155] created similar higher generation dendrimers starting with an aryl nonalcohol, as the core, which was treated with CH₂=CHCN and then reduced (BH₃·THF or BH₃·Me₂S) to give the corresponding extended nonaamine, which was subjected to the 1 → 2 branching procedure to give amine and nitrile dendrimers through G4 possessing 144 CN moieties. These polyamines at higher generations possessed diminished water-solubility. Formation of the corresponding metallocenes gave entrance to a series of efficient sensors capable of molecular recognition. Similarly, Sakai and Matile [156] introduced 1 → 2 branching onto cholestamine to investigate the potential of polyamines to enhance transmembrane ion transport; their results suggested that the protonated polyamines increasingly promoted ion transport relative to systems with more free amine moieties.

Several excellent reviews concerning the PPI family of dendrimers have appeared [46,157–165].

3.1.1. PPI's physical properties

Stöckigt et al. [166] investigated the composition and purity of the G2 PPI using capillary electrophoresis in combination with a sector mass spectrometer. Numerous obvious by-products were observed, derived from branching defects, cyclized arms, incomplete reduction products from the previous reactions, and dimers. It is noteworthy that procedural modifications in PPI synthesis have, in many cases, facilitated the development of purer materials. Analysis of a commercial (DSM) sample of the G2 PPI with amine termini by MALDI-TOF MS showed it to be defect-free, reflecting the synthetic improvements over time. High-performance liquid chromatography (HPLC) in conjunction with electrospray mass spectroscopy (ESI-MS) has also been used for the compositional analysis of the PPI nitrile intermediates [167]. The generational defects have been detailed, in which the complete PPI family has been analyzed by means of electrospray mass spectrometry [168]. Their gas-phase chemistry generated a unique molecular fingerprint that corresponds well to the observations shown after their prolonged heating in aqueous solution. These findings support the general globular shape of the dendrimers based on the observed linear relationship between the extent of protonation and molecular mass as well as unique fragmentation patterns. The fragmentation of various charged states of protonated PPIs has been investigated [169] by surface-induced dissociation; the charged species



Scheme 6. The commercial synthesis of poly(propylene imine) dendrimers [120].

have been proposed to fragment by a charge-directed S_Ni mechanism. The ions derived from ESI-MS of the PPI family were also subjected to ion-trap tandem MS [170]; all products from dendrimer parent ions were rationalized by dissociation processes associated with this S_Ni mechanism by the attack of the nearest neighboring atom on a carbon α to the site of protonation. A detailed tandem mass spectral study *via* post-decay and collisionally activated dissociation techniques of the G3 PPI dendrimer has been conducted [171]; the existence of distinct conformations was demonstrated. Thus in nonpolar solvent, one of the arms was pointed into the interior enabling *intramolecular H*-bonding; whereas in protic polar solvent, *intermolecular H*-bonding occurred. The electrophoretic mobility of the charged G3 and G5 PPIs was ascertained as a function of ionization, ionic strength, and hydrodynamic radius [172]. In general, the trends follow standard electrokinetic model predictions for an ion-impenetrable dielectric sphere of specified radius. Recently, use of a spray-jet technique to introduce neutral non-volatile solute molecules in a molecular

beam was successfully applied to a PPI dendrimer and 4-dicyanomethylene-2-methyl-6-[(*p*-dimethylamino)styryl]-4*H*-pyran, which enhanced multiphoton ionization of the dye in the dye/dendrimer molecular beam [173].

van der Wal et al. [174] analyzed the nitrile intermediates in this series using size-exclusion chromatography with a polystyrene-divinylbenzene stationary phase and THF, as the mobile phase. For the amine-terminated PPIs, the optimal systems were based on reverse-phase silica packing that was deactivated by tetraazacyclotetradecane using 0.25 M formic acid, as the mobile phase, at 60 °C; several by-products were also detected and analyzed by mass spectrometry.

Koper et al. [175] examined the protonation mechanisms of the G1–3 PPIs using ¹⁵N NMR spectroscopy. The *N*-nuclei “shells” derived from each nitrogen tier (the core nitrogens are the α -shell, the G1 nitrogens are the β -shell, *etc.*) were analyzed for their degree-of-protonation based on the number or availability of protons. Further, the distribution of *Z* protons on a structure possessing six protonation sites constitutes

a microstate (denoted as $n = 2$) comprised of the possible protonation positions for that structure. For G1, possessing six amine moieties, it was found that the first fully protonated shell is the β -shell; at $n = 4$, 90% of the microstate is comprised of complete terminal amine protonation. The interior is then left to protonate. For the $n = 1$ state, 80% of the possible structures are terminally protonated; while for $n = 2$ and 3, proton distribution is more prevalent. The data have later been considered by a simpler model involving a common microconstant for the tertiary amines [176]; the outer more basic amines protonate first, followed by the core, followed by those that are in-between, affording the odd-even shell protonation pattern [175]. Other potentiometric titration experiments with this PPI family were conducted at different ionic strengths [177–179]; the Ising model permitted a quantitative analysis of the titration curve around pH 6 and 10 supporting the stability of an onion-like structure, in which alternate shells of the PPIs are protonated as noted above [175]. The G2 PPI, composed of three shells, is initially protonated at the γ -shell (outer) and innermost α -shell; followed by the β -shell. The G3 PPI, at low proton concentration, exhibits some protonation at all levels other than the β -shell. The δ -shell is first to be fully protonated; at pH 8, the δ - and β -shells are nearly completely protonated; at still higher proton concentrations, the γ -shell fills.

Polyelectrolyte behavior [180] of these PPIs has been examined [181], and in general, potentiometric titrations showed the presence of two different amine functionalities possessing differing basicities and electrostatic interactions. Separate pH regions were noted and, for higher generation dendrimers, a polyelectrolyte effect dominates the protonated form such that a strong decrease in pK was observed during protonation.

Using Monte Carlo methods, Welch and Muthukumar [182] demonstrated that by varying the medium's ionic strength, the intramolecular density profile for these dendritic polyelectrolytes can be cycled from the “dense-shell” model (low ionic strength, Fig. 1a) and the “dense-core” model (high ionic strength, Fig. 1b). This is analogous to the expanded vs. contracted forms that are observed for the ionic- vs. neutral-terminated forms (e.g., carboxylate vs. carboxylic acid) [183]. Computer simulations [184] and theoretical principles were employed to show a molecular-level portrait of these host–

guest interactions and the conditions necessary for formation [185]. Molecular dynamics simulations were conducted on the G2–5 PPIs at 400 K to probe the molecular structure and melt morphology [186]; the radius-of-gyration scales with approximately cubic root of the number of monomers and interpenetration of individual dendrimers decreased with each increasing generation.

Infinite-dilution activity coefficients of polar and nonpolar solvents of these G2–5 PPIs using inverse gas chromatography, have been reported [187]. Solvent activity coefficients changed with dendrimer generation, *i.e.*, the maximum solvent solubility, that was shown for G4 in which protic solvents, EtOH and MeOH, were found to be better solvents than THF, toluene or EtOAc. Flory's interaction parameters were ascertained, as was the solvent activity for comb-burst-type macromolecules.

The amine-based G5 PPI formed more-conducting electrolytes with $\text{Li}[\text{CF}_3\text{SO}_2]_2\text{N}$ than similar complexes derived from the PAMAM family; these materials exhibited high ionic conductivity but high concentrations of salt increased the T_g temperatures with an attendant decrease in ionic conductivity [188].

The interactions of the poly(amine)s, as well as their corresponding surface-coated pyrrolidone analogs, with sodium dodecylsulfate (SDS), tetradecyltrimethylammonium bromide (TTAB), and hexaethylene glycol monodecyl ether (C_{12}EO_6) surfactants [189], based on electromotive force (EMF) measurements and isothermal titration microcalorimetry (ITM), were reported by Wyn-Jones et al. [190]. The SDS was found to bind these dendrimers at concentrations of $10^{-5} \text{ mol dm}^{-3}$; while, the C_{12}EO_6 and TTAB showed limited binding capabilities. The SANS data conducted on the supramolecular complexes derived from SDS and different PPIs were reported: for G1 and G2, the scattering data agreed with the SDS micelles being bound to the PPIs in which 3 or 4 dendrimers are bound to a SDS micelle; whereas for G3 and G4, they are inconsistent with small spherical micelles but rather, supported the formation of large aggregates [189,191]. Further, their SANS data with C_{12}EO_6 are consistent with spherical free C_{12}EO_6 micelles existing in solution [189].

Colligative properties and viscosity characteristics of the PPIs in MeOH have been evaluated [192] as well as the osmotic compressibility in CD_3OD [193] using low-angle laser light scattering and the self-diffusion coefficients by pulsed field gradient spin echo NMR [194]. Effective radii and partial specific volumes were determined; notably, solvent molecules resided within the structural interior. Comparisons of the rheological behavior of PPIs with those of either hyperbranched polyesters or poly(ether imide)s have been reported [195]; a fit of the Fox and Flory theory to the fractional free volume data suggested that the volume free fraction of the end groups is generation independent. Rietveld et al. [196] synthesized the G4,5 PPIs with terminal carboxylic acids, as well as possessing an inner deuterated shell, in order to probe the location of the terminal functionality *via* NMR and SANS; these studies also demonstrated that size changes could be a function of pH changes.

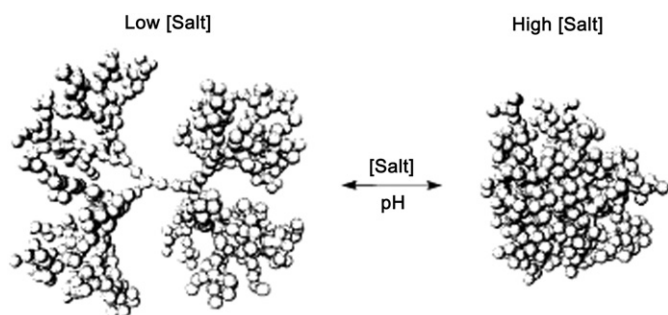


Fig. 1. Dense-shell model (low ionic strength) (a) and dense-core model (high ionic strength) (b). Reprinted with permission of the American Chemical Society [182].

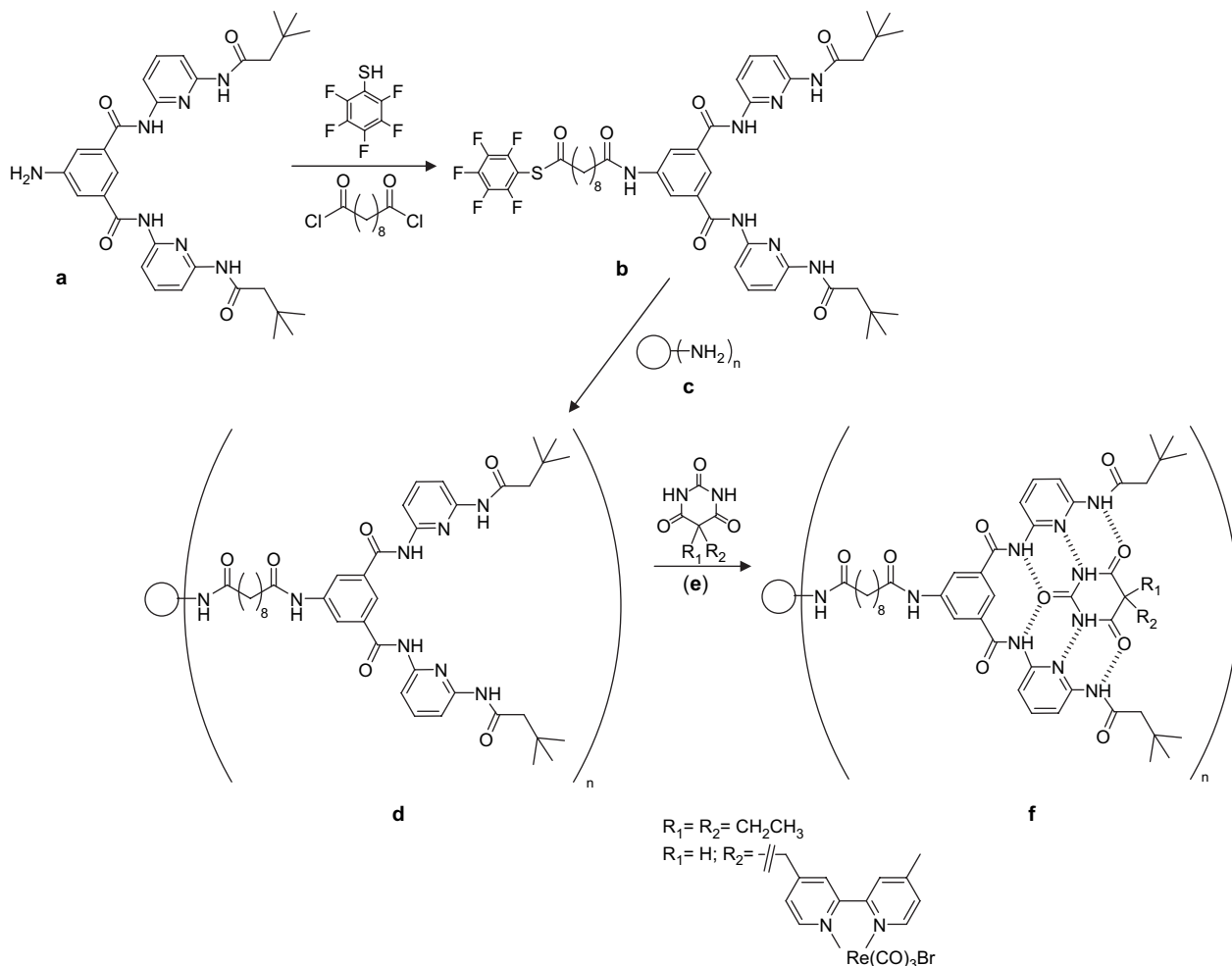
The use of PPIs, as pseudostationary phases for electrokinetic chromatography, has been evaluated [197] in which SDS micelles were compared with the G5 PPI possessing a CO₂H surface; mixtures of hydroquinone, resorcinol, phenol, benzyl alcohol, *o*-cresol, and 2,6-xyleneol generally revealed reverse retention times for the analytes.

The magnetic field effect on the photoinduced electron transfer reaction between benzophenone and PPIs has been evaluated in an aqueous environment by laser flash photolysis; in the presence of a 0.6 T magnetic field, relative yields of the benzophenone anion radical at a 4–7 μs delay increased by *ca.* 15% for G3–5 PPIs. It was concluded that the higher generation PPIs act not only as electron donors but also as a “super-cage” in the photoreaction [198]. Preliminary data on the optical properties of PPI colloidal films possessing thickness <1 nm using scanning angle reflectometry have emerged [199].

Static and time-resolved fluorescence studies have been used to evaluate the solubilizing capability of the PPIs with hydrophobic guests, *e.g.*, pyrene, in aqueous media [200]. Incorporation of water within the dendrimer was evaluated *via* the formation of emission exciplexes between pyrene and the internal tertiary amines. Host–guest interactions between

G5 PPI and different dyes in an aqueous solution have been evaluated by using surface plasmon resonance (SPR) in which a dendrimer monolayer was immobilized on a SPR sensor by means of carboxy-terminated self-assembled monolayers [201]. The surface uniformity was determined by AFM, then the absorption behavior of the dyes was measured – there was a strong affinity of the G5 PPI with Rose Bengal and erythrosine B suggesting that there is a strong affinity between the dendrimer’s cavities (the host) and guest dye. The host–guest ramifications of dendrimers have been reviewed [157].

The synthesis of 5-amino-*N,N'*-bis[6-(3,3-dimethylbutyryl)amino]pyridin-2-yl]isophthalamide (**7a**), an ideal “Hamilton receptor” for barbiturate guests [202], was accomplished and then treated with sebacyl dichloride and pentafluorothiophenol to generate **7b**, which was subjected to the G0–4 PPIs, *e.g.*, **7c** to give (*ca.* 85%) the receptor-coated dendrimer **7d** [203]. Then, treatment of **7d** with barbituric guests **7e** formed stable *H*-bonded complexes **7f**, which possess reasonable binding constants $1.4 \times 10^3 \text{ M}^{-1}$ for barbital and $1.5 \times 10^5 \text{ M}^{-1}$ for {Re(Br)(CO)[5-(4,4'-methyl-2,2'-bipyridinyl)-methyl-2,4,6-(1*H*,3*H*,5*H*)pyrimidinetrione]}, based on a single host–guest complex (Scheme 7).



Scheme 7. *H*-bonded surface complexation [203].

3.1.2. PPI's surface modifications

Treatment of the cyano-terminated PPIs with hydrochloric acid affords the simplest transformation of these dendrimers into their acid analogs, although amidation is another common conversion. Meijer et al. [204] utilized the reduced form of the G5 polyamine **8a** to construct a novel dendritic box which, as a result of surface steric hindrance, entrapped guest molecules. Initially suggested by Denkewalter et al. [5–7] by introducing the terminology “non-draining” spheres, the concept of “trapping topologically by shell molecules” was considered theoretically by Maciejewski [205], as well as the “unimolecular micelle” by Newkome et al. [23,206–209]. Dendritic boxes with molecular weights up to 24,000 amu were prepared [204] by increasing the surface congestion of **8a** through the introduction of bulky terminal chiral esters, such as the *N*-hydroxysuccinimide ester of phenylalanine (**8b**); the large interior void space and congested surface (**8c**) created the desired host pockets for guest entrapment. The addition of other amino acid surface groups, such as *L*-alanine, *L*-*t*-Bu serine, *L*-Tyr-cysteine and *L*-*t*-Bu-aspartic ester, has expanded the concept of dendritic boxes [160,210]. Additionally, studies including induced chirality of encapsulated guest molecules [211], the trapping of Rose Bengal [212,213], charge transfer [214], and triplet radical pairs [215], have been reported (Scheme 8).

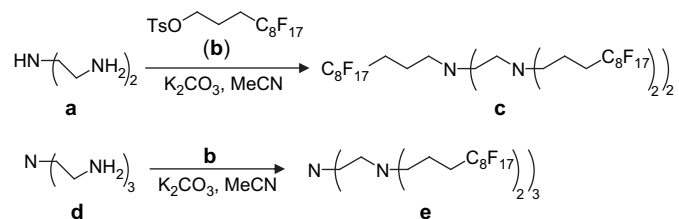
Goddard et al. [216] reported molecular dynamics calculations based on the dendritic box concept encapsulating Rose Bengal [160,204,210]; a concentration-dependent equilibrium was found between the interior and surface solvent regions for dendrimers that lack a “capping” periphery. Their experimental results regarding the number of guests within the dendritic host were supported by these theoretical calculations; moreover, bulky capping termini prevented the release of the molecular guests. Cavallo and Fraternali [217] used molecular dynamics to study the *H*-bonding, solvent-accessible surface area, and excluded volumes for G1–5 dendritic boxes terminated with *N*-*t*-BOC *L*-phenylalanine. Interestingly, self-inclusion of the termini within the inner shell was shown but these termini did not completely fill the internal void zones.

Interactions of the G5 amino acid surface-modified PPI between two mica surfaces have been evaluated across a toluene medium by means of a surface force balance [218]; frictional force vs. normal load profiles ascertained at different shear velocities revealed both solid- and liquid-like behavior of the confined dendrimer that is consistent with earlier NMR data [204]. Stimulated emission was evaluated using the G5 PPIs

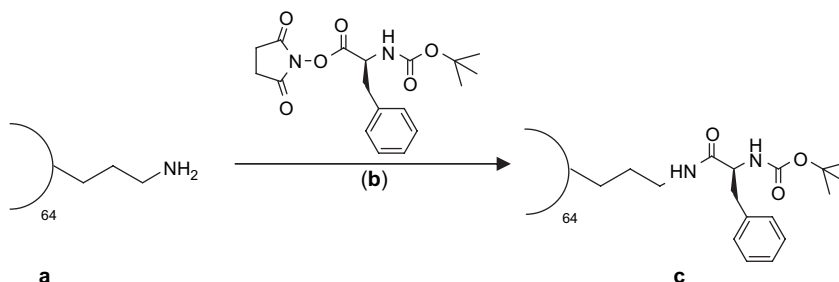
modified by the *tert*-butyloxycarbonyl-*L*-phenylalanine surface as the weak scattering source in the PMMA matrix with the external 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran, as the emissive moiety; a super-narrowing laser spectrum was observed [219]. The surface treatment of the G5 PPI with sarcosine *N*-carboxyanhydride gave a high (91–99%) yield of the AB_{*n*}-type dendrimer/linear polymer block copolymer [(CH₂)₂N[(CH₂)₃N[(CH₂)₃N[(CH₂)₃N[(CH₂)₃N[(CH₂)₃N(C(=O)CH₂NMe)_{*n*}-H]]₂]]₂]]₂]]₂]]₂ [220].

Verlhac et al. [221] reacted polyamines **9a** and **9d** with the linear tosylated monomer **9b** creating the perfluorinated alkanes **9c** and **9e**, respectively. These small dendrimers were then used as perfluorinated Cu(I) ligands for the intramolecular cyclization of alkenyl trichloromethyl esters catalyzed under “fluoro biphasic” conditions [222]. The PPIs have been coated with Freon 113 (a perfluorinated PEG-like material, the heptameric acid fluoride of hexafluoropropylene oxide) thus generating a “CO₂-philic” shell [223]; these materials were shown to facilitate the transfer of CO₂-insoluble, ionic, methyl orange dye from an aqueous media to CO₂ (Scheme 9).

Moszner et al. [224] surface-coated the G2, 4 and 5 PPIs with 2-(acryloyloxy)ethyl methacrylate, which generated a polyene that was subsequently polymerized in bulk solution to give cross-linked polymers with *T*_gs near, or below, ambient temperature. The properties of these dendrimers and polymers were further studied by exposing the polyamine surfaces to mixtures of methacrylate. The surface coating of PPIs with mixtures of 2-(acryloyloxy)ethyl methacrylate and hexafluorobutyl or 2-(trimethylsilyl)ethyl acrylate to obtain a “hetero-plurifunctional” or an early example of combinatorial-type materials was demonstrated [224]. Treatment of the terminal amines of G5 PPI with methyl acrylate by a double Michael addition, followed by hydrolysis generated the carboxylate-terminated series, which was characterized by ¹H NMR, ¹³C NMR, IR, and ESI-MS [225]; a characteristic onion-like shell



Scheme 9. Perfluorinated *N*-dendrimers [221].



Scheme 8. PPIs possessing *t*-BOC-protected phenylalanine termini [204].

protonation behavior was again observed. The influence of electrostatic interactions of the G5 PPI possessing the carboxylate-surface was studied [179] using scanning angle reflectometry, pH, and ionic strength; it was noted that charge density and the surface roughness must be considered.

Put et al. [226] functionalized the PPI's surface with second-order nonlinear optical chromophores, *e.g.*, 4-(*N,N*-dimethyl)-phenylcarboxamide, by a simple amidation using an appropriate acyl chloride. The hyperpolarizabilities of these coated dendrimers using hyper-Rayleigh scattering revealed the solution structure and symmetry to be flexible for lower generations – generally sphere-like. However, at higher generations, as the dendrimers became more spherical, they were also found to be quite rigid. These results support earlier reports [227] for the higher generation PAMAM dendrimers, which were said to become “globular” after G5. A related series of coated PPIs were prepared by a Michael reaction with ω -(4'-cyanobiphenyloxy)-alkyl acrylate [228] or 4'-cyanobiphenyl hydrogen glutarate [229] using diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)-phosphonate, as the condensing agent, generating the desired liquid crystalline dendrimers. A series of liquid crystalline azobenzene co-dendrimers were prepared by grafting 4-cyanoazobenzene and/or 4-cyanobiphenyl units to the periphery of G3 PPI; the synthesis utilized different percentages of randomly placed molecular caps on the outer surface [230].

In rheology studies, Wagner et al. [231] prepared G4 and G5 PPIs with acetyl and deuterated acetyl chloride-modified surfaces, which exhibited Newtonian properties at all concentrations in solution; however, the non-acylated dendritic solutions were less viscous. SANS data revealed significant chain backfolding and solvent penetration, as well as interdigitation and clustering. These dendrimers exhibited constant shear viscosities over a wide-range of shear rates; surface-capping with methyl or benzyl acrylates increased the T_g affording a noteworthy elastic modulus and nonlinear rheological behavior at enhanced shear rates [232]. Acetylated and hydroxy-terminated PPIs in aqueous poly(ethylene oxide) [PEO] solutions were subjected to similar experiments [233]. SANS measurements in a dilute PEO solution quantitatively showed that the dendrimers decorated the PEO chains possessed an unexpected necklace-like structure.

A series of star-shaped polymers, using the G1–5 PPIs as the core, was prepared [234,235] in order to investigate their miscibility properties with linear poly(styrene). After coating each member with tyrosine – possessing phenolic units – a “redistribution reaction” with poly(2,6-dimethyl-1,4-phenylene ether) (PPE) was conducted. The star-branched PPE length was regulated by controlling the phenol/PPE ratio; the average arm-length was determined to be 90 repeat units for each member. For star-polymers constructed from the G3–5 PPIs, inhomogeneous blends with poly(styrene) were obtained, while miscible blends were obtained using the G1,2-based stars. The T_g value for this series was shown to be *ca.* 210 °C. The unsaturated end groups of polyisobutylene were converted into anhydride termini by an ene reaction with maleic anhydride, and the product was reacted with the PPI dendrimers to generate PPI–polyisobutylene star copolymers

[236]. Polymerization of styrene in an aqueous dispersion of SDS and the amine-terminated G5 PPI initiated by potassium persulfate at 80 °C produced latexes with diameters of 26–64 nm and coefficients of variation of diameters of <10% [237]; the dendrimer was shown to be essential to produce the least polydisperse latexes.

Meijer et al. [238] described the treatment of PPIs with simple, long-chain (C_n , where $n = 5, 9–15$) acid chlorides to afford inverted unimolecular micelles. Dynamic light scattering experiments supported single-particle behavior (*i.e.*, no aggregation) and suggested a 2–3 nm hydrodynamic diameter using CH_2Cl_2 , as the solvent. Micellar characteristics were verified by molecular entrapment using the 5, 9, and 15 C -chain, with the modified G2 and G5 PPIs. Upon addition of Rose Bengal to the coated dendrimer in EtOH, followed by precipitation and copious washing, it was determined that the G2 inverted micelles entrapped *ca.* 1 dye molecule, whereas the G5 host trapped *ca.* 7–8 guests. Vapor–liquid equilibria for PPIs coated with dodecyl, octadecyl amides or polyisobutylene were measured by a classical gravimetric-sorption procedure; solvent absorption was found to be strongly dependent on structural composition and generation number [239]. The use of surface-attached octadecyl amine resulted in the formation of polyhedral aggregates that became embedded within an amorphous calcium carbonate phase that persisted in competition with the thermodynamic product, calcite; however, in combination with hexadecyltrimethylammonium bromide, small spherical aggregates were generated that induced the formation of vaterite. MALDI-TOF MS has been used to characterize related unimolecular micelles derived from C_{10} alkanoyl or C_{12} alkyl G1–G5 terminated PPI dendrimers [240].

Inverse unimolecular dendritic micelles, derived from the reaction of G1–5 PPIs with palmitoyl chloride, were demonstrated [241] to be very effective extractants of anionic xanthene dyes, *e.g.*, fluorescein, 4,5,6,7-tetrachlorofluorescein, erythrosine or Rose Bengal, from water to organic solvents at low pH, whereas at higher pH (slightly above pH 6.0) extraction yields dramatically fell; cationic dyes, *e.g.*, ethidium bromide, could not be extracted into the organic layer. The extraction behavior was attributed to the internal tertiary amine moieties. The translational diffusion and viscometry of these inverse micelles were evaluated in relation to generation [148]. These palmitoyl-functionalized PPIs in a liquid crystal (dendrimer-filled nematics) require extremely low switching voltages to change from scattering to the highly transparent state in which switching is totally reversible [242,243]. Using pyrene, host–guest characteristics similar to those of the palmitoyl-coated PPIs were reported [244]; the PPI–pyrene binding constants and pyrene's location were ascertained by fluorescence spectroscopy suggesting it to be near the PPI's core. Ramzi et al. [245] covalently, as well as noncovalently, coated these PPIs with fatty acids and conducted SANS experiments to elucidate single-chain factors of both the fatty acid and PPI component. The initial spherical inverse unimolecular micelles, derived from G5 PPI-coated with stearyl termini, were filled with $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ to form cylindrical

multidendritic structures, as revealed by SANS and SAXS data; the encapsulated gold salt was reduced by the addition of NaBH_4 in diglyme [246]. Simply treating an aqueous solution of G3 PPI with HAuCl_4 without added reducing agents gave one-step access to dendrimer-protected gold nanoparticles [247]. Blends were made by either solution or melt-mixing fatty-acid-modified PPIs with different olefins [248]; SANS measurements were used to determine the degree-of-miscibility from which the limiting power law behavior showed that all of the blends were immiscible. Treatment of the G5 PPI with lauroyl chloride formed the desired dodecanamide-modified inverse micelle, which produced stable polystyrene lattices when dispersed in an aqueous environment with styrene and SDS [249]. Several liquid-crystalline octopus-type mesomorphic materials were generated from the G1 PPI core and shown to possess a mesophase stability that is very sensitive to the nature as well as to the spatial juxtaposition of the mesogenic segments within the structures [250]. Treatment of the G2 PPI with $\text{HO}_2\text{C}[3,5\text{-C}_6\text{H}_3\text{-(OCH}_2\text{CH}_2\text{-N}_3)_2]$ in the presence of DCC gave rise to the corresponding polyazide, which was subjected to the Staudinger reaction in an attempt to generate the corresponding iminophosphine surface – the reaction stopped at the azidophosphine intermediate [251]; interestingly, this was shown to be an efficient catalyst for a Michael reaction. The G0–2 PPIs were treated with mesogenic materials [252–254], *e.g.*, 3,4-di(decyloxy)benzoic acid, affording the coated ligands that were subsequently loaded with Cu(II) salts to generate the corresponding complexes; these complexes were subjected to a magnetic field to evaluate the orienting effect [255].

The surface-coating of the PPIs with oligo(*p*-phenylene vinylene)s (OPVs) has been accomplished [256] to give amphiphilic globular species that were shown to self-assemble at the air–water interface forming stable monolayers. These OPV-coated PPIs act as hosts for guest dyes and the host–guest ratio can be easily tuned; the dendrimer-dye system can be mixed with OPVs, affording quality thin films suggesting the possibility of tuning the emission wavelength. This PPI OPV-terminated family has been evaluated *via* site-selective and time-resolved fluorescence [257], which showed that there was generation dependence and thus, a relationship to the number of OPV-termini. The OPV-coated G3 PPI was used to stabilize the fabrication of CdS nanoparticles that were shown to be spherical when CHCl_3 was used and plate-like using a $\text{CHCl}_3\text{–MeOH}$ (6:1, v/v) solvent mixture [258]. This OPV-coated G3 PPI formed spherical and rod-like aggregates that were manipulated by optical tweezers, resulting in the formation of novel nanoarchitectures [259]. Different generations of these PPI–urea–OPV materials were terminated with a mesogenic moiety, specifically 3,4,5-tri(dodecyloxy)phenyl, and were subsequently shown to possess weak π -bonding interactions in solution as well as increasing intramolecular *H*-bonding with increasing generation, indicative of increasing dense-shell packing [260]. The photoluminescence properties of the G3 [261] to G5 PPIs and poly(2,5-methoxypropyloxysulfonate phenylenevinylene) spin-assembled multilayer films were self-quenched with increasing film thickness. However,

in bilayer systems, a terminal dendrimer layer gave films with greater photoluminescence quantum efficiency when compared to those with terminal polymer layers [262].

Globular aggregates were formed when the $\text{C}_{16}\text{H}_{33}$ -coated G5 PPI was placed in an aqueous environment [263]; however, when single-chain surfactants, *e.g.*, octadecylamine (OA) or cetyltrimethylammonium bromide (CTAB) at concentrations below the c.m.c., different solid-reinforced aggregates were generated depending on the surfactant: with OA, a persistent polyhedral shape possessing a narrow size distribution arose or, with CTAB, spherical aggregates formed [264,265]. The combination of OA and alkylated PPI was shown to form aggregates that were demonstrated to stabilize the normally unstable amorphous calcium carbonate for extended periods of time [264,266]. The dendrimer/surfactant aggregates have been tuned to template the formation of different phases of calcium carbonate; however, the use of a negatively charged surfactant, such as SDS, resulted in growth retardation by the Ca^{+2} -induced agglomeration of these dendrimer/surfactant aggregates into giant spherical particles [265]. The formation of a hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] composite has been demonstrated to show plastic deformations while still retaining a high-degree of stiffness [267].

A comparative study of the G3 PPI dendrimer and related PAMAM each with sixteen imine-connected mesogens derived from mono-, di-, and tri-alkoxybenzoyloxysalicylaldehydes showed that it was the interaction between the rigid mesogenic moieties and the mesophase separation that governed the type of supramolecular organization, giving rise to nematic, smectic, and columnar mesophases [268]; also see an expanded study using the G1–5 families [269]. An overview of the relationship of these liquid crystals to nano-devices has appeared [270]. Diverse analytical techniques were used to evaluate the liquid crystal properties of these PPI dendrimers, each possessing mesogenic groups attached in different ways (end-on [271] and side-on) with the intent to tailor the resultant mesomorphic properties [272]. A series of nematic liquid crystalline networks was derived from G4 PPI with a mixture of chiral monosalicylaldehyde and an achiral disalicylaldehyde (prepared from 2,4-dihydroxybenzaldehyde and 1,10-dibromodecane) [273]; the thermoelastic measurements excluded the possible elastomeric nature of this network. A family of ionic liquid crystals originated from the treatment of the G1–5 PPIs, initially with three long-chain carboxylic acids [274], then 4-, 3,4-di-, and 3,4,5-tri(decyloxy)benzoic acids [275]. These resultant ionic liquid crystals were characterized by DSC, polarizing-light optical microscopy, and X-ray diffractometry. The attachment of *E*-stilbene chromophores onto a polyamine PPI core utilized a reactive red isocyanate [276] derived from a simple four-step procedure from 3,4,5-tri(propoxy)benzaldehyde and *N*-(4-iodophenyl)phthalimide. Vögtle et al. [277] treated the amino surface of the G1–3 PPIs with 5-formyl-4-hydroxy[2.2]paracyclophane forming the imine-connected chiral moieties on the surface; the CD spectra were compared to the starting aldehyde.

Partial amidation of the PPI family with stearic acid at 150 °C generated either compositional or positional heterogeneity. The lower generation PPIs showed a random distribution of dyads

(end-group substitution patterns); whereas at higher generations, a marked preference for a single substitution of dyads was realized and proposed to result from either intramolecular interactions or steric hindrance [278]. Notably, cotton fabric showed enhanced color enrichment with reactive dyes when pretreated with a G3 PPI in which *ca.* half of the surface sites possessed amido moieties [279]. The coating of the G5 PPI with 3,4,5-tri(ethoxy)benzamide moieties resulted in a molecular host capable of carrying Pd^{+2} , which could be chemically reduced to give a dendrimer-encapsulated Pd(0) nanoparticle that was able to act as a catalyst for the substrate-specific hydrogenation of polar olefins [280].

Meijer et al. [281] generated the *N*-*t*-BOC-protected glycine-coated PPIs in order to evaluate the issue of termini and branch back-folding. An X-ray structure of the G1 tetraglycine revealed a high degree-of-termini *H*-bonding; thus, concluding that end group localization was dependent on the dendritic structure and that secondary interactions had to be considered when using models that address this question. Meijer et al. [282] reported the preparation of a related series of glycodendrimers based on the G1–5 PPI family.

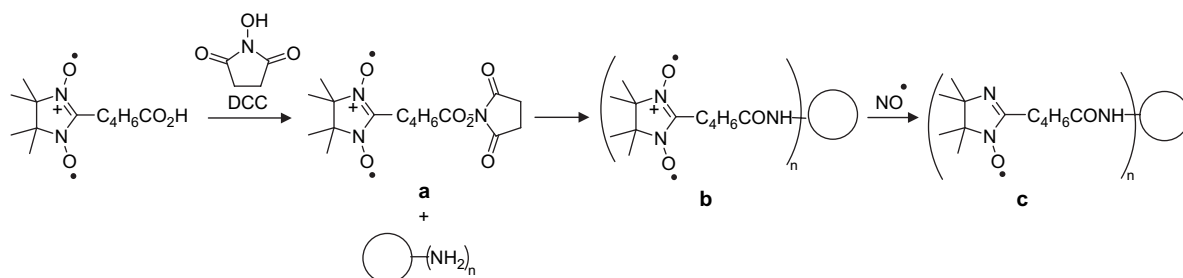
Meijer et al. [283] surface-modified the G1–5 PPIs with nitronyl radicals *via* reaction of the amino termini with 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (3-carboxy-proxyl) radicals. These polyradicals exhibited strong exchange interactions with lower generations, directly showing the number of hyperfine transitions, and thus the number of termini, by EPR experiments. The use of FT-IR further confirmed the presence of an amide-based, *H*-bonded network at the periphery. The introduction of nitronyl nitroxides that were developed to spin-trap $[\text{NO}^{\bullet}]$ was accomplished by the initial activation of 2-(4-carboxyphenyl)-4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide as well as *N*-hydroxysuccinimide in the presence of 1,3-dicyclohexylcarbodiimide to give 2-{4-[(2,5-dioxo-1-pyrrolidinyl)oxy]carboxyphenyl}-4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide (**10a**). Following addition of G1 or G2 PPI, the desired dendrimer coated with nitronyl nitroxide groups was prepared [284]. Treatment of the PPI poly(nitronyl nitroxide) (**10b**) with $[\text{NO}^{\bullet}]$ gave the corresponding poly(imidazolidinoyl) (**10c**), which was ascertained (EPR) by the notable shift for the nitroxide from a near exclusive broad-line to a narrow and defined pattern suggesting a potential route to biological spin-trapping agents for $[\text{NO}^{\bullet}]$. The quantitative evaluation of the radical's substitution was determined by EPR and electrochemical procedures [285] (Scheme 10).

The G3,5 PPIs were surface functionalized to generate nitric oxide (NO)-releasing dendrimer conjugates by their simple exposure to NO in 0.5 M NaOMe/MeOH with the maximum flux of NO release of 6760 ppb/mg [286]; the conversion efficiencies of these NO donor-modified dendrimers were low, however the proximity of adjacent neighbors slowed diazeniumdiolate decomposition. Remarkably, the total amount of NO released from the monoalkylated PPIs possessing surface secondary amines was significantly greater than that of the related parent, suggesting an enhanced stability of the secondary amine diazeniumdiolate.

Vögtle et al. [287] treated the G1–4 PPIs with either 3- or 4-(phenylazo)benzoic acid *N*-hydroxysuccinimide ester to afford (80–90%) the desired terminally modified dendrimers with up to (ideally) 32 surface photoisomerizable diazobenzene moieties. This was the first reported use of dendrimers as holographic materials; thus, thin films of these materials gave holographic gratings with diffraction efficiencies up to *ca.* 20%. The use of these poly(azobenzene)-coated materials, as molecular hosts for eosin Y (2',4',5',7'-tetrabromofluorescein dianion), has been examined [288]. Quenching of the encapsulated-eosin fluorescence, as well as hosting potential, was found to be more efficient in the case of the *Z* forms.

Kimura et al. [289] reported a temperature-sensitive nanocapsule when the G4 PPI was coated with 11-(thioacetyl)undecanoic acid; the terminal thiol was deprotected, and then subjected to *N*-isopropylacrylamide polymerization to impart the temperature-dependent solubility. The catalytic activity of encapsulated water-soluble Co(II) phthalocyanine complexes was studied, as it relates to controlled-by-response changes in the polymer's conformations. The G4 and G5 PPIs were coated with the related isobutyramide (IBAM) groups and compared to the similar PAMAM analogs; the PPI materials were shown to possess a higher density of IBAM moieties due to their smaller comparative size resulting from (1) an enhanced interaction of the terminal groups and (2) efficient dehydration at a relatively low temperature [290].

Other mesogens, *e.g.*, cyanobiphenyl using either a 5 or 10 carbon activated ester spacer chain, have been attached to the surface of these polyamines in order to study the resultant liquid-crystalline properties [291]. All of these mesogenic dendrimers formed a smectic A mesophase, while their thermal properties that were dependent on spacer length exhibited $g \rightarrow S_n \rightarrow I$ transitions (C_{10}). For the transition enthalpies and kinetics, mesophase formation was found to be more



Scheme 10. The preparation of nitronyl nitroxide- and imidazolidinoyl-coated PPIs [284].

favorable for the C₁₀ series. The coating of the PPIs with cholesterol termini attached *via* a carbamate linkage gave rise to the formation of smectic A phases over a broad temperature range and each layer of cholesterol termini was shown to stand erect both above and below the core [292]. Upon cooling, these materials were transformed into liquid crystalline glasses while retaining characteristics of the smectic A phase. Two related series of G4 PPI co-dendrimers have been described by grafting various proportions of either laterally or terminally attached promesogenic units [293]. The G4 and G5 PPIs have also been coated with larger mesogenic moieties possessing three, six, or nine terminal alkoxy chains, and these were shown to form hexagonal columnar mesomorphs from which a model was proposed [294]. X-ray diffraction studies showed that these materials exhibited either nematic or lamellar mesophases; whereas for intermediate proportions, the smectic C mesophase appeared [293]. The family of PPIs with hexasubstituted triphenylene-based mesogens, derived from C₆F₅OC(=O)C(CH₂)₁₀O-triphenylene-(OC₁₀H₂₁)₅, has been synthesized and studied for their mesomorphic properties [295].

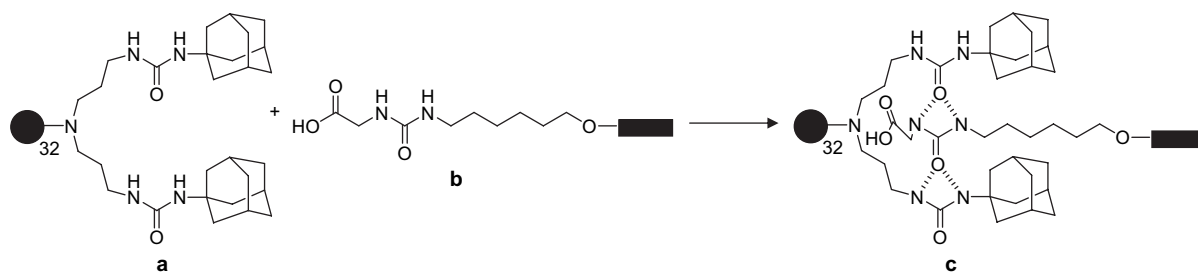
Peerlings and Meijer [296] reported one of the more fascinating chemical transformations in this field in which the amine surface of the G5 PPI was efficiently converted to the corresponding isocyanates. This was accomplished under very mild conditions by using di-*tert*-butyltricarboxylate [O=C(OCO₂-CMe₃)₂], which can be prepared [297] (84%) by the initial reaction of CO₂ with KO-*t*-Bu, followed by phosgene. The treatment of the G1 and G3 PPI terminal-isocyanates with 5-hydroxymethyl-1,3-phenylene-1,3-phenylene-32-crown-10 [298] afforded the “crowned”-PPIs in excellent yields [299]. The novel binding behavior of the poly-crown ethers with paraquat diol [300] [(C₅H₄N⁺CH₂CH₂OH)₂(PF₆)₂] demonstrated the formation of a mixture of [*n*]-pseudorotaxanes [299]. The treatment of the G1–4 PPIs with 4'-sulfonylchloride-benzo[15]-crown-5 in the presence of Et₃N gave the corresponding crowned dendrimer in 58–81% yield [301]; aqueous solutions of sodium pertechnetate and HgCl₂ were extracted with solutions of these crowned PPIs into chloroform.

Peripheral modifications with long (C₁₅) alkyl chains, C₁₀ chains possessing diazobenzenoid moieties, and adamantane [302–305] groups for the G1–5 PPIs have appeared [263]. Monolayer formation at the air–water interface was studied by X-ray diffraction of cast films, as well as electron microscopy and dynamic light scattering on acidic aqueous solutions, revealing a distortion of the dendritic core, further illustrating the highly flexible character of these materials. Surface-functionalized PPIs, with either palmitoyl or azobenzene-containing alkyl chains, were accomplished as well as a combinatorial-type coating (comprised of *ca.* 1:1 ratio) were designed to exhibit reversible, photoinduced switching (*syn* → *anti* conversion by IR irradiation and *anti* → *syn* at 365 nm) [306]. The G5 PPI with the same surface groups formed giant vesicles with 50 nm to 20 μm diameters and a multi-laminar onion-like structure in aqueous solution; the vesicles act like hard spheres and did not merge [307]. The adamantane-terminated G1–5 PPIs were dissolved in water in the presence of β-cyclodextrin and were shown to self-assemble as host–guest complexes in

a one-to-one arrangement for G1–4; the steric crowding in G5 prevented complete complexation [304,308]. These assemblies for G2–5 acted as supramolecular hosts for 8-anilino-naphthalene-1-sulfonate in water [308]. Employing a surface coated with bis-adamantane moieties and urea or thiourea [302] connectivity **11a** a convenient lock was developed for the insertion of a key **11b** comprised of an acid-terminated urea possessing pendant lipophilic component; this procedure offers a novel approach to a reversible self-assembly process (**11c**) [303,309]. Evidence of specific host–guest docking for these stable complexes was obtained from ¹H–¹H interactions exhibited in NOESY data [310,311]. Other hydrogen-bonding interactions using the substituted urea-terminated PPIs have led to self-assembled surfaces [312] and materials. Collision-induced dissociation in the mass spectrometer has been demonstrated to be an ideal route to study such multicomponent supramolecular interactions [313]. These adamantyl urea and thiourea surface-modified PPIs have been shown to act as hosts for *N*-terminal BOC-protected peptide guests to generate CHCl₃-soluble complexes, which readily decompose upon treatment with mild acid [314]. The synthesis of the G4 PPI core coated with an *N,N*-bis[(3-adamantylureido)propyl]amine binding site was accomplished, and shown to act as a host for π-conjugated oligo(*p*-phenylenevinylene) guests [315]. Novel applications of these adamantane-terminated PPIs, to generate molecular print boards for structured surfaces essential for nanotechnological, electronic or biochip applications, have appeared [316,317]; the delivery of these dendrimer-CD complexes in solution to CD SAMs has been demonstrated by utilizing a competition between solution and surface host sites. An approach to analyze the supramolecular assemblies, derived from a guest HOC*(=O)CH₂NHC(=O)NHAr (**12a**) or (HO)₂P(O)CH₂NHC(=O)NHAr (**12b**), where Ar = 3,4,5-tri(tetraethyleneoxy)phenyl and C* = ¹³C, and the host **12c**, utilized ¹³C and ³¹P NMR [318,319]. The statistical analysis showed that the guest **12a** formed a “polydisperse supramolecular aggregate,” whereas **12b** formed a “monodisperse supramolecular aggregate” at higher concentration; initial details concerning these supramolecular networks have appeared [320] (Schemes 11 and 12).

When treated with excess phenylisocyanate, the G3 PPI gave (60%) the desired phenylurea-coated surface, which with phenanthrenequinone generated the *H*-bonded host–guest complex, as determined by cyclic voltammetry data [321]. Phosphine ligands attached to urea acetic acid guests were supramolecularly bound to the surface of the dendritic polyhost, affording avenues to a coating of Pd-catalytic sites for an allylic amination reaction *via* either a batch process or continuous-flow membrane reactor [322].

Vögtle et al. [323,324] customized the surface of the G1–5 PPIs with dansyl groups. The resultant products were studied with regard to protonation, absorption [324], and photophysical [325] properties, as well as intradendrimer quenching and sensitizing processes; protonation was shown to initially occur within the dendrimer, then at the surface dansyl groups. The dansyl-coated G4 PPIs were shown [326] to exhibit a strong fluorescence that was quenched when the Co⁺² ion was

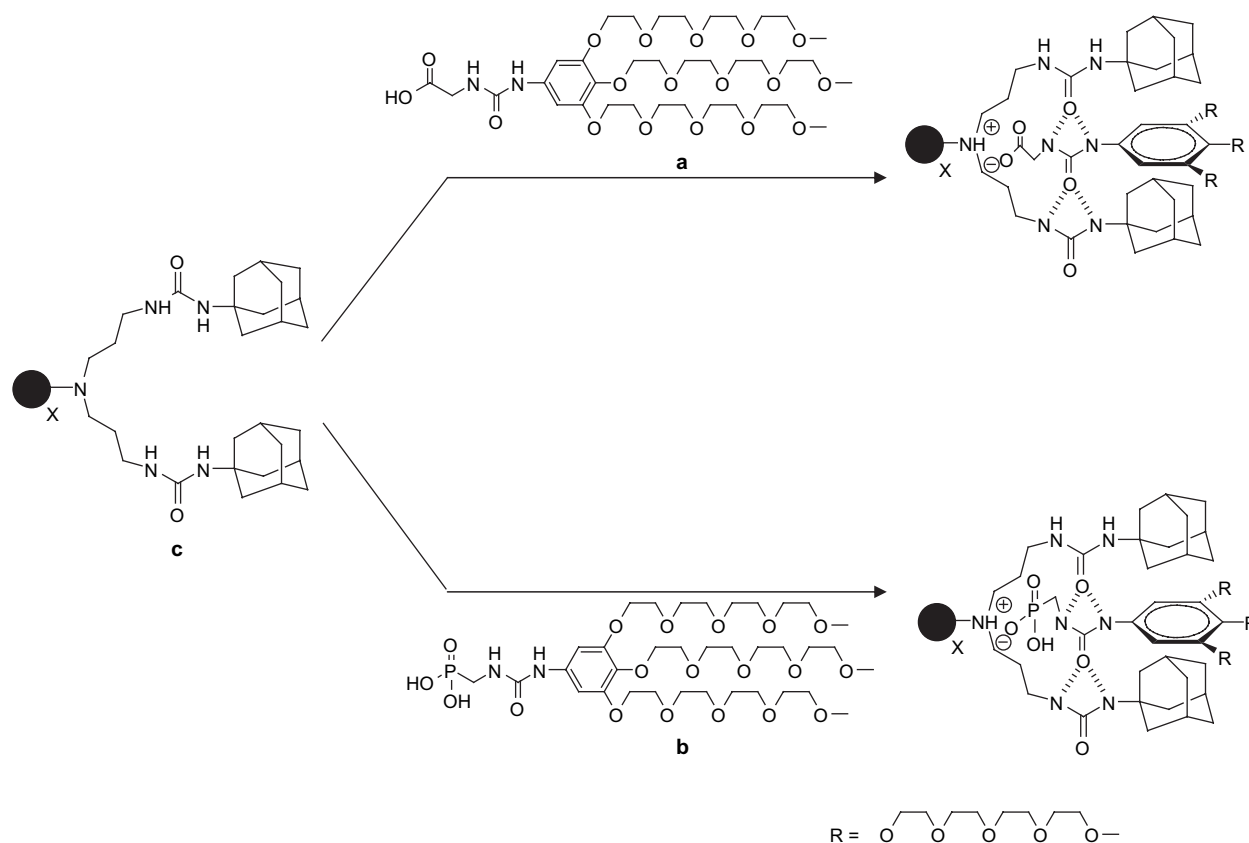


Scheme 11. A novel complex derived from host-guest surface locking.

N-coordinated within its interior; a Co^{2+} concentration of 4.6×10^{-7} M resulted in a 5% decrease in fluorescence intensity, revealing the potential to fine-tune this effect [324]. Utilizing eosin as a guest dye, these dendrimers in CH_2Cl_2 extracted eosin from water; the number of encapsulated dye molecules increased with generation size, up to a maximum of 12 at G5. The fluorescence of the surface dansyl groups was quenched *via* energy transfer with the added eosin; fluorescence of the hosted eosin was partially quenched; eosin can occupy two internal sites and the excitation of the eosin guest caused sensitization of the dioxygen emission *via* an eosin triplet excited state [327]. The molecular dynamics of this dansyl-coated G4 PPI, using a “cubic box” model with up to *ca.* 3500 solvent molecules and 12 eosin Y dye molecules, showed that multiple exits and entrances of the guests occur in less than a nanosecond until reaching the experimental number

of six, which are distributed at two different distances from the core [328]. The excitation energy transfer rates within G2–4 dansyl-coated PPIs complexed with eosin in CHCl_3 were characterized by time constants 1 and 6 ps and are independent of generation [329].

The PPIs coated with azobenzene-moieties embedded in a long alkyl chain have been shown to self-assemble in aqueous solution below pH 8 to give onion-like vesicles that are kinetically formed and can reach a thermodynamically relaxed state after light-induced isomerization [330]. Vögtle et al. [331] coated the surface of the G1–5 PPIs with related methyl orange moieties; molecular inclusion and subsequent release of the anionic substrates were controlled by modifying the pH. The protonation of these methyl orange surface-terminated PPIs clearly indicated that the higher generations dendrimers do not behave like methyl orange itself and that



Scheme 12. Methodology to evaluate the supramolecular aggregate.

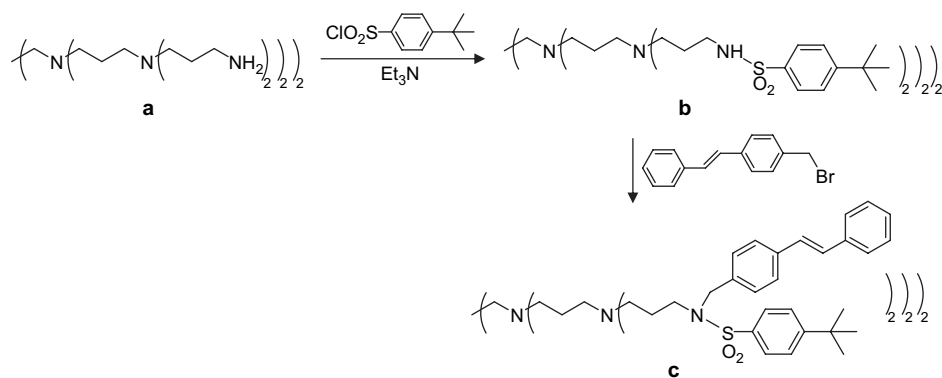
isomerization rates are extremely high and generation independent [332]. The reaction of the G1–4 PPIs with an excess of naphthylene-2-sulfonyl chloride gave the desired surface coated products, which were evaluated for the photophysical properties [333]. The G1–4 PPI family was also coated in a step-wise synthetic manner by the initial surface treatment with naphthylene-2-sulfonyl chloride forming the 2-naphthylsulfonamide moieties, followed by the N-alkylation with 4-bromomethylazobenzene, resulting in an equal number of naphthalene-2-sulfonyl and *trans*-azobenzene moieties [334]. The fluorescence of the naphthalene groups was quenched by the internal tertiary amines *via* electron transfer as well by the azobenzene units *via* energy transfer.

Vögtle et al. [335] terminally modified these dendrimers using various alkyl isocyanates (*i.e.*, hexyl, octyl, dodecyl, and phenyl) to produce efficient organic media hosts for oxyanions, specifically perchlorate, perchlorate, AMP, ADP, and ATP. Extractability rates were determined and the controlled guest release was demonstrated by pH dependent behavior, *e.g.*, greater host–guest binding occurred at a lower pH. Paleos et al. [336] described the novel use of these C₈- or C₁₈-coated G4 and G5 PPIs with urea connectivity as “nanosponges,” demonstrating their ability to encapsulate polyaromatic hydrocarbons from water down to a few parts-per-billion. These authors further demonstrated that the triethoxysilyl-functionalization of the G4 PPI followed by its reaction with porous ceramic filters generated a covalently bonded organosilicon dendritic polymer that was capable of removing polycyclic aromatics from water at a few ppb by continuous filtration [337]; the filter was effectively regenerated by treatment with MeCN.

The G1 PPI core was selectively *N,N*-bis(sulfonylated) with tosyl chloride and the mono-, di-, tri-, and tetra-*N*-tosylsulfonamides were isolated and characterized by a combination of MALDI-TOF and ESI-FT-ICR MS [338,339]. It is of interest to note that the related G2 PPI resulted in cleavage of the central

C–N bond upon similar persulfonylation; whereas N-alkylation with benzyl bromide was not selective but rather gave the completely alkylated product. The PAMAM counterpart was also shown to be stable during the sulfonylation and that no decomposition of the backbone was detected [338]. Treatment of the G3 PPI (**13a**) with 4-*tert*-butylbenzenesulfonyl chloride in CHCl₃ with Et₃N gave (90%) the yellow octa-mono-substituted **13b**, which was subsequently reacted with a slight excess of 4-bromomethylstilbene affording (29%) the desired **13c** [340]. It was observed that the dendritic specie **13b** possessed significantly different spectroscopic, photophysical, and photochemical properties than a monomeric reference, thus lending support to a “dendrimer effect” as described by others [341–347] (Scheme 13).

Amphiphilic architectures (Fig. 2) with a 1 → 2 *N*-branching motif as well as hydrophobic and hydrophilic terminal chains have been created [348,349]. These potentially water-soluble catalysts were generated by treatment of the G4 PPI initially (1) with octanoyl chloride, followed sequentially by (2) reduction (LAH) to the secondary amine, (3) addition of triethylene glycol acid chloride, (4) further reduction to give the polyamine precursor, and lastly (5) quaternization with MeI [and (6) I[−] → Cl[−]] to give the polyammonium catalyst [350]. These quaternary ammonium chloride dendrimers [349] were shown to act as hosts for diverse guests, *e.g.*, Reichardt’s dye and pyrene, in an aqueous environment and to enhance (500× over water alone) the rate of decarboxylation of 6-nitrobenzoxazole-3-carboxylic acid. The molecular dynamics (NMR) studies of the G2, 4, and 5 PPIs terminated with the hydrophilic triethylenoxy methyl ether were conducted, and it was concluded that the PEG moieties were preferentially located on the periphery extending into the external aqueous surroundings [351]. Reductive methylation of the G2 PPI with formaldehyde and formic acid produced predominately the terminal –NMe₂ functionality in



Scheme 13. A step-wise selective mono-substitution of the PPI surface [340].

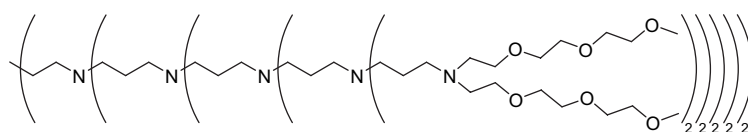


Fig. 2. Amphiphilic catalysts in aqueous media [348].

a *ca.* 6.3–1.7 (tertiary to secondary substitution) ratio. This mixture was then treated initially with octyl or dodecyl bromide in DMF, followed by ion exchange to afford a mixture of predominately terminal alkylation; notably, a minor amount of internal substitution was present [352]. For comparative purposes, decarboxylation of 6-nitrobenzisoxazole-3-carboxylate was determined to be 650 times faster in the presence of the PPI with eight dodecyl chains than in water alone [352].

The water-soluble, oligo(PEG)-terminated PPIs, derived from the 3,4,5-tris(tetraethylenoxy)benzoyl moiety, demonstrated unimolecular micelle character by the incorporation of anionic, water-soluble xanthene dyes, *e.g.*, 4,5,6,7-tetrachlorofluorescein or Rose Bengal [353]; the latter formed a stronger complex with the G5 dendritic host. The PEGing of the G5 PPI's surface was readily accomplished by its treatment with methoxypoly(ethylene glycol)isocyanate (MW 5000) in aqueous Me₃N [354]; these materials were evaluated as potential drug carriers for betamethasone corticosteroids [355]. The treatment of G2, 4, and 5 PPIs with 2-[2-(2-methoxyethoxy)ethoxy]acetyl chloride in DMF and Et₃N afforded (*ca.* 80%) the desired hydrophilic triethylenoxy methyl ether (TEO) coated materials [356]; the effects of diffusant size, polymer concentration, and temperature on the self-diffusion coefficients were studied by pulsed-field gradient NMR.

Noble and McCarley [357] treated the PPI series with 2,5-dimethoxytetrahydrofuran in AcOH and MeCN to transform the amine termini to pyrrole moieties. Exposure of this pyrrole-surface to gold resulted in surface adsorption, as evidenced by reflection–adsorption infrared (RAIR) spectra. The electrochemical oxidation of these polypyrrole films facilitated an *intramolecular* pyrrole oligomerization. Films formed on PPI–pyrrole₁₆/Au were found to be extremely scratch resistant, but these films could be partially removed by repeated attachment and removal with Scotch™ tape [358]. Ong and McCarley [359] coated the G5 PPI with redox-active donor functionality derived from 4-(dimethylamino)benzoyl chloride or 4-(dimethylamino)phenyl isocyanate; in that manner, there was a positive dendritic effect for the formation of charge-transfer complexes between the coated PPI and 7,7,8,8-tetracyanoquinodimethane. These authors further treated the PPI series with succinimidyl β,β-2,4,5-pentamethyl-3,6-dioxo-1,4-cyclohexadiene-1-propanoate to generate a redox-labile, trimethyl-locked termini that subsequently released these end-groups, as free 6-hydroxy-4,4,5,7,8-pentamethylnaphtholactone upon mild chemical or electrochemical reduction; in essence, to restore the initial dendrimer [360,361]. The synthesis and guest hosting of Nile Red in an aqueous media were accomplished by the surface coating of G4 and 5 PPI dendrimers with –NHC(=O)(CH₂)₄(NC₄H₃)-(CH₂)₂O(CH₂)₂OMe [362].

Surface coating of PPIs and PAMAMs with salicylate, catecholate, and hydroxypyridinoate has been accomplished and spectrophotometric titrations were used to investigate their metal binding properties [363].

The PPI family was surface-coated with pyrene and examined by fluorescence spectroscopy in order to evaluate the generational dependence of steric crowding on the surface; based on

pyrene–pyrene interactions, excimer emission showed little or no evidence for *intermolecular* interactions [364]. Evidence for preassociated pyrene moieties and protonation causing a slight increase in the excimer fluorescence was, however, observed.

The surface attachment of the redox-active phenothiazine has been reported [365] and shown to exhibit only one oxidation state due to severe Coulomb repulsion between the oxidized units. Treatment of G5 PPI with 2-(2,3-epoxy)propoxylthioxanthone in EtOH at 40 °C for 12 h gave (89%) the desired dendritic macrophotoinitiator while still retaining the thioxanthone coating [366]; the dendrimer was demonstrated to be a more efficient photoinitiator for free radical polymerization than the low molecular weight counterpart derived from the G1 PPI.

The perfluorinated PPIs have been used as phase transfer catalysts in supercritical carbon dioxide and shown [367] to be capable of catalyzing halogen exchange, *e.g.*, benzyl chloride into benzyl bromide, as well as the esterification of pentafluorobenzyl bromide with oxalic acid. It was demonstrated that the tier size of the PPI is important; if it is too large, it is difficult for the substrate to be encapsulated within the dendrimer.

Hybrid polymers were prepared by grafting living cationic poly(THF) onto the surface of the PPI dendrimers [368]; NMR studies permitted the estimation of the degree-of-grafting. A core-first approach to the preparation of well-defined dendrimer-star macromolecules as well as block copolymers, using the dithiobenzoate-terminated G2 and G3 PPIs, a multifunctional RAFT agent has been formed [369]; the polymerization kinetics was pseudo-first-order and the analyses showed that the dendrimer-star possessed low polydispersity (PDI < 1.3) [370]. These reagents were prepared (95%) by the treatment of the PPI with succinimidyl 4-cyano-4-[(thiobenzoyl)sulfonyl]pentanoate, which was prepared from 4-(4-cyanopentanoic acid) dithiobenzoate [371]. The kinetics and mechanistic aspects of ε-caprolactone and L,L-lactide polymerization initiated by Sn(2-ethylhexanoate)₂/G2 or G4 PPI amine-terminated dendrimers have also been investigated [372]. Polymer networks incorporating PPIs have been reported [373] in which either the bifunctional living poly(THF) was reacted with the aminodendrimer or the living poly(THF) was grafted to the PPI to form a star-like acrylate-terminated poly(THF) multi-macromonomer; the network was then formed by means a Michael reaction with the unreacted amino-termini.

The incorporation of the G5 PPI dendrimer into mesoporous silica was accomplished [374] by a HCl treatment of an anhydrous MeOH solution of tetraethyl orthosilicate (TEOS) with a 1-propanol solution of G5 PPI. After oven-drying at 373 K for 20 h, the solid was heated in a quartz U-tube under a nitrogen flow for 3 h at 803 K to give a brown powder, which was finally heated under a flow of air from ambient temperature to 833 K; the related PAMAM dendrimers were also used as templates [375]. The G5 PPI was used as a macrochelating agent to produce well-dispersed CuO nanoclusters within the silica sol-gel matrix [376]; the material was well-characterized and it was suggested to be applicable to other transition metals.

Multilayer films were prepared using G3 PPI with the NLO-active {poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamide]-1,2-ethanediy] sodium salt]} [PAZO], in

which the terminal layer was shown to be more loosely packed than the non-terminal layers possessing “interpenetrated zones” comprised of both PPI and PAZO [377].

The G4 PPI was surface-coated by its treatment with 2-diphenylphosphinobenzaldehyde in EtOH and CH₂Cl₂ under argon and in the presence of Na₂CO₃ yielding (100%) the –N=CHC₆H₄PPh₂ termini, which were subsequently reduced (NaBH₄) to the corresponding –NHCH₂C₆H₄PPh₂. Both of these *P,N*-ligands were demonstrated to activate electron-rich aryl bromides in the Heck reaction [378].

Chen et al. [379] functionalized the G3 PPI with dimethyldodecylammonium chloride units and demonstrated that these materials possessed strong antibacterial properties [380]. These novel dendrimers were further studied using Gram-negative *Escherichia coli* employing a bioluminescence protocol and shown to be very potent biocides [381]. The related G1–5 PPIs with surface dimethyl(do)decyl (chloride) moieties have been shown to be dendritic biocides that are more potent than their small molecule counterparts [382]. Surface modification of the G4 and G5 PPIs with glycidyltrimethylammonium chloride was accomplished in order to prepare pH-sensitive controlled-release systems; the studies of Paleos et al. [383] with pyrene support their prospects for drug delivery applications.

Interaction of the PPI series with linear polyanions, e.g., poly(sodium acrylate), poly(acrylic acid), poly(sodium styrenesulfonate) or native DNA, was evaluated by means of potentiometric, argentometric, and turbidimetric titrations [384], demonstrating that for flexible polyanions, interpenetration of the dendrimers was observed. Non-viral transfection systems based on the complexes of DNA and polycations (Superfect™ and Astramol™, as well as others) were evaluated [385] for their effectiveness, toxicity, and cell-type dependence in various *in vitro* models. In general, this study demonstrated the potential of these and related polycationic systems to be potential transfection agents with relatively low toxicity.

The interactions between salmon sperm (300–500 bp) and bacteriophage T4dC DNA (166 kbp) and G1–5 PPIs showed that G4 and G5 formed positively charged water-soluble interpolyelectrolyte complexes that revealed a wound double-helical structure [386]. Using fluorescence microscopy, compaction of individual ultrahigh molecular mass DNA interacting with excess G4 PPI was observed to form these interpolyelectrolyte complexes (“unimers”). Nanogels or aggregates of the DNA with dendrimers were also subjected to AFM analysis to certify their morphology and formation [387].

The synthesis of guanidylated G4 and G5 PPIs was accomplished by the treatment of the PPI with 1*H*-pyrazole-1-carboxamide hydrochloride [388] in the presence of diisopropylethylamine [389]. The interaction of phosphatidyl choline-cholesterol liposomes, incorporating dihexadecylphosphate [390], as the recognizable lipid with the guanidylated PPI, afforded the liposome-dendrimer aggregates, which were dispersed with added excess phosphate buffer. The surface functionalization of the PPIs with porphyrin moieties has been reported [391]. The time-resolved fluorescence anisotropy measurements on the G5 porphyrin-coated PPI are best

envisioned by a model that includes independent and simultaneous rapid electronic energy transfer between surface porphyrins and a slow energy transfer between porphyrins attached either inside or outside the sphere [391]. Larsen et al. [392] similarly reported the energy transfer process within a series of Zn-porphyrin-coated PPIs using this same technique and showed that energy transfer between the porphyrin units is limited to a maximum of four units as modeled by the Förster theory. The solvent-induced-optimization of this porphyrin series was studied by exciton–exciton annihilation; thus changing the solvent from polar to non-polar increased the energy transfer rate by 28–44%, which is related to a decrease in the hydrodynamic radius [393]. The surface-coupling of pheophorbide *a* (Pheo: a porphyrin-type structure isolated from *urtica urens*) to G3 PPI *via* an activated ester (*N*-hydroxysuccinimide) afforded a dendrimer with an average of two Pheo molecules per dendrimer [394]. The use of photosensitized-generated singlet oxygen was sufficient to destroy the dendrimer’s infrastructure *via* effectively releasing the surface dye molecule without additional chemical agents.

Twyman et al. [395] treated the G3 PPI with an excess of succinidyl 4-pyridinecarboxylate [396] affording a low yield of the coated dendrimer possessing 16-amidopyridino moieties in which the *N*-electrons were directed outward. The subsequent addition of a solution of a zinc porphyrin trimer generated a novel dendrimer–porphyrin complex possessing *ca.* 6 trimers to the pyridine ligands, suggesting a self-assembled porphyrin sphere containing 11 coordinated porphyrins and one uncoordinated Zn-porphyrin; the number of terminal porphyrins was limited by steric congestion. The PPI series with pseudorotaxane-termination was prepared in three-steps by initial treatment of the PPI surface with mono-Cbz-protected diaminobutane, followed by deprotection (HBr/AcOH) affording the protonated diaminobutane termini, which, with cucurbituril, generated the desired supramolecular assembly [397]. It was proposed that such a surface functionalization would be a convenient procedure to trap internal guests within the dendrimer, while dethreading of the surface will release the internal guest; all or part of the surface components are readily dethreaded with added base. The ternary complex of PPI–[NHC(=O)CH₂N⁺H₂(CH₂)₄NH₃⁺]_{*n*}, DNA, and cucurbituril was evaluated as a totally self-assembled gene delivery carrier [398]; this complex was able to transfect mammalian cells with high efficiency and possessed relatively low cytotoxicity.

The G5 PPI–(1B4M-Gd)₆₄ was synthesized from G5 PPI derived from the diaminobutane core conjugated with a bifunctional diethylenetriaminepentaacetic acid derivative for the complexation of Gd(III) atoms [399]. The dynamic micro-MRI of this complex was obtained in a mouse liver metathesis model using colon carcinoma cells and was shown to be a potential contrast agent [400]. Similar studies were conducted using G3–5 PPIs, in which these Gd MRI contrast agents were expelled by the kidneys more rapidly than the PAMAM counterparts [401]. A simple four-step preparation of Gd-DTPA-terminated G1, 3, 5 PPIs, as well as the mixed gadolinium and yttrium complexes derived from the G5 PPI, has been reported by Meijer et al. [402].

Fructose modification of these PPIs for heptacyte apoptosis suppression has been examined [403]. The covalent attachment of multiple phenylisothiocyanate derivatives of oligo-GM1 to the G1 and G2 PPIs generated derivatives capable of inhibiting adherence of the binding subunit of cholera toxin (cholera genoid) and heat-labile enterotoxin of *E. coli* to immobilized GM1 [404,405].

A recent proposed use of the PPI dendrimers as therapeutic agents for neurodegenerative disorders, such as prion and Alzheimer's diseases, in which the formation of amyloid plaques was shown to be the critical pathological event, has demonstrated that these dendrimers show the potential to be "very effective against fibril formations" for both of the peptides related to these diseases [406]. The direct attachment of the PPI that was surface activated with a cysteine residue to the C-terminus of a protein has been demonstrated [407]; the remaining cysteine residues can be further functionalized with other oligopeptides.

Preliminary *in vitro* transfection studies have shown that bifunctional cationic compounds comprised of trivalent galactosides (for cell targeting) and G2 PPI (as the DNA binding domain) could effectively deliver the genes to hepatocytes [408].

A series of G1–3 PPIs coated with polyphosphazene were prepared by a simple procedure in which the dendrimer was the core for *P*-growth [409]. Initially, triethoxyphosphoranimine [(EtO)₃P=NSiMe₃] was initiated with 2 equiv. of PCl₅ at 25 °C in CH₂Cl₂ to generate the initiator [(EtO)₃P=N–PCl₃⁺ PCl₆[–]], which with given amounts of [Cl₃P=NSiMe₃] created the [(EtO)₃P=N(PCl₂=N)_n–PCl₃⁺ PCl₆[–]] with specific lengths, in this case *n* = ca. 20 units. The addition of this living species to the G1–3 PPI–NH[–P=N–SiMe₃(OCH₂CF₃)₂]_{4,8,or16} gave the desired coating of polyphosphazene.

3.1.3. PPI-dendrons

A G3 PPI-like dendron has been prepared from ethylenediamine by its initial monoprotection with di-*tert*-butyl dicarbonate, followed by addition of CH₂=CHCN with subsequent reduction. This procedure was repeated, and then treated with bromoethanol to generate the G3 dendron with hydroxy-termini. Removal of the BOC-protection followed by addition of BrCH₂CO₂H gave the desired (HO₂CCH₂)₂NCH₂CH₂N–[(CH₂)₃N[(CH₂)₃N[(CH₂)₂OH]₂]₂] [410]. This was added to a CdSe/CdS core to generate water-soluble stabilized nanocrystals.

Poly(propylene imine)-like wedges through G5 have been assembled on one end of polystyrene, thereby forming a macromolecular surfactant. For polystyrene–PPI hybrids possessing multiple CO₂H termini, a pH-dependent [411] aggregation

was observed [*e.g.*, PS-dendri-(CO₂H)₈ formed "worm-like" micelles at high pH; PS = polystyrene, dendri = the PPI-dendron head group]. The amine-coated head groups [*i.e.*, PS-dendri-(NH₂)_n] led to generation-dependent aggregation [412]; aqueous solutions were observed to possess micellar spheres, rods, and vesicles for –(NH₂)₈, –(NH₂)₁₆, and –(NH₂)₃₂, respectively. Meijer et al. [413,414] constructed a PPI–linear polystyrene (*M*_n = 2 × 10³, *M*_w/*M*_n = 1.04) diblock polymer termed "macroamphiphiles" (Fig. 3). The construction was initiated from the carboxylic acid terminus of the polystyrene, which was initially reduced (LAH), cyanoethylated (CH₂=CHCN), and reduced again (Raney Co, H₂) to generate the amine surface. Standard iterative divergent PPI synthesis was exploited giving access to the series of PPI dendritic head groups. One of the more fascinating aspects of these copolymers was their aggregation behavior. As revealed by TEM imaging, aqueous aggregation for the G3–5 dendrons afforded flexible bilayers, rod-like micelles, and spherical micelles, respectively. Further study of these materials by SAXS and TEM supported the aggregation phenomena [415].

Tokuhisa and Crooks [416] covalently linked the PPIs to self-assembled monolayers in order to prepare chemically sensitive interfaces with the potential to detect volatile organic compounds (VOCs). Prior to monolayer attachment, dendrimer prefunctionalization was found to generate more sensitive surfaces due to the enhanced surface densities of the "active" termini. With benzamido-terminated dendrimers, the method of preparation and the π-stacking of the surface functionality with the VOCs were determined to be important factors.

The G3 PPI, acting as polycations, has been incorporated into linear poly(phenylene vinylene)-based, self-assembled polymer superlattices for the investigation of controlled unidirectional energy transfer [417]. The conjugated polymer–polyelectrolyte assemblies of G3 PPI and poly(2,5-methoxypropyloxysulfonate phenylenevinylene) [418] were prepared in an aqueous environment and characterized by absorption and fluorescence spectroscopy [261]. The photophysical properties of the polyelectrolytes were controlled by modifying the type and concentration of an added electrolyte.

The use of calixarene as a core for dendritic growth was shown by the treatment of the known aminoalkoxycalix[4]arene with acrylonitrile, followed by reduction and acylation with *p*-nitrophenyl(diphenylphosphoryl)acetate to generate the calix-{O(CH₂)₃N[(CH₂)₃NHC(=O)CH₂PPh₂(=O)]₂}₄ that was used for metal ion extractions [419].

A one-step activation [420] of silicon surfaces with 1,1'-carbonyldiimidazole (CDI) has been utilized to further attach the

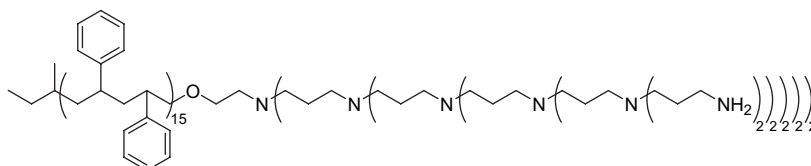


Fig. 3. PPI-capped polystyrene (27) by Meijer et al. [413,414].

amine-terminated PPI dendrimer, thus immobilizing the dendrimer on the surface [421]. The surface was evaluated by amine titration, protein coverage, and chemical activity; this procedure provides a route to a protein biochip fabrication.

Dendrons coated to the gold surface have also appeared [422], on which the surface was treated with a hydroxy-terminated G3 dendron $\{\text{HS}(\text{CH}_2)_2\text{N}[(\text{CH}_2)_2\text{N}(\text{CH}_2\text{CONHCH}(\text{CH}_2\text{OH})_2)_2]\}_2$, DSC activated and lastly treated with a G2 PPI coating. This is a different approach to the attachment of the PPI to a gold surface.

3.1.4. Catalytic activity

The surface coating of G1–3 PPIs with the reactive $\{[\eta^5\text{-C}_5\text{H}_4\text{COCl}]\text{Fe}[\eta^5\text{-C}_5\text{H}_4\text{CON}[\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_5]\}$ was accomplished by treatment with equimolar amounts of 1,1'-ferrocenedicarbonyl chloride [423] and 1-aza-18-crown-6 in the presence of Et_3N at 25 °C under an inert atmosphere [424]. Ferrocene-coating of PPIs has been accomplished [39,106,425–434] as well as the introduction of surfaces of ferrocenyl moieties [435–437], opening interesting pathways to molecular print boards utilizing β -cyclodextrin.

The surface-coating with diverse metal sites has taken many different forms in order to generate a recoverable homogeneous catalyst: initial attachment of bis-*P*,*P* sites for subsequent metal complexation with $\text{Ru}(\text{CO})_3/\text{Ru}(\text{CO})_4$ clusters [438], $[\text{Ru}_5\text{C}(\text{CO})_{12}]$ [439], $[\text{Au}_2\text{Ru}_6\text{C}(\text{CO})_{16}]$ [439], $[\text{Rh}(\text{cod})_2]$ [440], or $\text{Pd}(\text{II})$ [441–447], as well as $-\text{N}(=\text{CH}-2\text{-PyrPdCl}_2)_n$ [448], ferrocenyl-urea termini [426], directly connected ferrocenyl- $[\text{NHC}(\text{O})\text{cobaltocene}]_n$ [449], mixed ferrocene-cobaltocenes [450], $-\text{[NHC}(\text{O})\text{C}_5\text{H}_4\text{Co}(2,3\text{-Et}_2\text{B}_3\text{H}_5)]_n$ [451], $-\text{[NH}(\text{O})\text{COCH}_2\text{CH}_2\text{C}(\text{O})\text{C}_5\text{H}_4\text{Rh}(\text{NBD})]_n$ [452,453], $-\text{[NHC}(\text{O})\text{C}_5\text{H}_4\text{W}(\text{CO})_3\text{Me}]_n$ [454], $-\text{[Pt}(\text{NH}_3)_2\text{Cl}]$ [455], $-\text{[NHC}(\text{O})\text{CH}_2\text{CH}_2\text{P-Ph}_2\text{AuCl}]_n$ [456], $-\text{[NTfSc}(\text{OTf})_2]_n$ [457], and internal and surface *N*-complexation with $\text{Cu}(\text{II})$ [255,376,458–460], $\text{Zn}(\text{II})$ [460,461] or $\text{Co}(\text{III})$ [460].

The surface-coating of the PPI dendrimer with different combinations of triazacyclononane moieties afforded sites for $\text{Zn}(\text{II})$ coordination generating metallodendrimers that can act as active catalysts for the cleavage of the RNA model substrate: 2-hydroxypropyl-*p*-nitrophenyl phosphate [461].

The Fe^{+3} encapsulation within the G4 PPI was shown to form a Fe at dendrimer catalyst that was subsequently used in the production of carbon nanotubes [462], which were shown to possess an average diameter of 20–25 nm, smaller than those derived from previous procedures at lower temperatures.

The intramolecular segregation of G4 PPI and oxygen plasma modified high density polyethylene was studied with low-energy ion scattering (LEIS) and XPS [463]. The reaction of G4 PPI with $\text{Cu}(\text{II})$ was shown by LEIS to form a metallodendrimer in which the $\text{Cu}(\text{II})$ atoms are complexed by surface

tridentate coordination suggesting that there is high potential for these materials to be catalysts.

A series of metallodendrimers assembled by means of bis-(terpyridinyl) $\text{Ru}(\text{II})$ connectivity on G2 PPI scaffolds with homogeneous or heterogeneous surfaces were prepared [464]. The DSC and TGA studies were used to ascertain their thermal behavior, glass-transition temperatures, and decomposition kinetics and temperatures [465].

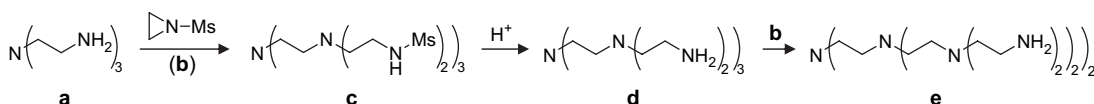
A perfluoropolyether coated G5 PPI [223] was converted to the corresponding $\text{Pd}(0)$ nanoparticle [466] possessing 1–2 nm catalytic centers in a pure, inexpensive and environmentally benign liquid or supercritical CO_2 ; the versatility of the encapsulated catalysts has been reviewed [467,468]. Examples are: styrene to ethylbenzene [469] and iodobenzene with methyl acrylate (Heck reaction) [466,469]. Palladium-based G1–5 PPI nanoparticles were prepared by treatment of the PPI dendrimer with an aqueous solution of K_2PdCl_4 , followed by reduction to the $\text{Pd}(0)$ nanoparticles [470]; the catalysis of the Suzuki cross-coupling reaction [471] was conducted.

The encapsulation of diverse metals within the PPI's infrastructure, although the PAMAM family are the dominate hosts, has been reported by many groups and the incorporated salts have been readily reduced to generate the desired nanoparticle: $\text{Pd}(\text{II})/\text{Pd}(0)$ [280,444,445,466,470,472]; $\text{Pt}(\text{II})/\text{Pt}(0)$ [472]; $\text{Ag}(\text{I})/\text{Ag}(0)$ [472–474]; $\text{Au}(\text{III})/\text{Au}(0)$ [246,475–480], and Ti or V doped [481].

3.1.5. 1 → 2 *N*-branched, alkyl connectivity (other than PPI-type)

The polyethylene imine (SPEI) dendritic series, possessing the shorter (than in the PPI series) ethano spacer, was prepared [482] by the nucleophilic addition of an amine to *N*-mesylaziridine (*i.e.*, **14b**). Addition of excess **14b** to a simple branched tetraamine **14a** generated the partially protected polyamine **14c**, which was easily deprotected to generate the terminal hexamine **14d**; further treatment of **14d** with excess **14b** created successive generations (*e.g.*, **14e**). Due to the very short distance between branching centers, the resultant dendrimers reached dense packing limits at a low generation [482] in which “divergence from branching ideality becomes significant as one approaches generation 3 or 4 and especially at generation 5” [227]. Treatment of the G3 SPEI with stoichiometric amounts of octanoic acid formed lamellar liquid crystals [483], as demonstrated by polarized optical microscopy and IR data, thus revealing the absorbance of carboxylate moieties. The liquid crystalline phase was postulated to give rise *via* a supramolecular ordering of the alkyl chains above and below the plane of the flattened dendrimer (Scheme 14).

Suh et al. [484] attached β -cyclodextrin (CD) units to the surfaces of the G3,4 poly(ethylene imine)s, similarly prepared



Scheme 14. The congested poly(ethylene imine) dendrimers generated with *N*-mesylaziridine [482].

except using *N*-tosylaziridine, by terminal amine reactions with mono-6-(*p*-toluenesulfonyl)- β -cyclodextrin; ^1H NMR data indicated the attachment of 0.87 and 1.05 CD moieties, respectively. *p*-Nitrophenyl esters possessing CD cavity affinity underwent rapid aminolysis when complexed to the CD-dendrimer complement; kinetic data suggest that diacylation occurred quickly and that two amino moieties were involved in the aminolysis.

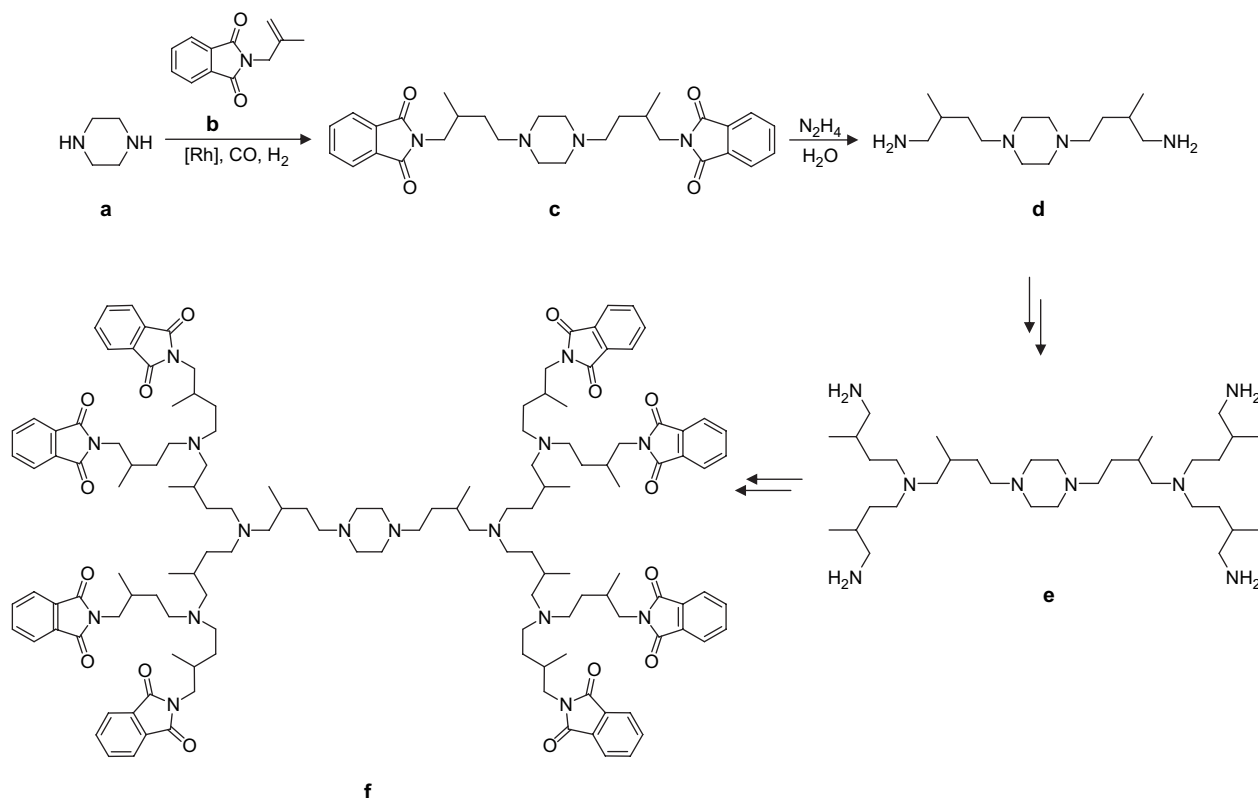
The Rh-catalyzed reaction of amines with olefins *via* a hydroformylation/reduction sequence has been applied, divergently, convergently, and on solid supports, to generate a new family of dendrimers [485]. The treatment of piperazine (**15a**) with methallylphthalimide [486] **15b** in the presence of $[\text{Rh}(\text{COD})\text{Cl}]_2$ gave (95%) the bis-phthalimide **15c**, which was cleaved (98%) in the presence of hydrazine to afford the desired tetraamine **15d**. Subjecting **15d** under this two-step sequence gave rise (94 and 84%) to the next generation **15e**; the octamer **15f** was then formed but in a diminished yield (35%) (Scheme 15).

3.2. 1 \rightarrow 2 *N*-branched, amide connectivity (PAMAM-type)

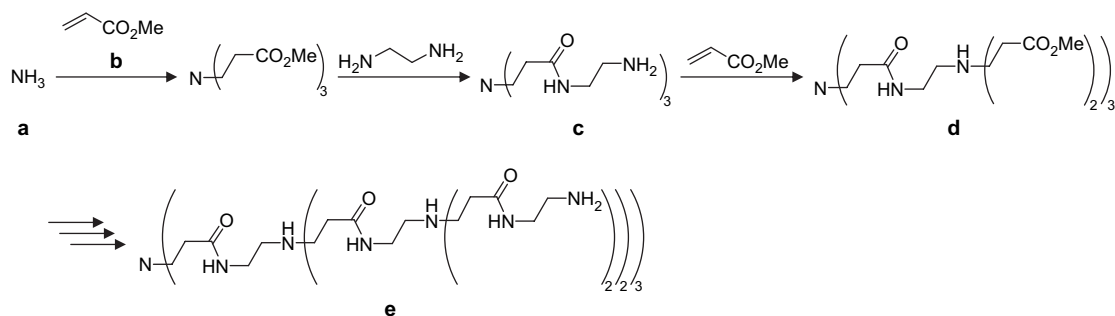
In 1985, Tomalia et al. [24,487] initially reported in the literature the synthesis of polyamidoamine dendrimers, which were generated from a three-directional core (*e.g.*, ammonia) and possessed 1 \rightarrow 2 *N*-branching centers as well as amide connectivity. Each generation was iteratively constructed by the exhaustive Michael-type addition of methyl acrylate to

the amine termini (*e.g.*, for an ammonia core, **16a**) to generate a β -aminoacid ester (*e.g.*, **16b**), followed by amidation with excess ethylenediamine to produce the new, branched polyamine **16c**. This general procedure was repeated to create the higher generations (*e.g.*, **16e**). Similar dendrimers were prepared by employing related cores, such as ethylenediamine as well as aminoalcohols and other functionalized groups, such as amino and thiol moieties [488]. This procedure is applicable to most primary amines, resulting in the 1 \rightarrow 2 *N*-branching motif and has been commercialized based predominantly on an ethylenediamine core resulting in the most readily available dendritic [PAMAM] architecture to-date. Other stable and practical frameworks have been considered [489–491] and will be demonstrated later in this review (Scheme 16).

In order to realize a high degree of synthetic perfection at each step (or a quest for monodispersity) in the intermediates and products, the potential synthetic problems associated with amidations using esters, such as *intramolecular* cyclization (lactam formation), *retro*-Michael reactions [492], incomplete addition, and *intermolecular* coupling have to be minimized; thus large excesses of the diamine, maintaining reaction temperatures ($<80^\circ\text{C}$), and avoiding aqueous solvents are critical to optimize the conversion at each branching termini [24]. This simple two-step procedure was noteworthy by allowing the preparation of high molecular weight dendritic polymers possessing a repetitive, fractal-branched infrastructure. It is important to note that even with optimized conditions, defects produced by these undesired reactions can be, for the most



Scheme 15. Preparation of polyamine dendrimers by means of a tandem hydroformylation/reductive amination procedure [485].

Scheme 16. Typical PAMAM construction *via* a divergent process [487].

part, suppressed but not totally circumvented. An ESI-MS study (reported in 1999) on the G4 PAMAM indicated that the analyzed sample possessed a structural purity of <8% [158]; this may bear out the statement “...the excess EDA required to make 95% or greater purity at generations higher than 4.0 becomes prohibitive experimentally” [493]. Although these dendritic structures derived from commercial sources possess low structural ideality at $G > 4$, Baker et al. addressed the question – if these commercial PAMAMs possess both generational and skeletal disparity due to the divergent synthetic methodology, how many terminal amine groups reside on the proposed spheroidal surface? Their conclusions, based on the G5 PAMAM used in their engineered nanodevices, were derived from acetylation studies from which it was concluded that the model G5 PAMAM had a “practical number of terminal amino groups” of 110 (calculated by NMR and potentiometric acid–base titration [494–496] *vs.* the theoretical number of 128). The use of capillary electrophoresis added further support to the assessment of the these nanoplatfroms for novel medical applications [494].

The related PAMAM-type dendrons have been conveniently and efficiently synthesized on a solid support, and the products possessed good homogeneity [497]. This solid-phase procedure demonstrated that peptides and drugs can also be attached directly onto dendrimer lattices or bound *via* a linker to its periphery. The G0–5 PAMAMs were synthesized and capillary zone electrophoresis was used to separate the different generations as well as for the characterization of specific generations [498]. Particularly, the hyperbranched PAMAM or the “dendrimer equivalent” has been reported [499,500] and shown to possess a M_n of *ca.* 2000 and a polydispersity of 2 [501].

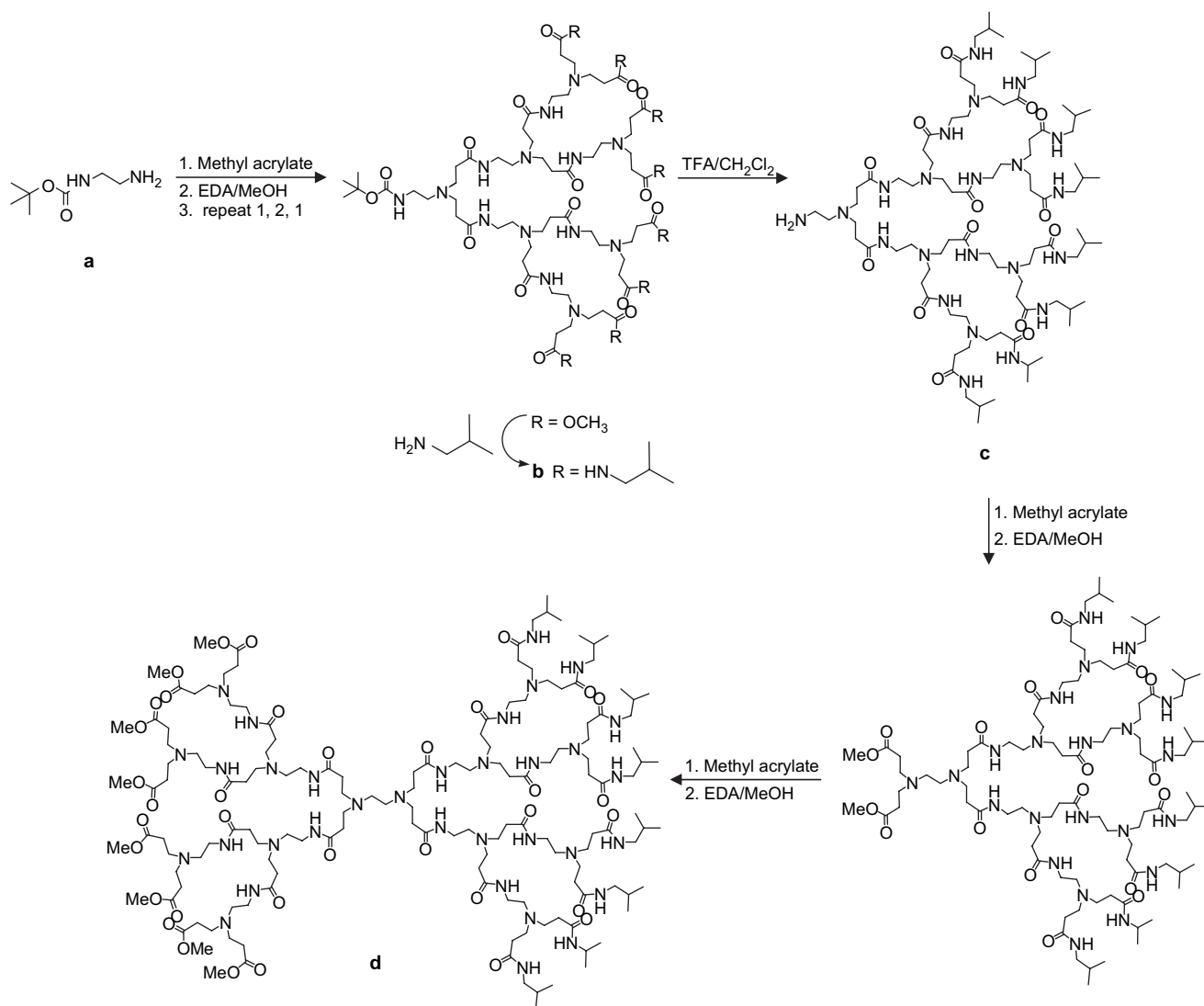
The “genealogically directed” synthetic nature of the PAMAM preparative protocol was elaborated by Dvornic and Tomalia [502]. This protocol was essentially comprised of an “excess monomer method” facilitating the isolation of dendritic intermediates (*i.e.*, generations) without excessive loss due to potential side reactions that may occur with the reagents that were not intended to be structurally incorporated. Thus, true molecular genealogy of this series can be examined from generation to generation by electrospray mass spectroscopy. These authors [503–505] further published a treatise describing the use of PAMAMs, as well as the concept of other dendritic systems, to branched macromolecular architectures.

Unsymmetrical PAMAM-like dendrimers **17d** have been crafted by a divergent/divergent strategy whereby after the focal site (**17a**) was *t*-BOC-protected, the typical sequential growth was terminated at the desired generation (*e.g.*, **17b**) by capping with *iso*-butylamine – the focal group was deprotected to generate a new starting point (**17c**) for elaborating the other direction [506]. This procedure also gave rise to the formation of the PAMAM-like dendron series (Scheme 17).

There have been numerous reviews over the structure, size, and shape of the PAMAM family by Tomalia et al. [227,504,507–533].

3.2.1. PAMAM physical and spectral studies

Computational [534–536] and Monte Carlo simulations [182,185,537–551], molecular modeling [552–554], molecular dynamics [546,555–559], atomistic molecular dynamics simulations [559], Rouse dynamics [560], comparative and electron microscopy [561], Brownian Dynamics simulation [562–564], holographic relaxation spectroscopy [565], and diverse physical characterizations [493,536] of these macromolecules have included standard spectroscopic methods, *e.g.*, ^1H , ^2H [566–569], ^{13}C [536,570], and PFG [571] NMR [572,573], IR, electrospray ionization (ESI) mass spectrometry [502,574–576], MALDI-TOF mass spectrometry [577–580] and with different matrices [581], Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) [582], HPLC, GPC, DSC, TGH, PAGE and CE electrophoretic methods [494,495,583–588], intrinsic viscosity measurements [589–591], rheology [592,593], vapor–liquid equilibrium data [594] by classic isothermal gravimetric-sorption [595], liquid–liquid equilibria in polar solvent [596], small-angle X-ray scattering (SAXS) [597–601], SANS analysis [602–606] of the G5 [607] or G7 [608] PAMAM, neutron spin-echo (NSE) spectroscopy [600], hyperpolarizabilities of G0 and G1 [609], atomic force microscopy (AFM) [610–614], quasi-elastic light scattering (QELS) [615], dielectric relaxation spectroscopy [616] and potentiometric pH titration [617]. Using SAXS, SANS, and TEM measurements, the G8 PAMAM with its 10 nm size has been considered as an aerosol calibration standard [618] and a review has appeared [601]. Comparative viscosimetric, hydrodynamic, and conformational properties of the PAMAM *vs.* other related dendrimer families is available [619]. Solid-state ^2D NMR studies of PAMAM-*n*DCI salts have been conducted in order to elucidate their structural and



Scheme 17. A route to unsymmetrical PAMAMs derived from an ethylenediamine core [506].

H(D)-bonding [567]. Variable-temperature dependent studies of G1–3, 5, 7, and 9 PAMAMs gave spectral characteristics of amorphous substances undergoing T_g s in the range of 25 and 65 °C. Internal *H*-bond lengths were estimated to be 2.2 ± 0.15 Å and were independent of generational level. A comparative molecular mechanics approach between the PAMAMs and related carbosilane dendrimers was used to evaluate the shape and steric interactions when the generation number (*G*) increases [620].

The hindered diffusion rates for PAMAMs and linear polystyrenes in porous glasses have been studied [621] in which the PAMAMs quantitatively agree with the hydrodynamic theory for a hard sphere in a cylindrical pore. The molecular, solution, and bulk properties of the important G5 PAMAM have been evaluated [622,623]. Also, the rheological behavior of the G1–8 PAMAMs has been investigated [624] under steady shear, creep, and dynamic oscillatory shear at different temperatures. It was shown that the PAMAM family exhibited (1) constant viscosity at small deformations, irrespective of the

applied stress, and (2) temperature- and generation-dependent non-Newtonian response at higher shear rates and frequencies from which a model was proposed that “involves dynamics of structural elements that are smaller than the overall dendrimer molecules” [624]. The Unifac- and Entropic free-volume models have been utilized to predict phase equilibrium for the PAMAM and related dendrimers; notably, the Unifac-FV model was better for the PAMAMs and shown to be influenced by the dendrimer’s density [625]. Using extensive molecular dynamics on the PAMAM family at 300 K, Goddard et al. [550] reported diverse structural properties including the radius-of-gyration, shape tensor, asphericity, fractal dimension, monomer density distribution, solvent accessible surface area, molecular volume, and end-group distribution functions. The structural and conformational properties of the G4–6 PAMAMs have been reported [626], concluding that “...significant back-folding of the outer subgenerations in the interior of the molecules at all levels of pH, contrary to original expectations and some SANS experiments, but in agreement with

other SANS experiments.” Based on ^2H NMR data, the termini of the G3 PAMAM are neither extensively interpenetrated as it is with G2 nor back-folded as with G9 [568].

Morgan, Stejskal, and Andrady [627] investigated the free volume of PAMAM and cross-linked polymers [poly(propylene glycol) – cross-linked with tris(*p*-isocyanatophenyl)thiophosphate] – by the absorption of ^{129}Xe . The fractional free volume (“void volume”) in these macromolecular architectures can be measured by means of xenon chemical shifts, since they are proportional to the collision rates within free-volume regions. Cross-linked poly(propylene glycol) exhibited typical polymer network-based Xe chemical shifts ($\delta = 217.2\text{--}222.2$ for prepolymer average molecular weights increasing from 670 to 2470 amu), while the PAMAMs showed a nearly linear Xenon chemical shift increase from $\delta = 214.8$ to 229.2 for G3 through G8 series. The fractional free-volume in the PAMAM series was shown to decrease with increasing generation; however, it was noted that these data are not indicative of the location of the free-volume within the dendritic structure [*i.e.*, core vs. outer region(s)].

3.2.2. Different PAMAM core constructs

The simplest two-directional core for PAMAM construction, as noted above, is derived from ethylenediamine, from which the largest commercial (Aldrich) diverse family of PAMAMs relative to size (G0–10) and intermediates (0.5–7.5), as well as hydroxy (G2–7) surfaces, are available. Similarly, but with limited series – generally G0–G6 – the 1,4-diamino-butane, -hexane, and -dodecane-cored PAMAMs are also available. Simple aryl esters have been utilized [490,401], as the core, upon which the PAMAM constructs have been assembled. Diverse PAMAM-type motifs have

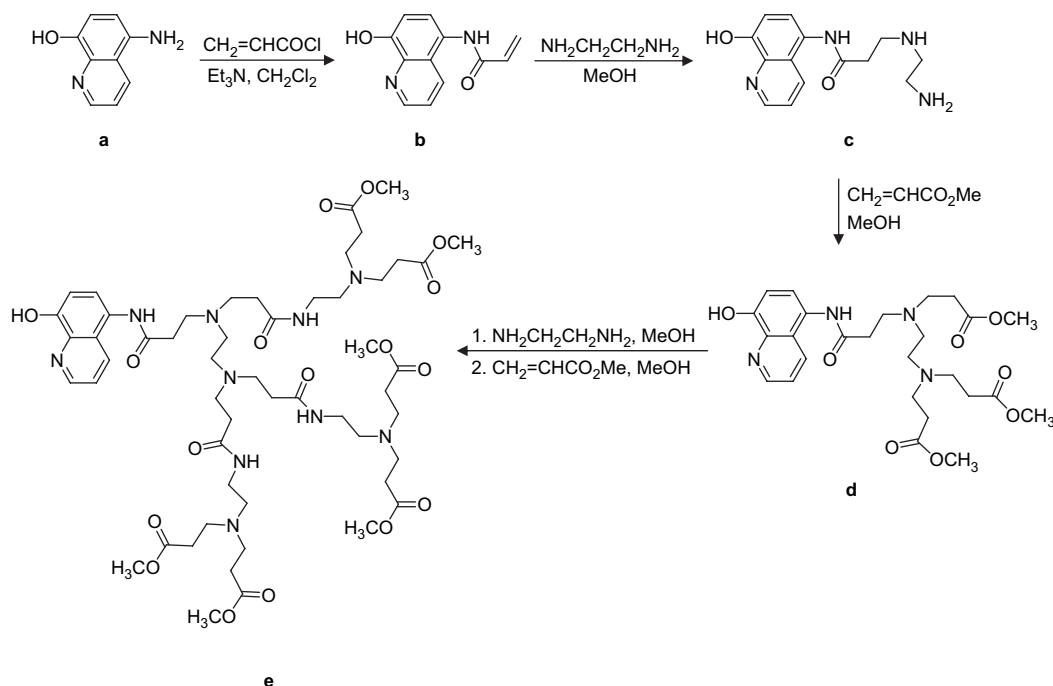
been created based on different cores in order to investigate the effects of the core on the ultimate structure. The core-shape and generation have been evaluated as related to *in vitro* gene delivery, as will be seen below.

The construction of G4–6 PAMAM-like dendrons with pyridoxamine at the core started with *N*-BOC- and phenolic-*O*-MOM-protected pyridoxamine to which different spacers possessing a free terminal amino moiety were attached [628]. Then, the typical step-wise synthesis of the 1 → 2 *N*-branched PAMAM-like infrastructure was assembled. The removal of the BOC and MOM protecting groups was accomplished in the last step, thus freeing the internal pyridoxamine site on the unnatural mimic of globular enzymes.

Starting with di-*n*-dodecylamine as the core, its exhaustive Michael reaction with methyl acrylate followed by amidation with ethylenediamine, gave the desired amino-terminated starting material. The repetition of this two-step sequence gave the unsymmetrical G1–4 dendrimer. The cationic lipid with the G2–4 PAMAM-like dendron exhibited an enhanced ability to form lipoplexes with plasmid DNA, based on agarose gel electrophoresis [629].

The 5-amino-8-hydroxyquinoline (**18a**), as the focal core for PAMAM construction, has been reported [630]. Treatment of **18a** with 1 equiv. of acryloyl chloride in Et_3N gave the solid acrylate **18b**, which with ethylenediamine gave diamine **18c**. Subjecting **18c** to the traditional methyl acrylate, followed by ethylenediamine gave rise to the desired framework **18d**; repetition gave rise to the larger **18e**. The reaction of the 8-hydroxyquinoline focal site with zinc(II) assembled the desired metallodendrimer (Scheme 18).

The assembly of two different PAMAM-type dendrons, each possessing complementary base pairs at the focal



Scheme 18. Dendron construction based on 5-amino-8-hydroxyquinoline [630].

position, led to the Watson–Crick base paired core, in which the base pair is the dendritic core [631].

p-Xylylenediamine (Fig. 4e) was used as a 2-directional core for the preparation of a G5 modified PAMAM; the ester surface was then either saponified or partially alkylated with octyl amine, followed by saponification of the residual ester moieties. When evaluated as a pseudostationary phase in electrokinetic chromatography (EKC), the retention and separation of the diverse components used in the EKC increased with each increasing generation and with the partial alkylated material [632]. The partially alkylated dendrimers can also be used in organic media, which can prove to be useful in certain environments.

A triblock copolymer, PAMAM (dendron)–PEG–PAMAM (dendron) was easily prepared by utilizing the traditional divergent treatment of the core H_2N –PEG– NH_2 with methyl acrylate at 37 °C for 2 days, followed by ethylenediamine under similar conditions [633]. The G1–5 series were created and shown to form highly water-soluble polyplexes with plasmid DNA possessing compact nanoparticles with a narrow size distribution.

A two-directional PAMAM dendrimer possessing a tris-hydroxy surface for water solubility and a core capable of a third attachment, specifically [(G5 dendron) $_2$]N–(CH $_2$) $_2$ –phthalimideN–(CH $_2$) $_2$ C(=O)NH(CH $_2$ O) $_2$ (CH $_2$) $_2$ [C(=O)] $_2$ (CH $_2$) $_3$ –Biotin, was synthesized. The binding of the central appended biotin with that of avidin was demonstrated, and upon binding, the number of other cages within the dendrimer decreased from

three to two, suggestive of unfavorable electrostatic interactions [634]. Interactions of avidin with biotin on a gold surface possessing G4 amine-terminated PAMAM have been evaluated using Fourier transform infrared reflection–absorption spectroscopy (FT-IRRAS); the procedure to generate the layered surface showed a high capacity for the binding of avidin with a relatively high specificity [635].

The use of a two-directional core derived from the by-product in the acrylation polymerization process, hexaacylonitrile, $[\text{=CHC}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_2(\text{CO}_2\text{Me})]_2$ [636], was treated with ethylenediamine to generate the G0 level; methyl acrylate, followed again by ethylenediamine, gave the next tier [637]. The sequence could be repeated to create the higher generations.

Although ammonia was utilized as a 3-directional core, the use of tri(ethanol)amine has also been utilized to generate a G2–8 PAMAM-like series [638,639]. A core using trimesic acid (1,3,5-benzenetricarboxylic acid, Fig. 4a) was initially transformed to methyl trimesate, which was amidated with ethylenediamine, followed with methyl acrylate; the iterative sequence was continued to G8 [640]. Also reported were PAMAM-type species up to G5 derived from pentaerythritol (Fig. 4b) and inositol (Fig. 4c). A series of PAMAM wedges through G5 were divergently assembled on a four-directional core, 1,4,7,10-tetraazacyclododecane (Fig. 4d), by the standard iterative approach.

Initial treatment of ultra-fine silica with γ -aminopropyltriethoxysilane introduced surface amino groups from which the two-step construction was conducted up to G4 [641–643] or

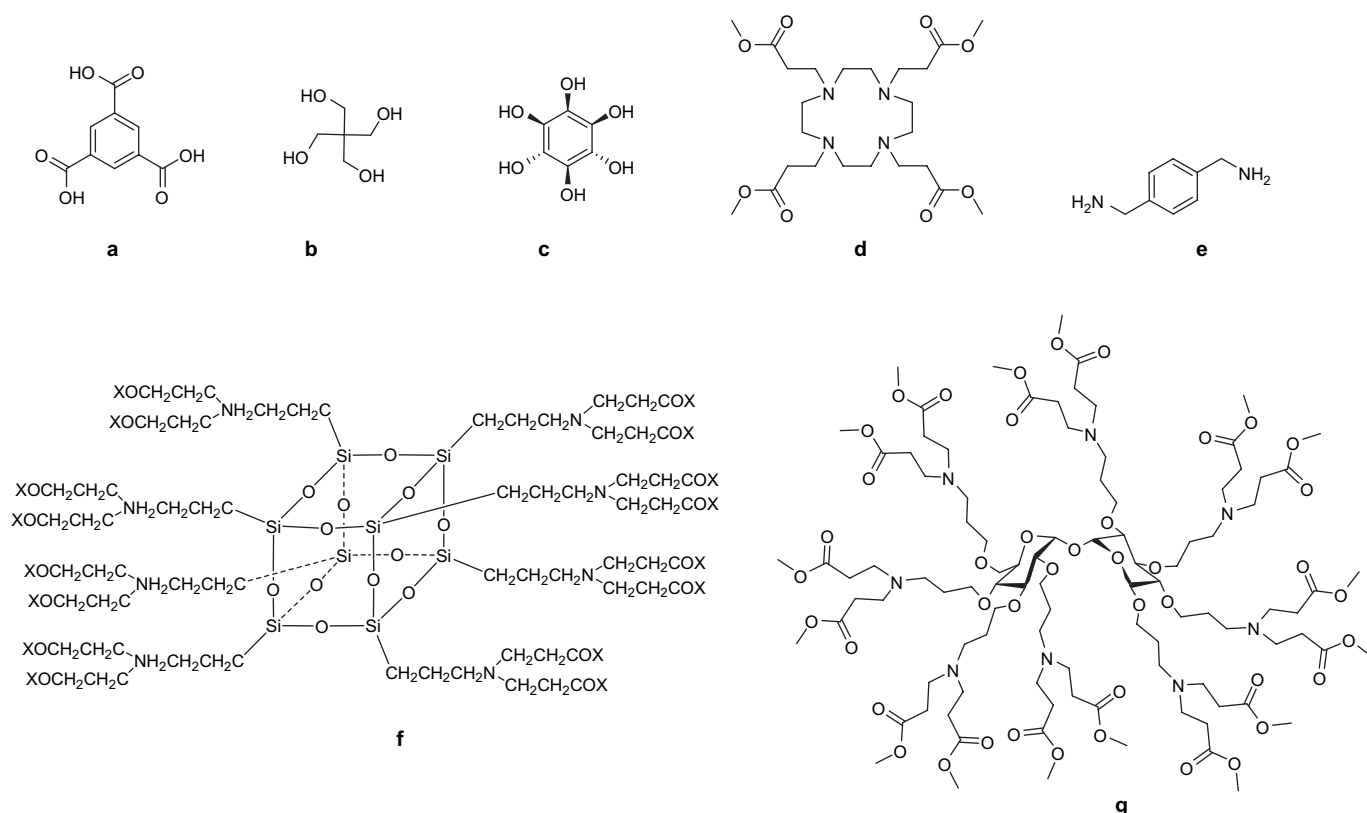


Fig. 4. Interesting cores.

G10 [644]. Propagation of the dendrimer grafting from the surface was much lower than theoretical expectation, and it might best be envisioned as hyperbranched rather than dendritic construction [645] also see [646–648]. The surfaces of these silica particles possessing the PAMAM-type dendrons were analyzed to give insight to the step-wise filling of the surface mesopores [647]. The initial immobilizing of the silica surface with 3-(triethoxysilyl)propionitrile before the step-wise construction of the PAMAM-like dendrons was shown to provide an internal standard to normalize the drift in the IR spectra for kinetics studies [649]. These types of PAMAM-coated silica substrates have themselves been surface-functionalized to accommodate the incorporation of catalytic metal centers [643,648]: typically, the terminal amine was transformed to a $-\text{N}(\text{CH}_2\text{PPh}_2)_2$ and then complexed with $\text{Pd}(\text{tmeda})\text{Me}_2$. Their catalytic properties depended to a large extent on the metal surface, *e.g.*, Pd: carbonylation of iodoarenes [648]; Heck reactions [650]; and Rh: hydroformylation reactions [651–653]. The introduction of silica-(G0–4) PAMAM-like- $\text{Pd}(\text{PPh}_2)_2$ surface has been reported in which the ethylenediamine was replaced with 1,6-diaminohexane; these were shown to be highly active, recyclable catalysts for the hydroesterification of olefins with MeOH and CO [654]. The encapsulation of different metal nanoparticles within the coated mesoporous silica has been demonstrated by the chemical reduction of impregnated metal salts by aqueous hydrazine [642].

Using a Fe_3O_4 nanomagnetite core [655] possessing a silica coating [655], the sequential step-wise generation of the PAMAM-type dendron was assembled [656]. The subsequent surface-activation of the amino-termini with diphenylphosphinomethanol, generated *in situ* from diphenylphosphine with paraformaldehyde, gave the ideal loci for conversion to the desired Rh-complexed dendrons by treatment with $[\text{Rh}(\text{COD})\text{Cl}]_2$; a series of hydroformylations was conducted, demonstrating the high conversion and selectivity of the vinylic substrate to the product, by these utilitarian dendronized magnetic nanoparticles [656].

The terminal amino moieties of this PAMAM-grafted silica were reacted with living poly(isobutyl vinyl ether) [poly-(IBVE)] or poly(2-methyl-2-oxazoline) [poly(MeOZO)]; poly-MeOZO was also post-grafted to the PAMAM surface whereby the percentage of overall grafting was determined to be 361.6%, based on silica [657]. Glass surfaces and Si(100) with 3-aminopropyltrimethoxysilane, G4 PAMAM, and poly(diallyldimethylammonium chloride) facilitated adsorption onto colloidal gold particles; these resultant films were subsequently exposed to mercury vapors and evaluated by X-ray photoelectron spectrometry and energy-dispersive X-ray spectroscopy [658].

The cubic, octameric oligosilsesquioxane [659] (Fig. 4f) and the related $[\text{H}_8\text{Si}_8\text{O}_{12}]$ [660] have been used as cores [661] for the construction of PAMAM shells. An interesting series of PEG-extended octakis (*e.g.*, ethylene glycol) octasilsesquioxane have appeared [662] and would extend the use of this core.

The use of a carbohydrate-core, the non-reducing disaccharide trelose, has been demonstrated [663]; however, instead of

the traditional PAMAM construction, the initial polyol was sequentially perallylated, ozonated, subjected to reductive amination with benzylamine, followed by deprotection. The treatment with methyl acrylate leads to a polydisperse product. The polyol was successfully treated with acrylonitrile [664] but the reduction again led to mixtures. However, treatment of the perallylated product with 9-BBN (83%), followed by the Gabriel synthesis [665] – CBr_4 , PPh_3 (63%), PhthNK (99%), and hydrazine (58%) – afforded the propylamine exterior, which with methyl acrylate generated (94%) the 1 → 2 *N*-branched ester (Fig. 4g) or with 2,3,4,6-tetra-*O*-acetyl- α -D-mannopyranosyl isothiocyanate [666] generated (87%) the thio-bridged glycoclusters.

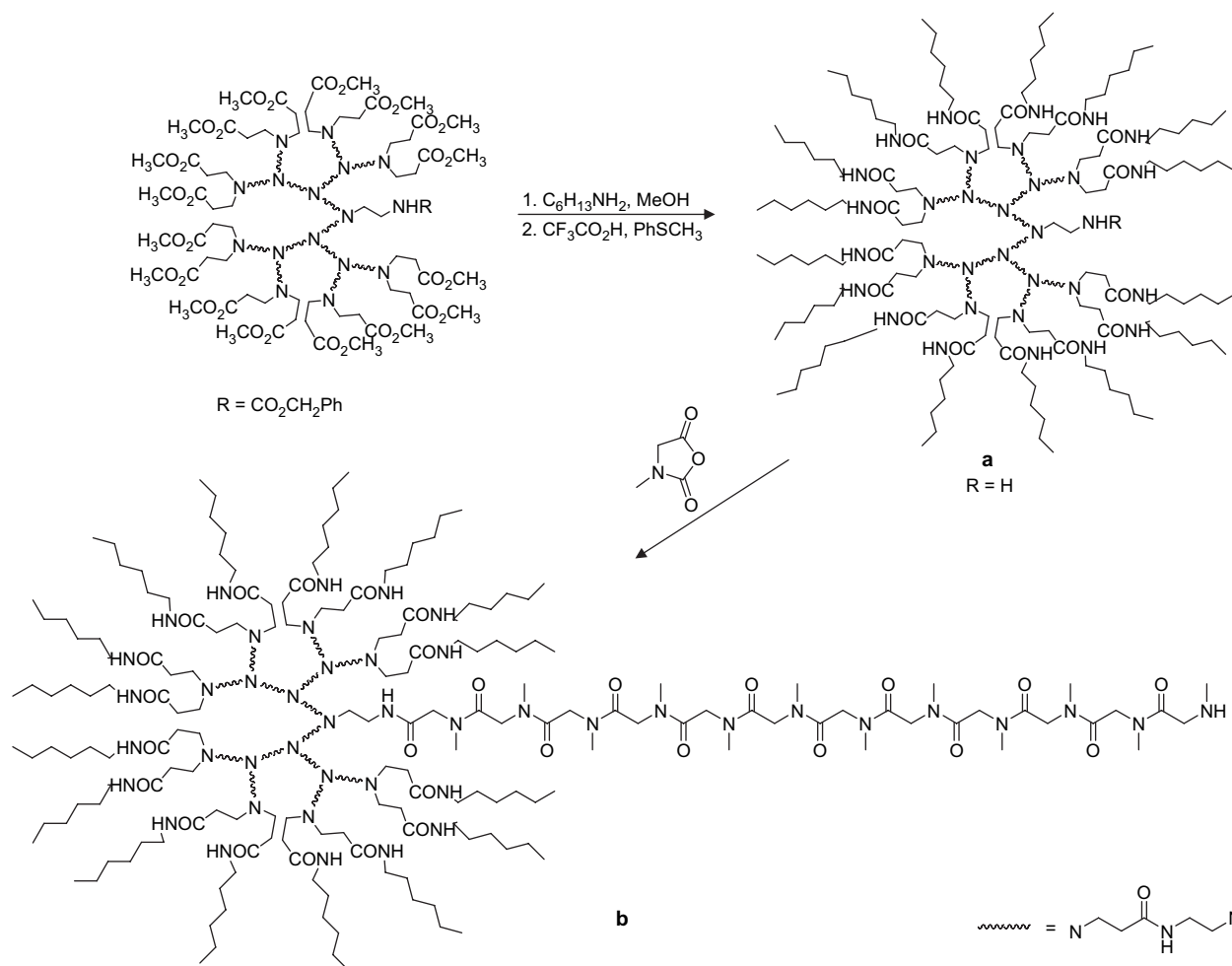
Derived from a monoprotected ethylenediamine as the half-protected initiator core, a PAMAM-like G2.5 framework was constructed [667] then capped with hexyl amine; deprotection of the core benzylcarboxy moiety with trifluoroacetic acid in the presence of thioanisole at 27 °C gave the desired free-amino group (**19a**), which was subjected to living polymerization of sarcosine *N*-carboxyanhydride in CHCl_3 at 27 °C for 60 h [668]. The larger G4, G5 and G5.5, “tadpole-like” materials (**19b**) have also been assembled [668,669] using a free-end of polyoxazolines; the surface tension measurements afforded insight to the disposition of the “tail” (Scheme 19).

3.2.3. PAMAM surface modifications

One of the two major sites for easy structural modification is the alteration of the multifunctional dendritic surface by simple covalent bond formation; the other is associated with the supramolecular properties associated with the internal void region(s) in which the dendrimer acts as the host for guests. The surface modifications have been broadly envisioned as transformations related to those of either non-biosurfaces or biosurfaces as well as those coupled with interactions with bio-related materials. Surface functionalization has most commonly occurred with the PAMAM series, since they were among the first commercially available dendrimers. The attachment procedures have generally followed traditional routes for derivatizing the ester/carboxylic acid (G#.5) and amine (G#) moieties, where # denotes the generation number.

3.2.3.1. PAMAM non-biosurface modification. The G2–3 PAMAMs have been stoichiometrically methylated (MeI) to afford both the internal and external quaternized materials, which exhibited a conductivity of 10^{-5} – 10^{-6} S cm^{-1} at ambient temperature and were shown to act as conductors [670]. Plots of conductivity vs. temperature were presented; their thermal and chemical stabilities were not addressed.

The initial treatment of *N,N*-dimethyl-*n*-octylamine with 2 equiv. of epibromohydrin, followed by removal of excess reagent and then addition of G4 PAMAM generated PAMAM– $[\text{NHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{N}^+\text{Me}_2(\text{C}_8\text{H}_{17})(\text{X}^-)]_{64}$ [671–673]; dissolution of this material with SDS in an aqueous solution was shown to possess very low surface tension and low micropolarity, even at extremely low SDS concentrations. The related G0 PAMAM core was treated with glycidyl dimethyloctylammonium bromide to generate a cationic tetrameric surfactant



Scheme 19. Tadpole-like PAMAM dendrimers [669].

possessing four octyl chains and four ammonium centers [673]. This tetraammonium salt possessed a critical micelle concentration (c.m.c.) of 13 mmol dm⁻³ at the concentration of one terminal group, a surface tension at the c.m.c. of 34 mN m⁻¹, and an occupied area of 1.94 nm². The addition of SDS to an aqueous solution of this tetraammonium salt enhanced the surface activities — these mixtures exhibited lower c.m.c., lower surface tension, and higher solubilization of pyrene than SDS alone. The adsorption of this tetraammonium salt and related G3 PAMAM has been studied by colloidal probe atomic force microscopy showing that the adlayer–adlayer interactions are very different even though they possess nearly equal hydrodynamic radii [674]. The related quaternized G1 PAMAM-type (C_{8qb}G1) surfactant with 16 octyl chains and 16 ammonium groups was similarly synthesized from the PAMAM and glycidyl dimethyl octylammonium bromide and various physicochemical properties were measured [675]. The G3 and G4 surface-terminated (amino/hexyl; hydroxy/hexyl; and *N*-acetyl-*D*-glucosamine/hexyl) block PAMAMs were investigated using various techniques. It was shown that the time-dependence for adlayer formation followed two-step adsorption kinetics [676,677] and the molecular orientation of the hexyl chains in the adlayers was in this order, also see [678,679]. EPR measurements were

conducted for different ionic surfactants/PAMAMs in water and it was concluded that cationic surfactants with dimeric character interacted with all PAMAM generations in comparison with those of monomeric character and the interactions were greater in basic media; whereas the interactions of SDS with the PAMAMs were stronger in acidic media [680].

Spindler et al. [681] functionalized the terminal amines of PAMAMs, using diaminoalkyl [with (CH₂)_{*n*}, *n* = 2, 4, 8, or 12] cores, with various epoxyalkanes to make them hydrocarbon-soluble, thus mimicking inverse micelles. Micellar behavior was exhibited by the transport of Cu(SO₄)₂ from an aqueous phase to an organic phase (toluene). In the absence of these two-directional dendrimers, no copper ions were transported as evidenced by a clear organic phase instead of a characteristic blue coloration. Also, Langmuir isotherm data for these materials were examined to gain an understanding of the properties at the air–water interface. Typical isotherm data revealed increasing surface pressure with decreasing available area until the monolayer collapsed resulting in multilayer formation. With additional compression, the surface pressure remained constant. This contrasts with the observations by Fréchet [682,683], whereby a nucleation phenomenon was seen albeit with different dendron architectures.

The surface modification of G3 PAMAM with benzaldehyde, benzyl chloride, and trityl chloride gave the corresponding imine, di-*N,N*-benzyl, and mono-trityl derivatives; the addition of TiCl_4 afforded catalysts capable of polymerizing α -methylstyrene [684]. The formation of G2.5 and 5.5 ^{14}C -labeled PAMAMs (between 30 and 45 mCi/mmol) was accomplished by the Michael addition of ^{14}C -labeled methyl acrylate with the appropriate amine-terminated precursor [685]. The stoichiometric analysis of the G5 PAMAM surface has been probed by a simple acylation in order to ascertain the average number of the terminal amines, which has been verified by using potentiometric titration, gel permeation chromatography, and NMR spectroscopy; yet, the acetylated PAMAM possessed a *smaller* molecular size and thus a more compact structure [686].

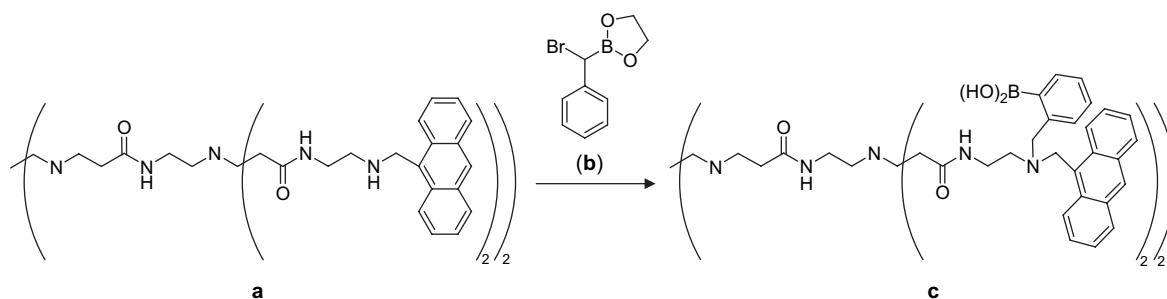
Shinkai et al. [687] created a series of dendrimers **20c** that were shown to act as “saccharide sponges,” which were prepared by the reaction of the PAMAMs with 9-formylanthracene, followed by imine **20a** reduction (NaBH_4), and then benzyl halide displacement followed by attachment of the boronic acid moiety **20b** (Scheme 20). In contrast to other flexible diboronic acid binding sites that show weaker binding, compared to the more rigid, preorganized host, these dendritic boronic acids form remarkably stable saccharide complexes. The simple condensation of G0–4 PAMAMs with 4-(4'-decyloxybenzoyloxy)salicylaldehyde generated air-stable, yellow dendromesogenic polyimines that exhibited a smectic A mesophase in which it was proposed that the mesogenic units possess a parallel orientation [688]; several larger mesogenic appendages possessing three, six or nine terminal alkoxy moieties have also appeared [294]. Treatment of G0–4 PAMAMs with 4-(3',4'-didecyloxybenzoyloxy)salicylaldehyde formed the related polyimines, which demonstrated a hexagonal columnar mesophase caused by the curved interface of the promesogenic surface units leading to a radial conformation and, therefore, the columnar structure [689]. A comparative study of the G3 PAMAM, as well as the related PPI dendrimer, with 16 imine-connected mesogens derived from mono-, di-, and tri-alkoxybenzoyloxysalicylaldehydes, showed that it was the interaction between the rigid mesogenic moieties and mesophase separation that governed the type of supramolecular organization affording the nematic, smectic, and columnar mesophases [268,269,690,691]. An overview of the relationship of these liquid crystals to nanodevices has appeared [270]. Fluorescence and aggregation studies were

conducted on the G1–5 PAMAMs after treatment with simple benzaldehyde [692]. The G3–5 PAMAM surface imines showed a dual fluorescence emission due to the phenyl ring and its excimer, and it was shown that the lower members of this series self-organize into spherical aggregates but no aggregation was realized when the size is $>G3$. The G4 PAMAM was similarly treated with a two-fold excess of 5,5''-dihexyl-[2,2';3',2'']terthiophene-5'-carbaldehyde, then reduced with excess NaBH_4 to give the terthiophene surface-coating [693]. This terthiophene-coated dendrimer was subsequently transformed to an encapsulated metal nanoparticle.

Cross et al. [694] prepared terminally-modified PAMAMs using tetracyanoquinodimethane (TCNQ), 2-naphthoyl chloride or 4-nitrobenzyl chloride to create materials with potential electronic or non-linear optical properties. Notably in electric field induced second harmonic (EFISH) studies, care must be taken to account for the volume fraction of the dendrimer in solution. Four generations of phenylene-fluorene-functionalized PAMAMs have been synthesized by coupling pentafluorophenol 4-[9',9'-bis(6''-tert-butoxycarbonylaminoethyl)-2'-fluorenyl]- or pentafluorophenol 4-[9',9'',9'',9''-tetra(6'''-tert-butoxycarbonylaminoethyl)-7',2''-bisfluorene-2'-yl]benzoates with the commercial PAMAM to generate a new family of light-harvesting macromolecules [695,696].

Mitchell et al. [697,698] converted (TRIS, DMSO, K_2CO_3) – the ester termini of the G#.5 PAMAMs – to their 1 \rightarrow 3 C-branched, surface-polyhydroxy derivatives in order to study their potential for drug delivery [699,700]; in essence, transforming the PAMAM dendrimers to arborols [23]. Inclusion complexes with a variety of hydrophobic molecular guests were reported [697]; *e.g.*, a 1:1 complex with benzoic acid was found to increase the aqueous solubility of the guest from 2.9 mg/mL to 305 mg/mL at neutral pH. Similarly, treatment of the simple ester-terminated PAMAMs with diethanolamine generated the related water-soluble, 1 \rightarrow 2 *N*-branched hydroxy-terminated dendrimer, which, upon treatment with excess benzyl bromide, underwent random quaternization at only four of the six internal nitrogens [701].

The G4 PAMAM has a 25-fold acceleration for aminolysis when compared to *N*-acetyl-ethylenediamine; the hydrophobic binding of the substrate at the closely packed polyfunctionalized surface has been proposed [702]. Aminolysis in water at pH 8.5 was shown to be greatly enhanced by the introduction of the G1–5 PAMAMs, in which the G4 gave the maximum



Scheme 20. Creation of a dendritic “saccharide sponge” [687].

rate enhancement [703]. A combination of hydrophobic binding of the substrate, methyl 4-nitrobenzoate, at the outer region possessing the terminal amino group, and close proximity of the internal amido groups, stabilize the transition state.

Self-diffusion and nuclear magnetic relaxation of the G3 and G4 hydroxy-terminated PAMAM were evaluated and it was shown that their generalized concentration dependence is similar to the curve for that of the large poly(allylcarbosilane) dendrimers [704]. The oxidation of the commercial hydroxy-terminated G2 or G4 PAMAM-based dendrimers with either $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ or Au(III) [705,706] was shown to give a strong blue luminescence [707]. Under an air atmosphere at 500 °C, the G4 hydroxy-terminated PAMAM completely decomposed as shown by TGA analysis; under an argon atmosphere, a greater fraction decomposed below 300 °C but not all fragments were removed until heating exceeded 550 °C [708]. The same dendrimer possessing *ca.* 40-atom Pt particle completely decomposed at 400 °C leaving only a residual platinum metal [708]. Interestingly, to realize a bistable memory behavior device, a hydroxyl-terminated G4 PAMAM device showed good memory performance, in that there was a 30 h retention time, low operating voltage <5 V, and the on-off ratio was controlled from 10^{-10} – 10^3 [709]. The interior tertiary amine branching centers of the G4 PAMAM possessing terminal hydroxy groups were methylated by the addition of methyl iodide in DMF in various molar ratios; the external hydroxy moieties were *not* methylated under these reaction conditions [710].

Crooks et al. [711] demonstrated the self-assembly of fatty acids about the surface of PAMAMs, in which the G4 PAMAM was sonicated in the presence of *ca.* 70–80 molecules of dodecanoic acid, thereby affording an ordered ionic array of terminally arranged aliphatic chains. Ramifications include nonpolar solubility as well as dye and metal encapsulation. The G4 PAMAM was coated with an average of 7–46 hydrophobic chains each possessing C_{10} – C_{14} from which it was based on Fourier transform pulse-gradient spin-echo NMR studies that these amphiphiles behave as unimolecular entities with their chains largely within the dendritic periphery [712]; only when the number of chains is very large (>34), are the chains externally forced to hydrophobically self-assemble. Treatment of G2, 4, and 6 PAMAMs with 1-ethyl-1'-(3-propionic acid)-4,4'-bipyridylium dibromide generated dendrimers possessing 13–34% viologen-surface functionalization, which upon chemical reduction, produced viologen radical-cations that were largely dimerized [713]. Five generations of PAMAM or PPI dendrimers possessing promesogenic termini derived from salicylaldehyde with one to three aliphatic chains were shown to demonstrate liquid-crystalline properties based on polarized-light microscopy, differential scanning calorimetry, and X-ray diffraction [269]. Polymer films were generated by electropolymerization of a thiophene-functionalized G4 PAMAM and the electrocopolymerization of this material with poly(3-methylthiophene) afforded a composite possessing 80% dendrimer [714]; the G4 PAMAM without a thiophene surface functionality was not incorporated into the polythiophene matrix.

Leblanc et al. [715] reported the surface functionalization of the G3 PAMAM with 10,12-pentacosadiynoic acid; these

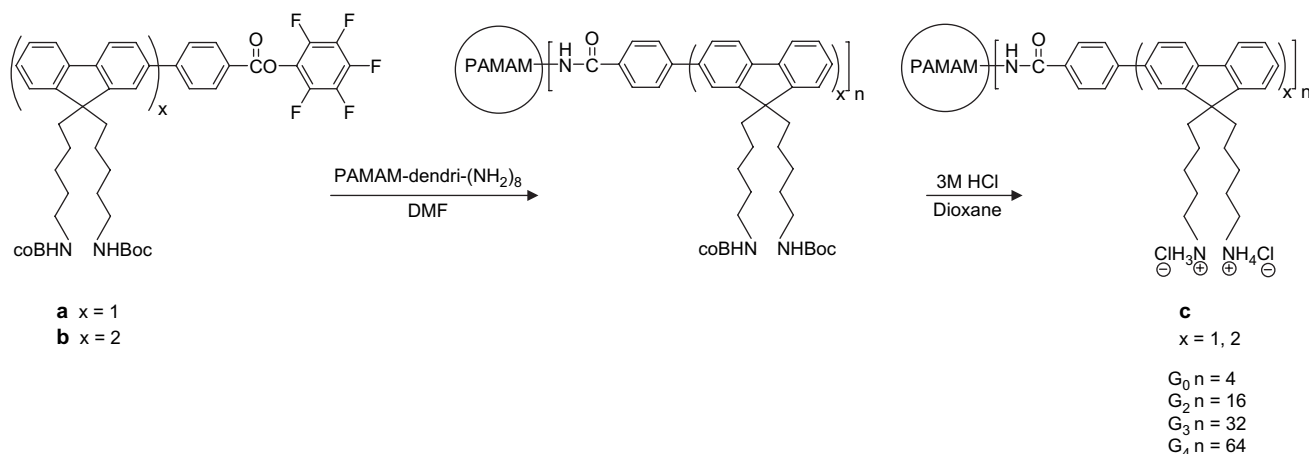
materials formed colloidal particles in CHCl_3 and were compressed into monolayers that could be polymerized by UV irradiation. There was good correlation between size and topology of the monolayer as measured by Brewster angle microscopy (BAM) and environmental SEM of a Langmuir–Blodgett film [716]. Coating the G3 PAMAM surface with cinnamoyl moieties permitted their surface dimerization upon irradiation with UV light using 5-nitroacenaphthylene, as an initiator; these shell-modified dendrimers possessed fluorescence properties, which increased upon photocyclization [717].

The tautomeric actions of surface-coated azo-functionalized PAMAMs, as well as the related model systems, were evaluated and shown to exist in an equilibrium mixture of azo and hydrazone tautomers [718]. The proportion of azo tautomer increases with dendrimer generation as well as in the presence of *H*-donor solvents, such as AcOH or 2,2,2-trifluoroethanol. The treatment of G3 PAMAM with pentafluorophenyl [4-(4'-hexylphenylazo)phenoxy]acetate afforded, in good yield, the dendrimer coated with $-\text{C}(=\text{O})\text{CH}_2\text{OC}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4\text{C}_6\text{H}_{13}$; the evanescent waveguide characterization and photo-alignment of this functionalized PAMAM, as well as a polystyrene blend ultrathin films, were measured [719]. The structure of these azo-coated dendrimers and its molecular interactions within the system were noted to be the primary factors leading to the highly aggregated domains.

The G0–4 PAMAMs were coated with either phenylene-fluorene (**21a**) or phenylenebis(fluorene) (**21b**) by amidation of the amine surface with the phenylene pentafluorophenyl ester [696]. The *N*-BOC surface groups were hydrolyzed with dilute HCl to generate the desired water-soluble products **21c** (Scheme 21).

The G4 PAMAM dendrimer was treated with *N*-hydroxy-succinimide ester of 3-mercaptopropionic acid to selectively place (an average of) two thiol groups on each dendrimer molecule [720]. The G1–3 PAMAMs were prepared and subsequently treated with 4-cyanobiphenyl hydrogen glutarate with diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate, as a condensing agent, to generate PAMAM-based liquid crystals, which exhibited a lyotropic LC property in 80 wt% DMF solutions of the dendrimers containing lithium bromide [721].

In the course to prepare efficient (7.72%) dye-sensitized solar cells [722], one of the components was polypyridinyl-pendent PAMAMs, which were synthesized by the treatment of the G1 or G2 dendrimers with either nicotinic or isonicotinic acid in the presence of 1-hydroxybenzotriazole (HOBT) and DCC; the second component was $[(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2-\text{CH}_2\text{I}]$. The use of PAMAMs with surface terpyridinyl moieties, prepared by a simple amidation procedure [723–725], has been demonstrated in interfacial coordination using transition metals, *e.g.*, Co(II) or Fe(II), to form highly ordered two-dimensional structures such as HOPG and Pt single-crystal surfaces *via* the two-dimensional packing of one-dimensional strands [726,727]. Dendrimer multilayers have been deposited on silica oxide wafers by alternately immersing the substrate into a solution of G2,3 PAMAMs terminated with terpyridine followed by Co(II) ions; the thin films were characterized by



Scheme 21. Preparation of light-harvesting dendrimers [696].

synchrotron-based X-ray reflectivity and X-ray fluorescence [728]. The interfacial reaction of PAMAMs terminated with terpyridine and 1,4-bis[4,4''-bis(1,1-dimethylethyl)-2,2':6',2'-terpyridin-4'-yl]benzene with aqueous Fe(II) or Co(II) gave highly ordered 2D hexagonal arrays composed of 1-dimensional polymeric strands [726,729].

The amidation of G0–4 PAMAMs with uracil-1-acetic acid successfully coated the surface with uracil moieties; the G1 functionalized dendrimer was treated with [3-(methylamino)propyl]trimethoxysilane to generate films possessing highly reproducible worm- or ribbon-like ordered structures on the micron length scale [730]. This self-assembly procedure offers an exciting new platform for the formation of hierarchically structured thin films.

Miller et al. [731] described preparation of a PAMAM series coated with aryl diimides that are capable of forming radical anions [732,733]; an overview of π -dimers and π -stacking in conducting polymers is available [734]. The vis-IR spectra of these anion radicals suggested the formation of diimide " π -stacks" and cyclic voltammetry further supported a diimide aggregation phenomena. It was shown [735] that the dendrimer-based, π -stacked diimide network led to a path for electrical conductivity, as opposed to the phenomenon being simply ionic. Films cast at 60 °C possessed conductivity value of $\sigma = 2 \times 10^{-3} \text{ S cm}^{-1}$, which is ten times greater than those cast at 120 °C suggesting that at lower temperatures stacking improved. It was postulated that the three-dimensional features of these coated dendrimers render the "isotropic nature of these films is of particular interest" [735]. Miller et al. [736,737] showed that the fully reduced (1.1 e/diimide) films of these cation-substituted naphthalenediimide modified G3 PAMAMs exhibited conductivities of $10^{-3} \text{ S cm}^{-1}$ (σ) while half-reduced films (0.55 e/diimide) showed $\sigma = 10^{-2} \text{ S cm}^{-1}$. Conductivity increased as a function of humidity approaching 18 S cm^{-1} at 90% humidity. The near infrared spectroscopy, X-ray powder diffraction, and quartz crystal microbalance assessment suggested that water absorption plasticized the film and facilitated a more rapid stack-to-stack electron transfer, thus increasing conductivity.

Initially, treating naphthalene dianhydride with 1 equiv. of 4-aminomethylpyridine (125 °C, DMA, 18 h), followed by reaction with SOCl_2 (DMF) afforded the pyridinium hydrochloride monoamide, which was subsequently treated with MeI to give the *N*-methylpyridinium iodide salt. Using a similar anhydride to imide conversion, this monoanhydride pyridinium salt was then attached to the G1–6 PAMAMs in an overall conversion of >70% [738,739]. Following the electrochemical or sodium dithionite reduction of these coated dendrimers, near-infrared spectroscopy indicated π -dimer and π -stack anion-radical associations in either D_2O or HCONH_2 solutions. Their cyclic voltammograms also supported aggregation; notably, dendritic size was shown to have little effect on the extent of aggregation. Several fluorescent derivatives of G0 PAMAM with substituted 1,8-naphthalimide-termini were prepared (93%) by treatment of the dendrimer with 1,8-naphthalic anhydride, followed by chemical functionalization [740]. The effect of Fe(II), Ni(II), Zn(II), and Pb(II) upon the fluorescent intensity of the G1 PAMAM with four 4-[(dimethylamino)ethyl]amino-1,8-naphthalimide moieties [740,741] has been reported [742]. The G2 PAMAM was also capped with a related 4-substituted 1,8-naphthalimides and their photophysical properties showed that the resultant fluorescence was related to this external fluorophore [743–746]. The surface-coating of the G3 PAMAM with 32 2,3-naphthalimide moieties has been reported and subsequently used in the coordination Eu(III) to generate luminescent lanthanide complexes in solution [747].

Budd et al. [748] treated the surface of the G2 PAMAM with 4-acetamidobenzenesulfonyl chloride to generate the corresponding sulfonamide, which was hydrolyzed to the sulfanilamide then diazotized and coupled with 2-naphthol-3,6-disulfonic acid disodium salt; the degree-of-substitution of this orange dye was determined to be *ca.* 85%. The treatment of G2 PAMAM with tosyl chloride in the presence of Cs_2CO_3 gave the desired octasulfonamide; whereas the corresponding PPI counterpart underwent a novel decomposition of the central C–N bond [338].

The interaction of G2 and G4 PAMAMs with anionic meso-tetrakis(4-sulfonatophenyl)porphyrin forms several dendrimer-

associated species depending on the ratios of the dendrimer to porphyrin. At ratios above the isoelectric point of the charge balance between the two components, only two spectroscopic species were detected [749]. Aging effects were noted in which different aggregation forms for the porphyrin are possible thus demonstrating that the intermediate dendrimer concentrations are thermodynamically labile systems [750]. The self-aggregation of porphyrins, *e.g.*, 5,10,15,20-tetrakis(4-sulfonato-[or 4-phosphonato-]phenyl)porphyrins, with G5 PAMAM is controlled by very minute differences associated with the acid–base properties of the porphyrin [751]. It has been further revealed that G1–4 PAMAMs can be used as stationary phases upon which the cationic 5,10,15,20-tetrakis(1-methyl-4-pyridino)porphyrin tetrakis(*p*-toluenesulfonate) intercalated in DNA can be deposited onto an ITO electrode; the resultant membranes were demonstrated to be stable under the reaction conditions [752].

Treatment of a G4 PAMAM with solid sodium 3,6-disulfonaphthylisothiocyanate (or 3,5-dicarboxyphenylisothiocyanate) generated the corresponding thiourea [753]; these polyanionic materials were evaluated as antiviral agents against HIV-1 strains.

Gray and Hsu [754] synthesized G2 sulfonic acid-terminated PAMAM by treating the amine termini with 1,4-butane-sulfone; these coated materials showed enhanced performance, compared to sodium dodecyl sulfate, when used as a pseudo-stationary phase in aqueous electrokinetic capillary electrophoresis to separate a series of neutral isomeric phenols.

The treatment of the G3–10 PAMAMs with *O*-[2-(vinylsulfonyl)ethyl]-*O'*-methylpoly(ethylene glycol) 5000 (“PEG-VS”) under typical Michael conditions gave dendrimer-[NHCH₂CH₂S(=O)₂(CH₂CH₂O)_{*m*}Me]_{*n*}, where the number of terminal PEG groups varied from 30 ± 1 (G3) to 750 ± 40 (G10) [755].

Turro et al. [756] studied the adsorption and aggregation behavior of methylene blue adsorbed onto the surface of G#.5, anionic (–CO₂[–]) PAMAMs; the dye was proposed to stack perpendicular to the dendritic surface.

The single state emulsion polymerization of styrene with added G 4.5 PAMAM in the presence of sodium dodecyl sulfate, as template, produced lattices with the diameters of *ca.* 33–66 nm and polydispersity indices of less than 10% [757]. The G0–5 PAMAMs have moreover been investigated as curing agents in epoxide resin systems [758]; the cure behavior of epoxide/PAMAM/imidazole at various temperatures and PAMAM concentrations agree well with theoretical predictions based on Flory’s gelation theory and the Avrami equation.

Wyn-Jones et al. reported the study of the interaction of the PPI dendrimers, as well as their corresponding pyrrolidone-modified analogs [189,190], and the PAMAMs and their surface functionalized derivatives with SDS [759,760], and also described the use of a surface ion-specific electrode [electromotive force (EMF) measurements] to determine the binding isotherm, isothermal titration calorimetry (ITC) to evaluate the interaction enthalpy, and SANS for structural studies [761]. The ITC studies monitored interactions of the PAMAMs with cationic dodecyltrimethylammonium bromide and non-ionic hexaethylene glycol-mono-*n*-dodecyl ether, which

showed no significant binding effects. The SDS binds to all dendrimers having different surface functionality, such as: amine, hydroxyl, or δ-glucolactone [761].

Gong et al. [762] described the ionic conductivities of G2.5 and 3.5 PAMAMs, prepared by treatment of the surface carboxylic acids with alkali (Li⁺, Na⁺ or K⁺) hydroxide; these metal carboxylates exhibited conductivities of 10^{–5}–10^{–6} S cm^{–1} at 30 °C. The temperature-dependence conformed to neither the Williams–Landel–Ferry nor Arrhenius equations; this was attributed to its molecular structure.

The incorporation of both surface PEG moieties and a methacryloyl group at every chain termini connected through an L-lysine group has been created; the polymerization of the termini was readily accomplished by free radical initiators, such as azobisisobutyronitrile or dibenzoyl peroxide [763]. A similar procedure was utilized to amidate the dendrimer surface with diverse alkylcarboxylic acids [764] or poly(*N,N*-dimethylaminoethyl methacrylate) [765] in an effort to control their temperature-sensitive properties. The treatment of G4 PAMAM with polyethylene glycol (*M*_n = 5000) with a terminal carboxylic acid group gave a spherical micelle-like assembly; these spherical constructs, when titrated with the dendrimer, gave rise to a supramacromolecular assembly [766].

Lamellar structures of anionic G2.5 and 4.5 PAMAMs with the cationic surfactant didodecyltrimethylammonium bromide were evaluated by SAXS at 25 °C [767]; the incorporation of these PAMAMs into the lamellar liquid crystals at surfactant concentrations in the range of 4–30 wt% resulted in a transition from monophasic liquid crystal to biphasic lamellar mixtures at similar [surfactant]/[–CO₂Na] ratios for the two dendrimers.

The surface of G3,4 PAMAMs was functionalized with *N*-methyl-2-ethynylpyridinium triflate resulting in core–shell copolymers (termed: “sea urchins”) possessing a coating of short ionic acetylenic chains and showing conductivities in the range of 10^{–4}–10^{–5} S cm^{–1}, when doped, as well as enhanced dendrimer thermal stability [768].

The surface modification of the G0–5 PAMAMs with naphthyl [769], pyrenyl [769], phenyl [769], dansyl [769,770] or 1-(naphthyl)-2-phenyldiazene (NAD) [770] chromophores has been accomplished and then spectroscopically studied. The aggregation and self-assembly of these hydrophilic cores bearing the hydrophobic aromatic peripheral chromophores were observed and systemically investigated. The aggregation behavior of these dendritic assemblies was ascertained using AFM and TEM [769]. The PAMAMs with the NAD coating have been electrochemically probed, and upon photoisomerization, there was a change in the aggregation size [770].

The surface of the G4 PAMAM was coated with buckminsterfullerene (C₆₀) by simply dripping a heterogeneous solution of the dendrimer with a homogeneous solution of excess of C₆₀ in pyridine. The mixture was stirred overnight and the solvent was removed *in vacuo* to give a brown-blackish solid, which was purified to give the desired product possessing *ca.* 30 C₆₀ molecules per dendrimer in 89% yield [771].

The inclusion of a G4 PAMAM in a silica sol–gel afforded a solid electrolyte that was used to encapsulate Prussian Blue [KFe(III)](Fe(II)(CN)₆] and [Co(II)Fe(II)(CN)₆] [772]; the

included dendrimer increased the lifetime of silica, as a solid electrolyte, from a few days to *ca.* three months.

The G2.5 PAMAM was surface-modified by initial treatment with a solution of diethylamine and piperazine in MeOH at 25 °C; after 2 days, they were concentrated to dryness and reprecipitated [773]. The partially aminated product was isolated and subsequently reacted with benzoylisothiocyanate to generate a new type of water-soluble chelating ion-exchange material capable of complexing Co(II), Cu(II), Hg(II), Ni(II), Pb(II), and Zn(II). All metals were retained, almost quantitatively, at pH9.

In order to attach the PAMAMs to a gold surface, PAMAMs possessing surface thiol groups were prepared by the simple treatment of commercial PAMAMs with excess methyl mercaptoacetate [774] and then demonstrated to generate stable self-assembled gold clusters in an aqueous environment. Cationic gold nanoparticles were coated with 3-mercaptopropyltrimethylammonium chloride, followed by the addition of either G3.5 or G5.5 PAMAM [775]; UV–vis, TEM, DLS, and zeta potential measurements demonstrated that these PAMAM dendrimers were attached to the activated gold surface by electrostatic attraction.

The encapsulation of diverse metals within the PAMAM infrastructure has been reported by numerous groups and the incorporated salts have been readily reduced to generate the desired nanoparticle [468,776–778]: Au(III)/Au(0) [477–479,705,706,775,776,779–812]; Cu(II)/Cu(0) [766,790,813–819]; Co(III) and Cr(III) [820]; Fe(II) and Ru(II) [821,822]; Co(III) and Ru(II) [823]; Cu(II) [766,824,826]; Cd(II) [786]; CdS [803,826–830]; CuS [831]; Sn(IV) [832]; Ni(II) [825,833]; Mn(II) [826,834,835]; Ag(I) [790,825,836]; Hg(II) [825]; Co(II) [837]; Co(III)/Co(II) [838,839]; Ru(II) [840–842]; Ag(I)/Ag(0) [472,785,802,808,809,843–847]; Pt(IV) or Pt(II)/Pt(0) [472,781,785,848–856]; Pd(II)/Pd(0) [472,711,776,792,814,848,851,857–870]; Fe(III)/Fe(0) [871], Au(III)/Au(0) and Pd(II)/Pd(0) [872–874]; Au(III)/Au(0) and Ag(I)/Ag(0) [802,875,876]; and Pt(II)/Pd(II) and Pt(0)/Pd(0) [877–880]. There is little doubt that the cavities within these dendrimer/dendron nanohosts will be a key factor in dictating and controlling the size and composition of the nanometalparticle guest(s) that will lead to numerous new avenues to diverse homogeneous/heterogeneous catalysts. The creation of dendritic inks or printed dendrimers take advantage of their cage-like properties with well-defined chemicals [881]; thus, they can selectively bind guests *e.g.*, palladium complexes, which open the door to easily creating patterns with chemical functionality. Metal coatings by means of metal ion coordination have also appeared: terpyridine–Fe–terpyridine [882].

There have been a few reports that have shown that dendrimers can serve as good nanotemplates for the precise synthesis of transition metal nanoparticles [776,883]. Using this procedure, nearly monodisperse F₂O₃ nanoparticles generated by interdendritic stabilization of Fe(III) within the G4 PAMAM, carbon nanotubes and nanofibers were successfully grown (200–400 °C) by microwave plasma-enhanced chemical vapor deposition [884].

The G3 and G4 PAMAMs were treated with stearyl acrylate *via* a Michael reaction to generate the inverse micelle

possessing the hydrophobic surface [885]. In a toluene medium, these micelles encapsulate organic polar dyes, such as Acid Red 1 and Cu(II) salts from an aqueous environment, to give red and blue toluene phases, respectively. There were *ca.* 8 (for G3) and 24 (G4) dye molecules for the globular dendrimers possessing a radius-of-gyration of 17.7 and 25.9 Å, respectively.

3.2.3.2. Bio-aspects of the PAMAMs. In a preliminary biological evaluation of the PAMAMs [886], the *in vitro* and *in vivo* toxicity along with immunogenicity and biodistribution have been investigated. Studies were conducted using either V79 cells or Swiss-Webster mice. Considering the use of G3, 5, and 7, only the G7 dendrimer exhibited potential biological complications. Biodistribution properties were unexpected with G3 preferentially accumulating in the kidneys; whereas G5 and G7 showed the highest concentration in the pancreas. It was concluded that the use of PAMAMs in biological applications was warranted with close attention to the generation employed, dose, *etc.*, along with further study of the biodistribution.

Jain et al. [34] addressed the use of dendrimers, including the PAMAM family, to enhance the solubility of poorly soluble drugs in the development of new drug delivery technologies in order to circumvent this critical dissolution obstacle. The G4 PAMAM in aqueous solution significantly enhanced the dissolution of ibuprofen when compared to 2% aqueous sodium dodecyl sulfate (SDS); the solubility was directly proportional to dendrimer concentration and inversely proportional to temperature [887].

The polymerization of lactide in the presence of G1 PAMAM with amine termini, as the initiator, has been shown to give a nonlinear PAMAM-*g*-PLA possessing enhanced hydrophilicity and faster degradation rate [888–890].

Singh et al. [891] coupled multiple antibodies to simple PAMAMs for use as multifunctional reagents in immunoassays in which the lower generation PAMAMs were most useful while the G5 was deemed to be a “product of unacceptable performance;” this highlights the critical dependence of generational size when dealing with bio-related materials. Antibodies have been readily coupled [892] to PAMAMs; these reagents have been shown to offer an attractive approach to the development of immunoassays in that these coupled antibodies are stable and retain full immunological activity, both in solution as well as when bound to a solid substrate; their analytical sensitivity is equal to or surpasses established methods. The radial partition immunoassays using dendrimers have been shown to possess the best features of both homogeneous and heterogeneous immunoassay formats. Dendritic thin film biosensors for live *Pseudomonas aeruginosa* detection have been described using hydroxy-terminated G4 PAMAM and SYTOX green fluorescent nucleic acid stain. The fluorescence increased with bacteria concentration and the intensity at 5.4×10^7 cells mL⁻¹ was 350% higher using the PAMAM–OH [893]. Methods for generating and detecting antibody response to the PAMAMs have been developed and recognition specificities of those antibodies have been partially defined. Since these antibodies were used in multiple immune detection

procedures [894], it was proposed to be able to generate antibodies as synthetic nanostructures.

The PAMAMs have been demonstrated [892] to enhance immunoassay sensitivity and to reduce, in some cases, the instrumental analysis time. The preparation of metal–carbonyl–G4 PAMAM dendrimer–antibody conjugates has been reported [895,896] by labeling the amine-surface with variable (η^5 -cyclopentadienyl)iron dicarbonyl (η^1 -*N*-succinimidyl) moieties; the detection levels were in the 5–200 pmol/membrane. Similarly, the G3 and G4 PAMAMs were tethered with both (η^5 -cyclopentadienyl)rhenium tricarbonyl and PEG chains [897] to create an infrared probe to be coupled to immunological reagents for amplification of the IR signal in carbonyl metalloimmunoassays.

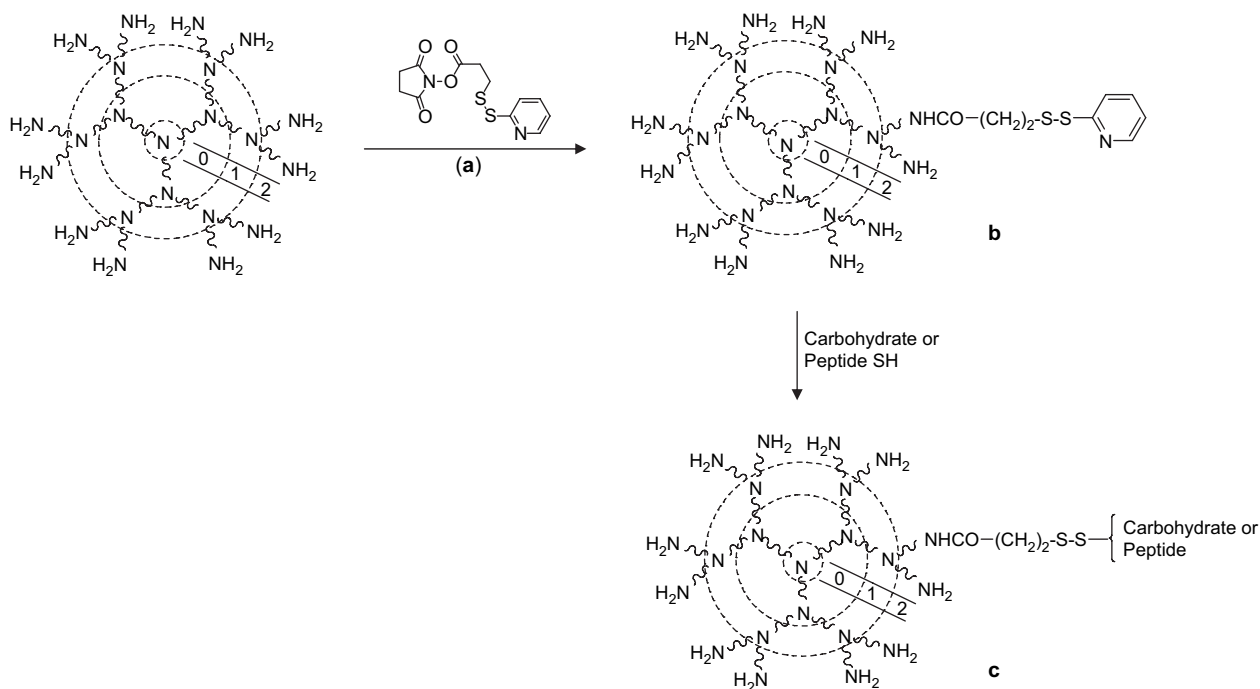
PAMAMs have been employed [898] as buffer additives on electropherograms of chicken sarcoplasmic proteins. Full- and half-generation materials were used through G5.5. The resolution of the protein electropherograms was shown to improve with concentration and generation of the anionic form; a G0 cationic form also improved resolution.

A series of PAMAM wedges through G5 has been divergently assembled on a 1,4,7,10-tetraazacyclododecane core by the standard two-step approach. The acetylated dendrimers were treated with 1-bromoacetyl-5-uracil to generate the dendrimer–5FU conjugates (fluorouracil); subsequent hydrolysis (pH 7.4; 37 °C) released the 5-fluorouracil units [899]. Studies derived from fluorescence *in situ* hybridization demonstrated that the eukaryotic assay vector pCH 110 (*LacZ* gene controlled by SV40 early promoter) plasmid DNA was transferred [900] into human small intestine cancer metastatic ascites (HICMA) cells induced by the G4 PAMAM dendron, based on this core, as a vector.

Early on, Haensler and Szoka [901] used the PAMAMs for the transfection of DNA into cultured cells. PAMAM-mediated transfection thus played a role in the area of hereditary disease treatment by gene therapy. Transfection depends on the dendrimer to DNA ratio as well as the dendrimer's diameter; a 6:1 terminal amine to phosphate charge ratio and molecular diameter of 68 Å were found to maximize transfection of firefly luciferase, an expression vector. When the membrane disrupting amphipathic peptides (GALA [902]) were attached to the PAMAM surface (*e.g.*, an average of 13 GALA residues/G5 PAMAM with a three-directional *N*-core), DNA transfections significantly increased using a 1:1 dendrimer/DNA complex. Szoka et al. [901,903] later reported that “degraded” or “fractured” cationic PAMAMs mediate an elevated level of gene transfection in a variety of cells. Fractured PAMAMs were prepared by heating them in a protic solvent, *e.g.*, H₂O, *n*-BuOH, *sec*-BuOH, or 2-ethoxyethanol. This process created branch defects by either amide cleavage or retro-Michael reactions to afford a heterogeneous end-mixture of products affording a wide range of molecular weights (<1500 to >10,000 amu). It was determined that the higher molecular weight components were responsible for facilitating the observed transfections, suggesting that the fracturing process increased dendrimer flexibility, thus allowing contraction and expansion necessary for DNA capture and release, respectively. De Long et al. [904]

found similar results for intracellular delivery, except that the G3 PAMAM was found to be an efficient oligonucleotide coupling agent. These specifically altered PAMAM-based mixtures were shown to efficiently transfer genes into mammalian cells [905–907], murine cardiac grafts [908,909], *Plasmodium falciparum* [910], lung epithelial cells [911], hairless mouse skin [912], selectable and nonselectable marker genes into human retinal pigment epithelium host cell DNA [913], and cultured human chondrosarcoma-derived HCS-2/8 cells [914]. These same factors of DNA-to-dendrimer ratios, as well as dendrimer generation, were the critical parameters that must be optimized for each model system. Similarly, the efficiency of PAMAMs, as masking membrane modifiers for DNA-based gene transfer due to membrane-destabilizing action, was found to be slightly enhanced by using endosomolytic agents [915]. The fractured cationic G6 PAMAM [903] has been used as well in gene delivery systems, specifically transfection and related physicochemical investigations with extracellular anionic glycosaminoglycans [916]. Although transfection efficiencies of cationic polymers, *e.g.*, either PAMAMs [901] or poly(lysine)s [917] depend on the degree-of-polymerization in which the sizes (10,000–60,000 amu) for the related poly(allylamine)s did not interfere with the mediation of *in vitro* gene transfer into cells [918]. There are, however, examples where cationic G6 PAMAM did not show any lipofection potentiation [919], suggesting that the internal amine branching centers ($pK_a \sim 6$) may prevent acidification inside the endosomes. The G7 PAMAM/DNA complex with a 1:1 ratio of surface amines to DNA phosphate groups was unable to induce leakage of 3:7 POPA–PE vesicles; however, extensive leakage was noted when the surface amine to phosphate ratio was $\geq 3:1$ [920]. The DNA/PAMAM complexes that typically encourage high levels of cell transfection are also able to induce increased levels of vesicle leakage. The modification of G5 PAMAM with biocompatible 3400 molecular weight PEG groups mimicked the fractured high-generation PAMAMs and produced a 20-fold increase in transfection efficiency when compared with partially fractured PAMAM controls [921]. Reports have indicated [922] that the PAMAMs are effective at membrane disruption when the membranes contain a significant proportion of non-bilayer forming lipids; membranes containing dioleoyl phosphatidylethanolamine and steric or oleic acid were very susceptible to disruption by the larger dendrimers, whereas membranes containing lipids with a preference for the lamellar phase were largely unaffected, as noted earlier [920]. The sequence-dependent complexation between single-strand DNA and various PAMAMs has been studied by atomistic molecular dynamics simulations along with free energy calculations, providing a detailed molecular level understanding of both the structure and dynamics of complexation [923].

The preparation of amphipathic peptide-modified **22c** was conducted [892] by treating the polyamine dendrimer with *N*-succinimidyl 3-(2-pyridinyldithio)propionate (SPDP: **22a**) to give the polypyridinyldisulfide **22b**. Subsequent reaction of the pyridinyldisulfide moieties with the GALA peptide possessing a cysteine amino acid afforded **22c** (Scheme 22). Wu



Scheme 22. Disulfide linkers for connecting amphipathic peptides and carbohydrates to amine-terminated dendrimers [892].

et al. [924] reported metal-chelate–dendrimer–antibody hybrids for use in radioimmunotherapy and imaging. PAMAMs were peripherally modified with a slightly less than stoichiometric amount of metal chelators, such as DOTA or DTPA. Lastly, the tumor-targeting antibody 2E4 was connected to the free amine moieties.

The fractured G6 PAMAM was tested for oligonucleotide delivery into a D407 cell line, specifically human retinal pigment epithelial cells, with transfected luciferase; in general, lipid carriers possessing a membrane-bound active component as well as have a small overall complex size proved necessary for the efficient cellular delivery of phosphorothioate oligonucleotides [925].

The resultant PAMAM-*block*-(polysarcosine)₆₄ possessed a narrow $\overline{M}_w/\overline{M}_n$ (1.0₁–1.0₃ by SEC) and a controlled polysarcosine chain length was realized by varying the molar feed ratio of reactants [669].

Double-stranded polynucleotides that were attached to PAMAMs included Calf thymus DNA, Poly(AT), Poly(GC), and 12mer-DNA. The results suggested that (1) DNA wrapped better with the higher generation structures; (2) increased protonation of large dendrimers decreased DNA interaction; and (3) increased protonation of small, more flexible structures led to greater DNA interactions. The ESR, CD, and UV data supported a proposed model for the generation of different supramolecular structures; the PAMAM/DNA interactions are electrostatic in nature and reversible suggesting that the DNA structure will not be permanently modified [926].

Baker et al. [927,928] studied complex formation of PAMAMs and DNA derived from electrostatic interactions between negative phosphate groups and positive protonated amine moieties. Attraction and repulsion were a function of

generation. Transfection was found to be effected by low-density soluble complexes that constituted only 10–20% of the total DNA aggregate. Hélin et al. [929] investigated the use of PAMAMs as vectors for oligodeoxynucleotides intracellular distribution; cell-cycle phase dependence was demonstrated. The DNA–(G2, 4, and 7) PAMAM complexes were studied [930] using ethidium bromide as a fluorescent probe for binding interactions. DNA was observed to wrap by electrostatic interactions around the G7 dendrimer but not G2,4 PAMAMs. Baker et al. [931] have further studied gene expression regulation by PAMAM-mediated *in vitro* transfection of antisense oligonucleotides and antisense expression plasmids. Using this technique, cell lines that permanently expressed the luciferase gene were obtained. In contrast, antisense oligonucleotide or *cDNA* plasmid transfection led to dose-dependent luciferase expression inhibition. These PAMAMs were evaluated [869] for plasmid-mediated gene-transfer efficiency in a murine cardiac transplantation model and were shown to increase the transfer and expression efficiency. The addition of β -cyclodextrin (β -CD) to G5 PAMAM–DNA complexes modified the distribution of those complexes within aqueous solutions [932]. These monodisperse formulations can be used as functional coatings on biodegradable membranes, and the immobilized dendrimer–DNA complexes facilitated *in vitro* transfection of cells. The introduction of α -, β -, or γ -CD–PAMAM conjugates demonstrated potent luciferase gene expression in NIH3T3 and RAW264.7 cells, especially with the α -CD conjugate, that was shown to be *ca.* 100 times greater than those of the dendrimer alone or of a simple physical mixture of dendrimer and α -CD [933]. The gene transfer activity of α -CD–G2–4 PAMAM conjugates was higher than that of the corresponding dendrimer alone in NIH3T3 and RAW264.7 cells; the α -CD

conjugate (G3) had superior gene transfer activity when compared to that of TransFast in NIH3T3 cells [934]. The α -CD conjugates with several α -CyD molecules with variable degrees-of-substitution were prepared [935] and investigated for physicochemical properties, membrane-disruption, cytotoxicity and *in vivo* and *in vitro* gene transfer of the α -CD conjugate in comparison to the dendrimer and TransFast [936]. This α -CD conjugate (G3) strongly interacted with a fluorescence probe, 2-(*p*-toluidinyl) naphthalene-6-sulfonate (TNS) suggesting that the conjugate possesses the inclusion ability with biomembrane constituents, *e.g.*, phospholipids, after transfection. Three sets of complementary oligonucleotides with 34, 50, and 66 base units were covalently conjugated [937] to partially acetylated G5 and 7 PAMAMs [513] and were characterized by agarose gel electrophoresis; these materials were compared to electrostatically bound oligonucleotide–dendrimer complexes [938]. The DNA-directed self-assembly of supramolecular clusters was created from the G5 and G7 conjugates. The G5 PAMAM dendrimer was conjugated to different biofunctional components, *e.g.*, fluorescein and folic acid, and then linked together by the use of complementary DNA oligonucleotides producing clustered macromolecules, which can target cancer cells [939] that over-express the high-affinity folate receptor [940]. A PAMAM dendrimer RGD-4C peptide conjugate was prepared and shown to be taken up by cells expressing $\alpha_v\beta_3$ receptors suggesting its use as a direct imaging agent or in chemotherapeutics to angiogenic tumor vasculature [941]. Baker et al.'s results demonstrated the ability to design and produce supramolecular arrays of dendrimers using oligonucleotide bridges. Their ability to design and produce polymer-based nanodevices for the intracellular targeting of drugs and imaging agents has been displayed [61,942–945]. A comprehensive evaluation of different surface functional groups, *e.g.*, acetamide, hydroxyl, and carboxyl moieties, on G4 and 5 PAMAMs using polyacrylamide gel electrophoresis (PAGE), capillary electrophoresis (CE), size exclusion chromatography (SEC), MALDI-TOF mass spectrometry, potentiometric titration, and NMR has appeared [946].

Initially Majoros et al. [947] partially acylated the amine surface of a G5 PAMAM using this controlled surface functionalization technique, then added fluorescein isothiocyanate as an imaging agent folic acid, and paclitaxel to create a polymer-based, engineered-conjugate for targeted cancer utilizing Taxol, as the chemotherapeutic agent. Polymer-bound adenine nucleotides were prepared by directly coupling of native adenine nucleotides with the carboxy-terminated PAMAM or the nucleotides were modified with a spacer containing a carboxylic acid moiety to be coupled with the amine-terminated PAMAM *via* CDI activation [948].

The permeability of G0–4 PAMAMs, labeled with fluorescein isothiocyanate, across the Madin–Darby Canine Kidney cell line was determined in the apical to basolateral direction and the order was shown to be $G4 \gg G1 \approx G0 > G3 > G2$; the permeability of mannitol in the presence of G4 increased by nine-fold [949]. The G0–4 PAMAMs exhibited a size and molecular weight dependence (*i.e.*, their increasing generation) that resulted in a corresponding exponential increase in extravasation time [950]. The permeability of G0–4 PAMAMs

across the Caco-2 cell monolayers in both the apical to basolateral and *vice versa* directions has been evaluated [951]: the permeability typically increased with the increase in donor concentration and incubation time; whereas the transepithelial electric resistance values decreased and mannitol permeability increased as a function of donor concentration, incubation time, and generation number.

A large number of fluorophores can be attached to an antibody by utilizing a dendritic linker (PAMAM) to form a water-soluble fluorescein–dendrimer–antibody bioconjugate; with added antigen, the fluorescence signals were enhanced when compared to the corresponding fluorescein–antibody analogs [952]. Water-soluble PAMAM derivatives possessing fluorine labels have been synthesized by a Michael reaction of the amine-termini in the presence of a mixture of ethyl 4,4,4-trifluorocrotonate and methyl acrylate; the G2.5 fluorinated product possessed a hydrated diameter of 26 nm. Their diffusion studies indicate that these dendrimers can diffuse rapidly enough in the water channels of bicontinuous cubic phases to be technically useful [953].

Balogh et al. [954] constructed a series of water-soluble, biocompatible, fluorescent, and stable silver-containing nanocomposites for *in vivo* cell biomarkers, thus the amine-terminated G5 PAMAM was transformed to the Ag(I)-dendrimer at pH7. Then, this complex was irradiated with UV light to reduce the bound Ag(I) to Ag(0) that was encapsulated within the dendrimer.

Duncan and Malik described [955,956] preliminary experiments focused on the biocompatibility of dendrimers [62]. The G3 and 4 PAMAMs were found to be cytotoxic toward CCRF and B16F10 cell lines while the corresponding carboxylate analogs were shown to be non-toxic. Complexes of the anionic G5 PAMAM with doxorubicin and cisplatin displayed *in vitro* cytotoxicity. The G2.5, 5, and 5.5 PAMAMs displayed serosal transfer rates that were faster than that observed for other studied macromolecules in the everted rat intestinal sac system [957]. Dennig and Duncan presented a short review over the use of activated PAMAMs in gene transfer into eukaryotic cells [958].

The layering of functionality on the dendrimer surface was demonstrated by the use of the G4 PAMAM that was initially treated with *N*-*tert*-butoxycarbonyl-*S*-acetamidomethylcysteine [BOC-Cys(Acm)], followed by BOC removal (TFA) and treatment with p -O₂NC₆H₄OC(=O)O(CH₂CH₂O)_{*m*}Me, possessing an average molecular weight of 2000, to afford PEG-Cys(Acm)-PAMAM that is lastly deprotected (I₂) to yield the final biocompatible PEG-Cys-PAMAM (G4) with environmental sensitivity [959].

Recently, the G2–8 PAMAMs possessing a N(CH₂CH₂-OH)₃ core have been shown to possess a strong binding affinity for RNA [638]. The ability of these dendrimers to form self-assembled complexes with siRNA was studied with agarose gel electrophoresis [960]. The dendrimers completely retarded siRNA in gels at ratios of [total dendrimer amine termini]/[total siRNA phosphate groups] >2.5 confirming the formation of an electrostatic complex. Their findings suggest the possibility of an effective siRNA delivery system and these complexes are able to produce efficient, as well as long-term,

gene silencing. Related G2–4 PAMAM-type dendrons with a triethylene glycol focal group and various amine termini have been shown to form stable complexes and well-defined nanoparticles with RNA *via* electrostatic interactions and self-assembly processes. The G5 PAMAM was also conjugated to the cell penetrating Tat peptide to generate dendrimer–oligonucleotide complexes, which were shown to be moderately effective for delivery of antisense oligonucleotides and poorly effective for the delivery of siRNA [961–963]. The influence of G2–5 PAMAM on the inhabitation of Tat protein/TAR RNA binding *via* the absorption of the PAMAM on TAR RNA, fixed on a gold substrate through an avidin-biotin connection, has indicated that G3–5 PAMAM have the possibility to be an inhibitors of HIV-1 transcription [964].

Tumor-specific targeting monoclonal antibodies (MoAbs) have been coupled to boronated dendrimers and evaluated for their effectiveness against the murine B16 melanoma using boron neutron capture therapy (BNCT) techniques [965,966]. The synthesis employed the amine-terminated PAMAMs and an isocyanate-based boron reagent, $\text{NaMe}_3\text{NB}_{10}\text{H}_8\text{NCO}$. It was concluded that these dendrimers do not seem to be well suited for the linkage of boron to MoAbs for immunotargeting if administrated systemically. Nevertheless, it was noted that they might be more useful as “linkers” for immuno-electron microscopy.

Barth et al. [967] utilized isocyanatododecaborane to surface modify the G4 PAMAM in a sub-stoichiometric manner, which was then subjected to maleimide–sulfide coupling of epidermal growth factor (EGF). The boronated starburst dendrimer (BSD)–EGF conjugate was prepared as a reagent for use with BNCT, which is used to destroy cancer cells by the production of tissue-destroying low-energy alpha (α) particles at the tumor site. Since increased numbers of EGF receptors are accumulated at the cancer cell surface, it was reasoned that high local concentrations of boron could be delivered by attachment to EGF. Binding of the BSD–EGF conjugate was shown to be EGF receptor specific, although the binding constant (K_A) was found to decrease slightly presumably due to steric hindrance.

Barth et al. [966] prepared the boronated dendrimer–monoclonal antibody immunoconjugates as a potential delivery system for BNCT [965,966,968–973]. Dendrimers have also been employed as linkers for the covalent connection of synthetic porphyrins to antibodies [974]. The PAMAMs have been utilized as a core for surface modification, *e.g.*, for glycodendrimers from *p*-isothiocyanatophenyl sialoside [975]; these constructs were successfully employed for probing multivalent carbohydrate–lectin binding properties. The breast cancer marker T-antigen [Gal(b1-3)GalNAc] was prepared as an allyl glycoside and subsequently transformed to an active ester and coupled to the PAMAM's surface. This glycoPAMAM was shown to strongly bind to mouse monoclonal IgG antibodies [976,977]. Multivalent ligands, including coated low generation PAMAMs, were used to evaluate the effects of structural architecture, *e.g.*, scaffold shape, size, valence, and density of binding elements, on inhabitation and clustering of lectin concanavalin [978]. In

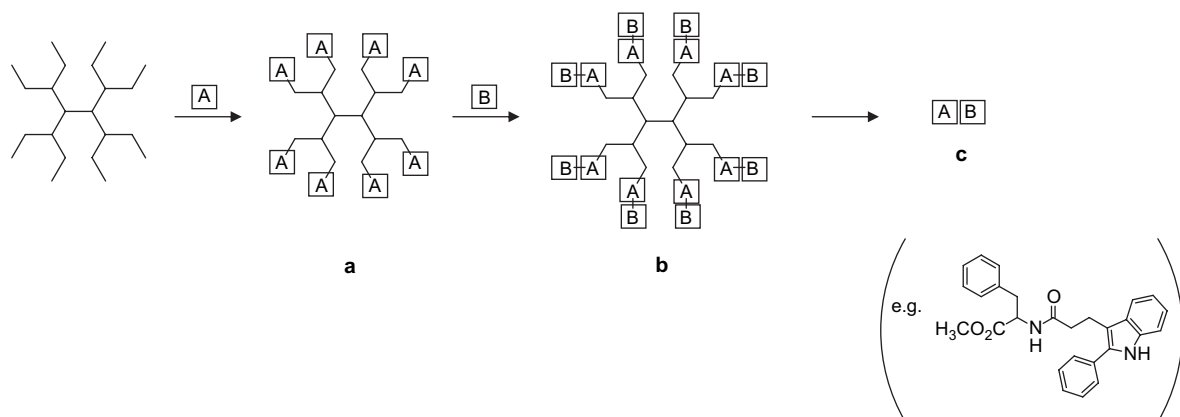
order to eliminate potential retro-Michael reactions associated with PAMAM construction, Zanini and Roy [979,980] devised a efficient modification to α -thiosialodendrimers in which the methyl acrylate step was replaced by simple alkylation with *tert*-butyl bromoacetate affording a $\text{RN}[(\text{CH}_2)_3\text{NHCOCH}_2\text{N}^<]_2$ motif; both divergent and convergent approaches were presented. Multivalent neoglycoconjugates have been shown to be valuable tools for studying carbohydrate-protein interactions. An evaluation of the interaction of HIV-1 gp120 with its reported alternate glycolipid receptors, galactosyl ceramide (GalCer) and sulfatide, galactose- and sulfated galactose-derivatized PAMAMs were prepared, then analyzed as ligands for rgp120 by surface plasmon resonance and lastly tested to inhibit HIV-1 infection of CXCR4- and CCR5-expressing indicator cells [981]. Numerous examples of carbohydrate- [977,982–992] or chitosan- [993–997] surface coatings, *e.g.*, mannose-based reagents [998–1002], have appeared, which have given rise to “sugar balls” [783,984,1003–1008].

Kim et al. [1009] used PAMAMs as scaffolding for the construction of a combinatorial library; the dendrimer-supported combinatorial chemistry was demonstrated through the production of a single species and a small library on the dendrimer periphery. To facilitate simple ester cleavage of surface constructs after their preparation, 4-hydroxymethylbenzoic acid was coupled (EDC) to the eight terminal amines; this provided the base-labile terminal hydroxy attachment starting points. Single molecule construction was exemplified by a sequential three-component synthesis of a biologically active indole. Thus, *N*-Fmoc-protected-L-phenylalanine was coupled (EDC/DMAP) to the hydroxy-terminated dendrimers and deprotected (piperidine/DMF) to give the supported aminoacid **23a**. Following the reaction with 4-benzoylbutyric acid, phenylhydrazine hydrochloride was added (Fischer indole conditions; $\text{AcOH}/\text{ZnCl}_2$) to complete the multi-component synthesis (*i.e.*, **23b**). After isolation, indole cleavage (MeOH/NEt_3) afforded the dendrimer, which was filtrated to give the desired phenylalanine-based indole **23c** (Scheme 23).

Similarly, a split synthesis protocol [1010] generated a $3 \times 3 \times 3$ (27 component) combinatorial library. Pertinent features of these methods include solution phase chemistry, homogeneous purification, intermediate characterization, and high support loadings.

Small hydrazide-terminated PAMAMs were prepared [1011] for use as cross-linkers in hydrogels created from hyaluronic acid. The amine-surface of the PAMAMs can be converted to an extended carboxylic acid moiety by its treatment with succinic anhydride in DMSO at 25 °C; the G3 PAMAM was so coated in 94% yield [505]. The use of this simple technique gave the acid-coated G7 PAMAM, which was employed as a nanoprobe of biological hydroapatite nanorod surfaces [613].

Margerum et al. [1012] treated the surface of the G2–5 PAMAM series with [1-(4-isothiocyanatobenzyl)amido-4,7,10-tetraacetic acid-tetraazacyclododecane; DO3A-bz-NCS] followed by Gd(III) complexation to generate a series of water-soluble materials possessing 11 Gd(III) complexes/G3 PAMAM or 57 Gd(III) complexes/G5 PAMAM based on wt%



Scheme 23. Scaffolding for molecular construction and combinatorial libraries [1009].

Gd, as determined by inductively coupled plasma (ICP) absorption spectroscopy. To improve the biocompatibility, the gadolinium chelating moieties and surface polyethylene glycol units were incorporated to investigate the effects of molecular weight on the biological and physical properties of MRI contrast agents [1013]. Thus for G2 and G3, unreacted terminal amines were treated with poly(ethylene glycol) (both the PEG₂₀₀₀ and PEG₅₀₀₀ analogs were prepared for each generation). Using NMR dispersion, non-PEG substituted dendrimers exhibited peak relaxivities as high as $18.8 \text{ mM}^{-1} \text{ s}^{-1}$ (25 MHz); the magnitude showed a linear increase with molecular weight. Half-life blood elimination in rats increased with molecular weight ranging from $11(\pm 5)$ min to $115(\pm 8)$ min for G3–5, respectively, and liver retention over a seven day period showed an increase with molecular weight (*i.e.*, 1–40%). The PEGed polychelated relaxivities ranged from 11 to $14.9 \text{ mM}^{-1} \text{ s}^{-1}$ (G2 and 3 PAMAM) while blood elimination half-lives dramatically increased to as much as 1219 min.; seven day liver retention decreased to 1–8% per dose. In this case, PEG modifiers enhanced the biodistribution and pharmacokinetics of the MRI contrast agents.

Peripherally modified PAMAMs with macrocyclic Gd(III) complexes for use as MRI contrast agents have been examined by Merbach et al. [1014–1016]. Rotational correlation times have been found to be 4–8 times greater for these agents when compared to smaller mono- or bis-complexes; however, the observed low H₂O exchange rates prevented a corresponding increase in proton relaxivities. The synthesis and evaluation as MRI agents of a related series of polymeric gadolinium complexes, including the surface-coated (DOTA) G3 PAMAM, have been reported [1017]; the blood half-life for these globular materials was longer than that of Gd-DTPA (Magnevist), but considerably shorter than the linear DOTA polymer. An alternative reagent, [2-(4-isothiocyanatobenzyl)-1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetate; *p*-SNC-bz-DOTA] [1018], was used to functionalize the G5, 7, 9, and 10 PAMAMs [924,1019]. The end result averages 127 chelates and 96 Gd³⁺ for G5 and 3727 chelate groups and 1860 Gd³⁺ for G10. *In vivo* ovarian tumor xenografts resulted in a 33%

contrast enhancement, following the folate-G4 PAMAM chelate administration [1020] that was significantly different when compared to the results with the non-specific, extracellular fluid space agent, Gd-HP-DO3A [1021]; whereas *in vitro* mouse erythroleukemia cells expressing the hFR bound the radiolabelled folate-G4 PAMAM chelate, affording a >2700% increase in binding when compared with untreated cells. The Gd(III) complex, derived from a DTPA-based chelate possessing one phosphinate moiety attached to a G5 PAMAM *via* a benzylthiourea connection, was shown to be a potential contrast agent for MRI [1016]. Folic acid was attached (CDI) to a G4 PAMAM surface and then loaded with the anti-arthritis drug, indomethacin [1022]; it was shown that the drug content and percentage encapsulation efficiency increased with increasing folate content for the dendrimer conjugates.

The biodistribution of ¹¹¹indium- and ⁸⁸yttrium-labeled G2 surface-modified PAMAM with 2-(*p*-isothiocyanatobenzyl)-6-methyl-diethylenetriaminepentaacetic acid (1B4M) has been reported [1023], whereby humanized anti-Tac IgC (HuTac) was conjugated to the PAMAM–1B4M complex and its *in vitro* and *in vivo* properties were analyzed. The dendrimer conjugates were shown to give greater liver, kidney, and spleen accumulation than that of native materials suggesting that the PAMAM dendrimer had potential detrimental effects on biodistribution. Different generations (G4–6) of the PAMAMs were utilized and a size-dependence factor was realized [1024–1028]; the ¹⁵³Gd-labeled G6-PAMAM conjugates remained in the blood longer and there was an increase in blood-to-organ ratio of the preparations that correlated to increasing molecular size. Two G6 PAMAM dendrimers possessing different cores were treated with 1B4M, then labeled with ¹⁵²Gd. In terms of intravascular contrast agents, the agent derived from the ethylenediamine core was deemed better due to a higher Gd(III) loading and a longer circulation time than the agent based on an ammonia core [1029]. The G4(PAMAM)–(1B4M-Gd)₆₄ has been previously prepared [399,401] and shown to be a useful vascular MRI contrast agent, as well as compared to G5(PPI)–(1B4M-Gd)₆₄, but in order to enhance hydrophilicity to increase its circulation

half-life and lower immunogenicity, the attachment of one and two PEG molecules has been reported [1030]. The G2 and 4 PAMAM–TU–1B4M vanadyl complex (TU = thiourea) was prepared and the molecular dynamics evaluated [1031]. Avidin–G6(PAMAM)–(1B4M–Gd)₂₅₄ was prepared and shown to accumulate and internalize into nude mice bearing intraperitoneally disseminated SHIN3 tumors; both *in vitro* and *in vivo* studies kill the cells using ^{157/155}Gd with external irradiation via an specific neutron beam with MRI monitoring [1032]. The G4, 6, and 8-1B4M–Gd biometric nanoprobe were recently used to detect vascular permeability in SCCVII mice tumors; the G8-size probe was shown to be an ideal candidate based on whole body clearance curves [1033].

The preparation of dendrimers possessing dual imaging modality has appeared in which a G6 PAMAM was initially treated with a two-fold molar excess of the 1B4M–DTPA bifunctional chelating agent connected by a thiourea linkage. The second step utilized Cy 5.5 (an NIR fluorescent dye) succinimidyl ester, which was reacted with the remaining free amine moieties of G6-1B4M, generating a new covalent linkage between the dendrimer and dye, and lastly, the 1B4M–DTPA moieties were complexed with Gd(III) from a solution of Gd(OAc)₃. The combination of MRI and FI within one molecule offers a novel approach to the mapping of sentinel nodes both before and during surgery [1034–1036]. A new bifunctional octa-coordinating ligand, 1,4,7,10-tetraazacyclododecane-4,7,10-triacetic-1-{methyl[(4-aminophenyl)methyl]-phosphinic acid} has been synthesized [1037] and applicable to dendrimer attachment [1038]. Reviews concerning MRI contrast agents have appeared [65,1013,1039–1045] and a series of remarkable papers from the Kobayashi groups is available [401,1046–1066]. Interestingly, quantum dots have recently been reported to perform multicolor images with high fluorescent intensity suitable for lymphatic imaging via direct interstitial injection [1067,1068]. These simultaneous multicolors for *in vivo* spectral fluorescence lymphangiography showed that using five different quantum dots with aligned sizes but possessing different emission spectra offer a new approach to diagnosis.

Novel water-soluble dendritic nanoparticles for computed tomography imaging have been prepared by surface-coating the G4 PAMAM with 3-*N*-[(*N*',*N*'-dimethylaminoacetyl)-amino]- α -ethyl-2,4,6-triiodobenzenepropanoic acid [1069]; the material has a hydrodynamic radius of 2.4 nm and an iodine content of 306% while still retaining an overall charge and water solubility.

Layer-by-layer films were composed of the branched architectures of either biotin-labeled-G4 PAMAM (14,215 amu) [1070] or biotin-labeled-PEI (of 45,000 amu) and avidin. The G4 PAMAM monolayer was first constructed on an 11-mercaptopoundecanoic acid self-assembled monolayer on gold, followed by surface-functionalized with the biotin-analogs, desthiobiotin or desthiobiotin amidocaproate [1070]. Surface plasmon resonance spectroscopy demonstrated a resonance angle shift for the formation of dendrimer monolayers on reactive self-assembled monolayers suggesting that 89% of the gold surface was covered by the dendrimer [1071]. Similar studies were

conducted based on the G4 PAMAM, which was partially coated with tethered ferrocenyl surface groups [1072–1074]. PAMAM-based films were shown to facilitate monolayer deposition of avidin; in contrast, the randomly branched PEI facilitated only multilayer avidin deposition [1075]. The loading of avidin in each layer of the multilayer films depended on the molecular geometry of the polymer, thus the PAMAM/avidin films were composed of monolayers due to the dendrimer's spherical shape [1076]. Biotin-coated G0–4 PAMAMs were prepared and cross-linked with streptavidin (SAv); an assessment was made of the quantity of [¹²⁵I]SAv, bound with polystyrene-bound SAv after treatment with the coated PAMAMs [1077]. The results of the biodistribution revealed that most tissues that were examined had low concentrations of biotinylated dendrimers, except for the kidney and liver. *In vivo* studies showed that the modified dendrimers had cleared the bloodstream within 4 h after administration.

The layer-by-layer assembly of [PAMAM–protein]_n films, in which the heme proteins were hemoglobin, myoglobin and catalase, was constructed with alternating adsorption of oppositely charged PAMAM and proteins from their aqueous solutions by electrostatic interactions [1078]. The use of a quartz crystal microbalance, UV–vis spectroscopy, and cyclic voltammetry permitted a critical insight into the assembly process.

The surface activation (with thiols, phenyliodoacetamido-, iodoacetamido-, and epoxy groups) of commercial PAMAM methyl carboxylate- and amino-terminal moieties has been described [1079] in the context of using these modified peripheries for attachment to alkaline phosphatase. Enzymatic and immunochemical properties of these protein–dendrimer reagents have been evaluated by immunoassay systems.

One of the few comparative studies [1080,1081] of PAMAMs, PPIs (with two different cores), and poly(ethylene oxide) grafted carbosilane dendrimers, was systematically conducted to probe the relationships of generation size and surface functionality as related to *in vitro* biological properties. This evaluation of dissimilar structural components of different dendrimers provided the first insight into the parameters that are critical to the rational design and tailoring of macromolecules for drug delivery. In general, cationic dendrimers are hemolytic and cytotoxic, depending on size and surface number; whereas the anionic dendrimers are neither hemolytic nor cytotoxic over broad concentration ranges and the dendrimers, irrespective of source, “essentially behaved very similarly according to their size and surface characteristics” [1080]. Cationic dendrimers typically have a higher surface charge density and are consequently capable of forming DNA complexes that are stable over various pH and salt concentrations; transfection efficiencies depended on the number and size of the dendrimers in each complex with the highest expression obtained using the 6.8 nm PAMAM (G6) at a $\pm 2.8/1$ charge ratio prior to liposome addition [1082].

Saegusa [1083] generated a PAMAM hybrid by a sol–gel reaction of ethyl orthosilicate in the presence of a PAMAM without a coupling agent. The G3.5 ester-terminated PAMAM was treated with tetraethoxysilane as well as a coupling agent, 3-glycidoxypropyltrimethoxysilane, by an *in situ* sol–gel

procedure affording a transparent nanocomposite [1084]. Another type of hybrid derived from multilayers of [poly(maleic anhydride)-*c*-poly(methyl vinyl ether), lightly cross-linked with 1% ethylenediamine], and PAMAM – beginning with an amino-functionalized silica/silicon surface [1085]. The use of G4 PAMAM, as a template for silica gels, was made from tetraethyl orthosilicate by means of a sol–gel method; X-ray diffraction and adsorption data demonstrated the presence of quasi-spherical dendritic “porogens” [375]. It was later demonstrated that the use of a G0 PAMAM cross-links the silica; whereas the larger G4 serves as a templating agent, leading to larger colloidal particles and does not necessarily strengthen the gel [1086]. These PAMAMs were coated with organosilicon to generate a family of materials possessing a hydrophilic core with a hydrophobic exterior [1087]. This novel family of dendrimers, abbreviated as PAMAMOS (polyamidoamine organosilicon), was recently reviewed [1088–1092] and, in part, is commercially available. Their synthesis was accomplished by either (a) Michael addition of organosilicon acrylates or methacrylates to the PAMAM polyamine surface or (b) haloalkylation with chloroalkyl- or iodoalkylsilanes. Variations of PAMAMOS’s composition are based on (1) the use of any amino-terminated PAMAM, (2) one or two organosilicon surface layers, (3) various inert or reactive end groups, and (4) different relative numbers of end groups. A covalently cross-linked, three-dimensional nanodominated network was prepared from radially layered PAMAMOS containing hydrophilic PAMAM interiors and reactive hydrophobic organosilicon exteriors [1093]. The interaction of Cu(II) with the diverse N and O sites within the PAMAMOS structures has been evaluated using near edge X-ray absorption fine structure characterization of the resultant copper-containing nanocomposite [1094]. Microcontact printing using the PAMAMOS–dimethylsilyl dendrimer multilayers onto silicon wafers, glass, and polyelectrolyte multilayers has been reported [1095]. A series of PAMAM–POSS hybrids (POSS = polyhedral oligosilsesquioxane) were generated by treatment of the G2–5 PAMAMs with varied amounts of isocyanatopropyl dimethylsilyl-isobutyl (or -heptacyclohexyl)-POSS in CHCl₃ at 25 °C [1096]. The hybrid’s thermal degradation was dominated by the thermal instability of the PAMAM component relative to the POSS component, suggesting that this could be a route to closed nanoporous silica structures. The inhibition efficiencies of PAMAMs, comparing either acid or amine surfaces, were ascertained in the formation of colloidal silica, and those with an amine surface were shown to be superior [1097] and offered a bioinspired approach [1098].

A combination of the G2 PAMAM covalently surface-coated to the mesoporous silica nanospheres (MCM-41-type) [1099] was used to complex plasmid DNA (pEGFP-C1 [1100], coded for an enhanced green fluorescence protein); its gene transfection efficacy, uptake mechanism, and biocompatibility with neural glia (astrocytes), human cervical cancer (HeLa), and Chinese hamster ovarian cells were investigated [1101]. It was concluded that this system could serve as a new transmembrane delivery system. The use PAMAM (G0–3 and G5) [or PPI (G1–5)] and have been used as templates in the biogenic silica

production to create a more robust, convenient, size-selective precipitation of silica nanospheres [1102,1103].

Yoon et al. [1104] prepared a thickness-controlled biosensing interface by multilayer (Schiff base) assembly of G4 PAMAMs and periodate-oxidase glucose oxidase on a Au electrode surface; the E5D5 (layers) electrode demonstrated a sensitivity of 14.7 $\mu\text{A mM}^{-1}$ glucose cm^{-2} and remained stable over 20 days with daily calibrations. Recently, amperometry has been used to study the properties – specifically, the kinetic parameters of the enzyme, response times, sensitivity, detection limits, linear ranges, and enzyme turnover – of glucose biosensors based on G1 PAMAM layers on a gold support [1105]. The G3 PAMAM–PEG–peptide conjugates have been reported [1106] for the specific control of cell aggregation.

Star-like *N*-(2-hydroxypropyl)methacrylate copolymers were constructed by conjugating poly[*N*-(hydroxypropyl)methacrylate], as arms, with a G2–4 PAMAM core. Doxorubicin was introduced into the resultant copolymer and evaluated as a drug delivery system, which was described as marginal [1107].

The interactions of G4 and G5 PAMAMs with bovine serum albumin (BSA) have been studied by evaluating the intensity of the intrinsic fluorescence of two tryptophane residues. Based on the shift of the emission maxima, it was demonstrated that G4 has a greater impact on the spectral properties [1108]. Interactions of BSA with sugar-coated G3 and G5 PAMAMs have been studied using surface tension, interfacial rheology, and circular dichroism [1109]. Comparisons between G3.5 and G4 PAMAM interactions with BSA have been evaluated and G4 was shown to have a greater impact on the spectral properties.

The synthesis and characterization of a complex composed of a gold quantum dot encapsulated by a G2 PAMAM conjugated electrostatically to an antibody designed as a major component of an immunofluorescent assay for the detection of the human IgG antigen, based on the polyclonal, goat-derived anti-human IgG antibody [791].

The surface coating of the G4 PAMAM with phenylalanine was accomplished by treating the PAMAM with either *N*-BOC-Phe or -Leu, using *N*-hydroxysuccinimide and DCC, followed by BOC-deprotection with trifluoroacetic acid and thioanisole; transfection and cytotoxicity studies were conducted [1110,1111]. Recently, the surface coating of the G5 PAMAM with alkylamide-termini, *e.g.*, isobutyramide moieties, has generated a proposed new polymer type possessing a thermosensitive surface enhancing their unimolecular micelle potential [1112].

Tethered ligands to polymeric macromolecules have been shown to significantly affect ligand access to the receptor; the use of PAMAM was evaluated as part of an estrogen–dendrimer-conjugate composition in which long or hydrophobic tethers impose considerable ligand shielding resulting in poor access to the receptor, however, those with short tethers permit exposure of the ligand thus enhancing receptor binding [1113].

3.2.4. PAMAM physical properties

Turro et al. [1114–1116] characterized the PAMAM series utilizing fluorescence spectroscopy, in which a photoluminescence probe, specifically pyrene, was used to evaluate the hydrophobic regimes. Their results were consistent with

theoretically predicted morphologies; thus, the G0.5–5.5 structures are open but G4.5–9.5 PAMAMs are closed, and the surface became more congested with increasing generation. Photoinduced electron transfer between species associated with the carboxylate surface supported the structural changes at the G5 level [1117]. Using single-photon-counting techniques through the monitoring of luminescence decay of the excited complex, the dynamics of electron-transfer quenching of photoexcited $[\text{Ru}(\text{phen})_3]^{+2}$ were evaluated using methyl viologen in solution with anionic PAMAMs [1118]. Kinetics of luminescence supported the structural change at G5 and, despite the structural differences with micellar aggregation, striking similarities were demonstrated. Reviews [517,1119] concerning the internal photophysics of the PAMAM series have appeared and should be consulted for the details.

Binding constant data of $[\text{Ru}(\text{phen})_3]^{+2}$ to carboxylate-terminated G#5 PAMAMs have been reported [1120]. Increased excited-state lifetimes were attributed to a decreased O_2 concentration at the surface relative to that of the aqueous media. Quenching rates of excited $[\text{Ru}(\text{phen})_3]^{+2}$ by dendrimer bound $[\text{Co}(\text{phen})_3]^{3+}$ were shown to be independent of quencher concentration. The statistical analysis of luminescence quenching of $[\text{Ru}(\text{phen})_3]^{+2}$ by $[\text{Co}(\text{phen})_3]^{3+}$ at the PAMAM surface has been examined [1121] showing that the donor and acceptor complexes bind in a non-random manner, preferring adjacent juxtapositions. The energy of attraction resulted from hydrophobic interactions. The emission-intensity and emission-lifetimes of $[\text{Ru}(4,7-(\text{O}_3\text{SC}_6\text{H}_4)_2\text{-phen})_3]^{-4}$ in solution containing a cationic PAMAM either in the presence or absence of potential quenchers have been investigated [1122]; the quenching constants between the various dendrimers and this Ru complex and methylviologen, $\text{K}_4\text{Fe}(\text{CN})_6$ or $\text{K}_3\text{Fe}(\text{CN})_6$ were ascertained by laser flash-photolysis. The use of high PAMAM concentrations relative to that of probe and quencher showed that the rate of quenching of $[\text{Ru}(\text{phen})_3]^{2+}$ by $[\text{Co}(\text{phen})_3]^{3+}$ bound to the dendrimer is independent of quencher concentration [1120].

In order to determine the colloid diameter and surface curvature, related to polyelectrolyte binding, Dubin et al. [1123] investigated complex formation between G5 PAMAMs and poly(dimethyldiallylammonium chloride). Based on turbidity experiments, their observations were consistent with those of Turro et al. [517,1118,1119] in which the higher generation dendrimers behave as closed Stern layer structures; whereas at lower generations, simple electrolyte characteristics were exhibited. Dubin et al. [1124] investigated the binding interactions of G0.5, 5.5, and 7.5 PAMAMs with poly(dimethyldiallylammonium chloride) with added NaCl; complex formation readily occurred at G7.5. This was attributed to its high charge density vs. that shown for the lower generations. The pH titration analyses gave estimates for the free energy of complex formation. The use of these G#5 PAMAMs as calibration standards for aqueous size exclusion chromatography demonstrated that there was a “remarkable correlation of the chromatographic partition coefficient with generation number” [1125,1126], due, at least in part, to the relationship between generation and molecular volume.

Tanaka et al. [1127] reported and Palmer reviewed [1128,1129] the use of PAMAMs as the pseudostationary phase in micellar electrokinetic chromatography. Uncharged aromatic analytes, including a series of aromatic hydrocarbons, were separated using water and water/MeOH mixtures, as the mobile phase. The surfaces of G#5 PAMAMs modified with *n*-octylamine and the products were evaluated for electrokinetic chromatography [1130]. These carriers facilitated efficient separations of aryl alkyl ketones and aldehydes, as well as exhibited reversed-phase liquid chromatography characteristics, allowing separation optimization by organic solvent content manipulation. Analytes were further examined [632] using dendrimers constructed from a *p*-xylylenediamine core and standard PAMAM-type construction. At the G5.5 level, the ester surface was treated with limited $\text{C}_8\text{H}_{17}\text{NH}_2$, followed by saponification giving a difunctional surface. A clear propensity toward separation of rigid aromatics from aliphatics was observed.

Chujo et al. [1131] used methoxycarbonyl-terminated PAMAMs to manipulate pore size in porous silica [1132]. Organic–inorganic hybrid materials were achieved by acid-promoted “sol–gel” reaction of $\text{Si}(\text{OMe})_4$ with added dendrimer. The amine-terminated dendrimers gave the phase-separated hybrid; whereas use of their ester-terminated counterparts produced transparent, homogenous blends. Heating the polymer hybrids to 600 °C for 24 h led to complete elimination of the dendritic frameworks, as shown by elemental analysis. Pore size distribution correlated with the size of the dendrimer employed. The SiO_2 –PAMAM hybrids were prepared [1133] by a Michael addition of the dendrimer and 3-(trimethoxysilyl)propylacrylate, dissolution in MeOH, and subsequent treatment with partially hydrolyzed tetraethylorthosilicate (PEOS); these hybrids were shown to possess metal ion complexing capacity. The covalent attachment of erythrosine isothiocyanate to the G4 PAMAM quantitatively eliminated the leaching of dye molecules from sol–gels prepared from tetramethylorthosilicate [1134,1135].

Ionic liquid crystalline dendrimers possessing a smectic A mesophase have been prepared from G3 PAMAM with steric, palmitic, and myristic acids [1136]. The characterization of these ionic liquid crystalline dendrimers derived from the spontaneous assembly of the G0–5 PAMAMs, or G0–5 PPIs, and $\text{Me}(\text{CH}_2)_n\text{CO}_2\text{H}$, where $n = 8, 12, 16$ [274,275], was appraised by DSC, polarizing optical microscopy, and X-ray diffraction.

Ottaviani et al. [1137] conducted extensive EPR studies on G#5 PAMAMs possessing a sodium carboxylate surface. Positively charged nitroxide radicals, attached to different length carbon chains, were used to evaluate the hydrophobic and hydrophilic binding loci. Mobility (τ_c) and polarity (A_n) parameters, as a function of pH, demonstrated electrostatic binding interactions at the dendrimer–water interface. The radical chain intercalated within the dendrimer and interacted at internal hydrophobic sites. Activation energies for the probe’s rotational motion were established. Aggregation behavior of the positively charged, TEMPO-functionalized, C_{16} surfactants (CAT16: 4-(*N,N*-dimethyl-*N*-hexadecylammonium-2,2,6,6-tetramethylpiperidine-*N*-oxyl iodide) in the presence of G#5

PAMAMs has been evaluated by EPR [1138]. For low aqueous concentrations of $G < 5.5$ dendrimers possessing smaller or comparable sizes to that of the CAT16 micelles, the guest dendrimers were postulated to bind to the host micelle; however for low concentrations of $G > 5.5$ dendrimers, the micelles act as the guests for the dendritic hosts. Bilayer surfactant-based aggregates at the periphery were proposed along the bridged dendrimer-bilayer-dendrimer complexes. Interactions of these anionic ($G\#.5$) PAMAMs and cationic surfactants were investigated using EPR spectroscopy; the spin–spin interactions supported the proposed model possessing more than one probe within the aggregates [1139]. The probes used consisted of alkylated (C_9 , C_{12} or C_{16}) TEMPO derivatives, while surfactants included either dodecyltrimethylammonium bromide (DTAB) or cetyltrimethylammonium bromide (CTAB). The results suggested two dendrimer-substrate models: (1) the surface adsorption of molecular probes by the PAMAM constitutes a primary structure, and (2) the monomer adsorption in surfactant aggregates adhered to the PAMAM periphery gives a secondary structure. Treatment of a G6 PAMAM with either an excess or a stoichiometric amount of *N*-hydroxysuccinimidyl-TEMPO generated the coated G6 PAMAM-TEMPO₁₉₈ or -TEMPO₈₀ derivatives, respectively, of which the degree-of-substitution was ascertained by MALDI-TOF-MS [1140]. A multi-angle, light scattering analysis showed that the fully substituted material aggregated to form particles of MW of 549,000 (degree-of-aggregation ≈ 5.4) with an 18.8 nm radius; whereas the less substituted sample revealed particles of MW 113,100 (degree-of-aggregation ≈ 1.6) and a radius of < 10 nm. An alternate route to G 2, 4, 6, 8 TEMPO- or fluorescein-labeled PAMAMs was by treatment of the free dendrimer with 4-(2-iodoacetamide)-TEMPO or 5-iodoacetamidofluorescein, respectively, in DMF [1141]; the mobility of the TEMPO-labeled PAMAMs was determined by EPR over a range of concentrations of added free PAMAM, resulting in the general observation that no significant interdendrimer interaction, *e.g.*, aggregation, occurred. Cloninger et al. [1142] recently, coated the G4 PAMAM with 5–95% of TEMPO in which the TEMPO was randomly distributed over the PAMAM's surface; however, in order to study the binding constants of mannose with lectin, the G4 PAMAM was initially treated with variable amounts of the mannose isothiocyanate derivative, followed by 4-isothiocyanatoTEMPO, to generate different surface concentrations of the carbohydrate (after deacetylation). The characterization of this heterogeneous coat was conducted with mass spectrometry [1143] and EPR studies [1144].

Turro et al. [1145] employed the alkyl core-based PAMAMs in host–guest complexation of the guest dye, Nile red. A hydrophobic core created by a C_{12} alkyl chain was observed to enhance significantly Nile red fluorescence emission in an aqueous media, while PAMAMs with cores derived from either shorter chains or ammonia showed no effect. Addition of anionic surfactants greatly increased the inclusion of Nile red due to the formation of a dendrimer–surfactant supramolecular host–guest assembly. Interactions between the smaller PAMAMs with several biologically important guests, such as pyridine, quinoline, quinazoline, nicotine, and trimethadone,

were evaluated [1146]. The association constants suggested that both internal and terminal interaction sites were possible; however, with ester-terminated PAMAMs, internal binding was inhibited.

Ottaviani et al. [1147] examined the interaction of PAMAMs with dimyristoylphosphatidylcholine (DMPC) vesicles. Structural modification of these vesicles was monitored by continuous wave- and pulsed-electron paramagnetic spectroscopy, using doxyl-modified stearic acids, as guest probes. Vesicle bilayer integrity was found, supporting their potential uses as drug and gene carriers. The TEM data for $[UO_2]^{+2}$ -negatively stained PAMAMs were analyzed with and without DMPC liposomes and mixed DMPC/DMP-colate sodium salt liposomes at different percentages [1148]; in general, the $[UO_2]^{+2}$ was complexed to the dendrimer rather than the liposomes. Nitroxyl radical probes were attached to the surface of G2 and 6 PAMAMs [1149] to facilitate EPR measurements. Their results showed that dendrimer–vesicle interactions (1) modified the fast rotation axis of the radical, (2) were greater for higher generation dendrimers, (3) were such that the mean vesicle size remained unchanged, and (4) were stronger with protonated dendrimers. Ottaviani et al. [1150] reported the interactions of polynucleotides with nitroxide-labeled PAMAMs by ESR. Cyclic voltammetric studies further indicated that the PAMAMs coated with nitroxyl termini are non-interacting and electrochemically equivalent in which the redox centers oxidize at the same potential [1151]. Both the hydrophobic 5-doxylstearic acid (5DSA) spin probe and the positively charged CAT16 were shown to insert into the vesicles and were used to monitor the formation of G2 and G6 PAMAMs mixed vesicle (DMPC/DMPA–Na) complexes; the spin probe showed a partial ordering of a double layer-like structure on the dendrimer's surface and the related EPR data suggested that the vesicles wrapped around the larger PAMAM, whereas the smaller PAMAM simply interacted with the vesicle's surface [1152].

Protonation of a G4 PAMAM coated with either amine or hydroxy functionality has been studied with potentiometric pH titration and was analyzed using either a multishell structural model [1153] or Frumkin absorption isotherm to ascertain the proton–dendrimer binding equilibrium [617]. The internal amine moieties in the hydroxyl coating have an average binding constant ($pK = 6.3$ compared to $pK = 9.23$ for the amino-surface) of 1–2 pH units lower than a single isolated binding site, which was attributed to hydrophobic internal microenvironments. The G1–4 PAMAMs were protonated and treated with a series of azo dyes in order to study the resultant aggregates resulting in the alignment of the electrostatically bound azo dyes [1154]. The adsorption spectra revealed a pattern of highly ordered spectrally distinct dye aggregates attributed to either H- or J-aggregation, resulting from blue- or red-shifted spectra, respectively; observations were made relating to the characteristics of the particular dyes used.

With the variance of generational size and acidity, the G2, 4, 6 PAMAMs have been shown to possess both specific and nonspecific binding properties. The use of 2-naphthol has been demonstrated to preferentially complex the *internal*

tertiary amines and can be released by lowering the pH of the solution [1155]. The supramolecular dynamics of the overall host–guest process was enhanced by increasing the solution's acidity; the degree-of-protonation of the internal branching amine sites was ascertained to be *ca.* 12, 10 and 1%, respectively, at pH6. The binding of 5-dimethylamino-1-naphthalenesulfonic acid (DNS) with a G6 PAMAM, which has the lowest average density in the family based on hydrodynamic measurements [570], was investigated [1156]; there is clear evidence for a conformational change but whether that change actually triggered the release of the DNS guest was not ascertained. The microscopic protonation of PAMAMs has shown that the surface primary amines are initially protonated at high pH, then the internal tertiary amines at lower pH, and lastly, the central tertiary amine groups [1157].

Yu and Russo [1158,1159] reported the fluorescence photobleaching recovery and dynamic light-scattering characterization of the PAMAMs in an aqueous environment. Agreement of their results suggested that attachment of a fluorescent dye does not significantly change the diffusion coefficient of the G5 PAMAM. At high salt concentrations, the measured hydrodynamic diameters *via* the Stokes–Einstein equation are close to those determined by size exclusion chromatography (SEC). Diameters have been measured using either SEC or SANS [467].

Employing SANS, the spatial distribution and location of PAMAM termini were obtained using partially deuterated G7 dendrimers and showed a larger radius-of-gyration of the terminal groups than that of the entire dendrimer ($39.3 \pm 1.0 \text{ \AA}$ vs. $34.4 \pm 0.2 \text{ \AA}$, respectively) indicating that the termini are located near the outer surface [608,1160]. These findings are in variance with many computer simulations [539,1161,1162], which suggested that a significant number of termini are backfolded into the interior cavities. The effect of solvent quality on the molecular dimensions of these PAMAMs was investigated [1163]; *e.g.*, using the solvent $D(\text{CH}_2)_n\text{OD}$, where $n = 0, 1, 2,$ and 4 , the radius-of-gyration for the G8 PAMAM was found by SANS measurements to decrease by 10% when going from $n = 0$ to 4 . Funayama and Imae [1164] reported the SANS data on a G5 PAMAM possessing hydroxyl termini suggesting that (1) the greatest density occurs at G4 and (2) the penetrated water reaches a maximum at G5.

Using holographic relaxation spectroscopy, solvent-dependent swelling of PAMAMs has been studied [565], whereby the influence of solvent quality on molecular dimensions was characterized. Low generation dendrimers were observed to possess similar hydrodynamic radii in various solvents studied; however in “good” solvents, the $G > 4$ PAMAMs showed significant swelling. It was suggested that this could be a useful tool for the controlled trapping and release of guest(s) molecules.

Low generation PAMAMs have been examined [1165] *via* fluorescence experiments with pyrene. Excimer fluorescence was observed at [pyrene]/[dendrimer] ratios as low as 10^{-3} . It was further concluded that the size of the dendrimer varies with the amount of solubilized pyrene in aqueous media.

Esumi and Gojino [1166] examined the adsorption of PAMAMs on either alumina/water or silica/water interfaces

[1167–1169]. The weight of dendrimer adsorbed was found to increase with increasing generation for both systems. For both alumina and silica dispersions, lower generations behaved as electrolytes, while higher generations exhibited ionic surfactant or polyelectrolyte behavior. The swelling response of the G8 PAMAM to polyelectrolytes in D_2O was evaluated using SANS; it was concluded that the PAMAM's size was independent of pH ($4.7 < \text{pH} < 10.1$) or ionic strength (up to 3 M aq. NaCl) and resembled a uniform sphere with a radius-of-gyration $R_G = 4.0 \pm 0.15 \text{ nm}$ [1170]. Maiti and Goddard [1171] pointed out that the above Nisato et al. [1170] conclusions are in disagreement with their findings derived from *ca.* 20–40 ns of molecular dynamics simulations for the G8 PAMAM in water under varying pH conditions as well as the observations of others [182,1163]. The stochastic molecular dynamics simulations have been conducted for the G5–7 PAMAMs and their radius-of-gyration was shown to explain the SANS data under different pH [556].

The interaction of the G0.5–5.5 PAMAMs with positively charged alumina particles was evaluated at pH 5; the smaller dendrimers act as electrolytes and the larger ones operate as anionic surfactants or polyelectrolytes [1024,1172]. Simultaneous adsorption of either G1.5 or G5.5 PAMAM and an anionic surfactant (SDS) on positively charged alumina was investigated at pH 5 by measuring adsorption amounts, ξ potential, and sedimentation rate of alumina suspensions; a competitive adsorption between these PAMAMs and SDS as well as a preference of G5.5 over 1.5 was observed [1173]. The relative viscosity measurements (η_r) of the small PAMAMs with SDS in water were conducted at 25 °C [1174]. Surface tension, fluorescence, and dynamic scattering measurements in aqueous solutions between the PAMAMs possessing surface carboxyl moieties were investigated with cationic surfactants [1175]. From the conductance measurements, the Krafft temperatures (T_k) of the cationic surfactants [hexadecylpyridinium bromide or chloride or hexadecyltrimethylammonium bromide] were studied by adding G0–2.5 PAMAMs at different concentrations. The T_k of the cationic surfactant decreased using any of these dendrimers; interestingly, the ester-terminated PAMAMs interacted more strongly than the amine-terminated series [1176]. The conductivity (κ), surface tension (γ), viscosity (η), dynamic light scattering (DLS) and Krafft temperature (K_T) measurements of aqueous dodecyltrimethylammonium bromide (DTAB) and di(dodecyl)dimethylammonium bromide (12-2-12) with the PAMAMs have been conducted at 25 °C [1177]. From the conductivity, κ , the apparent CMC for DTAB and 12-2-12 in an aqueous PAMAM solution was computed. Similarly, the κ , turbidity (τ) NMR, and K_T studies have been conducted with the cationic surfactants in the presence of G3, 3.5, 4, and 4.5 PAMAMs in aqueous media; the CMC values decreased in the presence of the PAMAM, relative to water, especially for the amine-terminated series [1178].

Amis et al. [1179] imaged these dendrimers by conventional TEM stained with sodium phosphotungstate from which *single* G5–10 PAMAMs were observed. A cryo-TEM technique was used for the G10 member in the series. Circular appearances were noted, with diameters following a Gaussian

distribution with increasing generation, although some broadening was observed at higher generations. Cryo-TEM generally supported the standard staining-based TEM, but it also suggested dendrimer shape variability, *e.g.*, polyhedral motifs frequently occur.

Dendritic (PAMAM) diblock copolymers, incorporating linear PEGs with molecular weights of 2000 and 5000 amu, have been prepared [1180]. Specular neutron reflectivity has been used to study the monolayers formed from these diblock copolymers at the air–water interface [1181]. For the shorter chain copolymer, intrinsic viscosity data resembled that of linear polymers; in contrast, data collected for those with longer PEG chains suggested the formation of “unimolecular micelles.” Hammond et al. [1182,1183] then examined the Langmuir thin-film behavior of PAMAMs coated with stearic acid and an arylvinyl acid. Transference of these monolayers onto hydrophobically functionalized surfaces afforded smooth, continuous, defect-free films. “Z-type” multilayer films were examined. The morphology and temperature dependence of diblocks containing G1–4 PAMAM-type dendrons with a linear PEG focal group have been reported, and the dendritic surface was functionalized with stearate groups to create an amphiphilic linear-dendritic diblock copolymer [1184]. The synthesis of hybrid diblock copolymers possessing linear-dendritic rod architectures has been reported [1185]. The normal ester and amine termini, as well as with the ester moieties, were transformed into alkyl groups of diverse lengths in order to tune the hydrophilic/hydrophobic nature of the construct. The G3 and 4 PAMAMs were coated with poly(ethylene glycol) monomethyl ether with average MW of 550–2000 by a urethane connection; these spheres encapsulated the anticancer drugs, adriamycin and methotrexate – specifically, the G4 PAMAM with a 2000 PEG surface could retain 6.5 molecules of the former and 26 of the latter [1186]. Encapsulation of drugs within liposomes was demonstrated by enhanced entrapment of dendrimer, which created a sink in the liposomal aqueous compartment where the methotrexate is located; the encapsulation increased with the G2–4 PAMAMs [1187].

Naka et al. [1188,1189] used G#5 PAMAMs as additives in the crystallization of CaCO₃ and observed the formation of spherical vaterite crystals [1190] in contrast to the rhombohedral calcite crystals formed in the absence of the additive. A linear poly(carboxylic acid) was found to inhibit crystallization.

Tucker et al. [1191] have conducted spectrochemical investigations with carboxylate-terminated PAMAMs to evaluate MeNO₂ as a selective fluorescence-quenching agent. Nitro-methane-selective quenching of alternate, as opposed to non-alternate, polyaromatic hydrocarbons (PAHs) was observed and rationalized in terms of different PAH locations within the dendrimer. The differentiation between unimolecular micelles and traditional micelles has been elaborated, based on the ability of pyridinium chloride to selectively quench alternate *vs.* nonalternate PAHs in these organized media [1192]. Using the fluorescent solvatochromic dye, phenol blue, to probe the interior of the G4–8 PAMAM, it showed that the dye was associated with the inside of the dendrimer and did not interact with the surface groups [1193,1194]. They

evaluated the “intrinsic” fluorescence of these carboxy-terminated PAMAMs by means of excitation-emission matrices (EEMs) and life-times. Larson and Tucker have shown a weak yet detectable fluorescence from the PAMAM with carboxy-termini by EEMs and life-time fluorescence techniques [1195]. Then, Wang and Imae reported [1196,1197] a strong fluorescence emission, not only for the G4 PAMAM possessing an amine surface but also for those coated with hydroxy- and carboxylate-termini, by simply adjusting the pH; there was a remarkable difference in the fluorescence between the G2 and G4 PAMAMs. The excitation and emission spectra for the polyprotonated G4 PAMAM (Tf₂N⁻)_n ionic liquid exhibited a strong blue photoluminescence at *ca.* 436 nm [1198].

Photochemical and spectroscopic probes have been utilized for the comparison of trivalent (ammonia)- *vs.* tetravalent (ethylenediamine)-based PAMAMs [1199]. Similar surface characteristics were observed, such as changing from an “open” to a “closed” architecture at G3 and G5, thereby suggesting ready extrapolation of earlier findings [756,1114,1117,1138,1200] predicated on these core constructs.

Striegel et al. [1201] examined and compared the dilute solution characteristics of PAMAMs and PPIs to that of polysaccharides by means of SEC, ESI-MS, and computer modeling. Intrinsic viscosities were observed to decrease in the order dextran_[η] > dextrin_[η] > dendrimer_[η]. Solution radii and molecular weights were found to correlate well with literature values.

Dvornic et al. [1202] evaluated the rheological properties of PAMAMs at medium to high dendrimer concentrations in ethylenediamine, as solvent, and demonstrated a typical Newtonian flow behavior. Interpenetration entanglements and surface sticking interactions were not observed; their findings support the encapsulation of small guests within the “soft and spongy” infrastructure. Klajnert et al. [1203] afforded added insight into the relationship between dendrimer and encapsulating capability by means of the interactions between the G4,6 PAMAMs and a fluorescent dye, 1-anilinonaphthalene-8-sulfonate; the size of the dendrimer had a notable impact on the number of incorporated dye molecules: the values of *k_b* and *n* for low- and high-affinity were 2.6 × 10⁵, 0.60 and 3.7 × 10⁶, 0.34, respectively, for G4; whereas for G6, these values were 1.2 × 10⁵, 76.34 and 1.38 × 10⁶, 22.73, respectively.

The rapid evaporation of solvent from a thin-cast film of an electrolyte solution on the dendrimer on mica produced aggregates in the form of nanometer-sized nanodots [1204]. The effect of PAMAM surface chemistry has been demonstrated by the structure of the self-assembled rings on a mica surface; the G4 PAMAM is diffuse and absent of layered growth. Whereas with 25% surface C₁₂ groups, there appeared an ordered ring structure and samples with 50% C₁₂ moieties show highly periodic scallops and very distinct monomolecular height terraced growth of the ring patterns [1205].

In order to attach peptide chains to G0–4 PAMAM cores [1206–1208], the PAMAMs were treated with *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline [1209] and chloroacetic acid in MeOH to give the perchloroacylated core to which the 20-residue peptide, R-HL4, was added by ligation [1210].

A Zn(II)-mesoporphyrin was subsequently coordinated. Electron-transfer was shown to be more effective with higher generations and that the *de novo* designed peptides with dendrimers can be utilized in artificial photosynthesis [1206,1207]. Using positively charged methylviologen as an electron-carrier, the photoinduced hydrogen evolution function of these positively charged peptide dendrimers was superior to the negatively charged counterpart [1211].

The simplest G0 PAMAM has been shown to function as a CO₂-selective molecular gate with highly humidified feed gas [1212], as well as for CO₂–N₂ separation [1146] and CO₂ separation with novel solvents as liquid membranes [1213,1214].

3.2.4.1. PAMAM dendrimers as attachments. Watanabe and Regen reported [1215] the use of these PAMAMs in the preparation of Iler-like arrays [1216], which were constructed on a (3-aminopropyl)triethoxysilane activated silicon wafer by a sequence of exposure to K₂PtCl₄, rinsing, treatment with a solution of the PAMAM, further exposure to K₂PtCl₄, and rinsing. Multilayers were constructed by the repetition of this simple (K₂PtCl₄, rinsing, PAMAM) sequence. Examination of a multilayer coating after five cycles by AFM demonstrated that the surface was smooth at the molecular level with an average roughness of 7.1 Å. The G5–10 PAMAMs have been imaged with a tapping mode AFM showing them to be monodisperse, dome-shaped, and randomly distributed on a mica surface [1217–1219]; the absolute molecular weight and polydispersity were estimated for each generation. Effects of substrate, volume, pH, as well as the size and shape of the G6–9 PAMAMs, were investigated by tapping mode AFM [610]; the effects of substrate and pH were discussed and discrete dendrimer aggregates were observed. An alternative approach to PAMAM surface-attachment is to use the anhydride [1220], derived from 3-cyanopropyltrichlorosilane with the PAMAM to give the amidation product, followed by treated with pyrometallic dianhydride that incorporated with the linker in order to attach the next tier of dendrimer [1221]. Similarly, an initial treatment of the quartz slides or silicon surface with *p*-aminophenyltrimethoxysilane, followed by the same dianhydride then dendrimer gave the dendronized surface. The activation of the silica surface with 3-glycidoxypropylmethoxysilane followed by the *n*th G PAMAM in refluxing MeOH gave the bound PAMAM, whose external surface was free for subsequent reaction with either (1*R*,2*R*)(+)-1-phenylpropylene oxide [1222] or CH₂=CHCO₂Me, followed by 1,6-diaminohexane, then the same chiral oxide generating a new silica-supported dendritic chiral catalyst for the enantioselective addition of Et₂Zn to benzaldehyde [1223].

Wells and Crooks [1224,1225] attached PAMAMs to self-assembled monolayers (SAMs) then demonstrated their usefulness in the construction of surface acoustic wave (SAW) devices. The G4 PAMAM was useful as a mass balance detector due to its globular architecture and accessible interior endoreceptors. Crooks et al. [1226] then revealed that PAMAMs could form high-density monolayers on gold platforms based on metal-terminated amine interactions without the requirement of an interfacial and supporting monolayer. Reduction of

tetrachloroauric acid in the presence of PAMAM dendrimers with a thiol-surface resulted in formation of water-soluble, dendrimer-stabilized, 1.5–2.1 nm diameter nanoparticles depending on the Au/dendrimer ratio [1227]. Dendrimer and mixed dendrimer–alkanethiol monolayers prepared on a gold surface have been reported [1228]. Single-component dendritic monolayers were described, as unlike the spherical form while the presence of hexadecylthiol appeared to compress the monolayer such that dendrimer conformation changed to an “end-on-oblate spheroid.” At pH 11, the redox probe [Ru(NH₃)₆]³⁺ is reduced to the Ru(II) specie on access to the Au surface *via* the dendritic interior; however at lower (6.3) pH values, the protonated dendritic terminal amines repelled each other and do not coordinate with the Au surface. Intradendrimer probe transfer was examined by cyclic voltammetry by following the deactivation of the amine monolayer surface using pH affects. These self-assembled dendrimers were described as a “molecular gate.” Cyclic voltammetry studies of the electrostatic binding of [Fe(CN)₆]⁴⁻ with full generation PAMAMs have been conducted in order to evaluate size and pH factors [1229]. Self-assembled films based on a G1.5 PAMAM carboxylates and nitro-containing diazoresin, as polycations, have been assembled [1230]; UV irradiation was shown to cause linkages between layers to switch from ionic to covalent bonding. Multilayer ultra-thin films deposited from phenolic shell-modified PAMAM and diazoresin were formed by hydrogen-bonding. UV irradiation altered the nature of the linkage to generate covalent bonds, enhancing the film’s stability [1231–1233].

Highly cross-linked dendrimer–polyanhydride composite thin films [1234] were prepared by treatment with either amine- or hydroxyl-terminated PAMAMs [or PPIs] with poly-(maleic anhydride)-*c*-poly(methyl vinyl ether) (also known as “Gantrez”). Essentially, the dendrimers were used as *in situ* thermosetting agents to cross-link the Gantrez copolymer. Prior to heating, the film’s permeability was found to be pH-dependent; however, after heat treatment during which the PAMAMs underwent typical retro-Michael reactions, the resulting films became “highly blocking.” These surfaces were shown to be pH-switchable permselective for both cationic and anionic redox-active probe molecules [1235,1236]. The Au, Si, and Al surfaces were used for film preparation. Employment of the amine-terminated PAMAMs as adhesion promoters between vapor-deposited Au films and Si-based materials has been reported [1237]; STM and CV were used to ascertain the surface roughness and the adhesive-tape peel test measured the effectiveness of the adhesion layer. Notably, significant improvements, such as increased hardness, decreased roughness, and better adhesion led to an enhanced quality of Au films on the self-assembled monolayer of G8 PAMAM on silica [1238,1239]. Ultra-thin titania films with molecular cavities, causing de-dendrimerization, were synthesized by treating an *ca.* 8 nm thick [(TiO₂)₃(hydroxy-terminated G4 PAMAM)-(TiO₂)₂] sandwich film with activated oxygen [1240].

The AFM has been used to examine G4 and G8 PAMAMs adsorbed on gold surfaces; exposure of the dendrimer-coated surface with alkylthiols results in a fully thiol-covered surface displacing the dendrimer [1241]. Dendrimer-coated surfaces,

upon exposure to the more strongly binding hexadecanethiol, showed a dendritic morphology change from oblate to prolate; monolayer surfaces showed gradual agglomeration ultimately producing dendritic pillars up to 30 nm in height upon alkyl thiol exposure [1242]. The aggregation of G4,5 PAMAMs from micromolar neutral aqueous solutions on either bare or thiol-coated [HS(CH₂)₂CO₂H or HS(CH₂)₂NH₃Cl] modified gold electrodes has been studied using the QCM technique [1243]. These thiol-coated surfaces promoted greater coverage over that of the simple bare surface and the models suggested that the main effect of surface attached thiols was a favorable lateral interaction between the adsorbed dendrimers. Godínez et al. [1244] built a tiered gold electrode surface in which the gold surface was activated with 2-aminoethanethiol hydrochloride, followed by a G5 PAMAM, and lastly Ni-tetraazamacrocycle (cyclam), giving rise to an electrocatalytic material that proved to be efficient for the electrochemical oxidation of MeOH in a basic aqueous medium. Gold bead electrodes were modified initially with either 3-mercaptopropionic acid or 2-aminoethanethiol, then either G4,5 PAMAMs, followed by the absorption of Prussian Blue to afford mixed and stable electrocatalytic layers [1245]. It was demonstrated by UV–vis spectroscopy and electrochemical experiments that Prussian Blue was located within the dendrimer's surface. These electrode-modified surfaces were used in the electrooxidation of L-(+)-ascorbic acid and were shown to be an improvement in both sensitivity and detection limits to that of the voltammetric response for a simple gold–Prussian Blue modified electrode [1245].

Bar et al. [1246] described a protocol using the G4 PAMAM adsorbed onto a surface of glass, silicon or indium tin oxide and then treated with colloidal metals, obtained by reduction (trisodium citrate dihydrate) of H₂AuCl₄·3H₂O or AgNO₃ aqueous solutions. The AFM, SEM, XPS, SERS, and UV–vis spectroscopy were used to characterize these materials. The thickness of the dendrimer layer was determined to range from 14 to 25 Å, while intercolloidal spacing could be controlled over a wide range (74–829 nm) by variation of particle size, concentration, and substrate immersion time. Adsorption of PAMAMs on clean gold has been studied [1247] using a quartz crystal microbalance; multilayers form on the gold surface increasing exponentially up to G6, whereas a drastic drop occurred at G7, which was postulated to be a result of surface crowding as related to the “dense-shell” transition of the dendrimer's outer surface. A comparative study of the PAMAMs vs. PPIs using a 27 MHz quartz crystal microbalance has been reported in which the formation of multilayer of the dendrimers occurred when the number of layers for the PAMAMs was greater than that of the PPI family [1248]. A thin, covalently assembled, hyperbranched poly(acrylic acid) graft on a gold surface has been shown [1249,1250] to swell reversibly by up to 300% in a pH 1.7 buffer and to 500% at pH 10.7. The solvated poly(sodium acrylate) films served as polyvalent ion-exchange substrates for immobilized polyvalent dendritic cations giving rise to self-assembled nanocomposites.

Hollow microcapsules composed of poly(styrenesulfonate) [PSS] and G4 PAMAM were prepared by the deposition of

PSS/PAMAM (G4) multilayers on melamine formaldehyde colloid particles through a layer-by-layer self-assembly procedure and subsequently dissolving the templated cores [1251,1252]; the conversion increased by increasing inter- and intramolecular attractive forces between the PSS chains in the capsules through electrostatic, hydrophobic, and a combination thereof. The UV/vis data afforded an adsorption–desorption phenomenon that was sensitive to pH and ionic strength of the PSS and dendrimer solutions as well as generation (G2–4) or PSS molecular weight and concentration [1253]. The effect of the G4 PAMAM present in an anionic phospholipid structure – comprised of hydrogenated soyphosphatidylcholine, cholesterol, dicetyl phosphate, and poly(ethylene glycol) (M_w ~ 2000) derivatized phosphatidylethanolamine – on the hydration and liquid crystallinity was investigated for which a model of dendrimer-doped mesophase structure and lamellae fusion was proposed [1254].

PAMAMs have been prepared by solid-phase synthesis using a polystyrene–PEG resin [1255,1256] by the initial reaction of methyl acrylate (2.50 equiv.) with a diamine linker followed by removal of excess reactant and treatment with 1,*n*-diaminoalkane (250 equiv.; where *n* = 2 or 3). Dendrimers up to G5 were realized.

The G3 hybrid was terminated with the super acid sensitive linker 4-[4-(hydroxymethyl)-3-methoxyphenoxy]butyric acid by Fmoc chemistry and sequentially treated with lysine and glycine in 1% TFA–CH₂Cl₂ to produce a dendrimer-bound dipeptide. This demonstrated the utility of these materials in applications such as combinatorial chemistry and chromatography based on high bead loading. Cleavage of the dendrimer from the resin was achieved by treatment with 50% TFA in CH₂Cl₂. Bradley et al. subsequently used these TentaGel (Polystyrene-PEG)-bound dendrimers as high-loading solid-phase scaffolds for the synthesis of a library of aryl ethers [1257] or amidine-based GP IIB-IIIa antagonists [1258]; ramifications of these resin-bound dendrimers include the potential to significantly increase bead loading [1259].

Tsukruk et al. [1260] described the self-assembly of multilayer films built-up of alternating layers of G4, 6 or 10 amine- and G 5, 5.5 or 9.5 carboxylic acid-terminated PAMAMs. Full generation PAMAMs were shown to form stable homogenous monolayers on silicon surfaces. By alternately immersing a clean silicon substrate in 1% dendrimer solutions, adjusted to an appropriate pH, films of up to twenty layers thick were assembled based on scanning probe microscopy and X-ray reflectivity studies. Monolayers were observed to possess smooth surfaces at the molecular level. Monolayers of G3 PAMAM with a C₁₂-surface were formed at the air/water interface and subsequently transferred onto silica wafers by a “horizontal lifting” procedure then evaluated by scanning force microscopy with X-ray reflectivity and X-ray photoelectron spectroscopy [1261,1262]. Dendrimer conformations in the monolayer were observed to be “collapsed” or “highly compressed,” which compares well with the “lateral compression” detected for other flexible dendrimers by means of neutron reflectometry [683]. Molecular dynamics simulations corroborated the compressed model that compared well with measured film thickness. Film thickness varied linearly with increasing

layer-by-layer deposition evidencing “organized multilayer films.” The structural states of PAMAMs at air–water and air–solid interfaces have been evaluated [1295]; for deformation-prone constructs, high interaction strength between “sticky” surface moieties and substrates was deemed responsible for compact monolayers and macromolecular compression. A model for the adsorption of rigid charged dendrimers with oppositely charged materials has been presented, which accounts for the small ion penetration into the absorbed layers [1263].

The AFM of the G0–2 PAMAMs and 2,2'-bis(3,4'-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA)-polyimide films has afforded insight into their morphology [1264].

Quartz or glass surface modification by layering has been demonstrated by initially coating the surface with 3-(triethoxysilyl)propylamine (APTS), followed by a G5 Majoral-type *P*-dendrimer (see Section 7.2) with an aldehydic surface, followed by G4 PAMAM amine-terminated dendrimers, and lastly, with one particle thick assemblies of poly(styrene-divinylbenzene-acrolein) ([P(SAD)] microspheres possessing surface aldehyde groups [1265]. The XPS and SEM studies indicated a saturation of the surface coverage with these particles. The XPS data showed that the thickness was low for the monolayer of PAMAM. It was concluded that the SiO₂–APTS–G5 substrate was incompletely covered with the PAMAM; the degree-of-coverage of the surface of SiO₂–APTS–G5–PAMAM plate with P(SAD) was found to be .60 (theory .62) for the microspheres, which were attached chaotically and irreversibly in a one microsphere thickness [1266]. Subsequent coating of the SiO₂–APTS–G5–PAMAM–P(SAD) surface with a 2 nm thick PAMAM adlayer has been accomplished [1266].

As the starting core (Fig. 5), Okada et al. [669] prepared poly(2-methyl-2-oxazoline) by “living” ring-opening polymerization, transformed the reactive termini to an amine moiety, and constructed PAMAM-blocks through G5 using this polymer. Aggregation behavior was studied by means of surface-tension measurements and small-angle neutron scattering analysis.

The mechanical properties of blends of PAMAMs with either poly(vinyl chloride) (PVC) or poly(vinyl acetate) (PVAc) have been assessed by Xe NMR, dynamic mechanical analysis, and tensile property measurements [1267]. Phase-separated dendrimer–PVC matrices facilitated mechanical relaxation, while the opposite was observed for the dendrimer–PVAc hybrid, suggesting enhanced compatibility.

Tsukruk et al. [1268] electrostatically self-assembled PAMAM monolayers on silver wafers using G5–10 dendrimers. Monolayer thickness, morphology, and stability were evaluated by scanning probe microscopy (SPM), while the proposed model assumed a highly deformed, ellipsoidal architecture for the monolayer. Imae et al. [1269] used SANS to determine the surface forces of mica-adsorbed PAMAMs terminated with hydroxy groups; the coatings were found to behave as surface-improvement agents by promoting fine particle dispersion stability.

The construction of PAMAM-type architectures onto low molecular weight linear poly(ethylene imine)s (accessed by

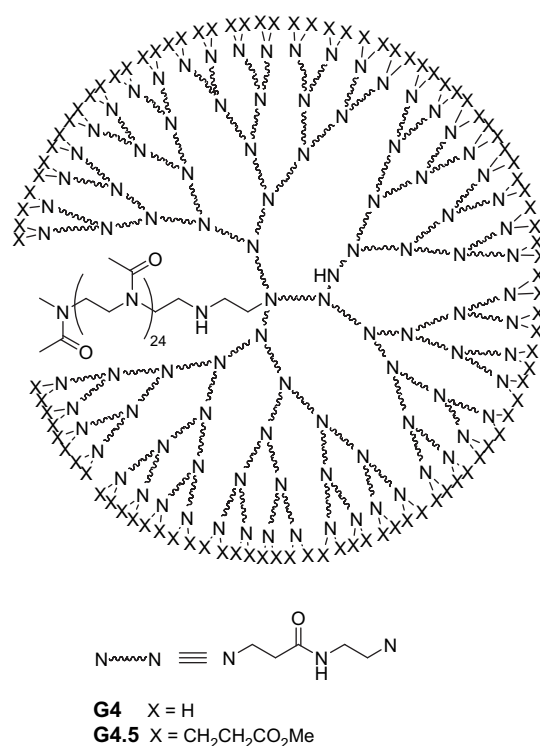


Fig. 5. Okada's polymer-dendrimer block copolymer [669].

“living” cationic polymerization of 2-ethyl-2-oxazoline) produced rod-shaped cylindrical motifs [1270]. These hybridized materials were termed “architectural copolymers” and their synthesis described as a “divergent, *in situ* branched cell” strategy. The necessity of large excesses of reagents and extended reaction times (*e.g.*, for ethylenediamine addition, 1260–10,000 equiv./ester group and 5–8 days, respectively) was critical to achieve complete reactions. Cross-linked products were also observed following long-term storage of the amine-terminated hybrids. The terminal amino groups were subsequently capped with hexyl acrylate in a molar ratio of 1:2 of amino group to acrylate in isopropanol at 25 °C, giving rise to the desired unimolecular amphiphiles [1271]; the encapsulation properties were evaluated and shown to be generation-dependent.

The layer-by-layer deposition technique was utilized to fabricate multilayers of the G4 PAMAM with a polyoxometalate (either [PMO₁₂O₄₀]^{−3} or [P₂W₁₈O₆₂]^{−6}) on quartz, pretreated with poly(diallyldimethylammonium chloride) or gold pretreated with 4-aminothiophenol [1272,1273]; these multilayer films mediated the reduction of iodate and nitrite. The multilayering of G4 PAMAM with an amine coating with conducting sulfonated polyaniline (“SPANI”) on solid substrates in an alternating pattern has been shown [1274].

The interfacial reactivity between vapor- and liquid-phase heptanoyl chloride and hydroxy-terminated G4 PAMAM monolayers has been demonstrated by Fourier transform IR-external reflection spectroscopy to yield ester-coupled bilayers. Real-time, quantitative SAW-based nanogravimetry indicated that the vapor-phase process was complete in <1 min [1275].

Thin layers of amine-terminated PAMAMs were prepared on either air or maleic anhydride plasma-treated poly(dimethylsiloxane) (PDMS) substrates generating either PDMS–dendrimer or PDMS–anhydride–dendrimer composite membranes [1276]. Gold nanoparticles have been attached to polymer substrates for imaging photomasks by the addition of HAuCl_4 in H_2O , followed by heat and ultraviolet light [1277]. The PAMAM dendrimers have also been immobilized onto an anhydride-functionalized pulsed plasma polymer surface by means of amide connectivity; the resultant materials were useful in surface fluorination [1278], adhesion, and gas barrier enhancement [1279].

The use of SAMs, in which the G4 PAMAM was directly coated on a gold surface for an immobilized matrix for glucose oxidase in the detection of glucose, has been reported [1105]. Treatment of a glass surface with 3-aminopropyltriethoxysilane afforded the desired amino-silylated base, which was treated with either 1,4-diisothiocyanatobenzene or disuccinimidyl glutarate, followed by G5 PAMAM to form a thin polymer film; the DNA microarray was subsequently prepared by the addition of an appropriate oligonucleotide [420,1280]. An alternative route appeared [1281] in which a gold-coated glass surface was treated initially with 11-amino-1-undecanethiol hydrochloride, then – after an ethanol wash and drying – treatment with the water-soluble, noncleavable cross-linker, bis(sulfosuccinimidyl) suberate (BS^3). This new activated surface was subsequently treated with G4 PAMAM, then a second treatment with BS^3 in order to covalently immobilize the amino-modified probe DNA oligonucleotides to the dendritic surface. The streptavidin protein has been linked to the PAMAM layer by using sulfo-NHS-LC-biotin instead of BS^3 . Other methods have been reported that utilize 11,11'-dithio-bis(*N*-hydroxysuccinimidylundecanoate) [1282]. Dendrons-coated to a gold surface have also appeared [422], in which the surface was treated with a G3 hydroxy-terminated dendron $\{\text{HS}(\text{CH}_2)_2\text{N}[(\text{CH}_2)_2\text{N}(\text{CH}_2\text{CONHCH}(\text{CH}_2\text{OH})_2)_2]_2\}$, followed by DSC activation and lastly, treated with a G2 PPI coating. PAMAMs have been attached to activated undecanoic acid monolayers that were covalently linked to silicon surfaces by means of Si–C bonds, resulting in the formation of ultrathin dendrimer films [1283].

The availability of single-walled carbon nanotubes (SWCN) has opened doors to their use as connectors for dendrimer constructs. Treatment of SWCN with strong acid converts them to $(\text{HO}_2\text{C})_n\text{–SWCN}$, which can be transformed to the $(\text{ClCO})_n\text{–SWCN}$ by treatment with SOCl_2 [1284]. These acyl halides, upon treatment with G10 PAMAM, generated a complex mixture of nanotube “stars,” as demonstrated by SEM images [1285].

Rotello et al. [1286] demonstrated that PAMAM dendrimers could be used to assemble nanoparticles by means of electrostatic interactions, and the average interparticle distance depended on the dendrimer's size. This technique was then applied to control interparticle spacing in the generation of cationic superparamagnetic iron oxide nanoparticles, showing that an increase in interparticle spacing altered the collective magnetic behavior by lowering the dipolar coupling between the particles [1287].

Megameric morphologies have been considered; however, structural-controlled assembly is predominately in the hypothesis stage [505,1288]. The statistical megamer construction is more easily envisioned at this stage, since this would be analogous to the packing of hard spheres; *e.g.*, marbles, in which the packing motif would be directly related to the size of the spheres in the assembly. As new utilitarian fields start to utilize the potential properties of megamer assembly, a better understanding of the required surface interactions will need to be addressed. The G4 PAMAM was cross-linked using glutaraldehyde to generate a formyl-surface activated PAMAM and the cross-linked G4 PAMAMs, which were called “premegamers” [1289]. These premegamers were subsequently grafted with octadecylamine to generate the stabilized products and were evaluated by TEM [1290].

The G4 amine-terminated PAMAM has been used as ink for microcontact printing; periodic lines with widths of 140 nm and interlines of 70 nm were directly printed on a silicon substrate [1291]. Increasing the dendrimer concentration up to 1 mmol resulted in stable multilayer structures up to *ca.* 60 nm in height, as determined by AFM. Dip-pen nanolithography employing an AFM tip with dendritic “inks” has generated patterns with 100 nm features or *ca.* 20 dendrimers on a Si/SiO_x surface; the resolution was evaluated on surface chemistry as well as the molecular weight of the dendritic ink [1292].

3.2.4.2. PAMAM-type dendrons. Kim et al. [1293] created a simple G1 PAMAM-type dendron *via* the initial activation of lauric acid with 1,1'-carbonyldiimidazole (CDI); then treatment with di[*N,N*-(3-aminopropyl)amine] produced the bisamide, which was reacted with succinic anhydride to give $[\text{C}_{11}\text{CONHCH}_2\text{CH}_2\text{CH}_2]_2\text{NCOCH}_2\text{CH}_2\text{CO}_2\text{H}$. The convergent process was also utilized to generate the G2 dendron and synthesis of these dendrons on a solid phase surface was previously reported [1294]. The focal attachment of 2-hydroxyethyl methacrylate to the focal carboxylic acid of the G1,2 PAMAM-type dendrons was accomplished and subsequently polymerized [1295]. The G2 dendron was further attached to different two-directional cores, *e.g.*, 1,5-dihydroxynaphthalene, 4,4'-biphenol, and 2,2-bis(4-hydroxyphenyl)propane, *via* a convergent process; Kim et al. [1296] reported the packing phenomena of their self-assembly.

The divergently generated G2.5 PAMAM-type dendron possessing a $\text{HOCH}_2\text{CH}_2\text{–[N<]}$ focal group [1297,1298] has been attached to a $(=\text{N–C}_6\text{H}_4\text{COCl})_2$ core to create a photo-switchable system [1297], to a 1,5-naphthalene core for acid sensitive fluorescence signal amplification [1299], and to tartaric acid to create chiral PAMAMs [1300]. The related G5 PAMAM-type dendron with ester termini was reacted with oligoisocyanates to generate oligourethanes possessing the pendent dendron [1301]. Creation of a diol core $[(\text{HOCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{–N<}]$ was reported and treated with sebacyl chloride or 2,4-toluidine diisocyanate to generate either the poly(ester) or poly(urethane) backbones, respectively, with pendent dendrons [1302]. An extension of this simple procedure [adding PEG (MW 6000)] in the presence

of dibutyl tin dilaurate has been shown to generate a dendritic polyurethane polymer possessing a PAMAM dendron side chain [1303]. Spherical vaterite crystals, prepared by the crystallization of calcium carbonate in the presence of PAMAM-type dendrons with an anthryl focal group [1304], upon irradiation, underwent photodimerization to form a PAMAM dendrimer possessing a dianthracene core [1305] or an attachment to a fullerene moiety [1304,1306]. Well-ordered thin films of these fullerodendrons were fabricated by the Langmuir–Blodgett and adsorption techniques and were characterized by X-ray reflectometry [1307]. A convergent route to fullerodendrimers was reported by the photochemical reaction of C_{60} with 5 equiv. of a disulfide core possessing the PAMAM-type dendrons [1308] under photoirradiation at >300 nm in the presence of 5 equiv. diphenyldiselenide in CH_2Cl_2 [1309].

The creation of a PAMAM dendron with a carboxylate surface and 9-anthryl focal group afforded spherical vaterite crystals; photodimerization of the anthracene groups within these crystals was demonstrated [1305]. Similarly in the presence of G2.5, 3.5, and 4.5 PAMAMs, the crystallization of the fluorescent dye, 4-*n*-octylamino-2-oxa-1,3-diazole, was drastically accelerated [1310].

The surface of carbon nanotubes (CNTs), possessing an oxidized surface, has been utilized as a base for the step-wise construction of $>G4$ PAMAM dendrons *via* a step-wise traditional procedure [1311]. Their conversion into silver nanoparticles was therein demonstrated. Recently, these authors reported that biotin-terminated PAMAM dendron was divergently constructed by the standard route from biotin [1312], then the asymmetric dendron was used to modify avidin *via* non-covalent bioconjugation. An alternative mode of initial attachment of the “foot” to the SWNT was conducted by a 1,3-dipolar cycloaddition by the formation of a pyrrolidine ring functionalized with a *N*-BOC-protected amine group, which was deprotected to permit the subsequent building of the dendron in the traditional way [1313]; the PAMAM-type dendron was capped with 5,10,15-tris(3,5-di-*tert*-butylphenyl)-20-[4-(carbonyloxy)phenyl]porphyrin. The use of carbon black [1314] has been utilized as the initial particle, rather than the structurally organized carbon nanotube. A simple one-step route to dendronized CNT recently appeared [1315] that utilized divergently or convergently prepared 1 \rightarrow 3 C-branched dendrons [1316].

Azide functionalized PAMAM dendrons, possessing the azidopropylamine focal substituent, were prepared by a traditional divergent process [1317,1318]; the use of a core with two alkyne moieties with two of these dendrons afforded the convergently created PAMAM-type dendrimers by means of click chemistry [1319,1320]. The combination of Fréchet [1321] and PAMAM diblock codendrimers has been constructed by the same process [1322,1323]. A series of propargyl-functionalized PAMAM-type dendrons were grown from $HC\equiv CCH_2NH_2$ and treated with azides, *e.g.*, 1,4-di(azidomethyl)-benzene generating the two-directional dendrimer *via* click chemistry [1324].

The scale-up preparation of up to G5 PAMAM-type dendrons was conducted on ultrafine silica *via* the traditional

step-wise procedure in a solvent-free, dry system [1325]. Extended G0–4 PAMAM-type dendrons have been easily constructed on commercial aminopropyl silica gel by the traditional two-step procedure using methyl acrylate and diaminoethane, followed by capping with diphenylphosphine and formaldehyde generating surface $-N(CH_2PPh_2)_2$ moieties [654,1326]. Treatment with Pd(II) salts generated the catalytic surface that was shown to be a highly active, recyclable catalytic system for the hydroesterification of olefins with MeOH and CO. These types of phosphino-methylated PAMAMs have been complexed with rhodium; the G0 and G1 species were shown to be very active catalysts for olefin hydroformylations [1327]. The synthesis and characterization of immobilized PAMAM-like dendrons onto a surface-modified silicon wafer surface using a divergent methodology have been reported [1328].

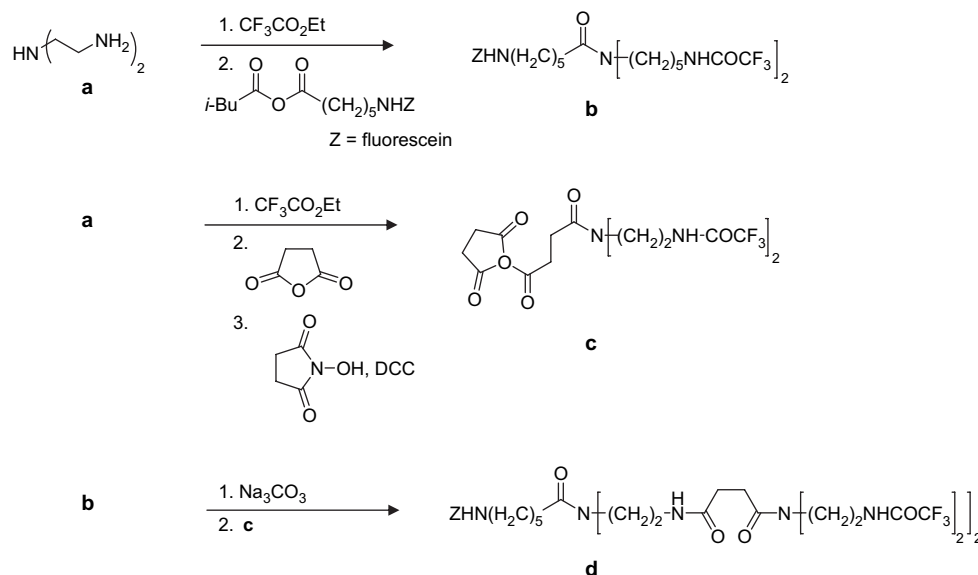
The assembly of the PAMAM-type dendron on the 9-anthracene has been reported [1329] using the standard synthetic protocol and then the anthracene-focal moiety was added to [60]fullerene in *o*-dichlorobenzene under ($\lambda > 300$ nm) irradiation [1330].

A series of small PAMAM-type sugar-coated dendrons was prepared from aminoacetaldehyde dimethyl acetal [$H_2NCH_2-CH(OCH_3)_2$] and following the traditional step-wise assembly to the G2 level, which was terminated with maltose lactone. Then this dendron possessing the protected aldehydic focal group was deprotected and treated with poly(vinylamine), followed by reductive amination using $NaCNBH_3$ [1331].

3.3. 1 \rightarrow 2 *N*-branched, amide-connectivity (other than PAMAM-type)

A series of simple triamines of $HN[(CH_2)_nNH_2]_2$, where $n = 2, 3$ or 6, was transformed into convenient *N*-branched monomers, *e.g.*, **24c**, *via* a facile two-step procedure [1332]. These bis-protected monomers were reacted with a liberated diamine derived from the core **24b** to generate **24d** (Scheme 24). Terminal deprotection of **24d** gave the tetraamine for growth to the next generation or the carbamate focal group could be released for attachment to a desired substrate, such as fluorescein. Such bis-functional monomers can be used in either a divergent or convergent pathway. These authors eventually transformed the octafluoroacetamides (G3) to the perguanidine-capped products, which were evaluated as dendritic molecular transporters. In general, the longer, more lipophilic as well as flexible spacers resulted in the most effective transport into cells – exceeding the oligoarginine transporters at high concentration.

Swager et al. [1333,1334] developed an approach to mini-dendronize a linear polymer *via* the functionalization of the critical monomer starting with 2,5-diiodo-1,4-di(ethoxycarbonylmethoxy)benzene that was initially saponified (NaOH/MeOH), then treated with $(COCl)_2$ to generate the corresponding bis-acyl chloride, which was reacted with diethyl iminodiacetate in the presence of NEt_3 , and lastly treated with TRIS [$H_2NC(CH_2OH)_3$] [23] in DMSO and K_2CO_3 . The resultant non-ionic, water-soluble, fluorescent conjugated polymers have been shown to be a novel platform for high specificity biosensory polymers.



Scheme 24. Formation of tunable polyguanidino dendrimers [1332].

Branched architectures were grafted onto ethylene–acrylic acid copolymer films using a grafting-from approach, in which DCC was used to activate the surface acid functionality followed addition of tri(aminoethyl)amine to generate the 1 → 2 *N*-branching center that was treated with succinic anhydride [1335]. Repetition of this two-step sequence would readily generate the desired dendron, which is, interestingly, isomeric with the PAMAM-type dendron described earlier.

The creation of a simple series of dendrons for the coating of CdSe nanocrystals has been reported as well as the dendrimer possessing a disulfide core. Treatment of diethyl iminodiacetate with ClCH_2COCl generated $\text{ClCH}_2\text{CON}(\text{CH}_2\text{CO}_2\text{Et})_2$, which with cystamine·2HCl generated the dendrimer $[\text{SCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CON}(\text{CH}_2\text{CO}_2\text{Et})_2)_2]_2$. The disulfide bond can be easily reduced to generate the dendrons $\text{HSCH}_2\text{CH}_2\text{N}[\text{CH}_2\text{CON}(\text{CH}_2\text{CO}_2\text{Et})_2]_2$ [1336]. Related 1 → 2 *C*-branched dendrons were also prepared by the treatment of $(\text{SCH}_2\text{CH}_2\text{COCl})_2$ with serinol generating $\text{HSCH}_2\text{CH}_2\text{CONCH}(\text{CH}_2\text{OH})_2$; different combination dendrons can be synthesized and subsequently coated onto the CdS particles [1336,1337].

Pittelkow and Christensen [1338] have created a small series of PAMAM-type dendron and dendrimers *via* a convergent process from 1,2-propanediamine $[\text{MeCH}(\text{NH}_2)\text{CH}_2\text{NH}_2]$ by taking advantage of the different reactivity of each amine termini. Initial BOC-protection of the less hindered primary amine moiety, followed by treatment with benzyl acrylate gave $(\text{BOC})\text{OCOHNCH}_2\text{CHMeN}(\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{C}_6\text{H}_5)_2$ permitting either the cleavage of the benzyl moieties by hydrolysis (Pd/C/H₂) or removal of the BOC-focal group ($\text{CF}_3\text{CO}_2\text{H}$). With the resultant two building blocks possessing the free acids or amine, respectively, the convergent process led to the construction of appropriate dendrons and dendrimers. Rennard et al. [1339] convergently prepared a family of dendrons and dendrimers using $[\text{Me}(\text{CH}_2)_3(\text{Et})\text{CHCH}_2]_2\text{NC}(=\text{O})-$

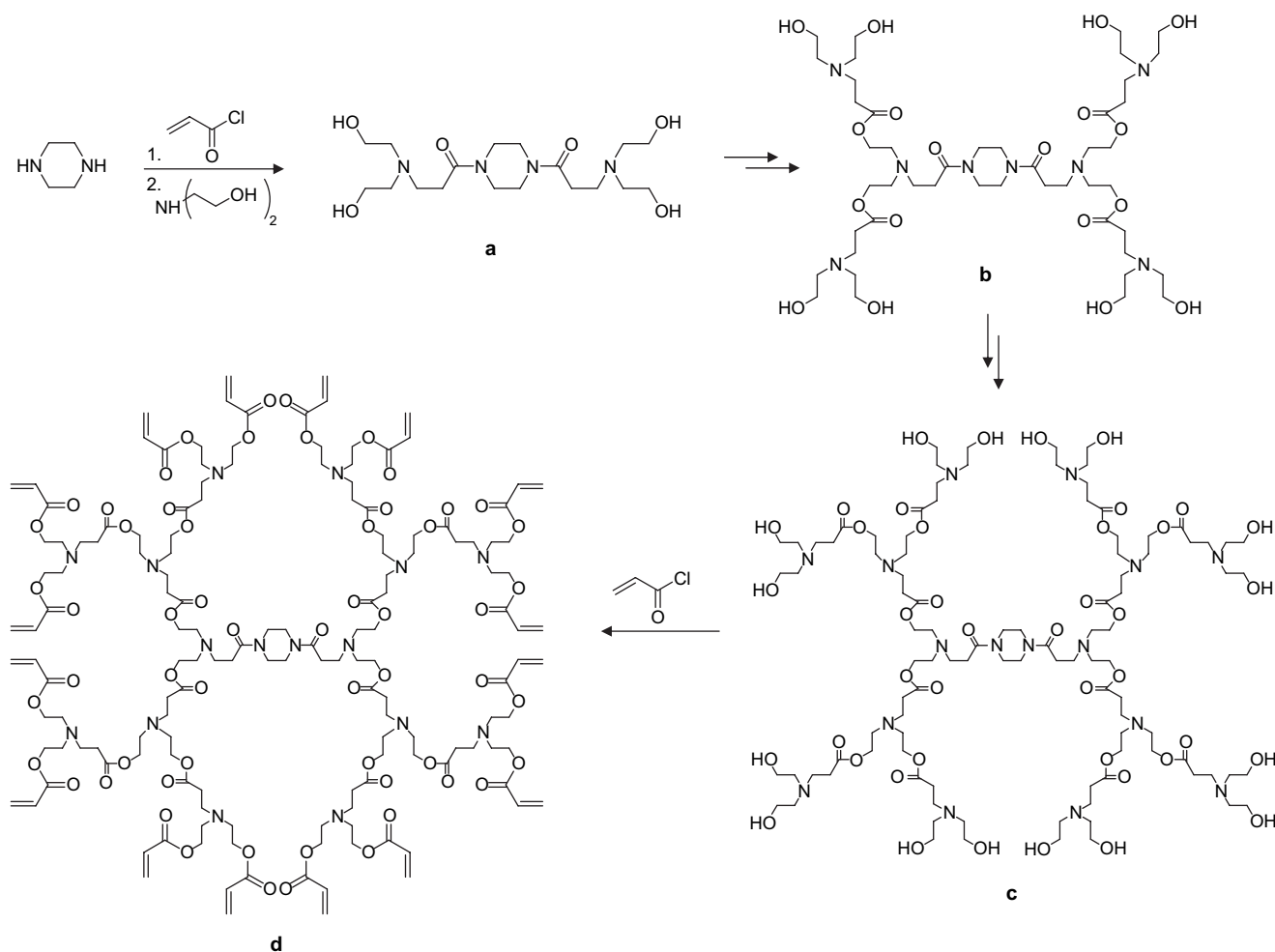
$\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, as the key monomeric building block; the resultant products are closely related to the PAMAM family but each arm possesses an additional carbonyl moiety.

3.4. 1 → 2 *N*-branched, ester-connectivity

Treatment of piperazine with acryloyl chloride followed by diethanolamine gave the G1 tetraol **25a**, as the core, which with acryloyl chloride, then diethanolamine, generated the desired octaol **25b** possessing the internal ester linkage [1340]. The repetition of this sequence gave the G3 with 16 terminal hydroxy moieties (**25c**); the G3 acrylate surface (**25d**) was also created but the yields decreased with increasing generation: G1 (79%), G2 (62%), and lastly G3 (48%) (Scheme 25).

3.5. 1 → 2 *N*-branched, ether-connectivity

The creation of poly(propyl ether imine) dendrimers (PETIM) has been accomplished by a series of simple iterative steps demonstrated by treating an ammonia core with *tert*-butyl acrylate to give (98%) triester **26a**, which was hydrolyzed (AcCl , H₂O) to afford (99%) the triacid **26b** that was quantitatively reduced (LAH) giving the intermediate triol, which was then subjected to a Michael reaction with acrylonitrile to give (90%) **26c**; reduction (Raney Co, H₂) and treatment with *tert*-butyl acrylate gave (90%) the hexaester **26d**. The sequence is repeated until the G3 24-acid **26f** is realized [1341] (Scheme 26). Dendrimers up to G6, possessing theoretically 128 terminal ester moieties, have been reported [1342] based on their preliminary work using $\text{O}[(\text{CH}_2)_3\text{N}(\text{CH}_2)_3\text{OH}]_2$, as the core [1343,1344]. The procedure is long but the overall yields are quite good; however at the higher generations, the yields are lower, as expected. The terminal phosphonated dendrimers were synthesized by conversion of the surface



Scheme 25. The formation of amine-branched dendrimers with ester connectivity [1340].

hydroxyl moieties to corresponding chlorides, followed by treatment with Ph₂PLi; subsequent reaction with Pd(COD)Cl₂ gave the desired Pd(II) complexes [1344].

3.6. 1 → 2 *N*-Branched, carbamate-connectivity

A simple divergent approach [1345] to two-directional dendrimers has appeared in which the 4-nitrophenyl chloroformate derivatives (*e.g.*, from diethylene glycol; **27a**) can be reacted with the readily available diethanolamine, followed by 4-nitrophenyl chloroformate to give (83%) the G1 protected tetraol **27b**. When this simple procedure is repeated, the G2 **27c** was generated in 68% yield. This procedure easily allows access to the incorporation of other (monoprotected) bis-nucleophiles, such as ethylenediamine [as the mono-protected BOC-derivative with **27b** gave (80%) **27d**] and di[2-(2-hydroxyethoxy)ethyl]amine (Scheme 27).

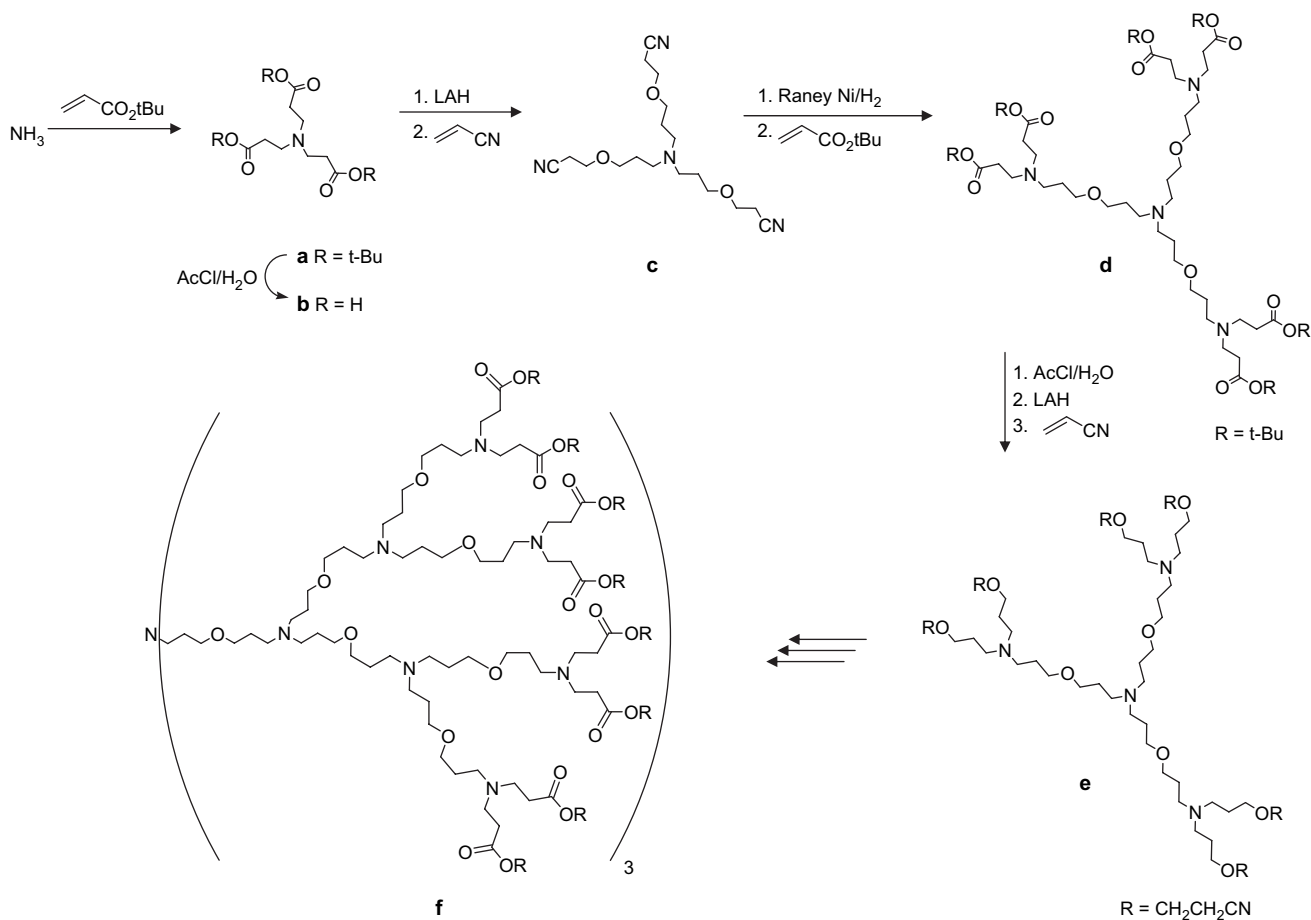
3.7. 1 → 2 *N*-branched, aryl connectivity

A simple series of mesomolecules, based on 4,4',4''-tris(*N,N*-diphenylamino)triphenylamine, has been prepared and characterized [1346]. The ESR of the cationic triradical of the related 1,3,5-tris(diphenylamino)benzene has been shown

[1347] to agree well with the theoretical prediction of a quartet ($S = 3/2$) spin state with a zero-field splitting parameter of 11 G (0.0012 cm⁻¹). 1,3,5-Tris[*N*-(4'-methylbiphenyl-4-yl)-*N*-(diphenylaminophenyl)amino]- and 1,3,5-tris[*N*-[4-bis(4-methylphenyl)aminophenyl]-*N*-(4-diphenylaminophenyl)amino]benzene have been found to be thermally and morphologically stable amorphous materials that exhibit unique multi-redox properties [1348]. The synthesis and femtosecond excitation energy transport studies of these highly electron-rich materials have been studied [1349] and it was demonstrated that they can produce highly delocalized radical cations. A review of the synthesis and applications of these hole-conducting oligomeric and polymeric, including dendritic, triaryl amines has appeared [1350].

Although small by normal dendrimer standards, the 4,4',4''-tris[*N*-methylphenyl-*N*-(9-ethylcarbazyl-3)amino]triphenylamine was synthesized (90%) from 4,4',4''-tris(*p*-bromophenyl)amine with *N*-(9-ethylcarbazyl-3)-2-methylaniline [1351]. This material was successfully applied to the preparation of an organic light-emitting device. The simple all *trans*-C[C₆H₄-CH=CHC₆H₄N(C₆H₅)₂]₄ led a low band-gap molecular glass that retained the optical and electrochemical properties of individual components [1352].

Treatment of hexa(4-bromophenoxy)cyclotriphosphazene with *N-p*-tolylpyrene-1-amine in the presence of Pd[P-



Scheme 26. Synthesis of poly(ether imine) dendrimers [1341].

(*t*-bu)₃]₂ conducted *in vacuo* using the Buchwald–Hartwig amination procedure gave (>93%) the monodisperse G1 dendrimer possessing high glass transition and decomposition temperatures as well as a high photoluminescent quantum efficiency [1353].

3.8. 1 → 2 *N*-branched, Si-connectivity

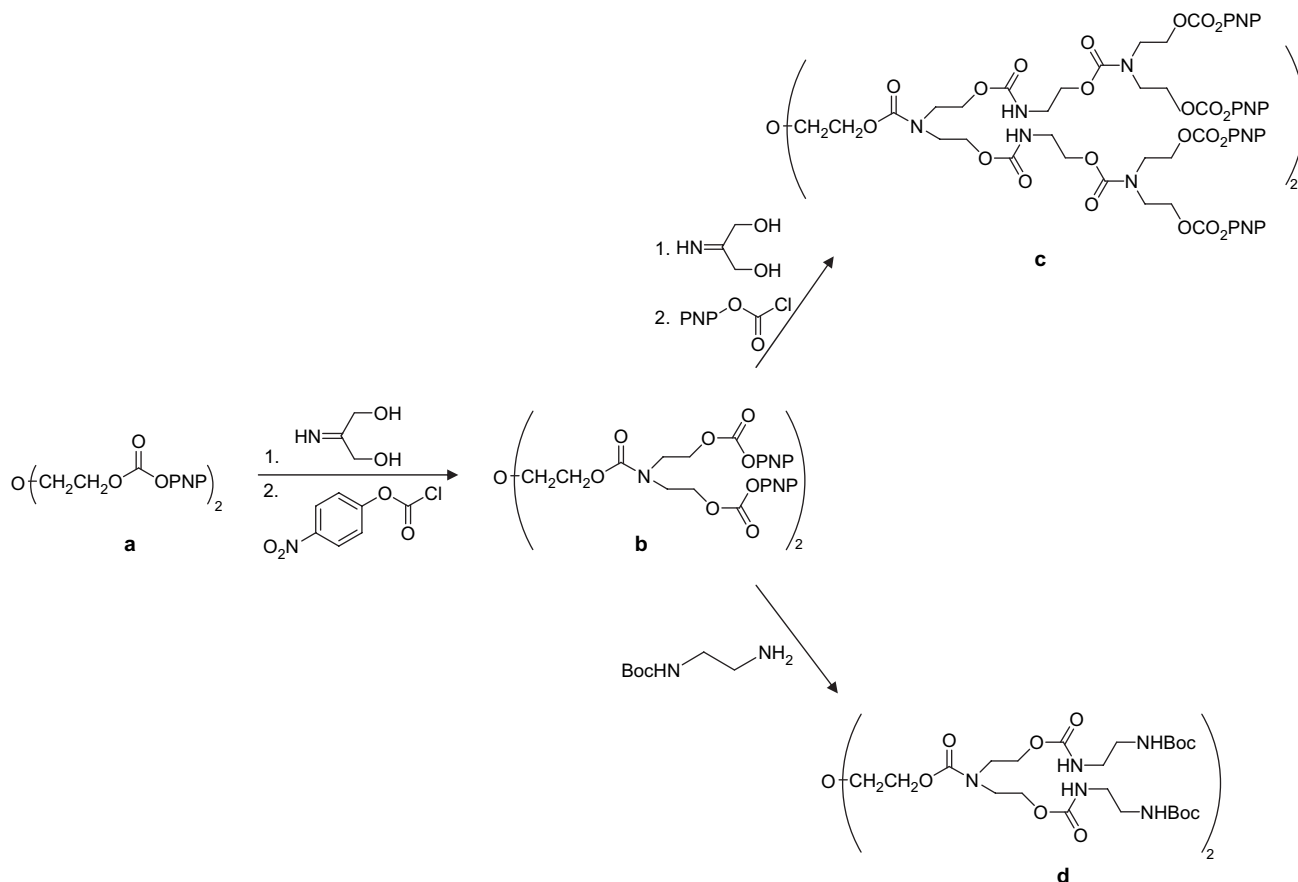
Hu and Son [1354] employed the traditional hydrosilylation–chlorosilane procedure in concert with silazane monomers for the construction of *N*-branched, silane-based structures. This iterative procedure is exemplified by the Pt-mediated (Karstedt's catalyst) [1355] reaction starting from a three-directional core **28a** with HMe₂SiCl, followed by treatment with lithium (dimethylvinylsilyl)amide (**28b**); repetition then afforded the G1,2 constructs **28c** and **28d**, respectively (Scheme 28). Notably, the hydrosilylation steps required three days to proceed to completion, although quantitative yields were realized. Complete reaction for access to a defect-free G3 was not, however, realized. Interesting features of this architecture includes the known planarity of the N(Si)_{*x*} units (*x* ≥ 2) [1356] and the facile hydrolytic degradation of the Si–N moieties. This initial synthetic work was expanded by Veith et al. [1357] to the G4 level possessing the vinyl surface that was transformed to a mesogenic surface [1358] by hydrosilylation using Karstedt's catalyst

[1355] thus generating nematic dendrimers possessing liquid crystalline properties [1359–1361]. The birefringence, refractive indices, and dielectric measurements have also been conducted on these liquid crystals [1362].

3.9. 1 → 2 *N*-branched, amide and alkyl-connectivity

Synthesis of the fluoros support **29f** was prepared in a multi-step sequence and used as a convenient platform for the construction of peptides [1363] and polysaccharides [1364]. The initial acid [1365] **29a** was treated with amine [1365] **29b** to give (97%) the bis-amide **29c**, which was quantitatively saponified to give acid **29d**. To assemble the core, diethylenetriamine was treated with trityl chloride to protect the primary amines; the internal secondary amino moiety was reacted with monomethyl glutarate, followed by deprotection to give the core **29e**, which with 2 equiv. of acid **29d**, followed by saponification, gave the desired support **29f** (Scheme 29).

The treatment of benzylamine with *tert*-butyl acrylate *via* a neat Michael reaction in the presence of Yb(OTf)₃ [1366] gave rise to the desired tris-protected iminodipropionic acid [1367] **30a** [1368]. Selective deprotection *via* debenzoylation (Pd/H₂) gave (90%) the free amine **30b**, which was extended with Fmoc-GlyOH to furnish amide **30c** that was *N*-deprotected to give the *N*-extended diester **30d**. Hydrolysis of the



Scheme 27. Carbamate connectivity [1345].

tert-butyl groups with TFA/anisole/water gave (75%) the *N*-protected diacid **30e**, which was transformed into the G2 dendron **30f** by reaction with the extended amine **30d**, derived by deprotection of **30c** with piperidine in MeCN (Scheme 30).

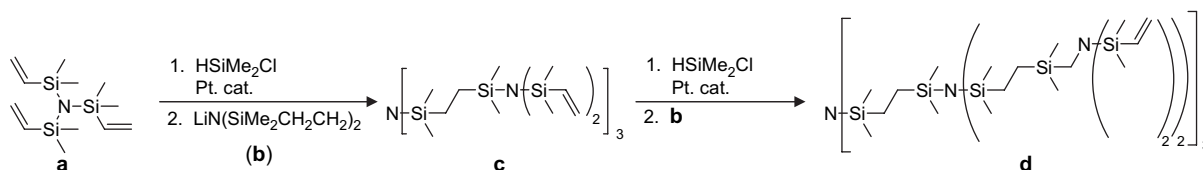
3.10. 1 → 2 *N*-branched, *N*- and amide-connectivity

Beer and Gao [1369] created the G1,2 poly-1,4,7-triazacyclononane-based architectures, which easily gave the Cu(II) and Ni(II) complexes. The initial 1,4,7-triazacyclononane **31a** was readily transformed to either triamine core **31f** or, by selective protection/deprotection steps, the key 1 → 2 branched macrocyclic ring **31b**, which can be subsequently either hydrolyzed to give the free acid **31c** or catalytically reduced to generate the diamine **31d**. Combinations of the different heteromacrocycles were connected divergently using traditional acid–amine coupling procedures (EDC, HOBT, DMF) to generate the G1 hexa-amine; the easy conversion of these monomers to the larger

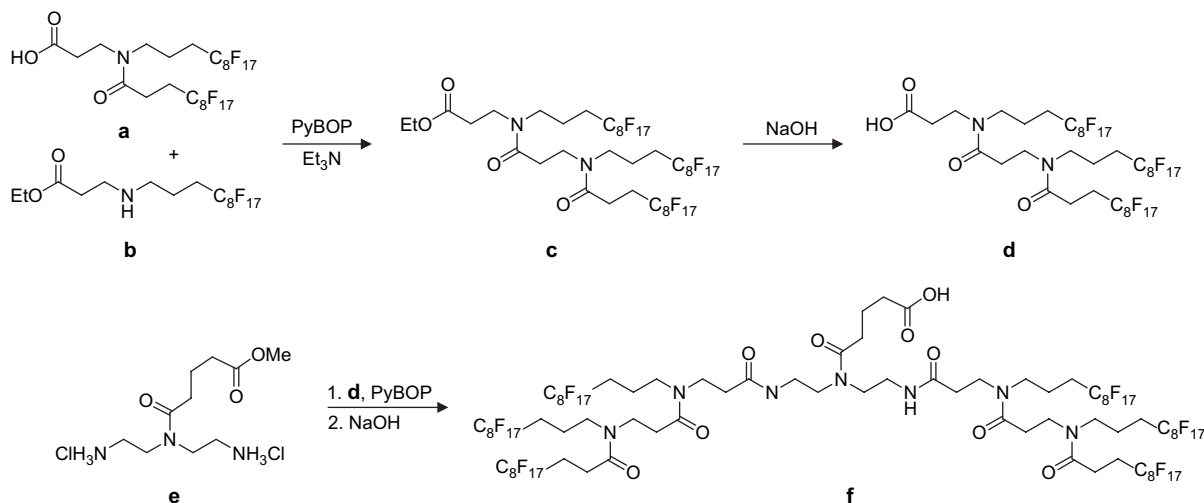
monomers, *e.g.*, **32a**, permitted the convergent assembly of this dendrimer family **32b** (Schemes 31 and 32).

3.11. 1 → 2 *N*-branched, carbamate and urea-connectivities

The key reagent used in this divergent process [1370,1371] was *cis*-4-isocyanatomethyl-1-methyl-1-isocyanatocyclohexane (**33a**), which was prepared from the corresponding diamine upon treatment with di-*tert*-butyltricarboxylate [296]. Treatment of 1,1,1-tris(methanol)ethane, as the three-directional core, with **33a** using [Zr(acac)₄], as a catalyst, in refluxing CHCl₃ for two days afforded the G1 tris-isocyanate **33b**; the addition of diethylamine terminated the reaction to give (100%) urea **33c**. If, however, instead of termination, bis(ethanol)amine was added, followed by additional **33a**, the G2 terminal hexa-isocyanate **33d** was generated, followed by capping with diethylamine to give **33e**. The G3 derivative



Scheme 28. Carbosilazane dendrimers [1354,1357].



Scheme 29. Synthesis of the useful fluorinated support for peptide construction [1364].

33f and products derived from an alternate core, 1,1'-ferrocene-dimethanol, were also reported [1370] (Scheme 33).

3.12. 1 → 2 *N*-branched, sulfone and aryl-connectivity

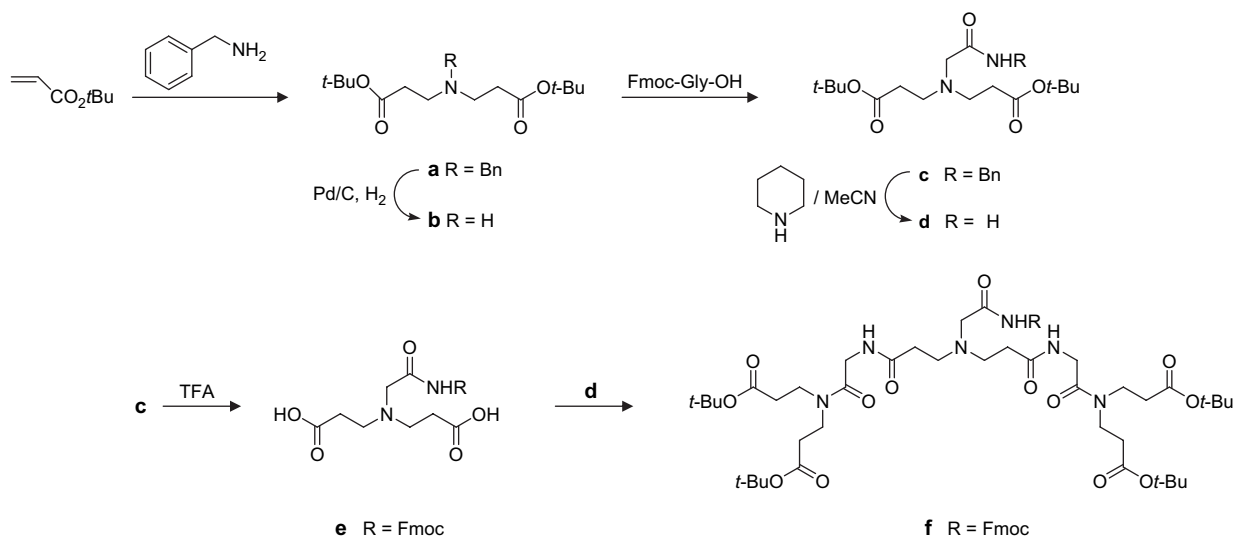
Treatment of tris(2-aminoethyl)amine (**34a**) with 4-nitrobenzenesulfonyl chloride in the presence of Et₃N gave (80%) *N,N,N'*-trisulfonamide **34b**. It was then reacted with 4-nitrobenzyl bromide with Cs₂CO₃ in MeCN to afford (70%) **34c**, which was reduced (79%; SnCl₂/HCl) to the desired hexamine **34d** [1372]. Sulfonylation of **34d** with either tosyl chloride or *p*-*tert*-butylbenzenesulfonyl chloride gave low yields of the G2 dendrimer **34e** (R = Me) and **34f** (R = *t*-Bu), respectively (Scheme 34).

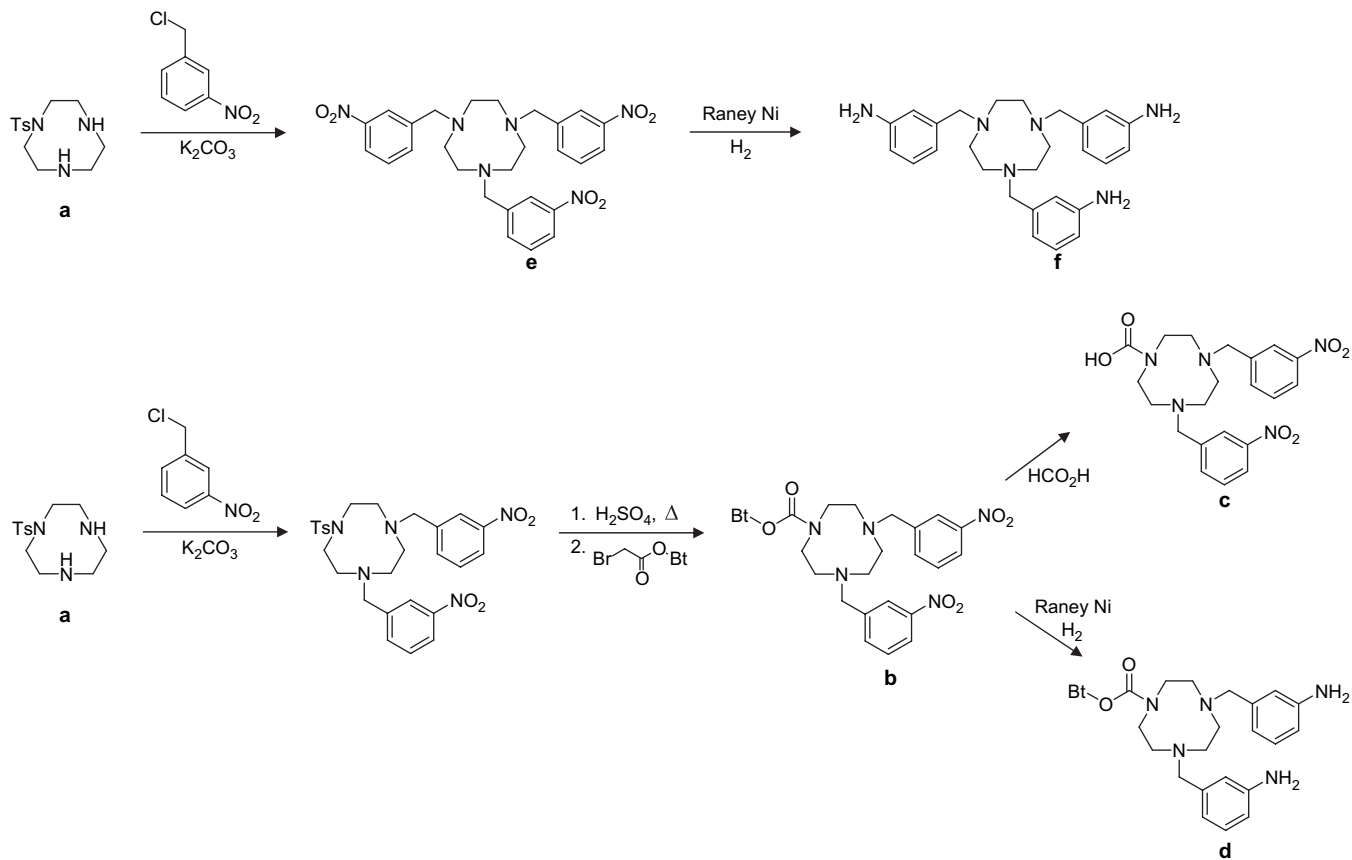
Lukin et al. [1373] expanded the synthesis of oligosulfonimides by the treatment of an *N*-alkylamine with 2 equiv. of *p*-nitrobenzenesulfonyl chloride in the presence of NEt₃, followed by catalytic reduction (10% Pd/C) of the nitro moiety

to the corresponding aryl amine; this sequence can be repeated to generate the next tier. The introduction of a terphenyl core was accomplished *via* a double Suzuki cross-coupling reaction using 1,4-phenylene diboronic acid diester. Photophysical properties of three of these dendrimers possessing the terphenyl core were studied [1374] and shown to exhibit high steady-state anisotropy.

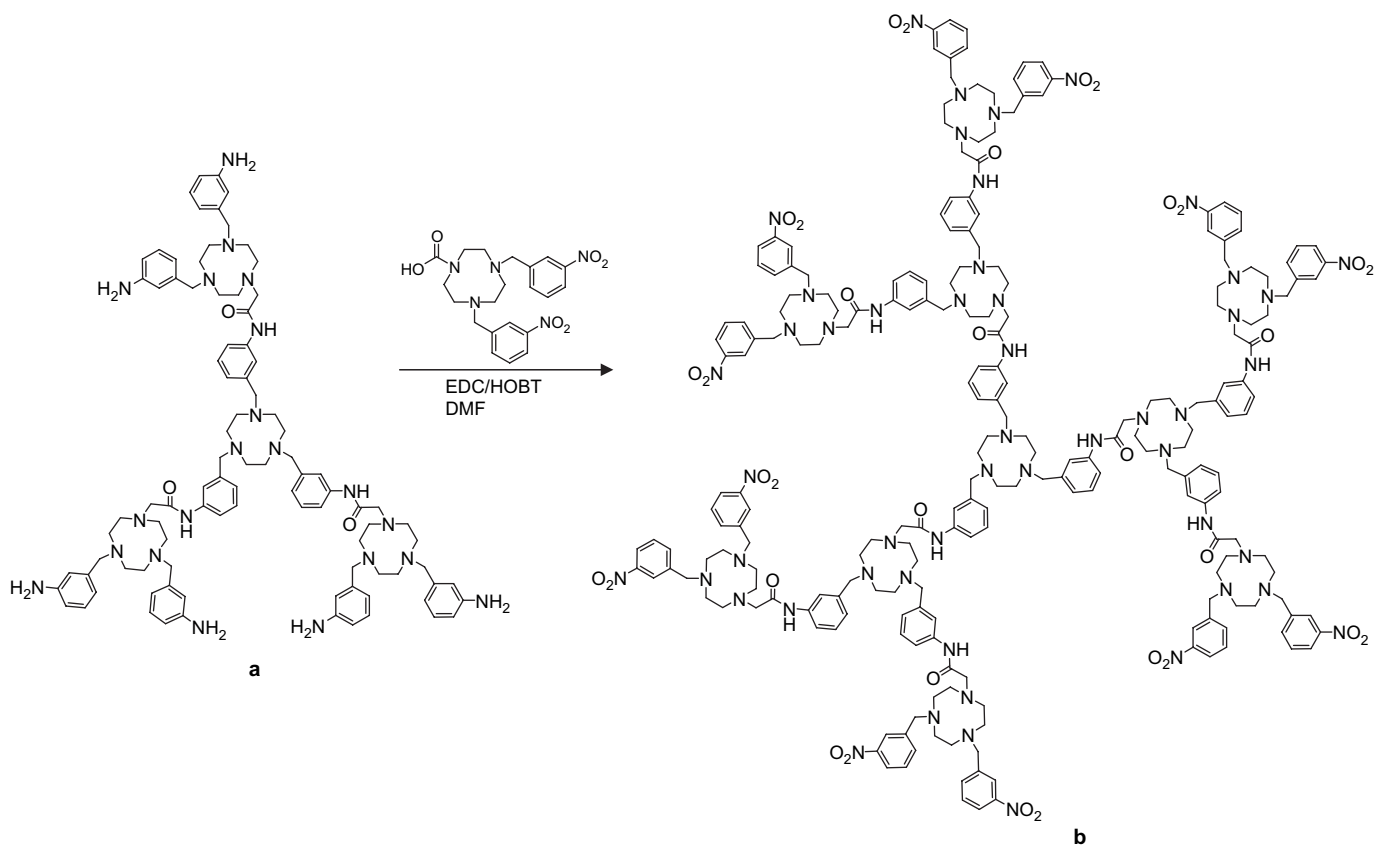
3.13. 1 → 2 *N*-branched, amide, ether, and calixarene-connectivity

Vicens et al. [1375] synthesized the 1 → 2 *N*-branched diamido *N*-dicalixarene-CH₂CH₂NH₂ monomer and the mono(methoxycarbonyl)calix[4]arene as starting materials of hyperbranched systems possessing the calixarene spacer group. By clever control of ring substitution, a divergent preparation of calix[4]-dendrimer **35a** was created [1376]. The *N*-calix[4]arene **35b** was transformed (37%) with 4 equiv. of BrCH₂CO₂Me

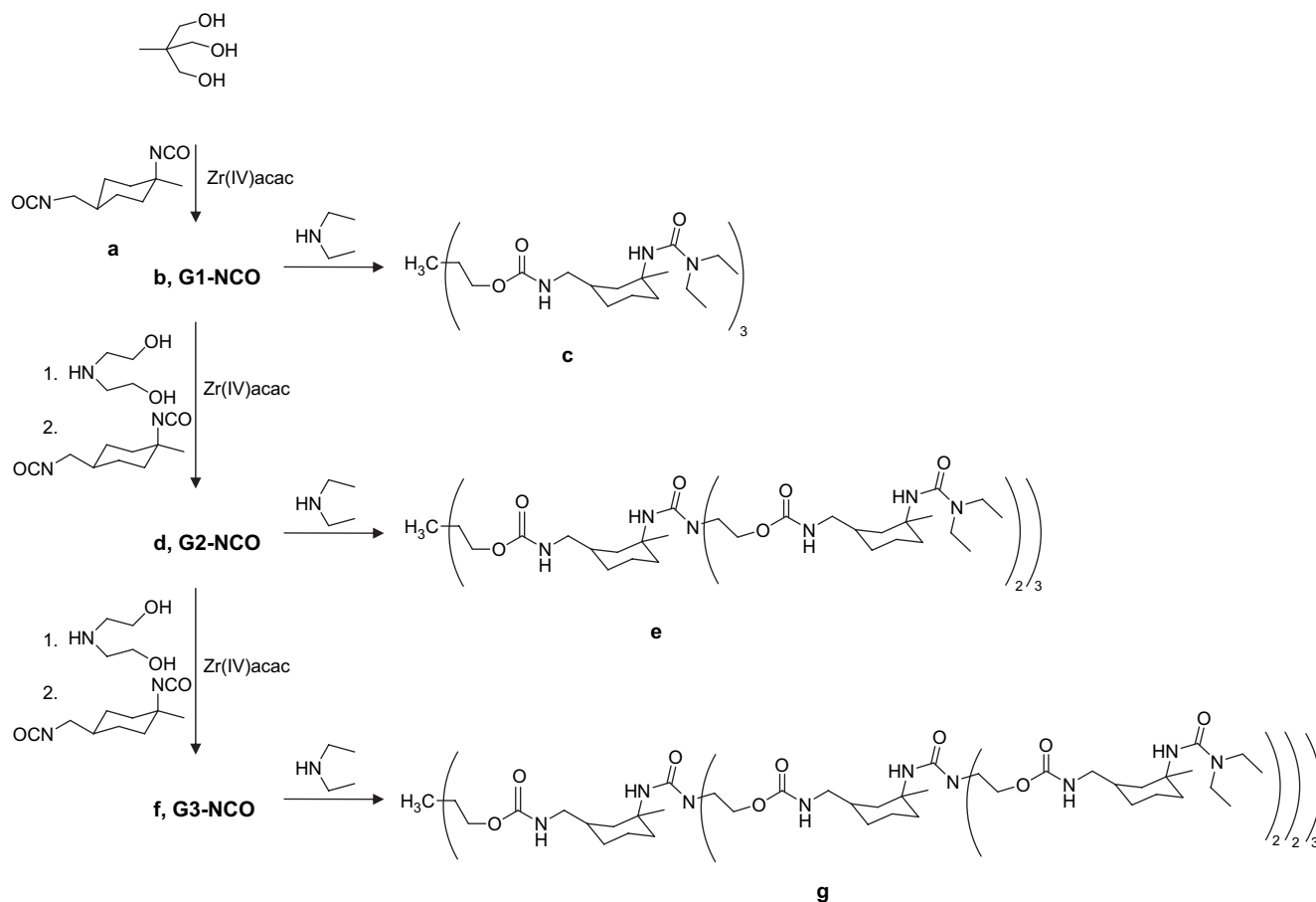
Scheme 30. Synthesis of a new *N*-branched dendron system, based on iminodipropionic acid [1368].



Scheme 31. Azomacrocyclic dendrimers [1369].



Scheme 32. Combination of triaza-building blocks [1369].



Scheme 33. Synthesis of polycarbonate, urea-based dendrimers [1370].

and 1.5 equiv. of K_2CO_3 in MeCN into the *N*-calix[4]arene-triester **35c**. This triester was reacted with 6 equiv. of the monomer **35d** to afford (5%) the desired dendrimer **35a**. Reaction conditions were shown to be important since using a step-wise process *via* a hyperbranched intermediate, the dendrimer **35a** was isolated in 74% yield (Scheme 35).

4. 1 → 2 Aryl-branched

4.1. 1 → 2 Aryl-branched, *N*-connectivity

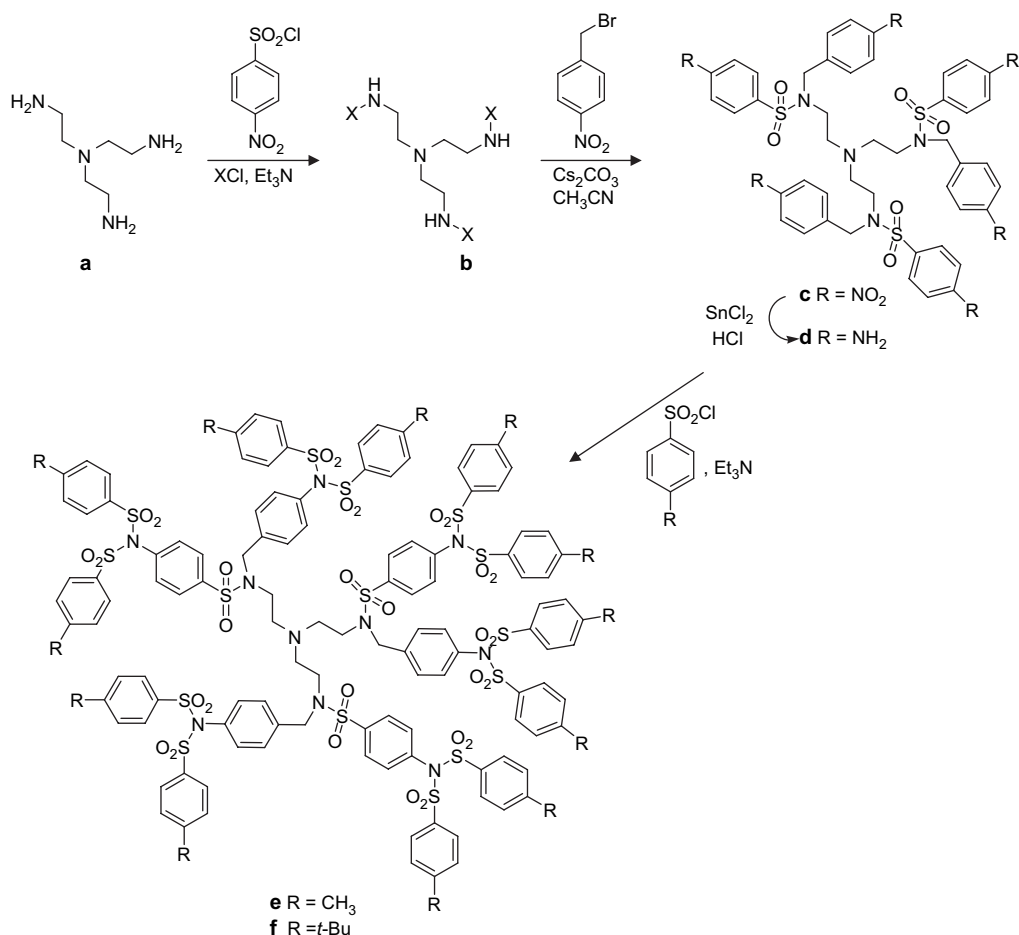
By the use of an aromatic nucleophilic substitution–reduction sequence, Hall and Polis [1377] synthesized a series of polyarylamines by treatment of 2,4-dinitrofluorobenzene (**36b**) with *p*-diaminobenzene (**36a**) in DMSO at 25 °C to give the tetranitrodiamine **36c** that was reduced (Pd/C/H₂ in MeCN) to afford the initial G1 amine **36d**. The G2 octanitro and tetradecaamine constructs **36e** and **36f** were readily prepared by repetition of this simple procedure (Scheme 36). These polyarylamines were examined by cyclic voltammetry and shown to be (1) unstable in the presence of either air or light and (2) semiconducting materials when complexed with iodine.

Blackstock et al. [1378] generated stable, isolable polyradical cations that were derived from a small poly(phenylenediamine), which was prepared (21%) by condensation of phloroglucinol with *N*-phenyl-*p*-phenylenediamine using the

Ullmann reaction with iodobenzene. When *p*-iodoanisole was used in this procedure, the corresponding methoxy-terminated analog was prepared. A larger poly(aryl amine) dendrimer was similarly synthesized [1379] and electrochemically oxidized and shown by cyclic voltammetry to possess a redox-gradient caused by the outer shell of the difficult-to-oxidize aryl amines surrounding the more readily oxidized internal phenylenediamino moieties. Other small, related triarylamines have been reported [1380,1381].

The one- and two-electron transfer processes in triarylamines with multiple redox centers were reported by Lambert and Nöll [1382]; the hexakis[4-(*N,N*-di-*p*-methoxyphenylamino)phenyl]benzene was easily synthesized from 4,4'-bis(*N,N*-di-*p*-methoxyphenylamino)tolane in the presence of $[Co_2(CO)_8]$. Thelakkat et al. [1383] also reported the formation of various low molecular weight triarylamines possessing photoconductive and non-linear optical properties; the OLEDs derived by this procedure exhibited a high efficiency and large current carrying capacity.

Walder et al. [1384] utilized a divergent procedure using preformed branching units to construct a dendritic-type electron sponge that exhibited generation-dependent intramolecular charge-transfer complexation; the basic architecture was comprised of viologen (4,4'-bipyridinium) spacers with aryl branching centers **37b** derived from the viologen core **37a**. Capping with a viologen moiety **37a**-PF₆ initiated

Scheme 34. Synthesis of *N*-branching dendrimers [1372].

a two-directional branched core **37d**, which with **37e** gave G1 product possessing 5 viologen moieties. The treatment of **37d** with the branched viologen monomer **37f** gave rise to the G2 level, which was terminated with 4 equiv. of **37e** (Scheme 37). The related series of dendrimers was constructed up to G3 possessing 45 benzyl viologen subunits. Ramifications for molecular recognition, signal transduction, and charge trapping [1385] were considered.

The functionalization of a Wang polystyrene support with 1 → 2 aryl branched dendrons has recently appeared [1386] in which the surface CH₂Br moieties (Wang Bromo resin) were treated with dimethyl 5-aminoisophthalate, followed by LiBH₄ reduction to generate the G1 dendron with a hydroxy surface. Oxidation of these CH₂OH moieties to the corresponding aldehydic functionality with a pyridine·SO₃ complex, then conversion to the imine and subsequent reduction gave the G2 dendron with an ester surface. The same reduction, oxidation, and imine-reduction sequence afforded the G3 level.

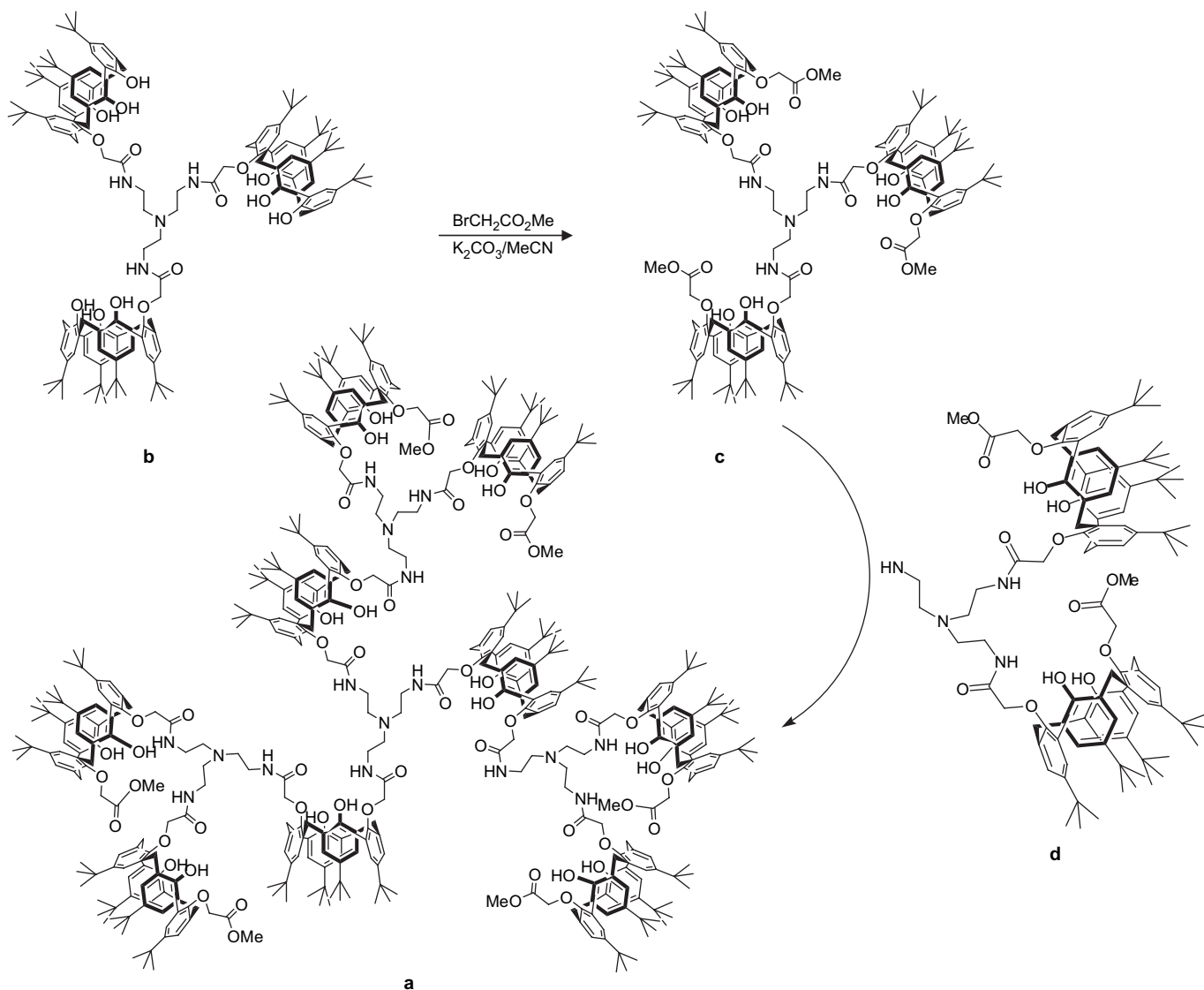
4.2. 1 → 2 Aryl- and C-branching and connectivity

Veciana et al. [1387–1393] reported the formation of perchlorinated polyradicals through G2. The 1st tier triradical **38e** was obtained by subjecting 1,3,5-trichlorobenzene (**38a**)

to dihalomethylation conditions to provide the Reimer-Tiemann intermediate, *i.e.*, tris(α,α -dichloromethylbenzene) (**38b**), which, upon treatment with pentachlorobenzene in the presence of AlCl₃, afforded the desired polychlorinated heptaaryl radical precursor **38c**. Deprotonation at the triphenylmethane loci using a large excess *n*-Bu₄N⁺OH⁻ at 25 °C for 35 days gave the trianion **38d**, which was subsequently transformed with excess *p*-chloranil to the corresponding triradical **38e** (Scheme 38).

The static [1392] and dynamic [1393] stereochemistry of these structurally complex materials characterized by three propeller-like moieties has been analyzed by a unified theoretical methodology, based on a symmetry-adapted symbolic notation. The above triradical **38e** was isolated in two isomeric forms possessing *D*₃ and *C*₂ symmetries. Thus, due to steric shielding provided by the chloro groups, the polyradicals exhibited exceptional stability in the solid state at temperatures up to 250 °C. The G2 (Fig. 6) perchlorinated polyradicals were similarly prepared, although the authors noted that several structural defects disrupted some of the desired ferromagnetic couplings.

Rovira et al. [1394] generated the G2 perchlorinated tetra-radical using a modified Friedel–Crafts reaction with elevated reaction temperatures as well as a large excess of reagents



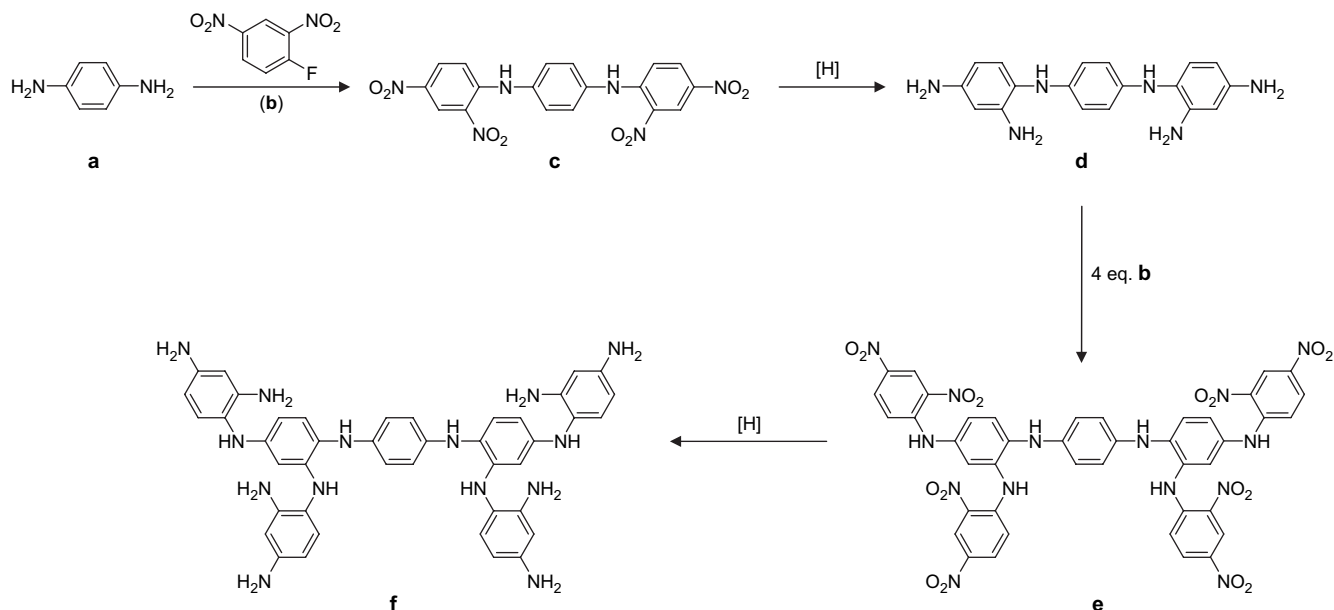
Scheme 35. Synthesis of a dendrimer possessing a calix[4]arene spacer [1376].

(such as benzene and AlCl_3 in >60:1 and 3:1 molar ratios, respectively) to produce (*ca.* 90%) nonaarylmethane **39c** starting from the tris(dichloromethyl) precursor **39a**. Exhaustive chlorination (SO_2Cl_2 , SCl_2 , AlCl_3) of the Friedel–Crafts product **39b** gave the desired, highly overcrowded dendrimer **39c**. The deep-red purple solid polyradical formation (*i.e.*, **39d**) was achieved by the formation ($i\text{-Bu}_4\text{NOH}$) of the initial carbanion, followed by oxidation ($p\text{-chloranil}$) (Scheme 39). These radicals were studied by using X-band ESR. A crystal structure was determined [1395] for a small high-spin triradical, which revealed the presence of diastereoisomers possessing either C_2 or D_3 symmetry. Employing linear solvation free-energy relationships, the molecular surface characteristics of the quartet 2,4,6-trichloro- $\alpha,\alpha',\alpha'',\alpha'''$ -hexa(pentachlorophenyl)mesitylene, existing in two atropisomeric forms, were studied based on its interactions with adjacent solvent molecules [1396]. Both the shape and structural fractality were shown to be important molecular characteristics; whereas the cavitation effects were found to be unimportant.

Iwamura et al. [1397] reported the synthesis of a branched-chain nonacarbene possessing a nonadecet ground state with the intention of preparing superparamagnetic polycarbenes initiated by the photolysis of 1,3,5-tris[diazo(3-(diazo(3-diazo(phenylmethyl)phenylmethyl)phenylmethyl))]benzene. Bock et al. [1398] reported the preparation of three-directional, diradicals, while a tetraphenylmethane tetrakisgalvinoxyl-type tetradical was prepared by Kirste et al. [1399] The perchloro-2,6-bis(diphenylmethyl)pyridine- α,α' -ylene biradical has been shown to possess exceptionally high stability [1400].

4.3. 1 → 2 Aryl and aryl-branching and connectivity

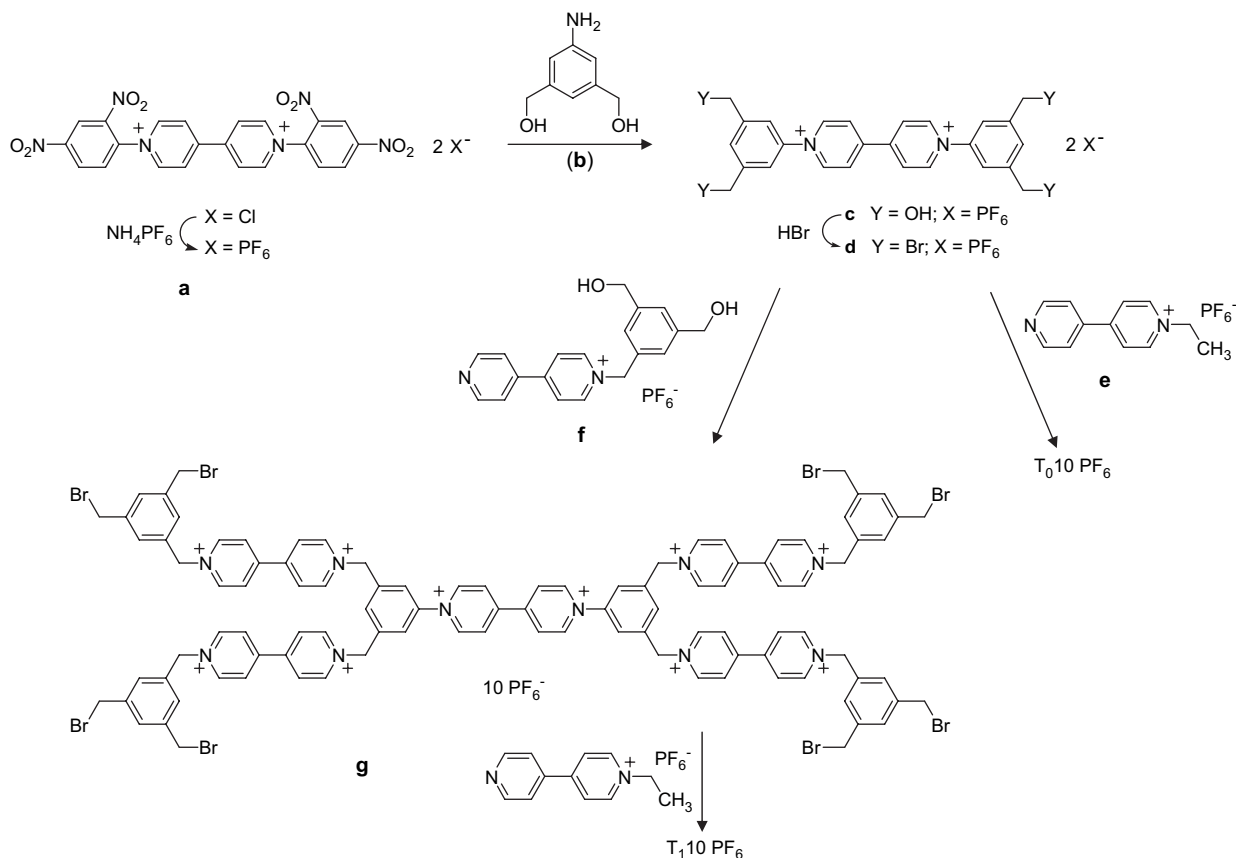
Müllen et al. [1401–1404] described the synthesis of polyphenylene dendrimers using an irreversible construction via the Diels–Alder cycloaddition of an alkyne dienophile to an activated diene. Key monomers included dienone **40d**, accessed by coupling [$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , Et_3N , toluene] [1405] of triisopropylsilylacetylene (TiPSA) to 4,4'-dibromobenzil, followed



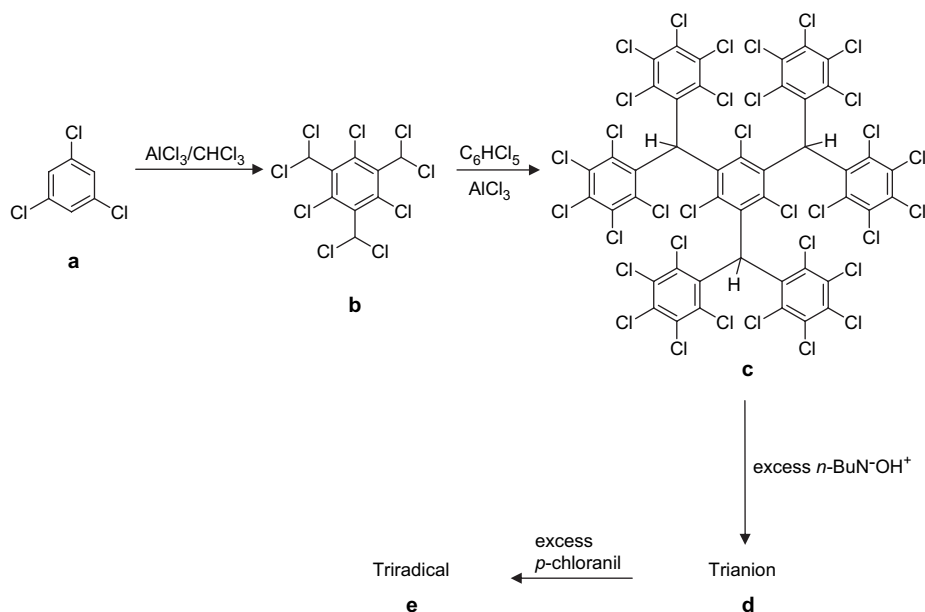
Scheme 36. Poly(aryl amine)s [1377] prepared by aromatic nucleophilic displacement ion.

by condensation (KOH, EtOH) with 1,3-diphenylacetone, and diene **40a**, prepared by [4 + 2]-cycloaddition of **40c** with diphenylacetylene and subsequent alkyne deprotection [Bu₄NF]. Preparative iteration is demonstrated: 2 equiv. of diene **40a** were

reacted with bis(alkyne) **40c** to give, after silyl deprotection, the tetraalkyne **40e**; repetition of the sequence yielded the octaalkyne **40f**. Analogously, the rigid dendrimer **41c** was constructed starting with the tetraalkyne core **41a** (Schemes 40



Scheme 37. Synthesis of dendritic electron sponges utilizing benzyl viologen [1385].

Scheme 38. A perchlorinated triradical possessing D_3 and C_2 symmetries.

and 41). All silyl-protected intermediates, as well as the free polyalkynes, were freely soluble in common organic solvents. Notably, the dienophile was added portion wise to an excess of diene to produce the large polyalkynes. An alkylated series

of related dendrimers was synthesized by this general procedure [1406]; their organization of graphite has been investigated using AFM showing the formation of a stable, almost pinhole-free, monolayer. A single-molecule spectroscopic study was

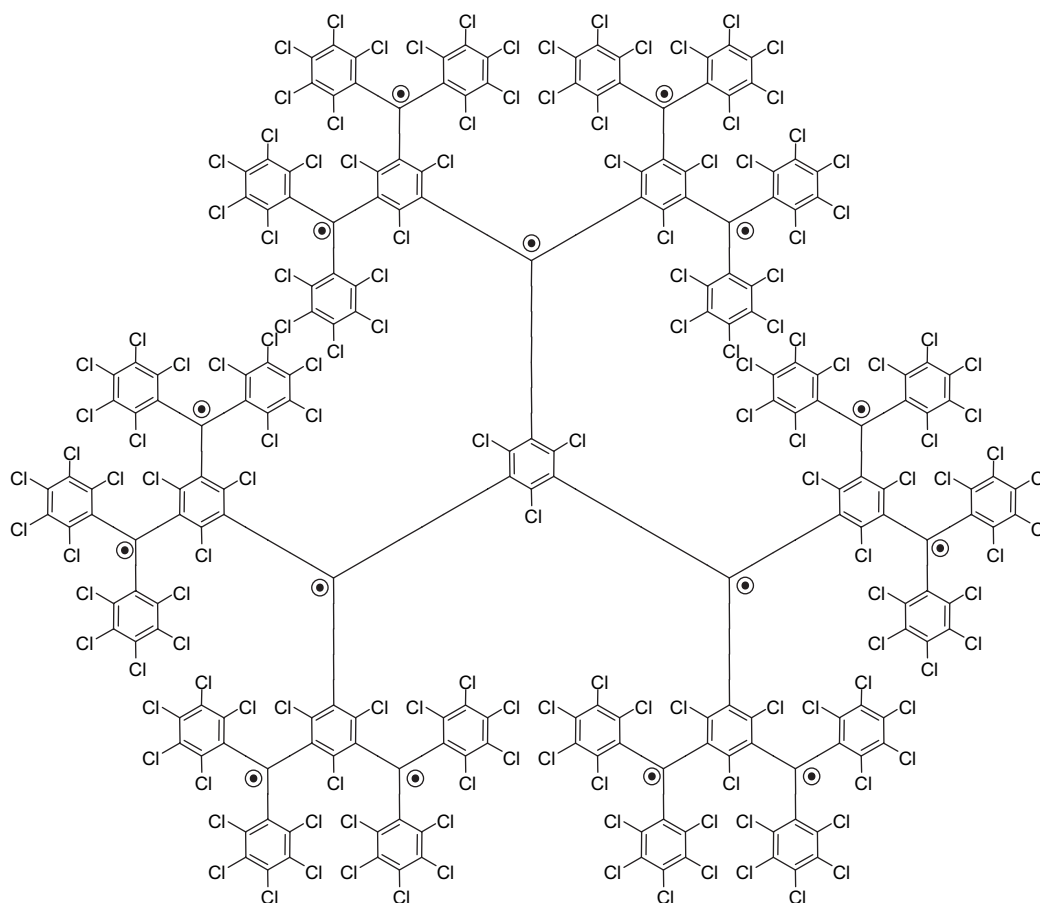
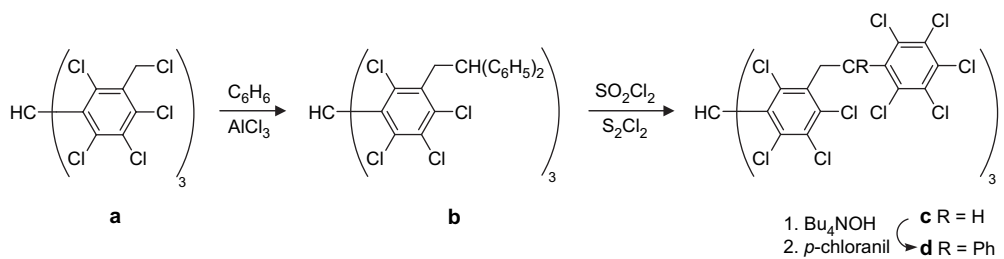
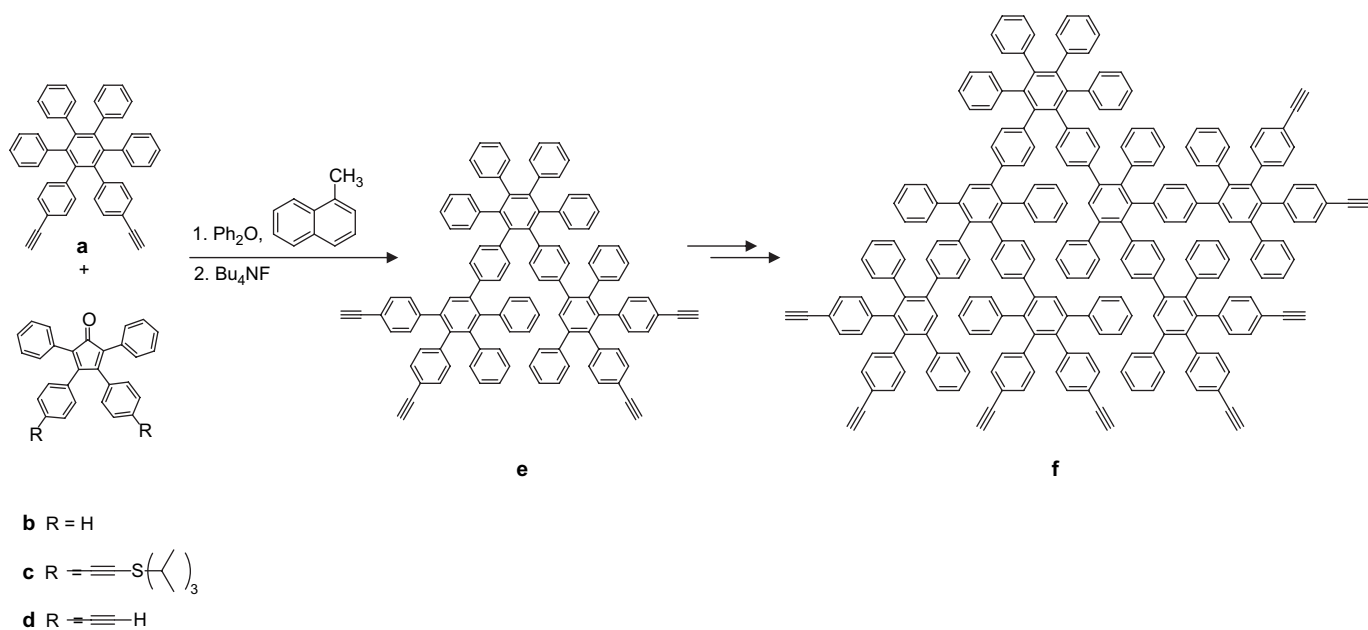


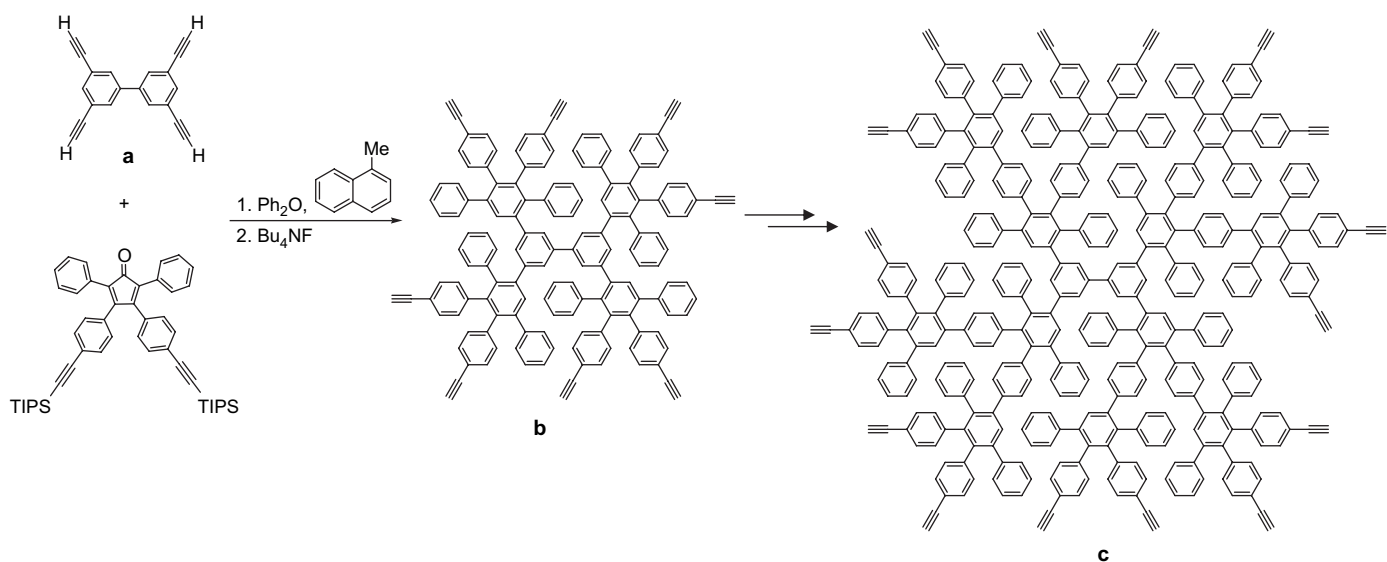
Fig. 6. A dendritic G2, perchlorinated polyradical used to investigate solid radical stability.



Scheme 39. Creation of a congested perchlorinated poly(aryl methane) [1394].



Scheme 40. Polyaromatic hydrocarbon-based dendrons (e) and dendrimers (f).



Scheme 41. Cyclodehydrogenation generated unique 2-D architectures.

conducted with the G2 polyphenylene dendrimer possessing 16 carboxylate moieties on the periphery and the cyanine dye, pincyanol; at low concentrations, a 1:1 complex was present, whereas at higher ratios, ion-pairing resulted [1407].

Improved procedures for the synthesis of their polyphenylene dendrimers using a [2 + 4] cycloaddition–deprotection protocol have appeared [1408]; excellent, detailed reviews are accessible [1409–1412]. Phenylene dendrimers possessing an increasing number of chromophores on the surface have been generated up to G2 [1413,1414]. The G1–3 dendrimers were prepared consisting of 22, 62, and 142 benzene rings, respectively; dense packing for G2,3 was shown by molecular mechanics to limit the conformational degrees-of-freedom, thus providing support for infrastructural “shape-persistence.” The diameters of these structures were determined to be 7, 21, 38, and 55 Å for the G0–3, respectively. Individual polyphenylene dendrimers have been spin-coated onto a mica surface; the size of a single molecule measured using noncontact AFM was in agreement with that calculated by molecular dynamics simulation [1415]. Solid-state NMR with magic-angle spinning (MAS) as well as fast-MAS recoupling techniques of these G1–4 shape-persistent polyphenylene dendrimers with different functionalities have been reported [1416]. Their results support the observation that the radial segment density distribution was caused by extended arms and that the dense-shell packing limit was reached at G4; see below. The single-molecule fluorescence spectroscopy of numerous peryleneimide polyphenylene dendrimers has been conducted in order to determine whether these dendrimers can be used as single-photon sources at ambient temperatures [1417]. All G1 dendrimers were shown to behave “as single-photon emitters when more than one chromophore is excited by a single-excitation pulse regardless of the number of constituent chromophores.” The G2 polyphenyl dendrimers possessing multiple peryleneimide chromophores attached to the *para* position of the outer ring were studied with steady-state and femto- to nano-second time-resolved fluorescence spectroscopy, affording insight to the average distance between the chromophores [1418]; also see [1419] for the related G1 polyphenylene dendrimer. Wide-field imaging of individual multichromophoric molecules and photo-bleaching was used to determine the end-to-end distribution of the end-capped polyfluorene moieties [1420]. Detection of single molecules, *e.g.*, a simple peryleneimide derivative, was reported [1421]. Two new routes to highly fluorescent peryleneimide chromophores imbedded within the infrastructure of phenylene dendrimers by means of the iterative Diels–Alder reaction have recently appeared as an extension of their approach to create brilliant light emitters with a large number of fluorophores [1422]; in one case, the peryleneimide was used as a spacer leading to an extended dendrimer with a molecular diameter of >12 nm and 24 chromophores within the scaffold.

The “desymmetrized” polyphenylene dendrimers were initially reported [1413]; however, to circumvent some inherent synthetic problems, the symmetric tetrakis(4-ethynylphenyl)-methane (**42a**) was treated with less-than stoichiometric quantities of functionalized cyclopentadienones, thus circumventing

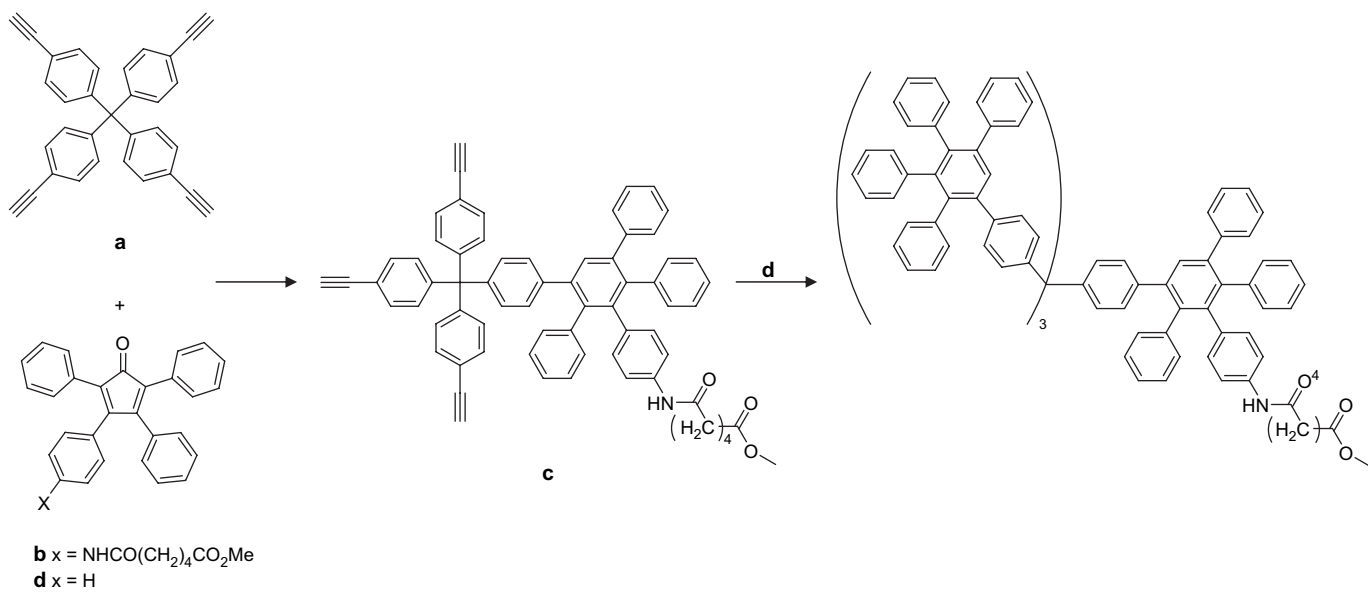
the original synthetic limitations [1423]. Treatment of **42a** with a monosubstituted tetraphenylcyclopentadienone (*e.g.*, **42b**) gave a mixture from which the mono-substituted **42c** was the major (55%) product, followed by the di-product (35%), and negligible quantities of the more highly substituted components. Subsequent treatment with tetraphenylcyclopentadienone (**42d**) gave the desired tetrasubstituted product. The use of the four-directional core **42a** with a masked AB₂ monomer, 3,4-bis(2',5'-dimethyl-4'''-triisopropylsilylethynyl-1,1':4',1'':4'',1'''-quaterphen-4-yl)-2,5-diphenylcyclopentadienone generated a G1 protected “exploded” polyphenylene dendrimer, which with the same protected monomer gave (96%) the next tier, followed by deprotection and repetition of this simple two-step sequence that furnished up to G5 the related family of dendrimers [1424]. Amazing as it may seem, this G5 dendrimer possessing 128 triisopropylsilyl moieties was deprotected (*n*-Bu₄NF·3H₂O in THF at 25 °C) then treated with excess of the above AB₂ branching protected monomer [1424] to generate the “largest chemically monodisperse” G6 macromolecule having a molecular weight of 271,600 amu and 256 terminal groups [1425]. Using the tetrakis(pentafluorophenyl)-cyclopentadienone, as an end capper for the outer shells of these dendrimer, a series of polyphenylene dendrimers possessing pentafluorophenyl moieties has been synthesized [1426].

Core **42a** was reacted with 3,4-bis[4-(triisopropylsilylethynyl)phen-1-yl]-2,5-dipyridin-2-ylcyclopentan-2,4-dienone to start to introduce the pyridinyl-functionality into these rigid poly(phenylene) dendrimers [1427]. Deprotection gave terminal alkyne moieties, which can be reacted with this same dienone to provide the larger generations or may simply be capped with tetra(2-pyridinyl)cyclopentadienones [1428]. The interesting 2,3,4,5-tetraphenyl-4'-bromophenylbenzene has recently been reported [1429] and subsequently transformed into either the related fluorescent poly(phenylenevinylene) or copolymer with 2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene (Scheme 42).

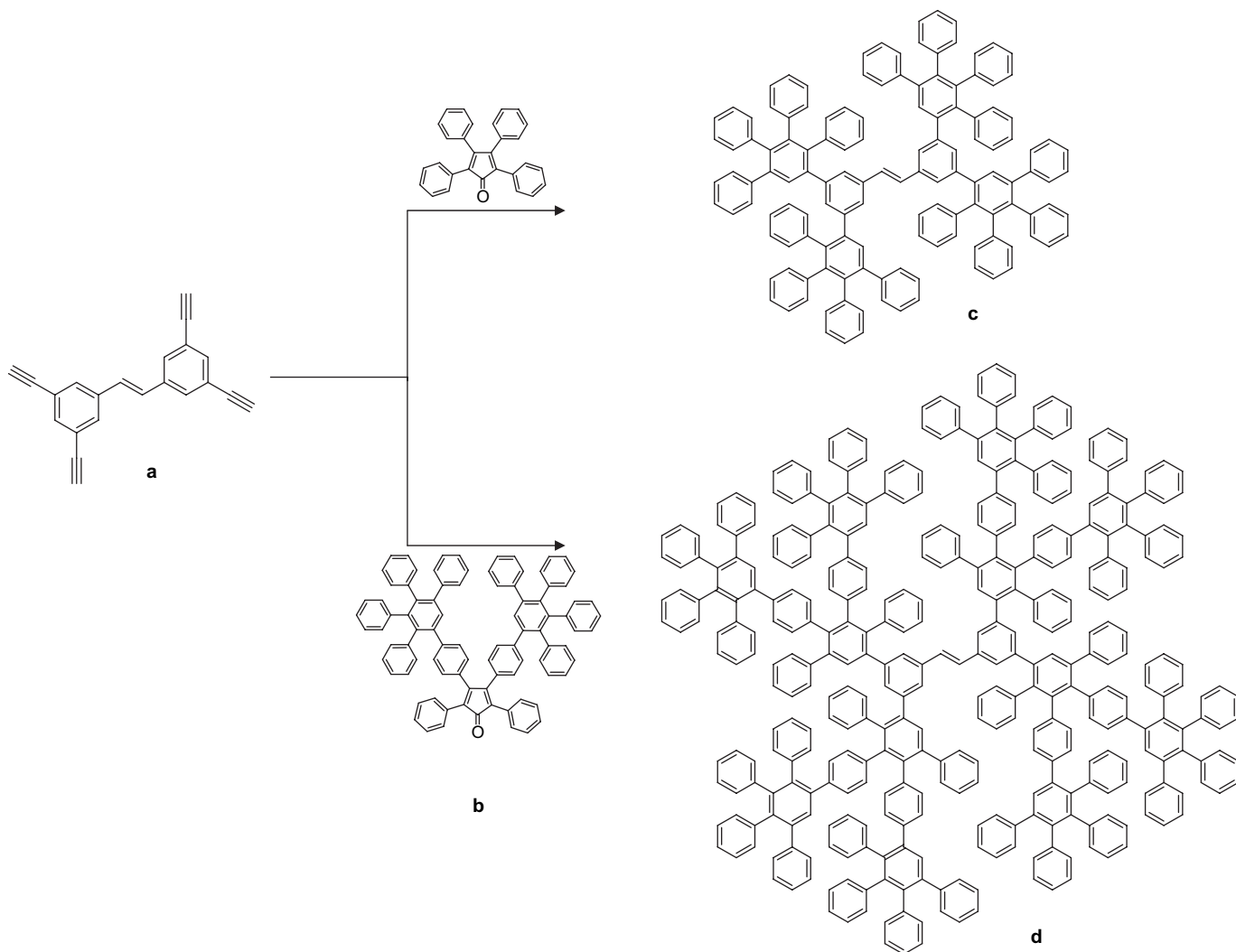
A series of azobenzene-cored polyphenylene dendrimers has been constructed and shown to exhibit a photoresponsive behavior upon UV and visible irradiation, resulting in a reversible change depending on the generation and degree-of-branching [1430]. A SANS study of the G4 dendrimer in this series has shown that all of the termini are located at the periphery of the macromolecule and that only truly stiff chemical structures can realize such an orientation [1431]. The inclusion of a central olefinic center has been constructed, starting from **43a** with tetraphenylcyclopentadiene and **43b**, to give the desired hindered olefin products **43c** and **43d** [1432], which both exhibit fluorescence emissions with considerably higher quantum efficiency and longer fluorescence lifetimes than that of the parent stilbene [1433] (Scheme 43).

Novel, shape-persistent, glycopolyphenylene dendrimers [1434] possessing either the internal or external sugar moieties have been accessed by utilizing the Schmidt glycosylation [1435] as well as Diels–Alder reactions; remarkably, these glyco-dendrimers exhibited water-solubility despite the sugar location.

The photophysical properties and excitation energy transfer process of the G1 polyphenylene dendrimers possessing a rigid



Scheme 42. Preferential synthesis of desymmetrized polyphenylene dendrimer cores [1423].



Scheme 43. Synthesis of a polyphenylene dendrimer possessing a stilbene core [1432,1433].

tetrahedral core and an increasing number of peryleneimide chromophores have been evaluated by steady-state and time-resolved fluorescence spectroscopy; with one chromophore, the dendrimer decays monoexponentially with a time constant of 4.2 ns; whereas with the multichromophoric species, an additional long decay time of 7.4 ns was observed and described as an “excimer-like” state, which increased with the number of chromophores [1436]. If a teryleneimide chromophore [1437] was introduced onto the surface of the dendrimer along with three peryleneimide chromophores, more than 95% of the energy harvested by the peryleneimide chromophores [1438] was transferred and trapped in the teryleneimide [1439]; the energy-transfer processes were rationalized by Förster resonance energy transfer (FRET) theory [1440–1442]. Single-molecule spectroscopy was utilized to investigate energy hopping and transfer in these dendritic systems [1443]. Initially using fluorescence up-conversion [1444] and anisotropic transient adsorption measurements on the G2 of these dendrimers (8 chromophores), a faster decay time of 5 ps was observed [1445]; thus the time-resolved fluorescence up-conversion

study of G3 (Fig. 7) possessing 16 peripheral peryleneimide chromophores showed that the existence of a ground state interaction led to a directly formed complex [1446]. The ensemble and single-molecule dynamics of FRET in multi-chromophoric rigid polyphenylene dendrimers [1442] with spectrally different “rylene” chromophores of distinct adsorption and emission spectra covering the visible spectral range have been studied based on a terylenediimide, as the core, four perylenemonoimides, as the spacer, and eight surface naphthalenemonoimides [1447–1449]. Time dependent spectral properties of the G1,2 dendrimers possessing peryleneimide chromophores at the rim and a terylenediimide core were studied by time resolved polychromatic transition absorption measurements [1414]. A new terylenediimide dye, 1,6,9,14-tetra(4-sulfonylphenoxy)-*N,N'*-(2,6-diisopropylphenyl)terylene-3,4:11,12-tetracarboxydiimide [1450], that is water-soluble and forms H-type nonfluorescent aggregates in an aqueous environment, has appeared; however, upon addition of surfactants, *e.g.*, CTAB, a strongly fluorescent species assigned to a monomeric dye incorporated within the micelle

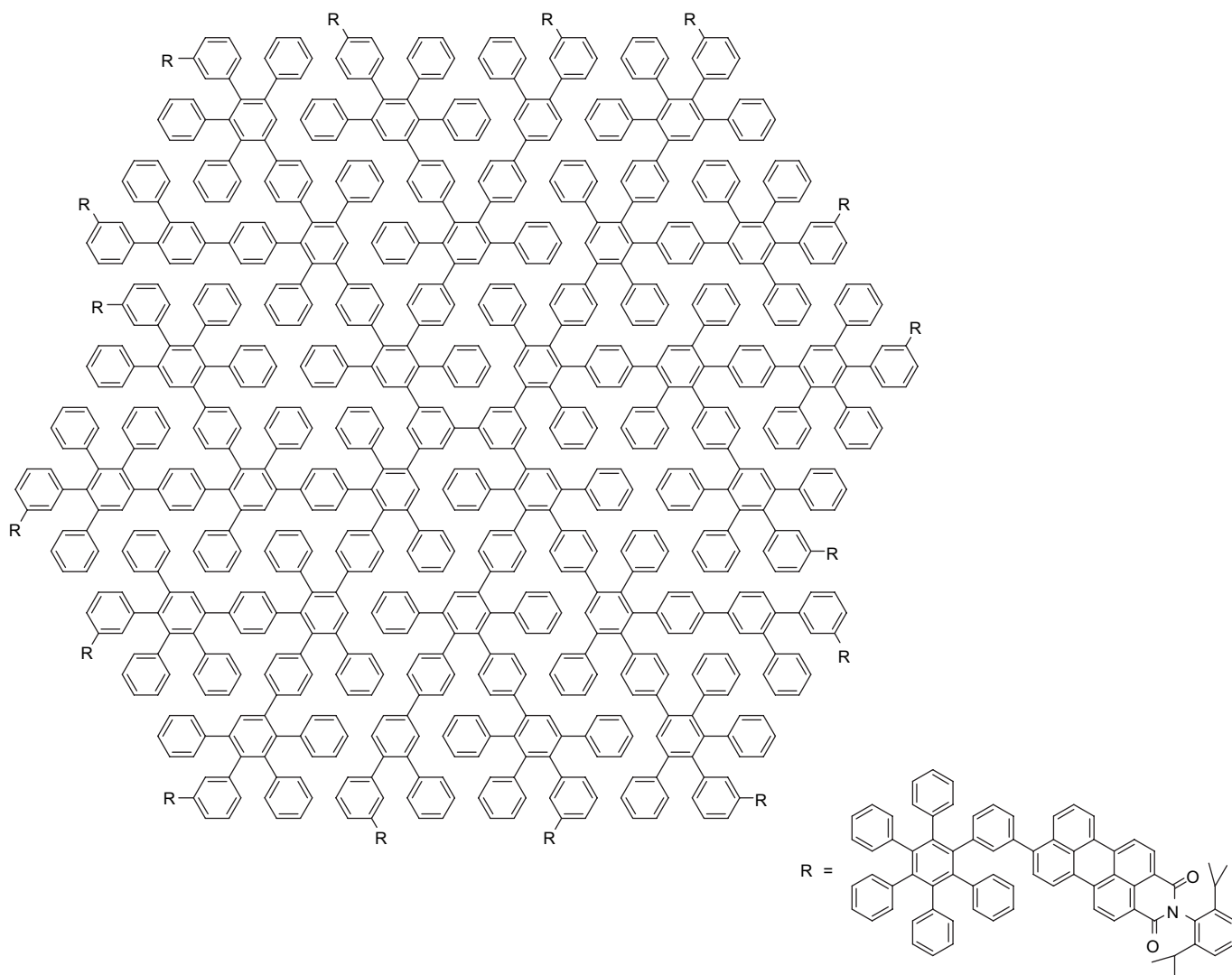


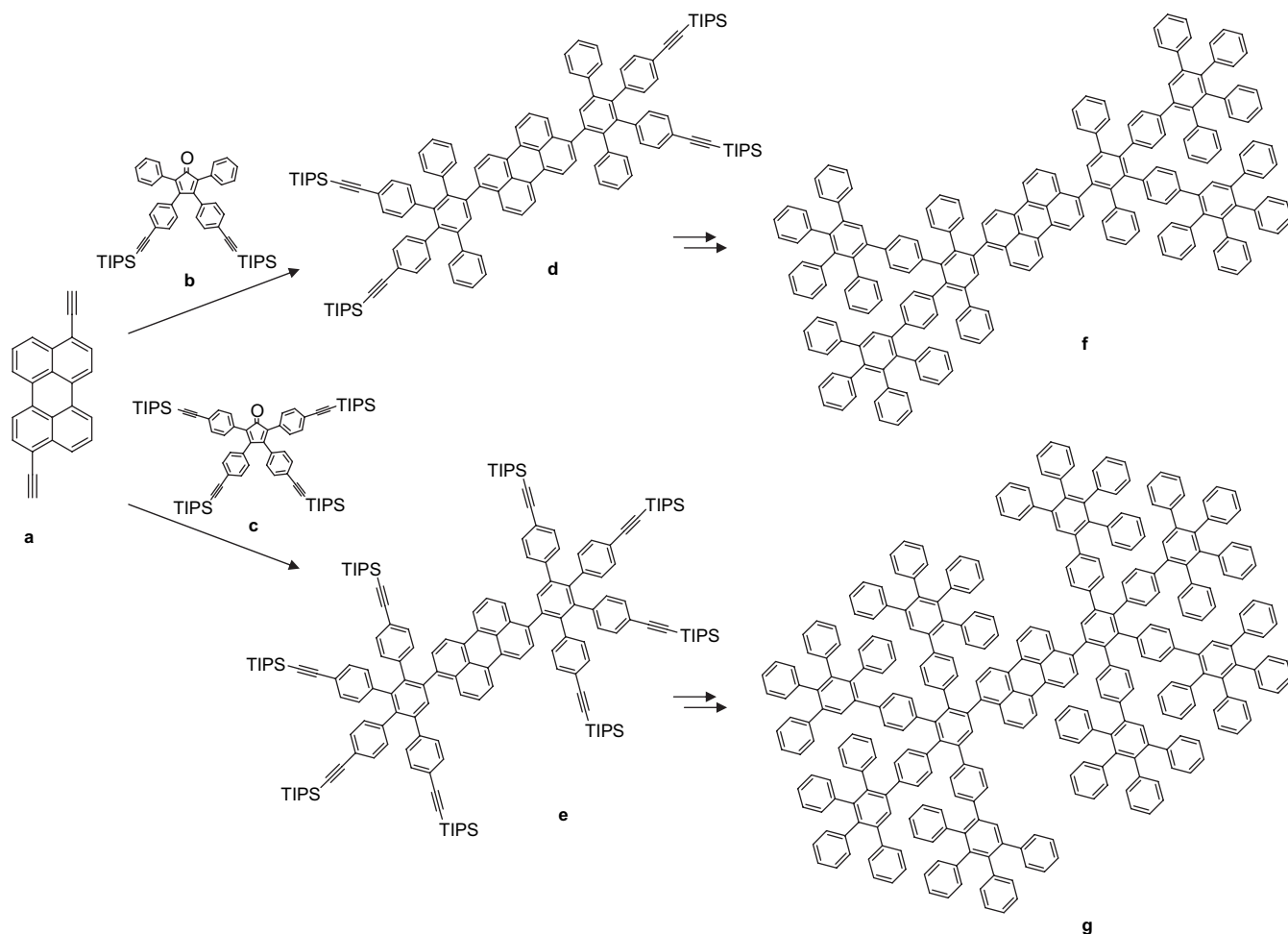
Fig. 7. The G3 polyphenylene core dendrimer with 16 perylene surface chromophores [1446].

appeared [1451]. The availability of *N,N*-di(*n*-butyl)-1,6,7,10-tetrachloroperylene-3,4:9,10-tetracarboxylic acid bisimide [1452] and its easy nucleophilic substitution of the chlorine atoms gives easy access to diverse substituted perylene bisimides [1453].

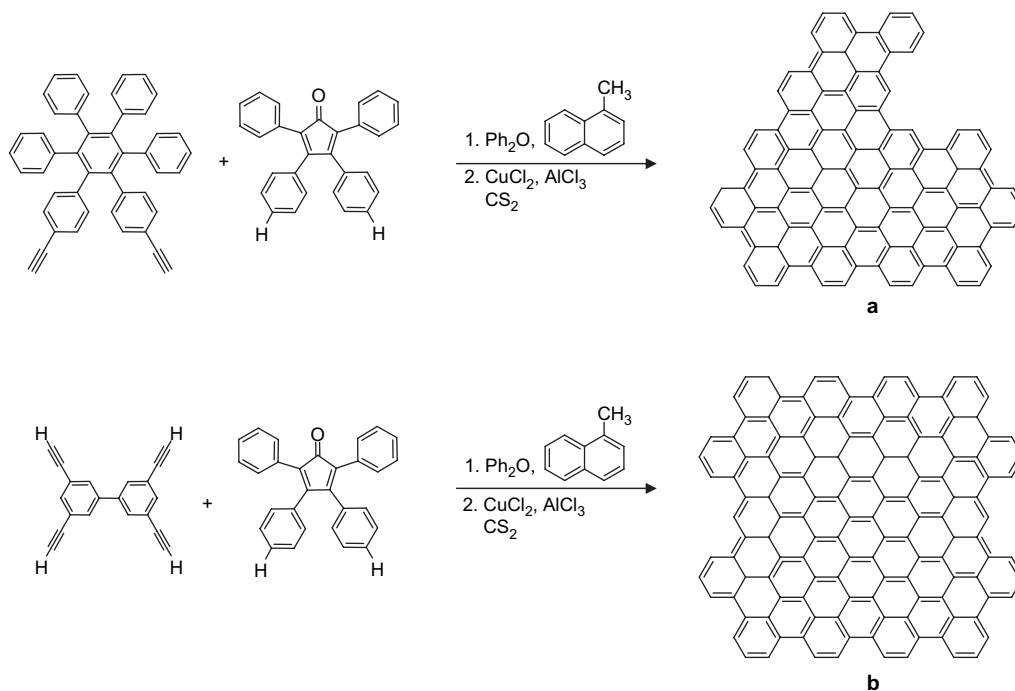
A series of polyphenylene-dendronized perylenes has been synthesized from the 1,7-diethynylperylene core **44a**, which when treated with either 1 → 2 (**44b**) or 1 → 4 (**44c**) branched cyclopentadienone gave **44d** or **44e**, respectively. Deprotection followed by capping with tetraphenylcyclopentadienone gave good yields of the highly substituted perylenes **44f** and G2 dendrimer **44g**, respectively [1454]. These highly functionalized dendronized perylenes possessed enhanced solubility in common organic solvent and were spin-coated to form films (Scheme 44).

The synthesis of the PAHs **45a** and **45b** has been reported by reaction of dienone **40b**, possessing only terminal *H*-moieties, with core units **40a** and **41a**, respectively, followed by cyclodehydrogenation under Kovacic [1455] conditions (Scheme 45). Spectroscopic analysis of these materials was hindered by their poor solubility; however, the M^+ signal of the mass spectrum of **45b** was 56 amu less than that of the precursor Diels–Alder adduct (*i.e.*, 2X 28H atoms were lost during the formation of the 28 new C–C bonds). Müllen et al. [1456] later extended

their work in this area to include construction using the AB₄ monomer, 2,3,4,5-tetrakis(4-triisopropylsilylethynylphenyl)-cyclopenta-2,4-dienone; thus, facilitating a more rapid synthesis of these spherical polyphenylenes. Additionally, their synthetic protocol has been used to prepare organic-soluble C₆₀ polyaromatic hydrocarbons bearing dodecaalkyl chains [1457]. A polyfluorene possessing the bulky dendritic polyphenylene appendages has been prepared and when instilled into a LED; it showed a pure blue emission with onset voltages below 4 V [1458]. The photophysical aspects of these dendronized poly(fluorene)s have been investigated, to date, but no conclusive verdict about the singlet migration in these materials was found [1459]. By variation of the core, stiff and shape-persistent dendritic structures possessing dumbbell-, tetrahedral-, and propeller-like constructs have been prepared [1460,1461]. Highly ordered monolayers of these segments were prepared and subsequently analyzed by STM. Müllen et al. have elegantly generated numerous specifically tailored, large polycyclic aromatic hydrocarbons, for example: “superbenzene” [hexa-*peri*-hexabenzocorene] [1410]; alkylated hexa-*peri*-hexabenzocoronenes [1462–1464]; “supernaphthalene” [1465]; “superbiphenyl” [1466]; elongated “superbenzene” [1467]; molecular propellers (“blades”) [1468,1469]; “star-like” and “butterfly-shaped” dyads [1470]; “graphite ribbons” [1471];



Scheme 44. Formation of polyphenylene-dendronized perylenes [1454].



Scheme 45. Rapid polyaromatic hydrocarbon synthesis.

“superacenes” [1465]; and “nanographene shapes” [1472] have been reported. The diverse real and potential applications of these novel polyaromatic hydrocarbons (graphenes) in electronic devices, batteries and energy storage have been presented [1461,1473–1476]; even their monomeric precursors are of interest as synthetic precursors [1477–1479], dyes for biolabeling [1480], and energy transfer [1481].

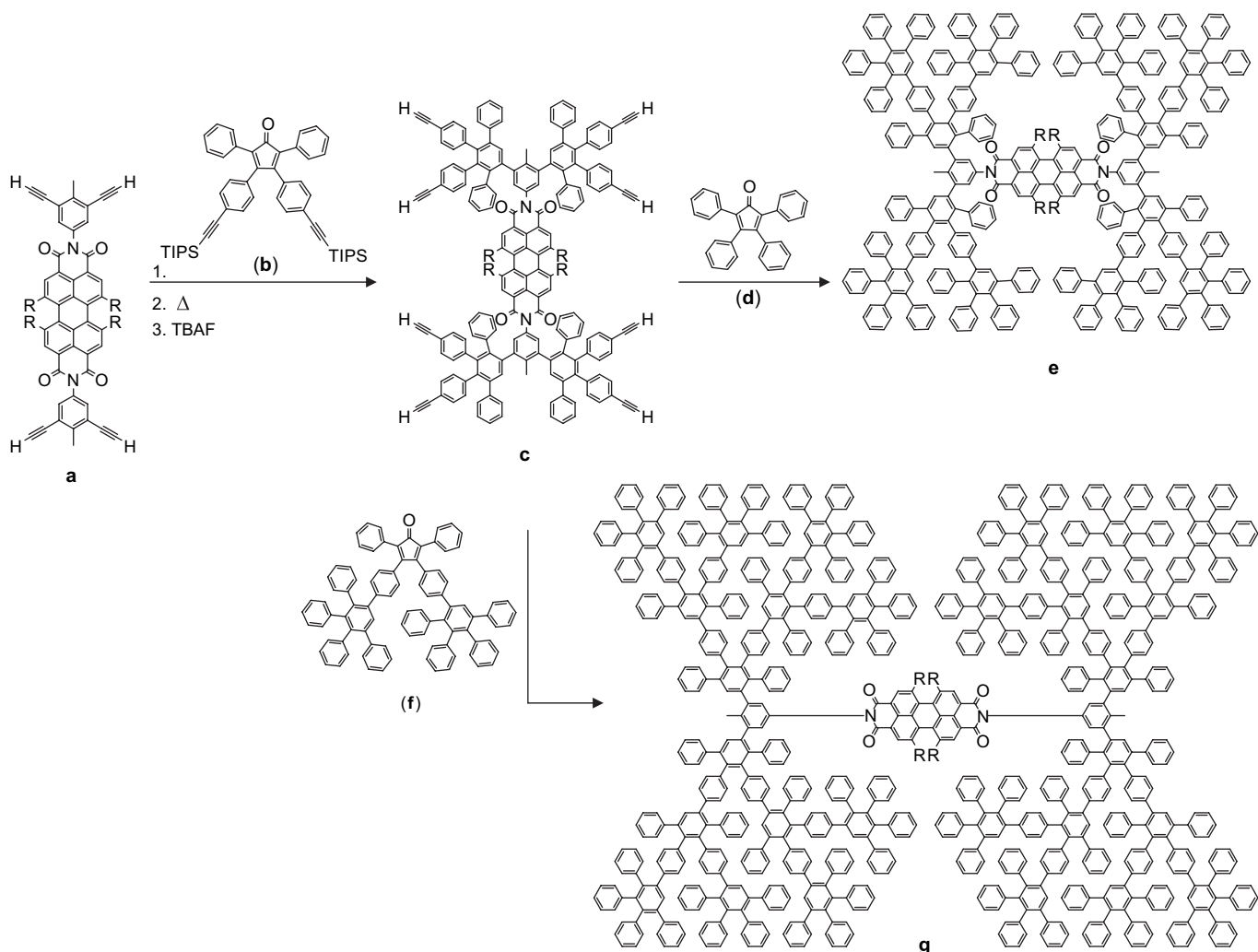
A novel approach to extremely large polycyclic aromatic hydrocarbons [1482] has been realized by the simple cyclodehydrogenation of selected polyphenylene dendrimers, which were controlled by varying the cyclopentadienones used in the last growth step. These large oligophenylenes, possessing either benzene or tetraphenylmethane cores, were shown to undergo oxidative cyclodehydrogenation to give structurally novel propeller-shaped species [1468], which are themselves precursors to different large polycyclic aromatic hydrocarbons. The synthesis of core–shell nanoparticles with the shape-persistent polyphenylene dendrimers as the core with different surface polymers, such as polyethylene oxide, polystyrene or polyisoprene, giving rise to mono- or double-shells have been devised; hydrodynamic radii of these particles were ascertained by dynamic light scattering to be in the range of 5–20 nm [1483]. The fourfold ethynyl-substituted chromophore, 1,3,6,8-tetraethynylpyrene, has been incorporated into the these polyphenylene dendrimers *via* both divergent and convergent procedures [1484]. Another interesting core was that of bis(3,5-diethynylphenyl)ketone (a tetraalkynylbenzophenone), which opened the door to spatially well-ordered spherical nanoparticles possessing single isolated, central internal functional groups [1485].

The G1–3, shape-persistent polyphenylene dendrimers, possessing terminal methyl groups as probes, have been

investigated using high resolution, solid-state NMR with rapid magic angle spinning [1486]. These dendrimers do not follow the de Gennes and Harvet dense packing model but their NMR data supported the presence of structural shape-persistence.

The incorporation of a fourfold ethynyl-substituted perylene-diimide core permitted the construction of G1–3 polyphenylene dendrimers possessing a luminescent core [1487]. Therefore, treatment of the core **46a** with reagent **46b** followed by deprotection with *n*Bu₄NF (THF, 25 °C, 87%) gave **46c**, which with either **46d** afforded (85%) the G2 dendrimer **46e**, or with **46f** gave rise to (58%) the very dense G3 **46g** (Scheme 46). Derivatives of perylene-3,4,9,10-tetracarboxydiimide dyes functionalized with G > 2 polyphenylene and substituted with triphenylamine moieties were moreover reported [1488]. A series of processable perylene-3,4,9,10-tetracarboxydiimides, substituted with polyphenylene dendrons with external alkyl chains, was constructed in order to evaluate their optical and electronic properties [1489]; these new materials with the G1 and G2 dendrons showed good solubility and film-forming properties as well as displayed strong red-orange photoluminescence with reduced chromophore interactions indicative of the dendronized exterior shielding of the emissive core. Introduction of peptide surfaces followed the simple modification of their procedures [1490]; the self-assembly and molecular dynamics of these poly-L-lysine-functionalized polyphenylene dendrimers were studied in detail by means of X-ray data, NMR, calorimetry, and dielectric spectroscopy [1491].

A polyphenylene dendrimer possessing three perylenemoinide dyes as well as a biotin moiety was shown to be highly hydrophobic; however with added detergent, it formed a dendrimer–detergent complex that was soluble in aqueous media [1492].



Scheme 46. Synthesis of the hindered polyphenylene dendrimers on the perylene-3,4,9,10-tetracarboxylic diimide core [1487].

Two generations of the dendritic dyad consisting of the extended core terrylenetetracarboxydiimide (TDI) [1437] possessing a stiff polyphenylene scaffold, and a peryleneimide exterior were created [1493]. The TDI **47a** was functionalized by initial bromination, followed by treatment with 4-iodophenol with base, then triisopropylsilylacetylene under Sonogashira conditions and lastly, deprotected with tetrabutylammonium fluoride to give the desired tetraalkyne **47b**. Treatment of this alkyne **47b** with different tetraphenylcyclopentadienone monomers (e.g., **47c**) afforded the desired extended constructs, such as **47d** (Scheme 47).

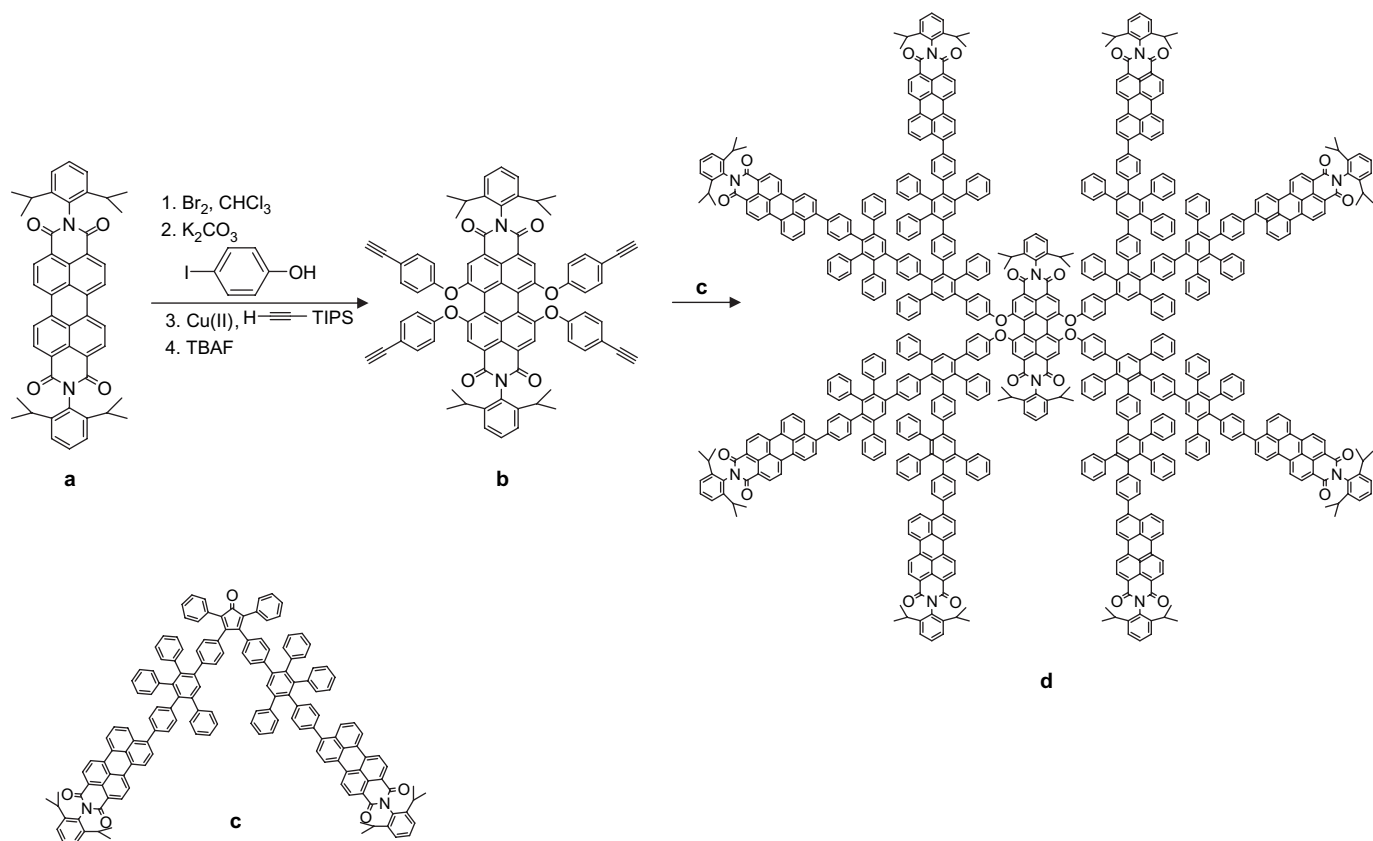
The coating of a tetraphenylmethane core with an outer layer of terthiophene has been accomplished to produce a stiff as well as shape-persistent “hedgehog-like” core–shell material **48c**, which was derived by the high-temperature reaction of the core **48a** with **48b** (Scheme 48).

In general, postfunctionalization after the infrastructure had been assembled was difficult, but recently, Müllen et al. [1494] put forth a synthetic route to the incorporation of a defined number of benzophenone as well as ketal derivatives. Reactions of these ketonic moieties with organolithium reagents

afforded monodisperse alcoholic products, which were suitable precursors for the generation of trityl cations and radicals as well as the ketyl radical anions [1485]. The introduction of internal methoxycarbonyl groups has been accomplished then their conversion to the free acid moieties permitted entry to novel host–guest chemistry within these rigid species [1495].

A poly(*p*-phenylenevinylene) core with pentaphenylene dendrons has been synthesized from 1,4-dibromomethyl-2,5-bis{3,4-bis[4-(2-ethylhexyloxy)phenyl]-2,5-diphenylphenyl}-benzene, derived from the 3,4-bis[4-(2-ethylhexyloxy)phenyl]-2,5-diphenylcyclopentadienone and 1,4-diethynyl-2,5-dimethylbenzene, followed by NBS bromination [1496].

Suzuki et al. [1497] reported the synthesis of perfluorinated polyphenylene dendrimers using ArCu-promoted cross-coupling with aryl bromides. A G3 dendrimer was created along with smaller, less branched materials. These constructs, due to their electron-transport properties, were prepared in order to examine their potential as field-effect transistors and OLED materials. In general, perfluorinated non-dendritic phenylenes gave more amorphous films and showed better electron-transport capabilities than their related dendritic counterparts.



Scheme 47. Synthesis of a multiphoric dendritic architecture [1493].

Assemblies of L-lysine/carboxylic acid functionalized polyphenylene dendrimers and hybrid multilayers of L-lysine dendrimers and colloidal gold nanocrystals were created by alternating multilayers on a gold surface coated with 3-mercaptopropionic acid [1498]. The permeability properties of these dendritic polyelectrolyte layers were electrochemically characterized in the presence of [Fe(CN)₆]^{3-/4-}, as the redox couple.

4.4. 1 → 2 Aryl-branched, ether-connectivity

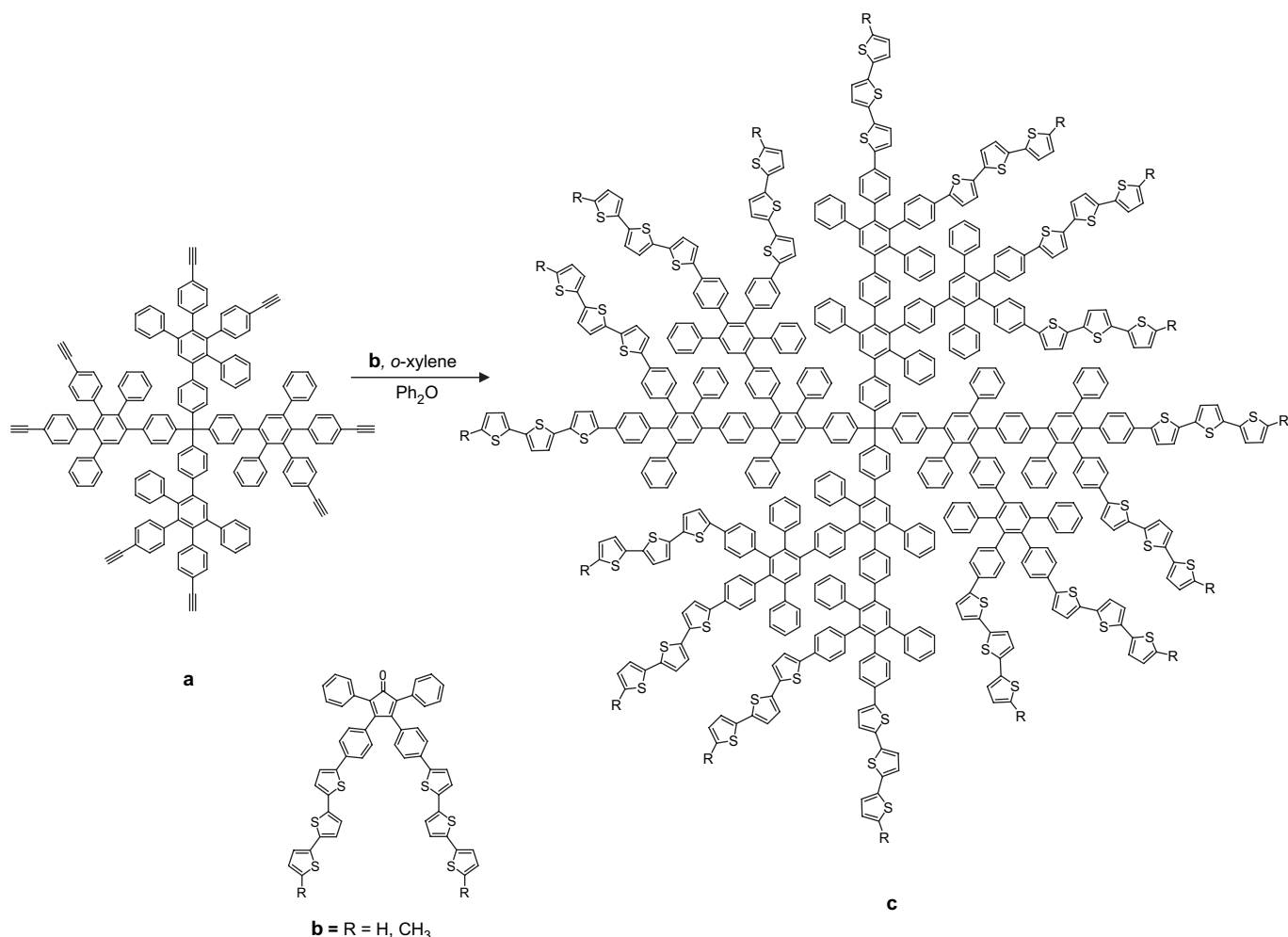
The G1,2 poly(aryl ether) dendrons have been divergently incorporated onto a calix[4]resorcinarene (**49a**) core by initial treatment (K₂CO₃, 18-crown-6) with 3,5-bis(allyloxy)benzyl bromide **49b** to give the G1 polyether **49c** [1499]. Subsequent deallylation [(Ph₃P)₂PdCl₂, HCO₂NH₄] gave rise to the poly(phenoxy) intermediate **49d** that was next reacted with bromide **49b** to give (52%) the desired G2 construct **49e** (Scheme 49). Due to the core's numerous hydroxyl groups, *M_w*s of 7171 and 9345 amu were realized for the G1 and G2 constructs, respectively. Employing the related calix[4]resorcinarene core [1500], a G1 poly(aryl ether) motif was designed to function as a negative-working, alkaline-developable photoresist, which upon UV irradiation exhibited an unmistakable negative pattern following post-baking (110 °C), and subsequent treatment with aqueous Me₄NOH (0.3%, 25 °C).

Functionalization of a Wang polystyrene support with 1 → 2 aryl branched dendrons was shown (see Section 4.1) in

which the surface CH₂Br moieties were treated with dimethyl 5-hydroxyisophthalate followed by LiBH₄ reduction to generate the G1 hydroxy surface. The Mitsunobu coupling and an ester reduction sequence were shown to give rise to the G2 and G3 dendrons [1386,1501].

4.5. 1 → 2 Aryl-branched, thioether-connectivity

A series of G1–4 poly(phenylene sulfide)s has been prepared [1502] from the 1,3,5-tris(4-chlorophenylthio)benzene core (**50c**), prepared in 70% from 1,3,5-tribromobenzene and the sodium salt of 4-chlorothiophenol in DMAc at 150 °C, and using the 1,3,5-trichlorobenzene (**50d**), as the monomer building block. Treatment of the core **50c** with **50d** with lithium sulfide and *N*-methylpyrrolidone at 180 °C gave (65%) the key intermediate to the G1 dendrimer, which was converted (85%) to the G1 dendrimer **50f** by reaction with sodium 4-chlorothiophenoxide in DMAc at 150 °C; the subsequent generations (G2–4) were prepared in a similar manner and in remarkably high yields (60–80%) [1502]. The G1 and G2 dendrons in the series were also reported starting from 3,5-dichlorobenzoic acid, which were transformed to the 3,5-dithiolbenzoic acid (**51b**). Ensuing treatment of **51b** with 3,5-dichlorobromobenzene (**51c**) in the presence of NaOH in DMAc at 140 °C gave the G1 dendron **51d**. The two-step procedure was repeated to form the G2 dendron **51e** in 90 yield; further oxidation with H₂O₂ generated **51f** [1502]. These G1 (**50d**) and G2 (**50e**) dendrimers were



Scheme 48. The synthesis of a novel dendritic “hedgehog.”

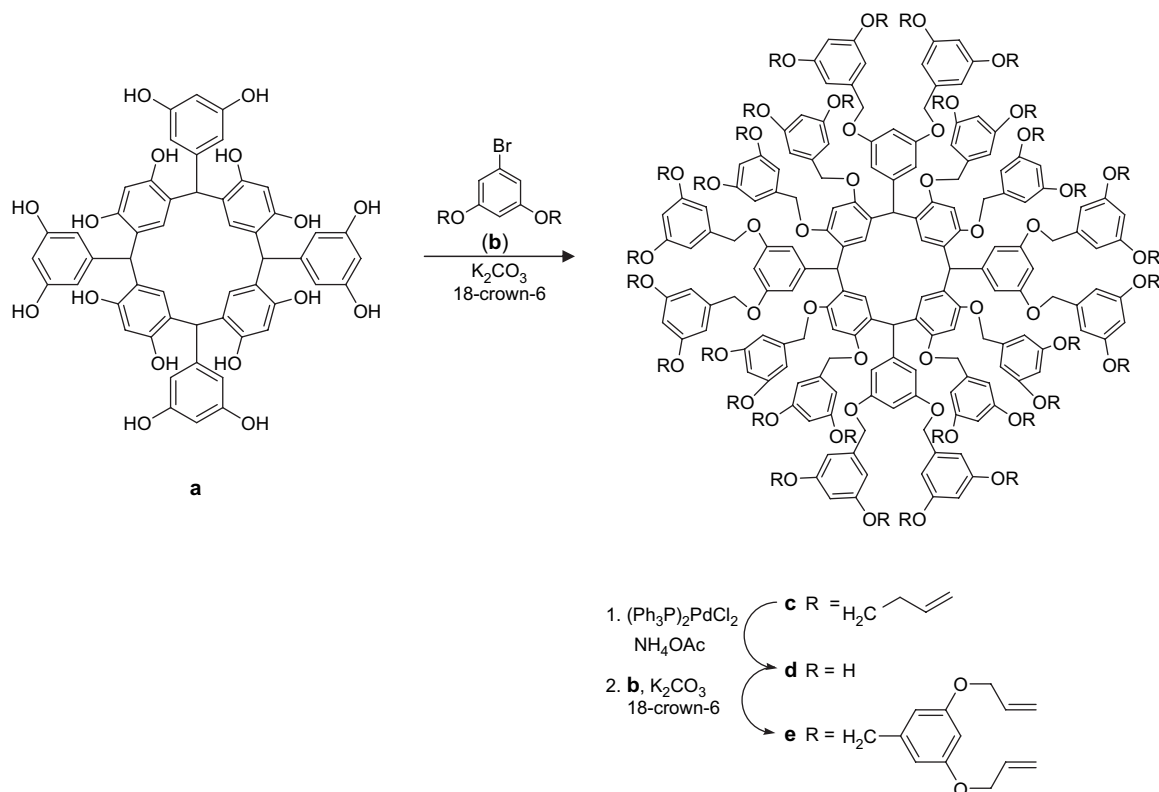
subsequently terminated with immobilized lipase derived from *Burholderia cepacia* using CDI as the coupling agent, then their hydrolysis activity was evaluated by the conversion of olive oil to the corresponding fatty acid. This immobilized enzyme was shown to be a biocatalyst for batch hydrolyses of olive oil retaining 80–90% activity even after 20 cycles [1503] (Schemes 50 and 51).

4.6. 1 → 2 Aryl-branched, amide-connectivity

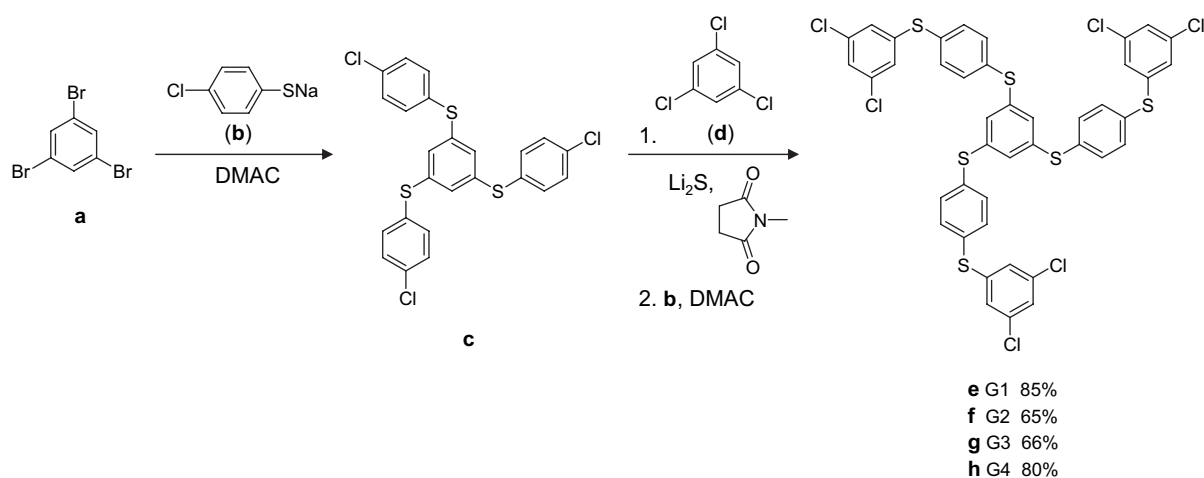
Vögtle et al. [1504–1507] devised a simple route to a series of small dendrimers employing the *N*-tosylate of dimethyl 5-aminoisophthalate (**52b**), which with 1,3,5-tris(bromomethyl)benzene [1508] (**52a**), as the core, gave (81%) the hexaester **52c** ($X = \text{CO}_2\text{CH}_3$). Reduction (49%, LAH/THF) of **52c** and subsequent bromination (55%, $\text{PBr}_3/\text{HCCl}_3$) formed the hexakis(bromomethyl) derivative **52e**, which, in turn, was treated with 6 equiv. of monomer **52b** to afford (43%) the dodecaester **52f**. The three-step divergent reaction sequence was repeated, ultimately achieving (33%) three generations, e.g., **52i**. An X-ray structure (Fig. 8) of hexaester **15c** afforded insight into the congestion imparted by its infrastructure. The structural

homogeneity, associated with further tier construction beyond the G3 **52i**, is problematic due to steric requirements associated with the bulky monomer **52b** and the diminished surface spatial availability (Scheme 52). In order to surface-attach azo-moieties, the hexakisbromo intermediate was treated (40%, $\text{K}_2\text{CO}_3/\text{DMF}$) with 3-(tosylamino)azobenzene to give the hexaazo product; irradiation of the all-*E* isomer at 313 nm for 5 min gave the photostationary equilibrium that is largely the *Z*-form. An overview of polyamide and polyimide dendrimers has appeared and considers the divergent as well as the more favored convergent routes to their preparation [1509].

Branched aryl imides comprised of tetrahydro[5]helicene units were prepared by Wang et al. [1510] The initial necessary monomer **53a** was synthesized by the nitration of anhydride **53b**, followed by treatment with 2-aminoethanol and subsequent reduction of the nitro moiety. This monomer was reacted (*m*-cresol, 200 °C) with anhydride **53b** to generate dendron **53c**. Treatment of monomer **53a** with the corresponding dinitro anhydride **53d**, followed by reduction (Fe, HCl) generated tetraamine **53e**, which was subsequently terminated with **53b** to form dendron **53f**. Linear analogs (up to 10 units)



Scheme 49. Coated calix[4]resorcinarenes [1499].



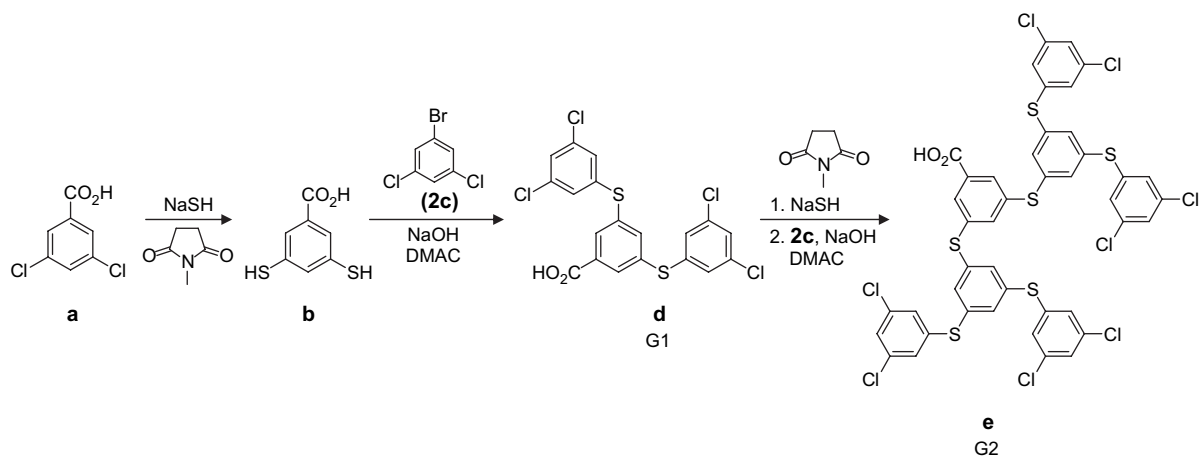
Scheme 50. The divergent synthesis of poly(phenylene sulfide) dendrimers [1502].

were reported. All of these materials exhibited reversible redox behavior as well as generation-dependent fluorescent emission (Scheme 53).

The use of a silica particle, as the core for dendrimer growth, has been shown to give access to recyclable catalysts. The use of branched monomers, *e.g.*, **54a** [1511], gave access to G1–3 dendritic beads whose surface can be readily transformed to the bis-*P*-ligand exterior **54b** upon treatment of the $-\text{NH}_2$ surface with H_2CO and HPPH_2 via the *in situ* generation of $\text{HOH}_2\text{CPPH}_2$ (Scheme 54). Introduction of a catalytic surface locus was accomplished by the addition of $[\text{Ru}(\text{CO})_2\text{Cl}]_2$ giving rise to the metal-coated particle that

was successfully employed in hydroformylation reactions [1511,1512].

Treatment of core **55a**, derived in two steps from 1,3,5-tribromobenzene followed by hydrolysis, with 3 equiv. of the aryl monomer **55b** gave the protected G1 dendrimer **55c** that was readily deprotected (98%) with trifluoroacetic acid [1513] (Scheme 55). The next generation could be formed by repetition of this simple sequence. The incorporation of chirality was further accomplished by addition of protected amino acids or dansylation was possible by treatment of these terminal amines with dansyl chloride in the presence of Et_3N at ambient temperature. A series of bifunctional surface groups was also created [1514].



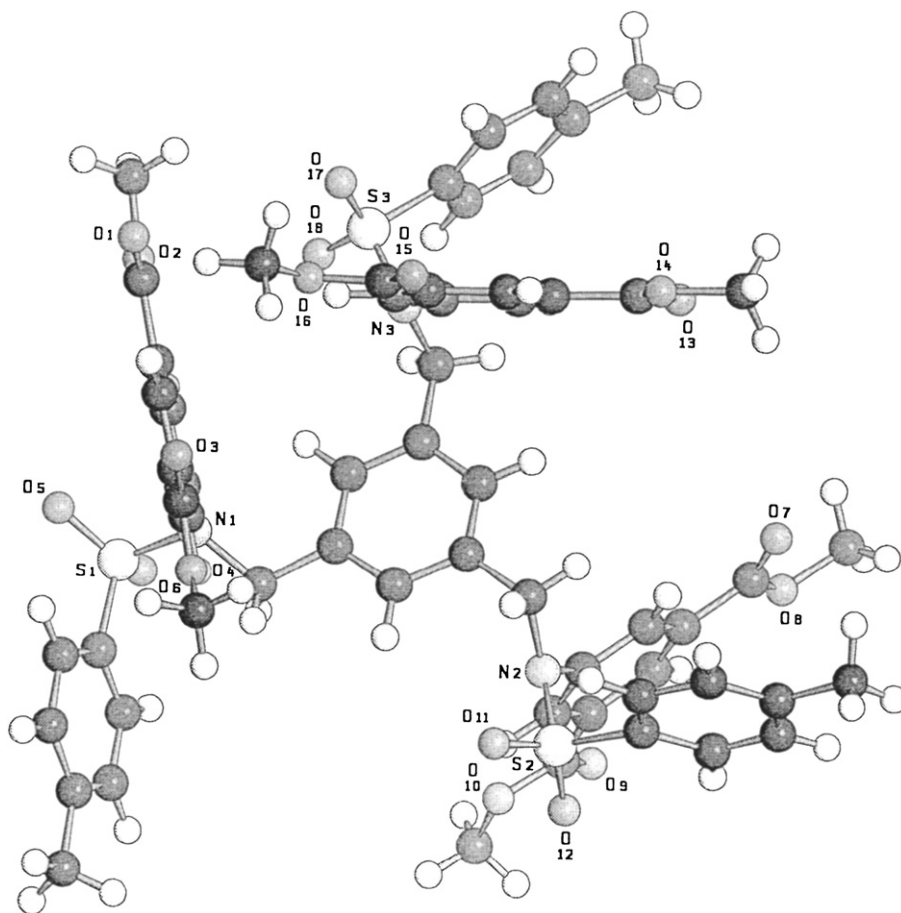
Scheme 51. Dendron formation [1502].

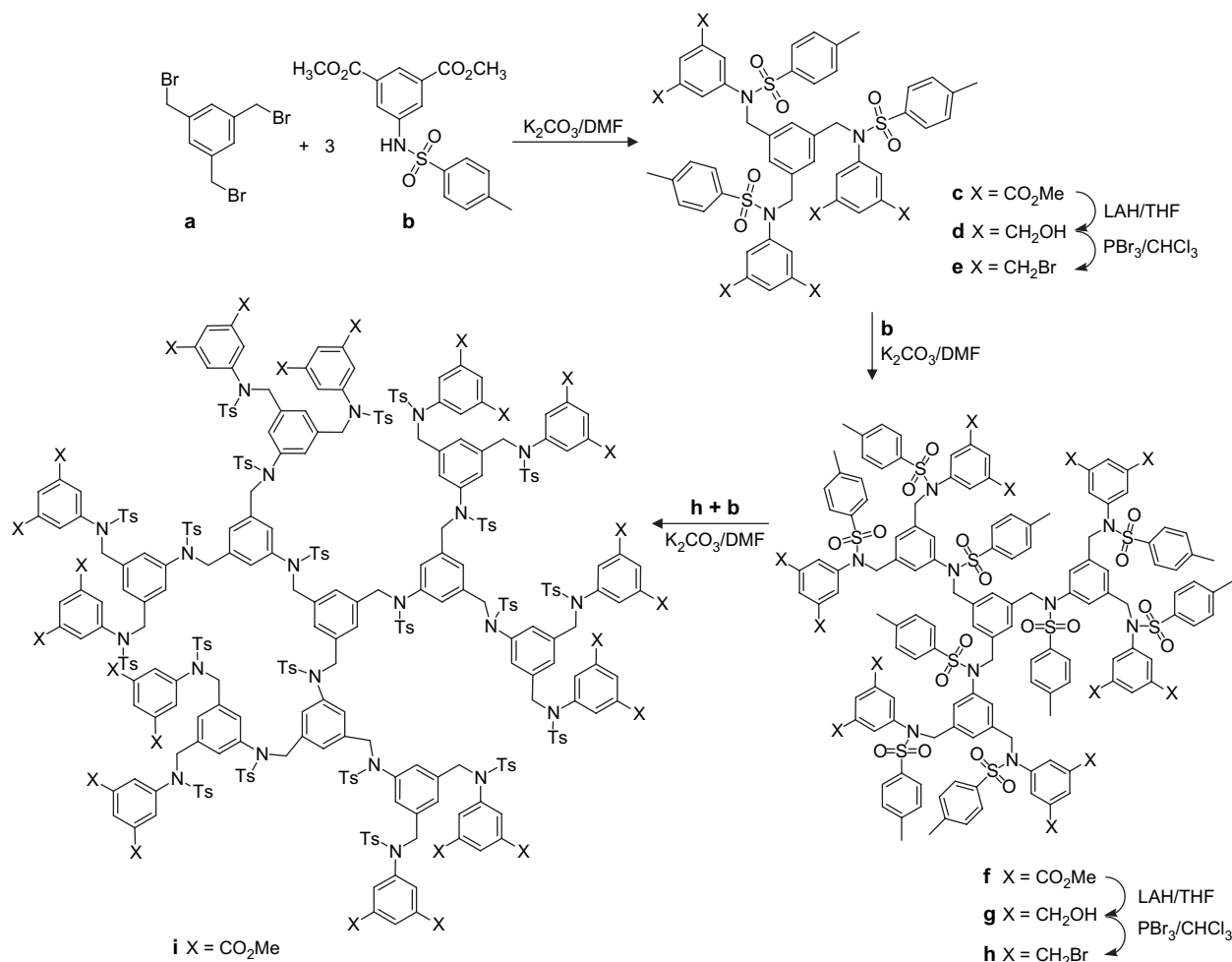
The computer-aided simulations of these dendrimers afforded the desired structure–activity relationships derived from their observed (non)cytotoxicity with molecular features such as the radius-of-gyration, molecular shape, and structural dimensions [1515].

Activation of silica with 3-(aminopropyl)triethoxysilane gave an aminated silica gel (now commercially available) that was initially treated with 1,3,5-tris(chlorocarbonyl)benzene in the presence of DMAP, followed by (1*R*,2*R*)-(+)-

1,2-diphenylethylenediamine [1516]. The resultant terminal amines can be capped with phenylisocyanate or subjected to another equivalent of the tris(chlorocarbonyl)benzene, followed by the above diamine to build the next tier. Although this example is based on a chiral reagent, the use of achiral diamines is quite feasible. The enantio-separation using these chiral stationary phases was evaluated by HPLC.

An attractive alternative to generate aryl dendrimers was from 3,5-diaminobenzoic acid, which was converted to the

Fig. 8. X-ray structure of the G1 tris-*N*-tosylated dendrimer **52c** [1507].



Scheme 52. Synthesis of dendrimer **52i** using the *N*-tosylated aminoisophthalate diester monomer [1504–1507].

desired reactive, crystalline monomer, 3,5-bis(trifluoroacetyl-amido)benzoyl chloride [1517]. This aryl halide readily reacted with aryl amines, *e.g.*, 1,4-diaminobenzene, in NMP at 0 °C for 5 min, then 1 h at 25 °C. Deprotection of the trifluoroacetyl groups was readily accomplished by treatment with excess hydrazine at 50 °C for 2 h. The dendritic family was readily prepared in high overall yields by this simple iterative sequence: G2 (94%), G3 (95%), and G4 (95%). Use of the related monomer, 3,5-dinitrobenzoyl chloride, with 4,7,10-trioxa-1,13-diaminotridecane gave the simple two-directional G1 dendrimer, which on catalytic hydrogenation gave the tetraamine [1518]; the amidation of 3,5-dinitrobenzoyl chloride with 3,5-diaminobenzoic acid gave the G2 dendron, which upon treatment with thionyl chloride gave rise to the desired monomer necessary to create the two-directional G2 dendrimer possessing a PEGed core.

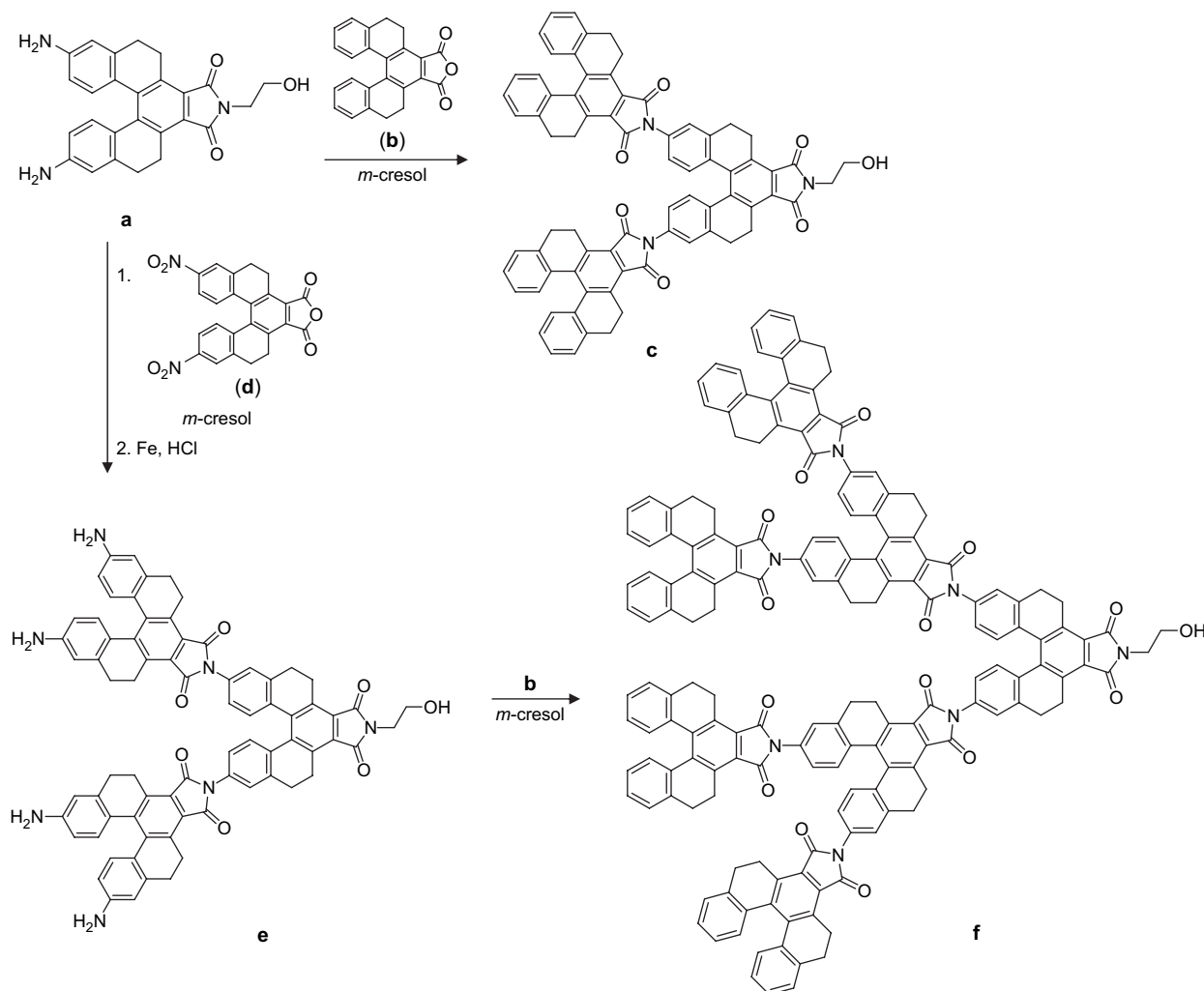
Functionalization of a Wang polystyrene support with 1 → 2 aryl branched dendrons was shown above in 4.5 in which the surface CH₂Br moieties were treated with dimethyl 5-hydroxyisophthalate, followed by LiBH₄ reduction to generate the G1 hydroxy surface. Conversion *via* rearrangement [1519] of the dimethylcarbamoyl derivative derived from dimethyl 5-hydroxyisophthalate gave the 5-thiol derivative, thus permitting

direct entrance to thioetheral derivatives. The nucleophilic substitution of the benzyl halide with the thiophenolate, followed by reduction, and chlorohydroxylation, permitted the creation of the G1–G3 dendron series [1386].

4.7. 1 → 2 Aryl-branched, ester-connectivity

Haddleton et al. [1520] reported a divergent route that utilized either phloroglucinol (1,3,5-trihydroxybenzene) or hydroquinone (**56a**), as the core, and the benzyl protected 3,5-dihydroxybenzoic acid (**56b**), as the building block. Thus, treatment (DCC) of diol **56a** with 2 equiv. of acid **56b** gave the bis-ester **56c**, which was deprotected to liberate the tetrahydroxy diester **56d**. Repetition of the esterification afforded hexaester **56e**; ultimately, three tiers were constructed and characterized by MALDI MS studies, which showed no evidence for dimer or trimer formation either during the synthesis or within the mass spectrum.

Taylor et al. [1521] constructed a series of dendrimers based on naphthalene-2,6-diol, as the core (Fig. 9a). For the phloroglucinol-based dendrimer (Fig. 9b) derived from a 3-directional core, the dense-packed de Gennes limit [1522] occurred between G3 and 4; while for the 2-directional cored



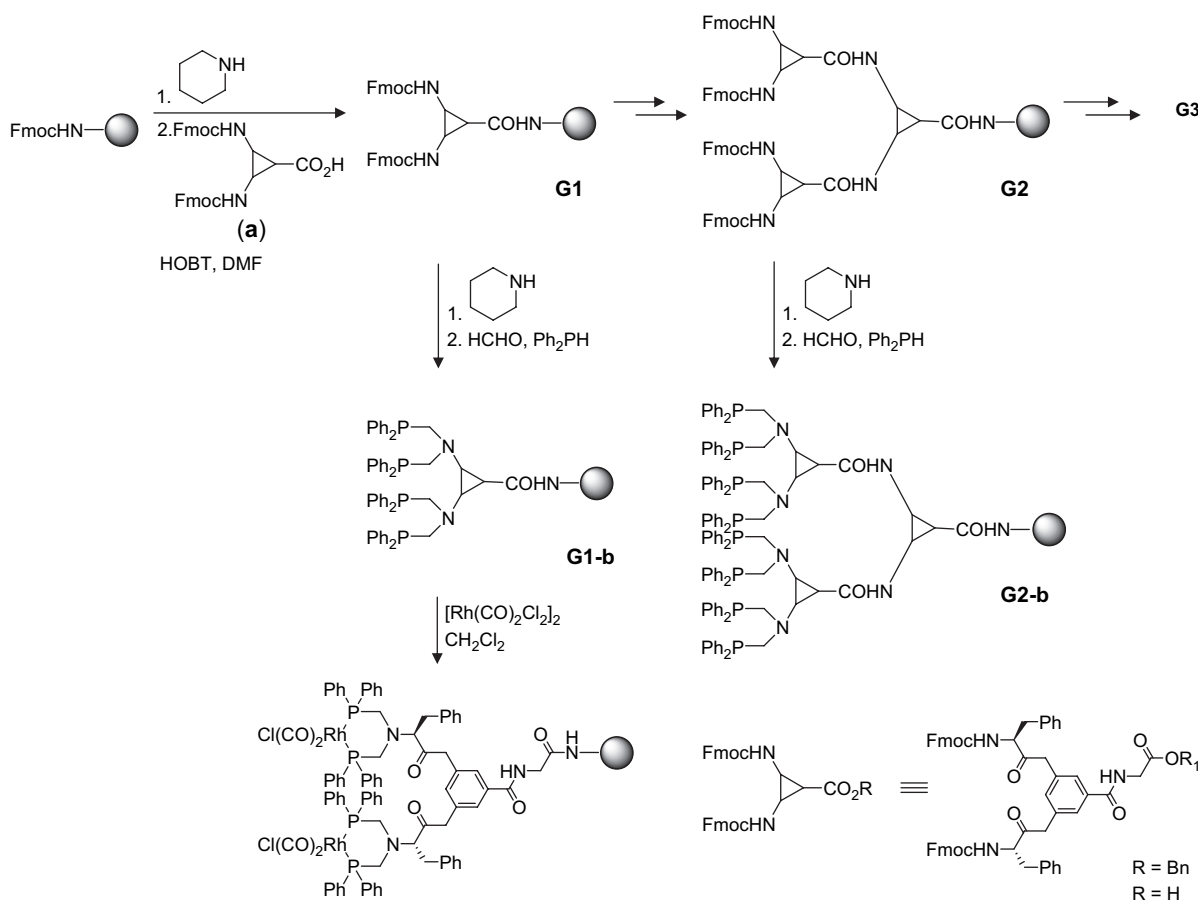
Scheme 53. Helicene-based dendrimers [1510].

dendrimers (including the hydroquinone-based dendrimer as shown in Scheme 56), the limit was extended to between G4 and 5 due to a slightly diminished congestion. It was observed that comparable coupling procedures were more useful during different stages of dendrimer construction; notably, acid halide coupling of building blocks afforded improved yields during higher generation steps, while DCC-based coupling gave superior results at the lower generations.

Shi and Rånby [1523–1525] prepared the polyester dendrimers, beginning with the esterification (SnCl_2 promotion) of pentaerythritol with 1,2,4-benzenetricarboxylic anhydride, followed by treatment with glycidyl methacrylate in the presence of benzyl dimethylamine and hydroquinone, as a radical inhibitor, to give octakis(hydroxymethacrylate)-terminated dendrimers. Reaction of the hydroxyl groups with methacrylic anhydride afforded the corresponding *ca.* 12 (incomplete reaction) and 16 alkene-terminated dendrimers. The T_{gs} of the UV-cured films of these materials were found to increase with increasing terminal functionality [1524]. With 3% benzyl dimethyl ketal, as a photofragmenting initiator, the UV polymerization occurred rapidly (75% conversion after 0.15 s); however, a 10–40 wt% addition of the multifunctional

monomer trimethylolpropane triacrylate did not enhance the curing efficiency, which is in contrast to the effect seen with conventional linear acrylate-based oligomers [1523]. Mixtures of these polymethacrylate dendrimers, TMPTA, and BDF were coated over Mylar-surfaced, glass fiber mats and subjected to UV radiation to produce polyester composites envisioned to potentially replace metals in industry [1525]. Liquid crystalline fulleropyrrolidines, based on poly(aryl ester)s, are also known [1526].

Conversion of L-DOPA to the desired protected building block **57a** was accomplished *via* a simple four-step sequence [1527]. Its transformation to the branching monomer **57b** as well as the structurally related core **57c** has been accomplished in 58% and 73%, respectively, each in two steps. Treatment of monomer **57b** with core **57c** formed (76%) the deprotected intermediate, which was debenzylated to provide the *N*-protected G1 dendrimer **57d**. Hydrolysis of the *N*-BOC protecting groups generated the free G1 L-DOPA dendrimer **57e**; whereas the related G2 and G3 dendrimers were prepared from the *N*-protected polyphenolic intermediates in very good overall yields. These L-DOPA dendrimers are more soluble in water than the parent L-DOPA, more photostable, and hydrolysis



Scheme 54. A divergent route to solid phase heterogeneous catalysts for hydroformylation [1511,1512].

led to a sequential degradation mechanism for these prodrugs (Scheme 57).

4.8. 1 → 2 Aryl-branched, sulfone-connectivity

Treatment of 1,3,5-trichlorobenzene (**58b**) with thiolate **58a** at 80 °C generated the initial core **58c** in 56% yield. Its quantitative oxidation gave sulfone **58d** that was accomplished by the *in situ* generation of peracetic acid. Subjecting **58d** with thiolate **58a** gave very low yields (6%) of the desired octachloride **58e** along with several mono-, di-, and tri-substituted byproducts. Subsequent oxidation of **58e** afforded a high conversion of the pentasulfone **58f** [1528]. Attempted preparation of the G2 oligo(aryl sulfone) was unsuccessful due to single electron transfer processes (Scheme 58).

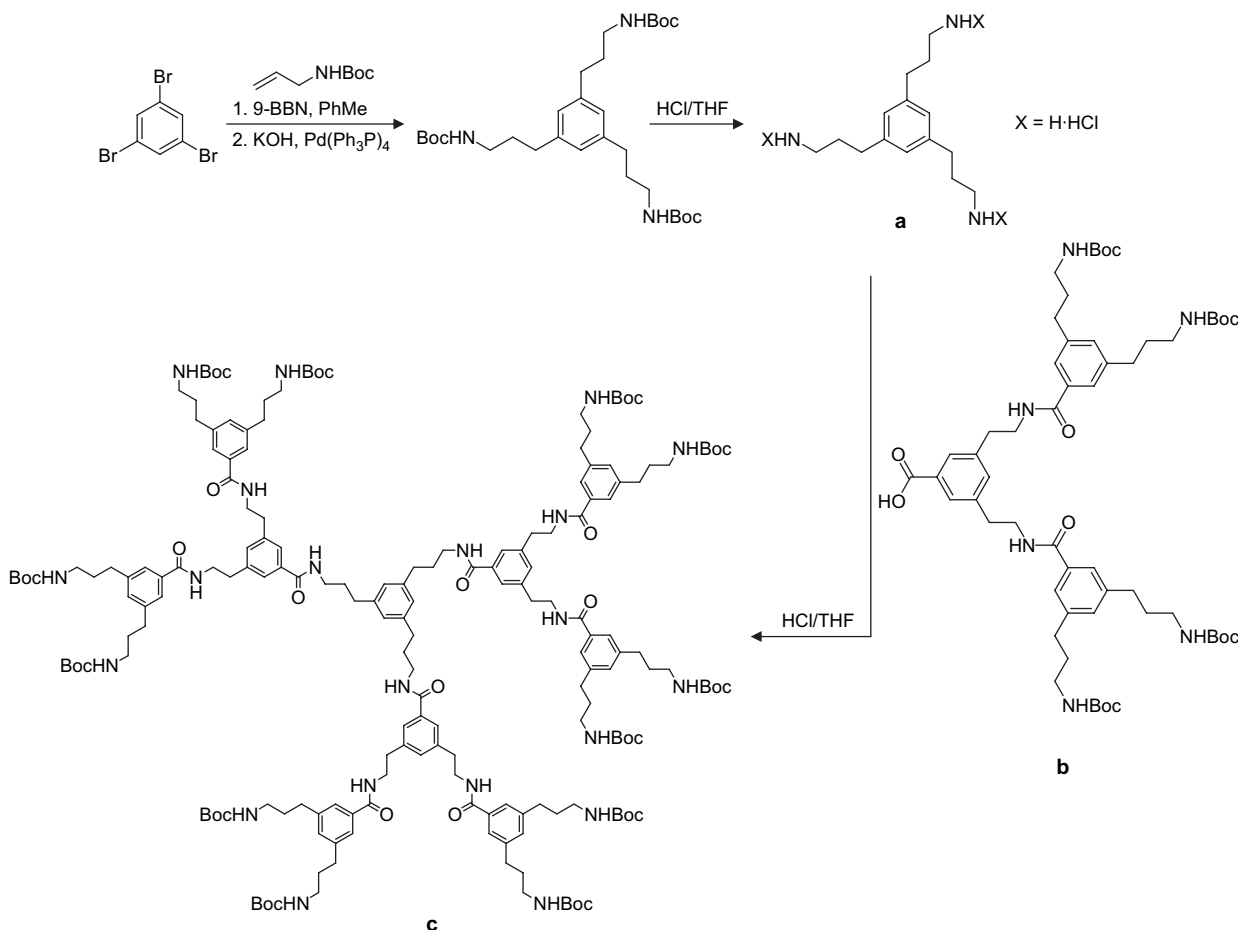
4.9. 1 → 2 Aryl-branched, ester and ether-connectivity

Dendrimers possessing multiple 9,10-anthracene bridging moieties have been prepared by divergent [1529] as well as convergent [1530] pathways. Bromomethylation of **59a**, followed by treatment with 3,5-di(benzoyloxy)phenol (**59b**) in the presence of Cs₂CO₃ gave (90%) **59c**, which was subsequently debenzoylated with butylamine in THF under reflux generating **59d**. Capping of this diphenol monomer with

9-chloromethyl-10-*n*-hexylanthracene afforded **59e**, which was de-esterified and transformed to the desired chloromethyl derivative **59g**. Attachment of **59g** to the hexaphenolic core [1530] **59h** gave the dendrimer **59i** possessing six internal and 12 terminal anthracene moieties. Such dendritic architectures, also see [1531], underwent an intermolecular energy migration over a large portion of their infrastructure (Scheme 59).

4.10. 1 → 2 Aryl-branched, sulfone and ketone-connectivity

Percec et al. reported the use of (1,1-dimethylethyl){[1-[3,5-bis(*S*-phenyl-4-*N,N'*-diethylthiocarbamate)phenyl]ethenyloxy]}dimethylsilane [1532] (**60a**), as an irreversible terminator multifunctional initiator [TERMINI, which is a masked multifunctional specie that can quantitatively and irreversibly interrupt a living polymerization or chain reaction] [1533] that was prepared in five steps from 4-methoxyphenylboronic acid and 3,5-dibromoacetophenone in 55% overall yield. The tridirectional core, 1,1,1-tris(4-chlorosulfonylphenyl)ethane (**60b**) [1532], was subjected to a metal-catalyzed living polymerization with methyl methacrylate to generate **60c** that was subsequently capped with **60a**. The deprotection was realized by an oxidative chlorination that transformed the *N,N'*-diethylthiocarbamate into the terminal sulfonyl chloride moieties. The



Scheme 55. Synthesis of aryl polyamidoamines [1513].

sequence was repeated to generate the elongated G1 polymer **60d**, which was subsequently capped or converted into up to the G4 branched polymer. The replacement of **60a** with a TERMINI that was easier to make was accomplished in three-steps, giving diethylthiocarbamic acid *S*-{3-[1-(*tert*-butyldimethylsilyloxy)vinyl]-5-diethylcarbamoylsulfanyl}phenyl ester [1534]; the use of $\text{Cu}_2\text{S}(\text{bpy})$ over $\text{Cu}_2\text{O}(\text{bpy})$ as the self-regulated catalyst, gave rise to an accelerated route to dendritic macromolecules (Scheme 60).

4.11. 1 → 2 Aryl-branched, ether and triazole-connectivity

Recently, the application of Huisgen's 1,3-dipolar cycloaddition reaction ("Click Reaction") of azides and alkynes has been demonstrated to be an excellent route to the building of macromolecular structures. Hawker et al. have demonstrated [1535] the divergent assembly of aryl branched dendrimers by using a simple 1 → 2 aryl branched monomer **61a** and a diazido core **61b**, easily derived from bis(2-chloroethoxy)ethane and NaN_3 . The monomer **61a** was prepared in two steps from dimethyl 5-hydroxyisophthalate by treatment with propargyl bromide, followed by reduction (LAH). The reaction of **61b** with a slight excess of **61a** was catalyzed with Cu(II) and in the presence of sodium ascorbate for 46 h at 25 °C to give (94%) the G1 **61c**,

which with SOCl_2 , followed by NaN_3 generated (87%) the tetraazide **61d** that was subsequently subjected to 4.2 equiv. of monomer **61a** to give (91%) the G2 tetraol **61e**. The sequence was successfully repeated to afford the G3 **61f** possessing 16 terminal azido moieties. Click chemistry has recently been used for the chemoselective and accelerated, layered approach to the 1 → 2 aryl-branched dendrimers [1536] with both ether and triazole connectivity (Scheme 61).

4.12. 1 → 2 Aryl-branched, amide, urea, and ether connectivity

The one-pot model reaction sequence to dendritic aromatic poly(urea-amide)s based on 5-[3-(4-aminophenyl)propionyl-amino]isophthalic acid hydrochloride [1537] (**62a**) and 5-[3-(4-aminophenyl)propionylamino]isophthaloyl azide hydrochloride (**62b**) was investigated [1538]. Treatment of **62b** and *p*-tolyl isocyanates gave (93%) the urea with two acyl azide termini, which when subjected to the Curtius rearrangement [1539] (30 min, 140 °C) generated the intermediate bis-isocyanate that can readily react with aniline. This procedure utilized activation of the 1,1,1-tris(4-carboxymethoxyphenyl)ethane (**62c**), as the core, with the condensing agent, diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate [1540], followed by 3 equiv. of the aminodicarbonyl azide **62b**, then *via* the Curtius

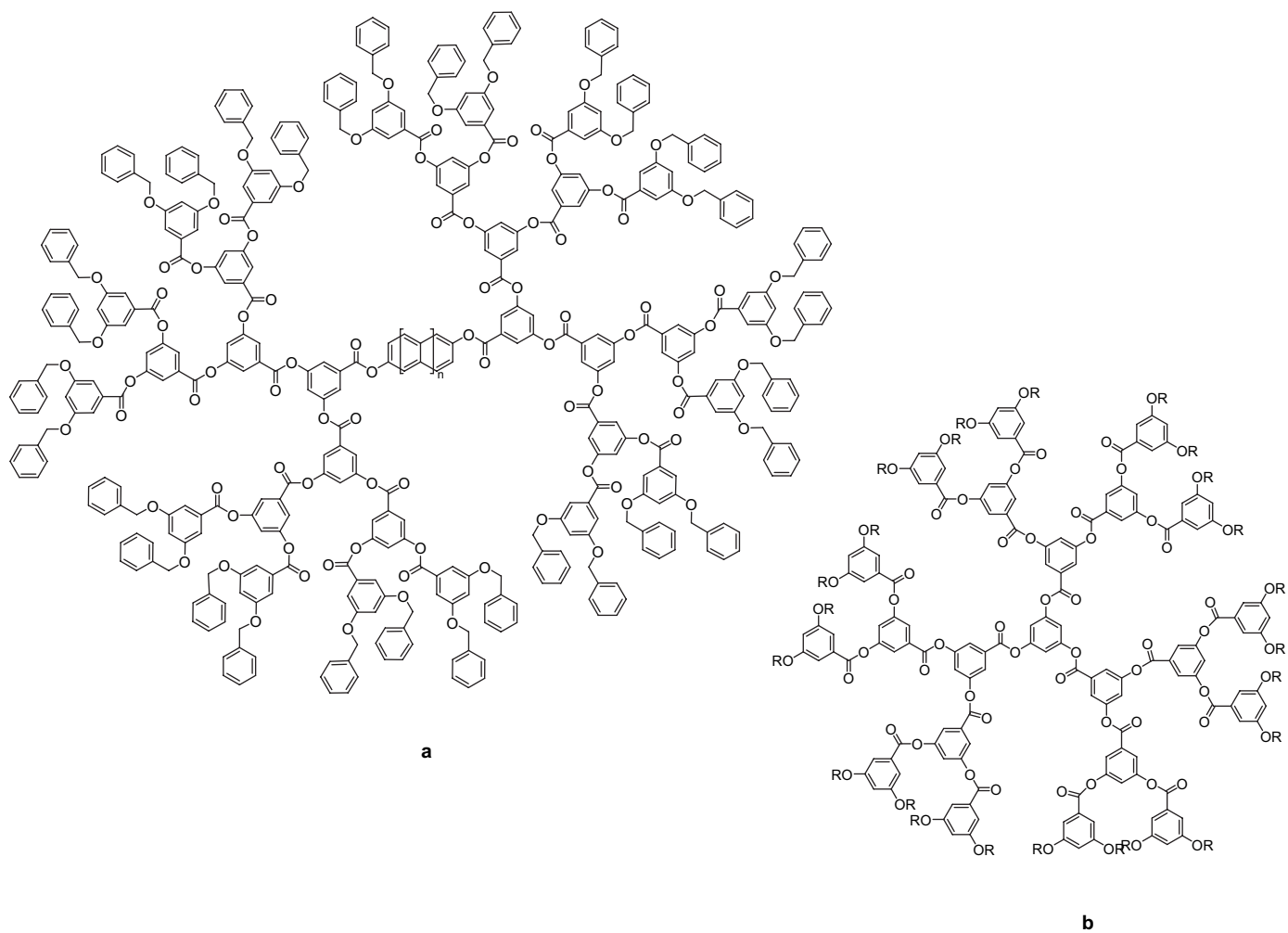
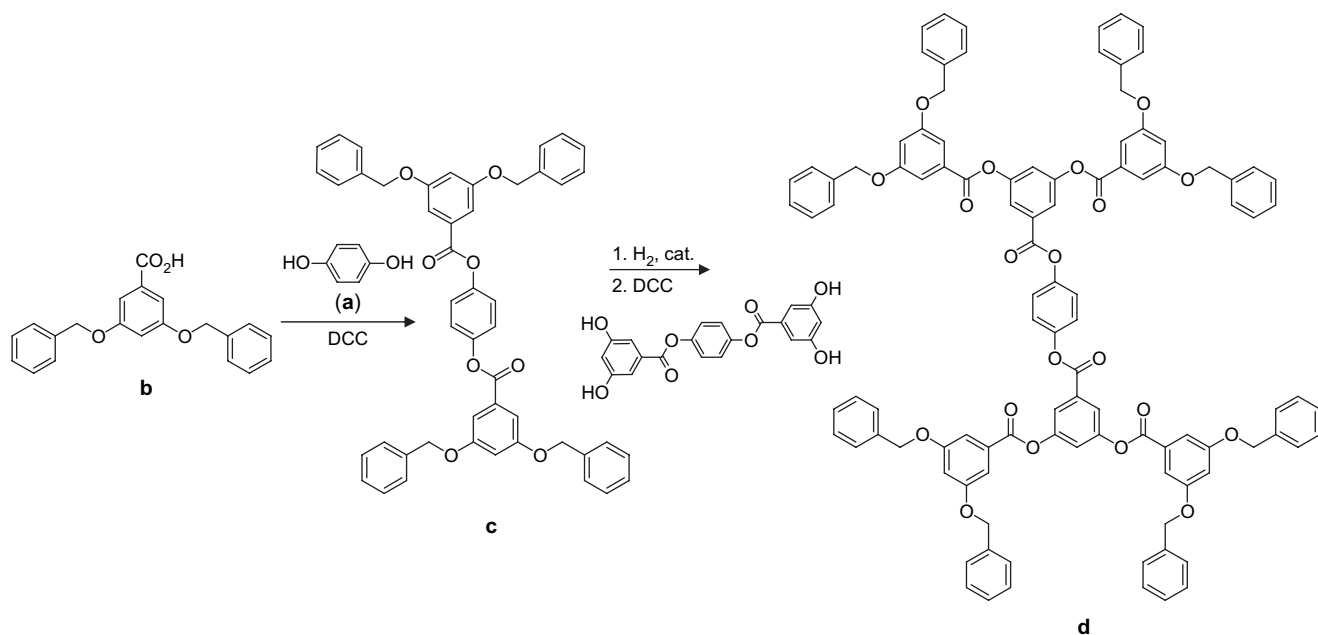
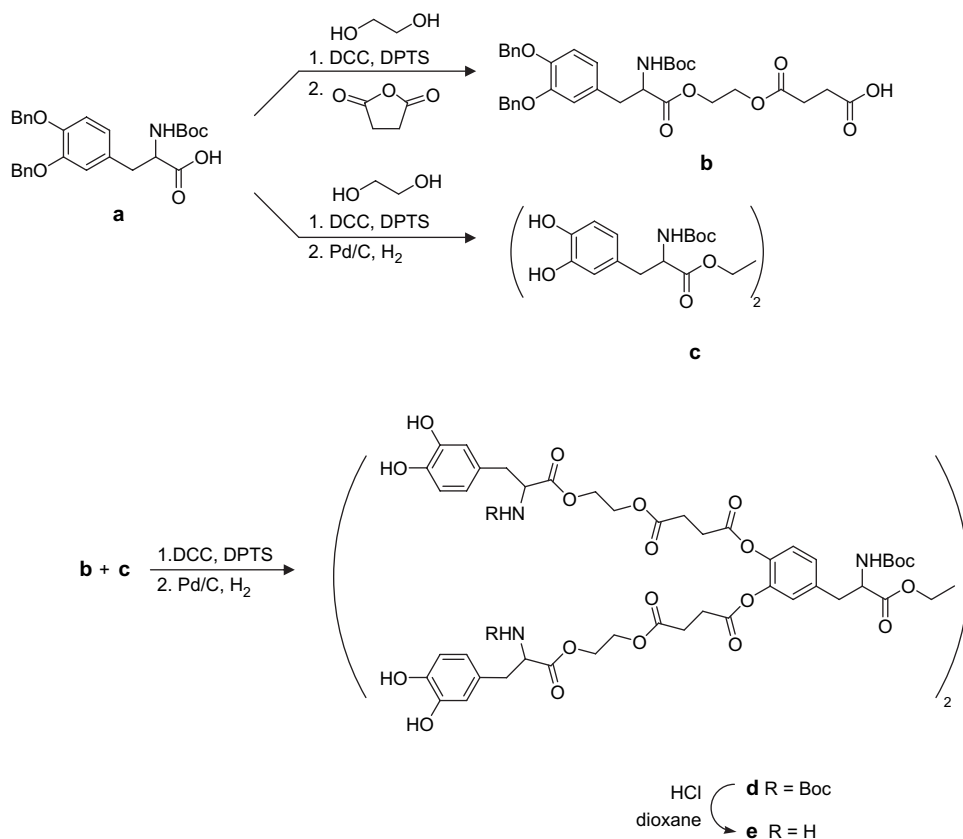


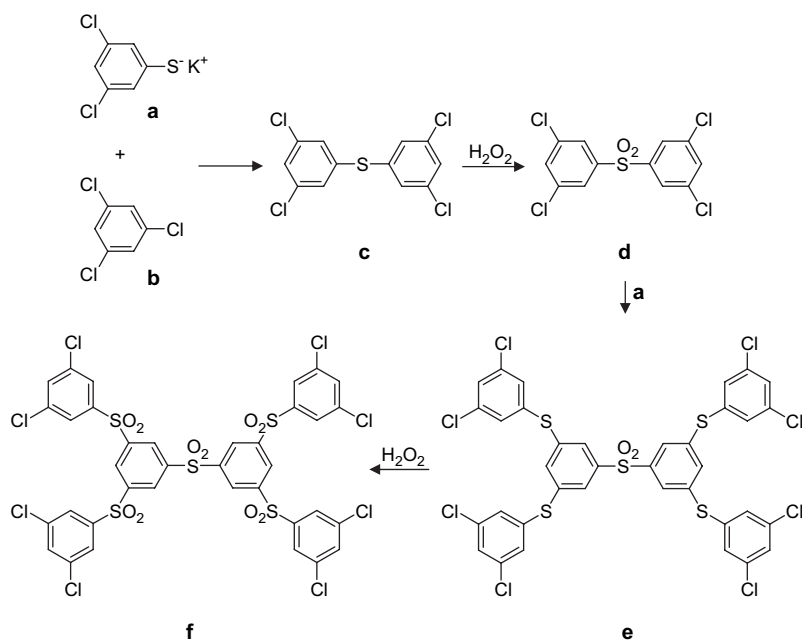
Fig. 9. Poly(ester) dendrimers possessing naphthalenediol (a) and phloroglucinol (b) core units [1521].



Scheme 56. Construction of aryl-branched polyesters dendrimers [1520].



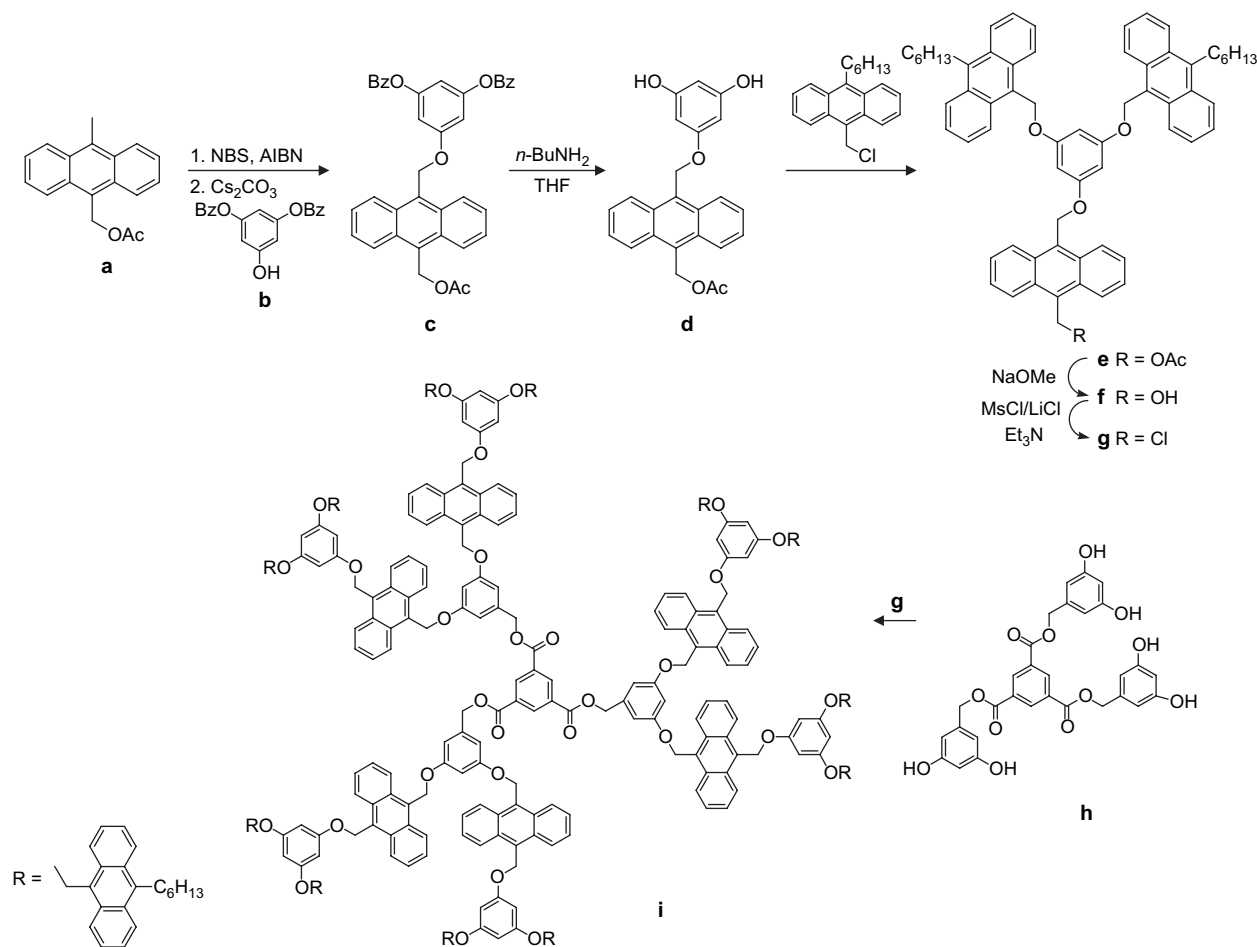
Scheme 57. The creation of novel L-DOPA prodrugs [1527].



Scheme 58. Preparation of the first generation aryl sulfone [1528].

rearrangement to generate the new core **62d** possessing the desired branching isocyanate groups. In order to prepare the higher generation dendrimers, the core **62d** was initially activated then subjected to 6 equiv. of **62a** to afford dodecaacid

62d; repetition of this process gave rise to the G3 poly(amide-urea) **62e** with 24 surface isocyanate groups [1541]. The G4 species was also formed; interestingly, all of the steps were in greater than 90% conversion and the terminal groups



Scheme 59. Divergent synthesis of dendrimer possessing 9,10-anthracene spacers [1530].

were also capped with *p*-*tert*-butylaniline or dihexylamine. The M_w/M_n values were narrowly in the range of 1.08–1.15 (Scheme 62).

4.13. 1 → 2 Aryl-branched, amide, ester, and ether connectivity

Starting with the octahydroxy porphyrin core **64a**, treatment with the bis-protected mono-acid **63b** in the presence of a polystyrene-bound carbodiimide reagent along with DMAP and DPTS [1542] generated the initial dendrimer **64b** in 83% yield. Deprotection of the hydroxy groups with $[(NH_4)_2Ce(NO_3)_6, MeCN/borate\ buffer\ mixture\ at\ pH\ 7]$ [1543,1544], followed by esterification with **63c**, again possessing the acetonide moiety formed the internally functionalized dendrimer [1545] **64c** with eight internal naphthopyranone (from **63b**) and 16 external coumarin-3-carboxylate (from **63c**) donor chromophores (Schemes 63 and 64).

4.14. 1 → 2 (Hetero)aryl and amine-branched

A series of diiodoaryl compounds **65b** has been treated with 2 equiv. of 2,6-bis[*N,N*-bis(carboxymethyl)aminomethyl]-4-ethynylpyridine (**65a**) in the presence of traces of $(Ph_3P)_2PdCl_2$

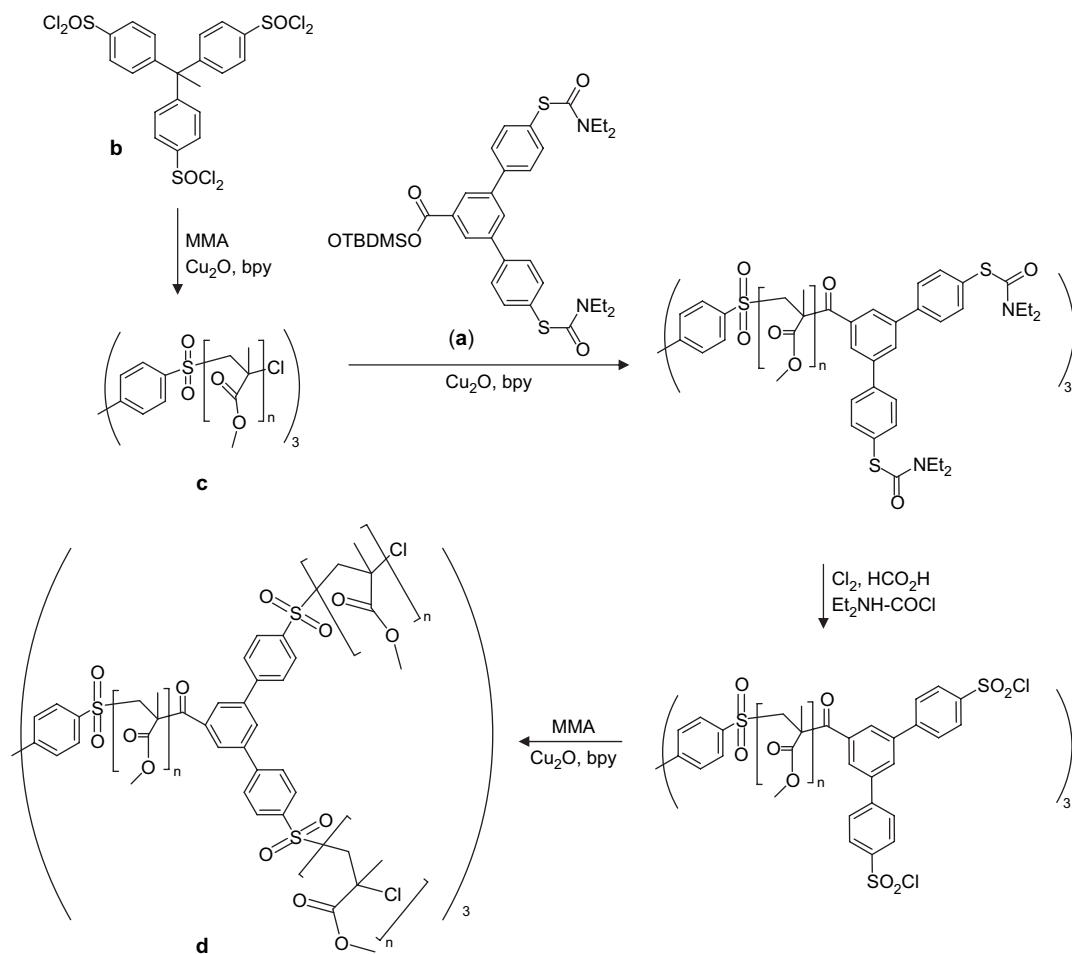
and CuI in a mixture of Et_3N and THF to generate the simple two-directional dendrimer [1546] (Scheme 65).

4.15. 1 → 2 Heteroaryl-branched, amine, ether-connectivity

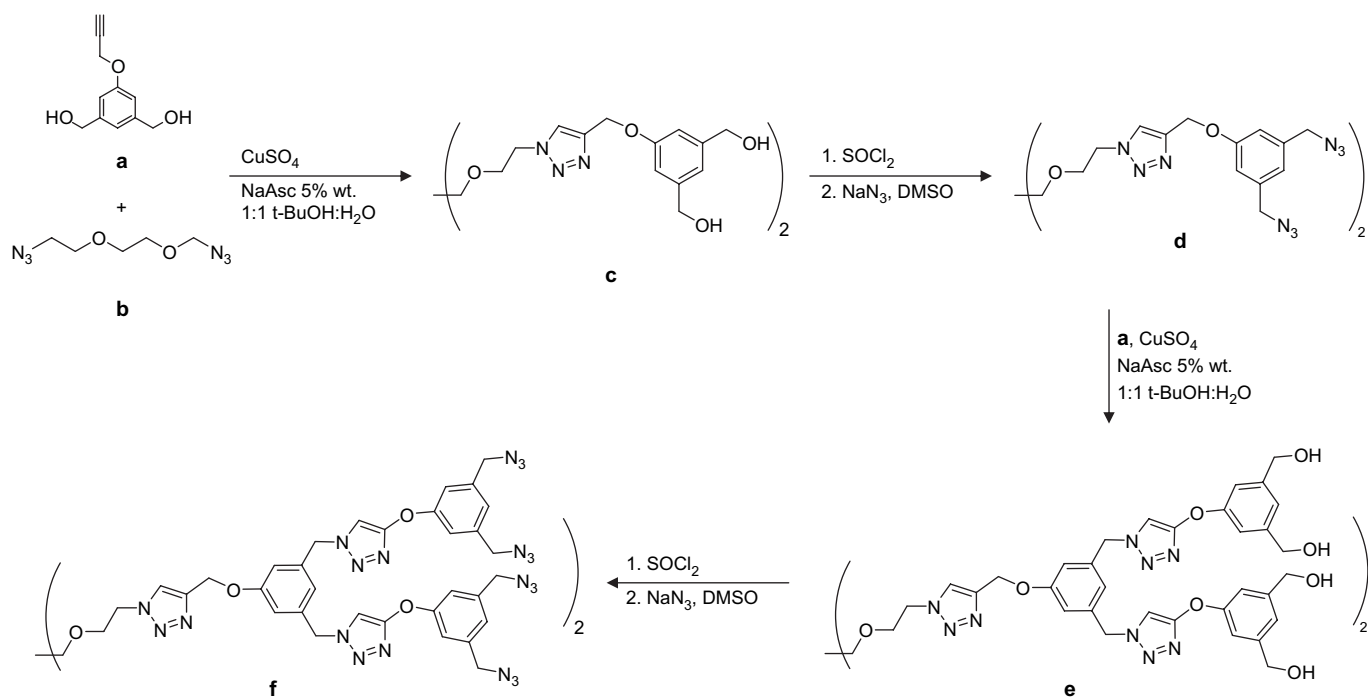
The use of a PEG core to create linear-dendritic triblock copolymers has been reported [1547]. When commercial PEG 1000 in aqueous base was treated with cyanuric chloride (**66a**) in CH_2Cl_2 at 0 °C, the white solid **66b** was generated (100%). By controlling the reaction temperature permitted monosubstitution from which **66b** was treated with excess ethanolamine at 25 °C, followed by 4 equiv. of **66a** generated the G2 product **66c**. The G2 **66c** was subjected to the same two steps, then capped with phenol to give the G3 level **66d**. All of the steps were reported to be >90% (Scheme 66).

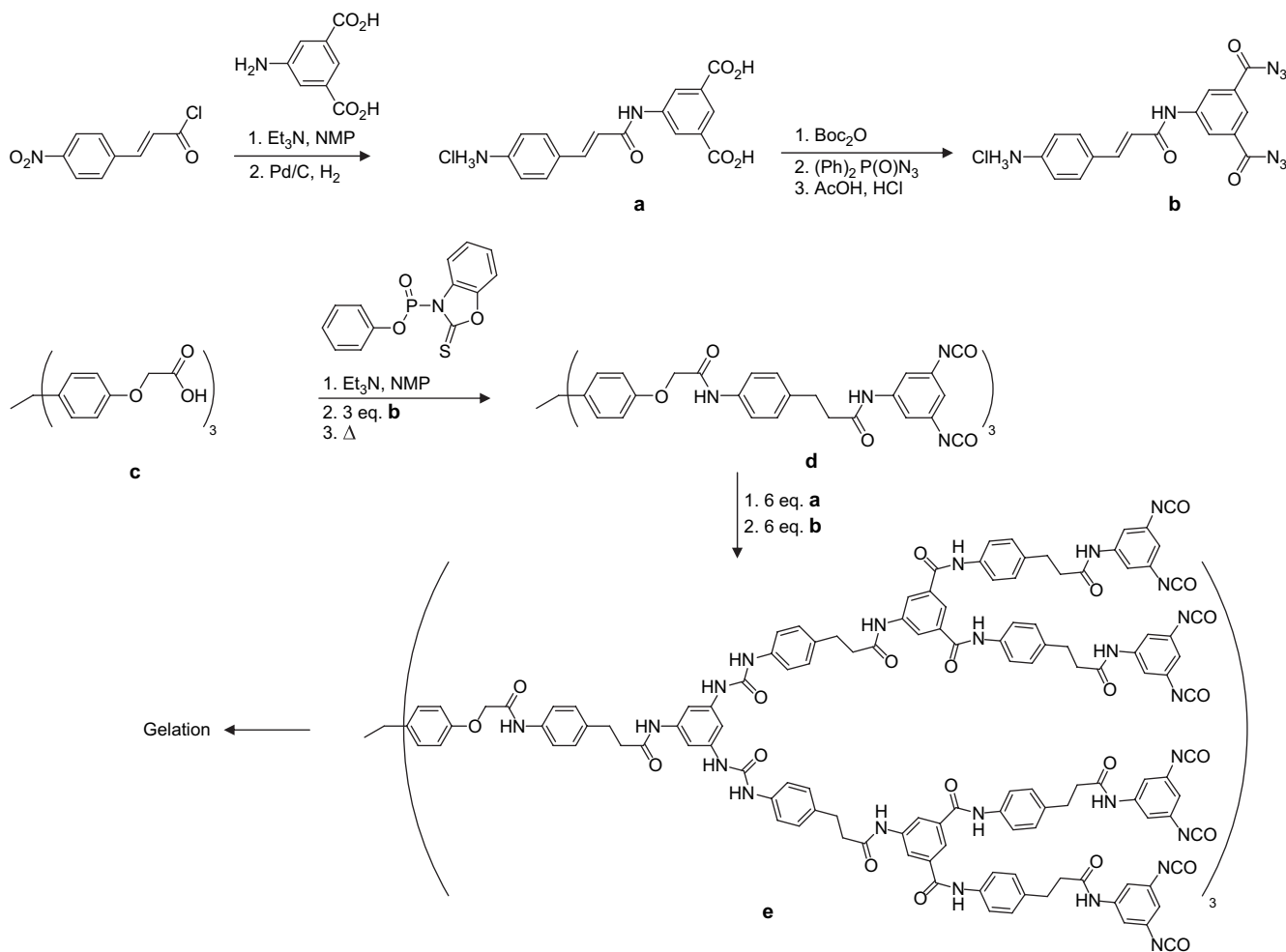
4.16. 1 → 2 (Hetero)aryl triazine-branched, amine-connectivity

An excellent review covering triazine-based dendrimers has been presented by Simanek et al. [1548] in which the rationale for using triazine is considered in detail. The selective reactivity of cyanuric chloride has been well-known for decades in that it



Scheme 60. Divergent route to dendritic PMMA by a combination of living radical polymerization and terminator multifunctional initiator [1533].

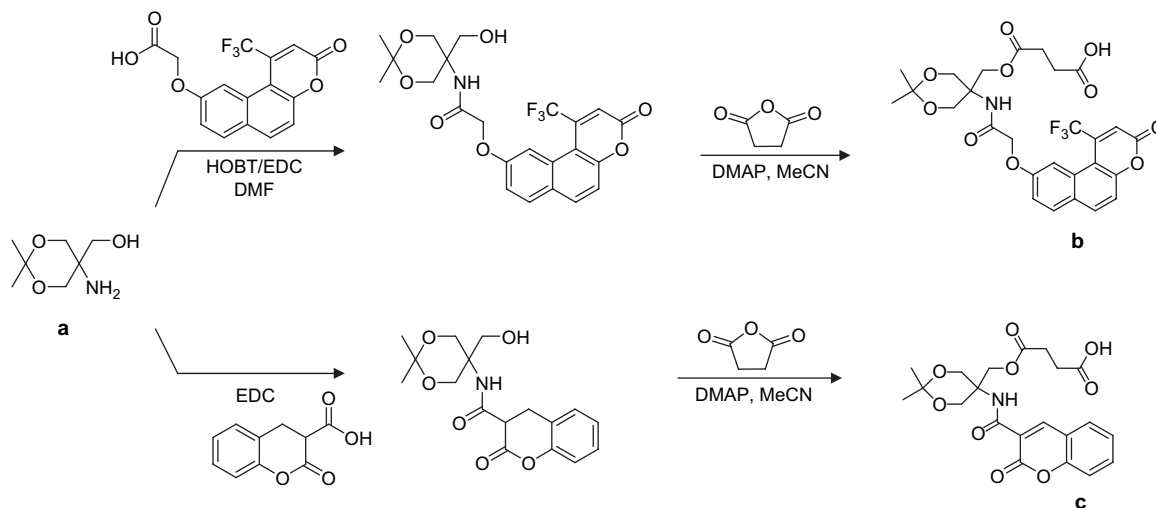
Scheme 61. The divergent approach *via* Click Chemistry [1535].



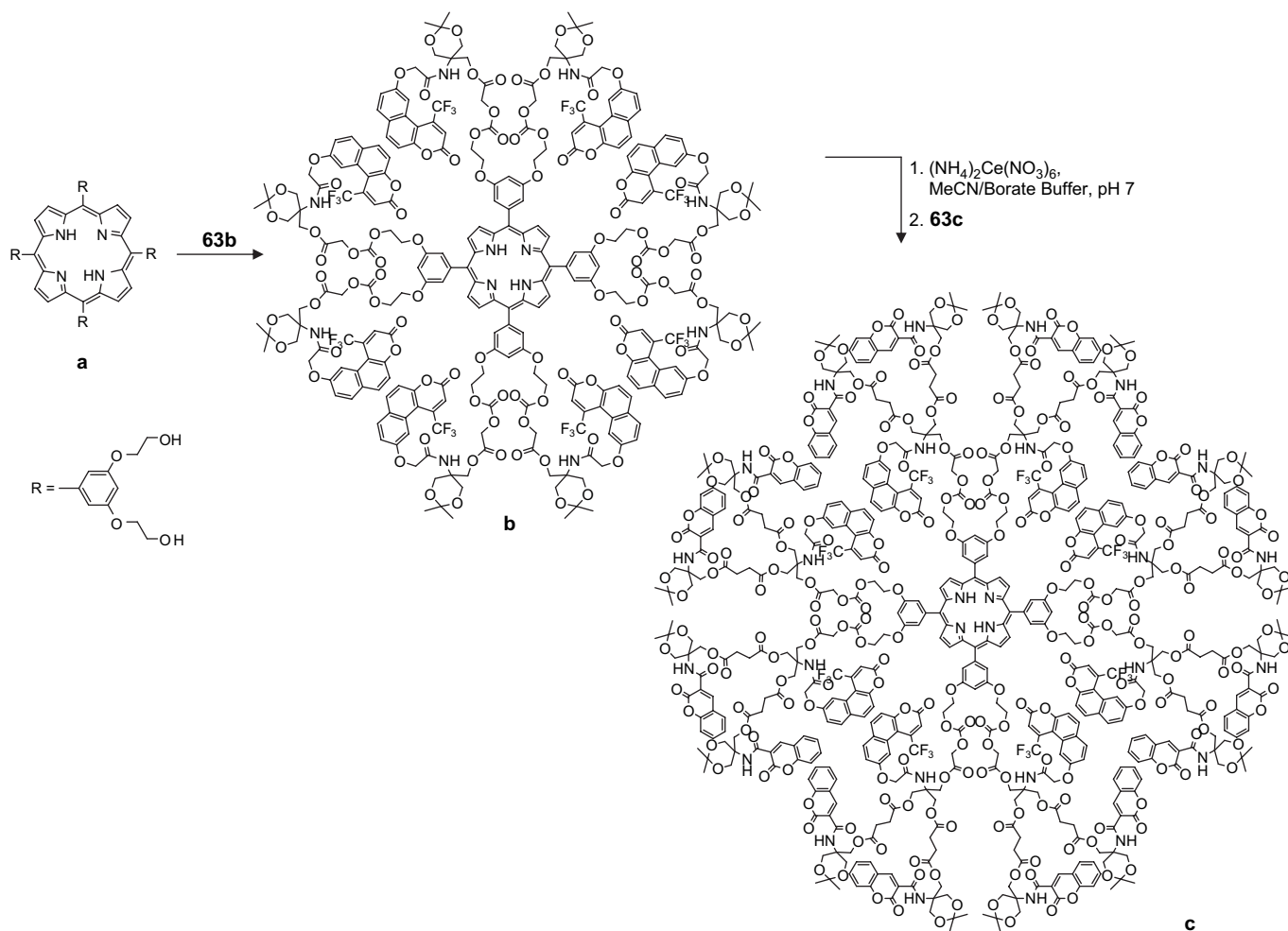
Scheme 62. The creation of the initial diacid (**a**) and diacyl azide (**b**) intermediates [1538] and the one-pot dendrimer construction *via* the Curtius rearrangement [1541].

can be treated with a nucleophile and, depending on the reaction temperature, then selectively replace one (low temperatures), two (room temperature) or three (high temperature) chloride(s) predictably. Although there are examples of simple multibranch

reactions utilizing benzoguanamine, the first non-patented route was described by Zhang and Simanek [1549] demonstrating the construction of melamine-based dendrimers possessing diamine linkers and cyanuric chloride. Treatment of a monomer **67b**,



Scheme 63. Synthesis of key reagents for chromophoric monomers [1545].

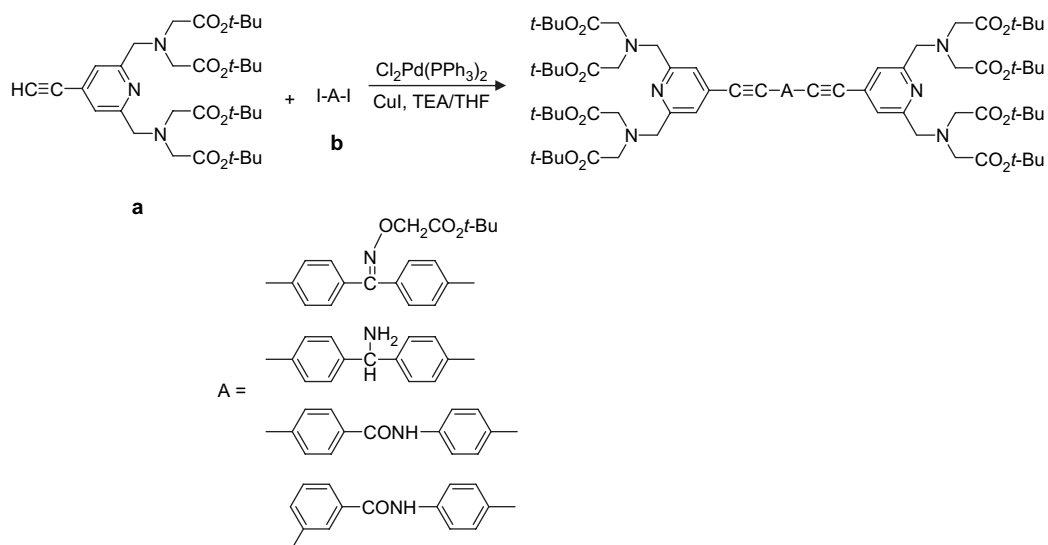


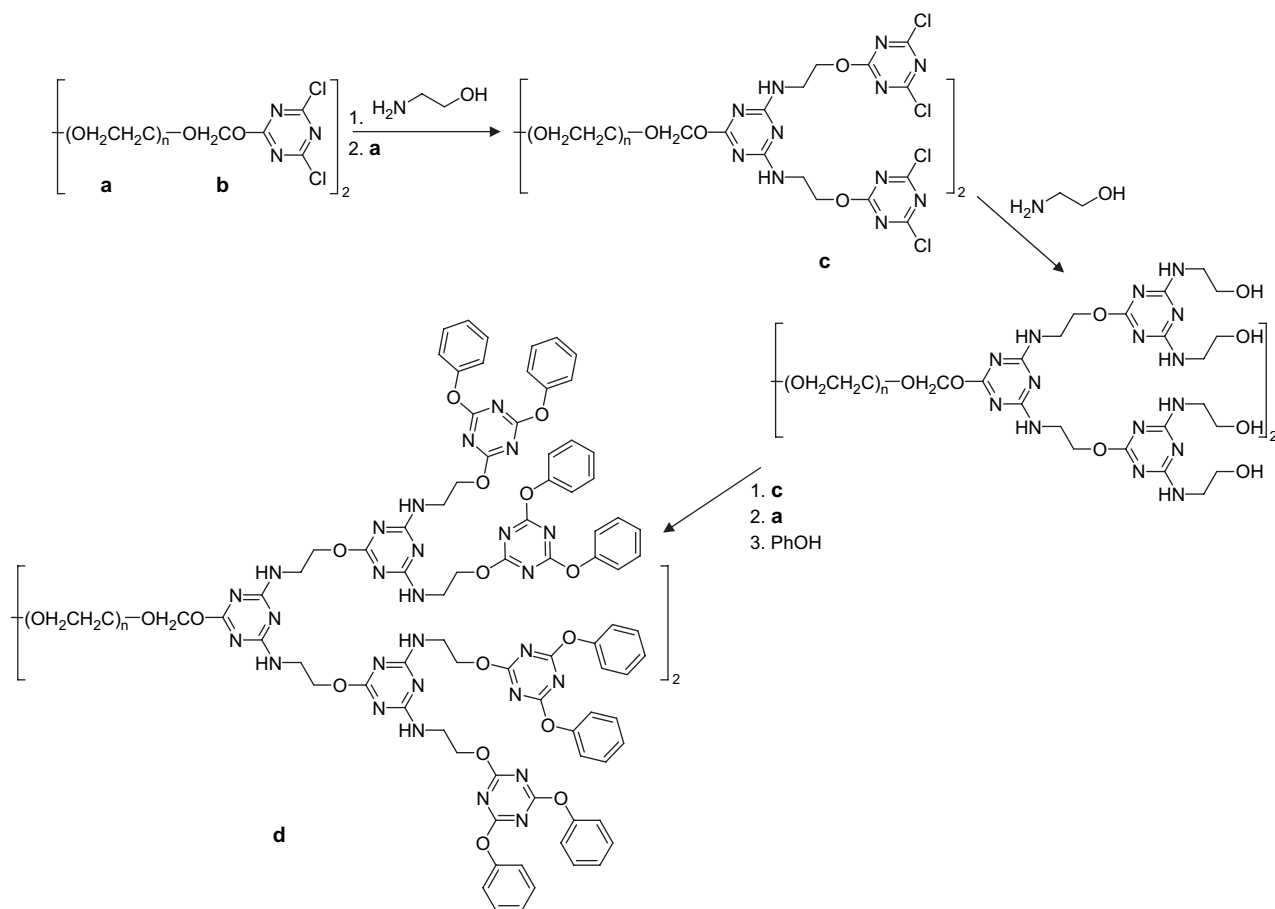
Scheme 64. A modular synthetic approach to complex dendritic architectures [1545].

derived from cyanuric chloride and 2 equiv. of the BOC-amino-methylaniline at 0–20 °C, gave rise to the desired core **67a**, which with 4 equiv. of the same monomer generated the G2 dendrimer **67c** (Scheme 67). In general, these dendrimers and

dendrons have been more conveniently assembled *via* a convergent process [1550–1555].

A similar divergent approach utilized the three-directional core **68a**, formed in two-steps from cyanuric chloride with

Scheme 65. 1 → 2 heteroaryl and 1 → 2 *N*-branched species [1546].



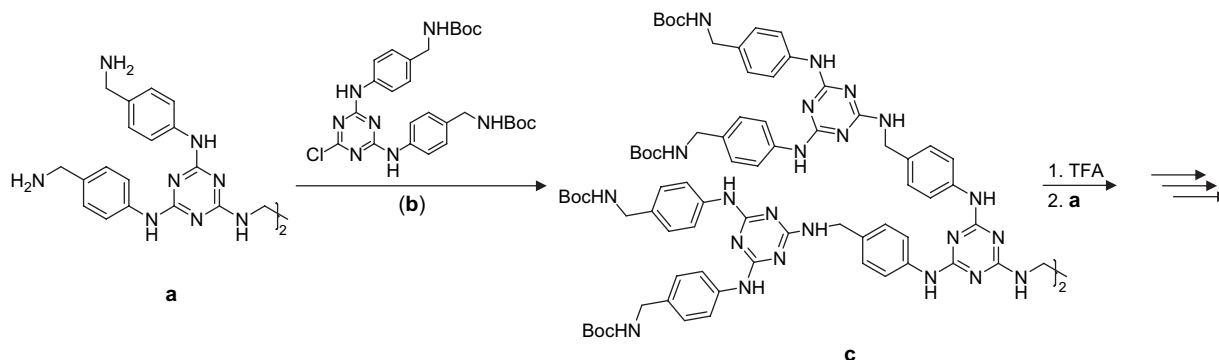
Scheme 66. 1 → 2 Heteroaryl branching using cyanuric chloride [1547].

p-nitroaniline, followed by SnCl_2/HCl reduction that was treated with monomer **68b** in collidine and NMP at 100 °C to give the desired G1 product **68c** [1556,1557]. Subsequent reduction followed by 6 equiv. of monomer **68b** gave the G2 dendrimer after reduction. Capping of **68c** with 1-chloro-3,5-aminophenyltriazine was also accomplished. The use of phenolic linkers was further described leading to ether connectivity (Scheme 68).

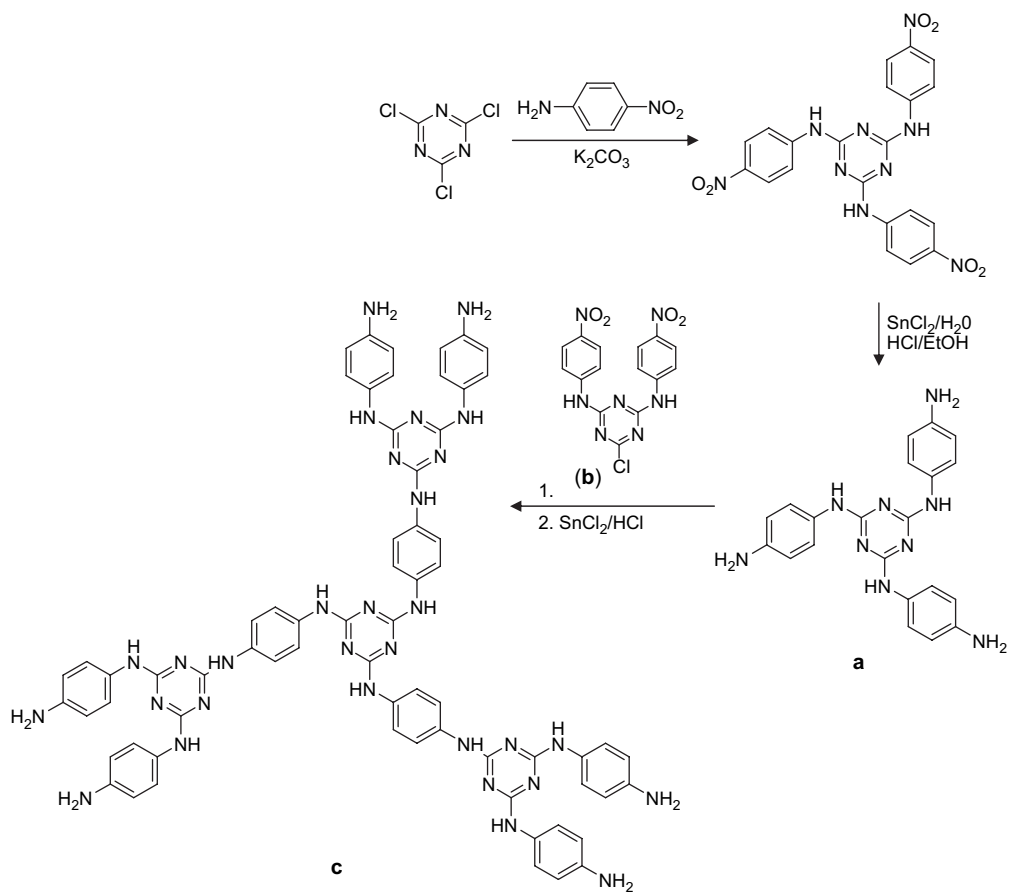
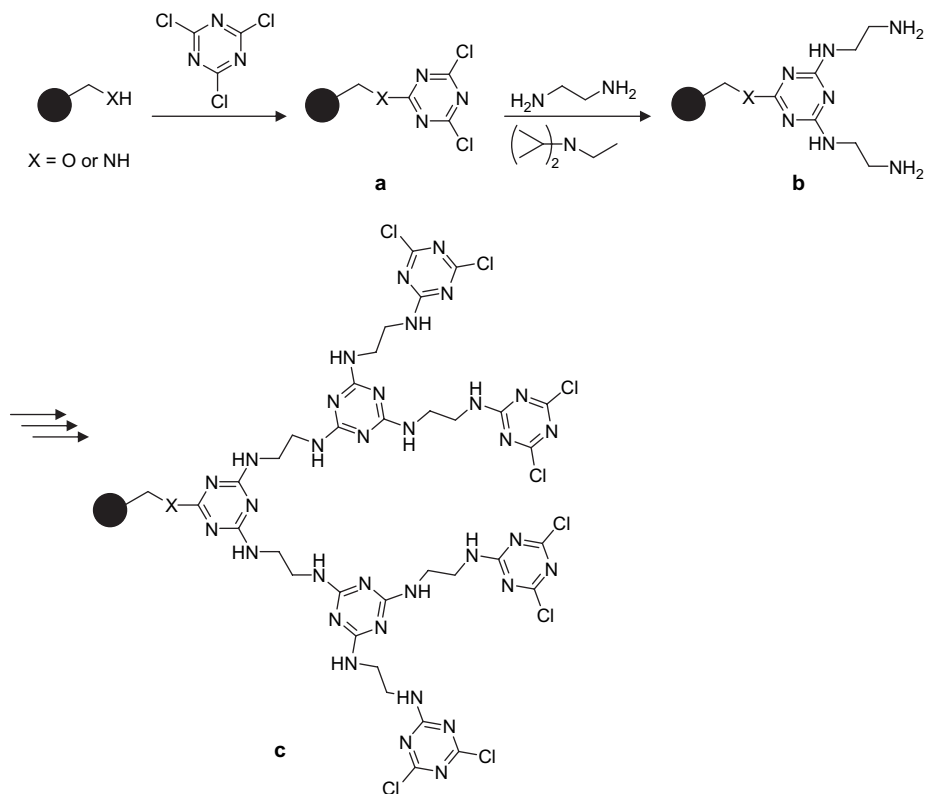
The synthesis of these melamine-based dendrimers was divergently constructed upon ordered mesoporous silica (OMS) surface (SBA-15) by initial activation [1558] with

3-(aminopropyl)triethoxysilane. The step-wise growth of the triazine dendron followed by the addition of cyanuric chloride with diisopropylethylamine, as the base, then 4-(aminomethyl)piperidine is known [1559,1560]; the sequence is repeated to generate the desired level of construction.

Similarly, the attachment of cyanuric chloride to the surface of a Wang resin, aminopropyl silica or SynPhase lanterns has been reported to generate **69a**, which with ethylenediamine, followed by cyanuric chloride gave **69b** [1561]. Treatment with ethylenediamine and then cyanuric chloride generated the next tier product **69c**. The capping of these



Scheme 67. Divergent construction of triazine dendrimers [1549].

Scheme 68. Another approach to triazine dendrimers *via* a reductive step [1556].

Scheme 69. The divergent construction of triazine dendrons on different solid supports [1561].

materials with diverse reagents, *e.g.*, *N*-acetylenediamine, 3-aminopropanol, 2-[2-(2-aminoethoxy)ethoxy]ethanol, and *N*-acetyl-4-(3-aminopropyl)morpholine, has also been reported (Scheme 69).

Since dichlorotriazines react selectively to afford either mono- or di-substitution, depending on reaction conditions, Hollink and Simanek [1562] utilized this controlled approach to introduce different components to these macromolecules. In general, the tris(piperazyl)triazine core [1563] was treated with 1-(*N'*-BOC-piperazyl)-3,5-dichlorotriazine to give (83%) the G1 dendrimer possessing three 3-(*N'*-BOC-piperazyl)-5-dichlorotriazinyl termini, from which the chloro moieties were displaced (97%) with 2-(2-aminoethoxy)ethanol, then, after deprotection (HCl/MeOH) afforded the free secondary amine, which can be used to create the next tier. They noted that gram quantities can be prepared without either humidity considerations or the need for inert conditions.

There are numerous monomers that are envisioned using either the selective substitution approach noted above, or alternatively, a potent new class of gelators that have been reported [1564] which are derived from salts of 4,6-bis(aryl amino)-1,3,5-triazine-2-carboxylic acids by the condensation of 1,5-diarylbiguanides with excess dimethyl oxalate in MeOH [1565].

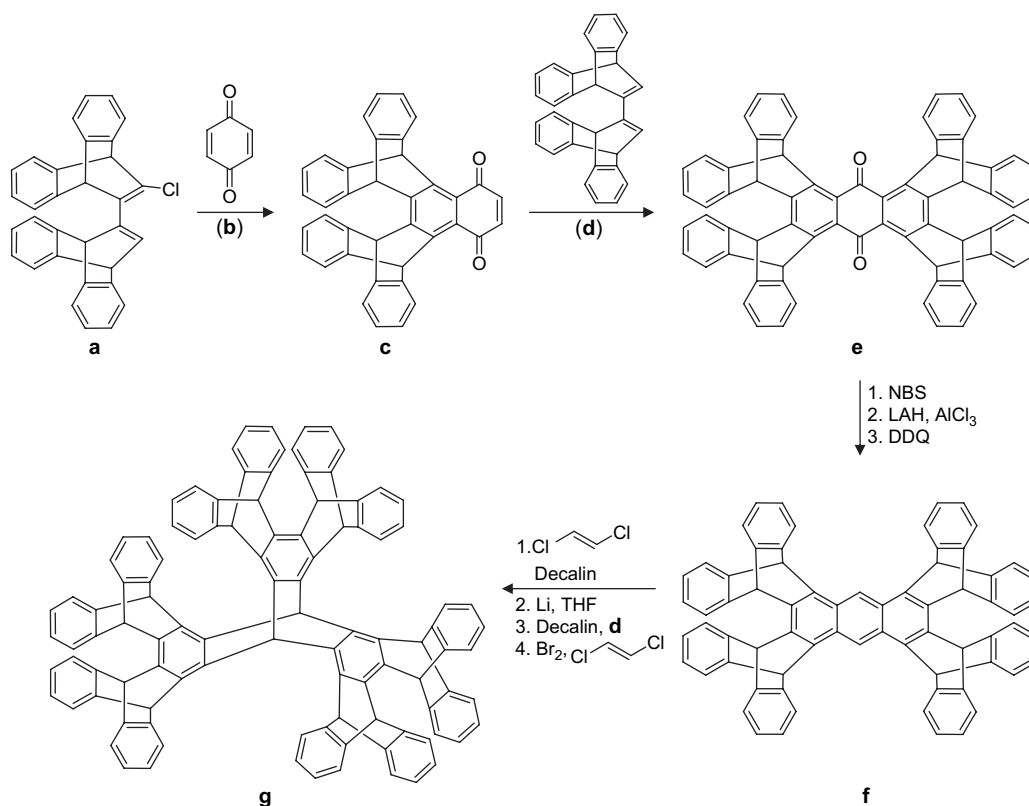
The review of the applications and supramolecular assemblies of these novel triazine dendrimers, constructed either divergently or convergently as well as their related hyperbranched species, has been covered in the above mentioned critique [1548].

5. 1 → 2 C-Branched

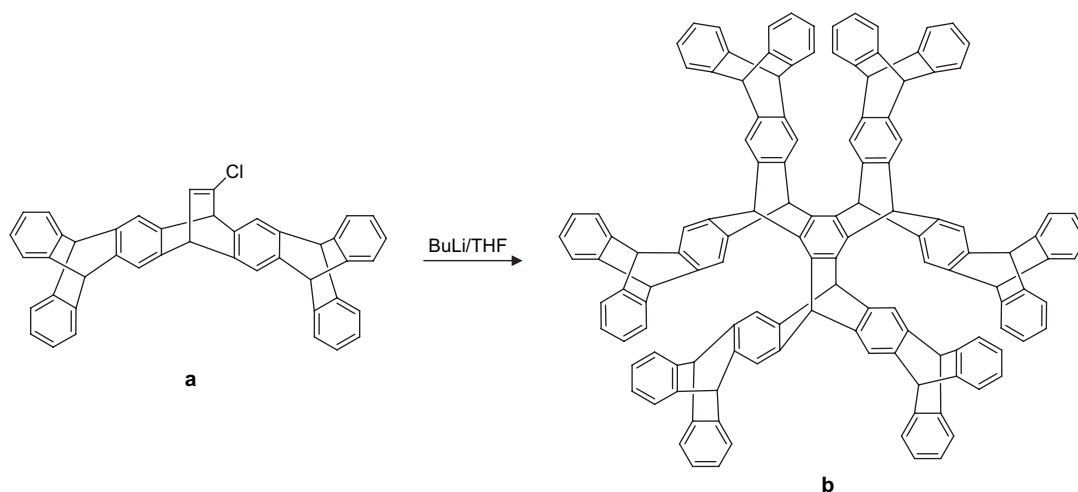
5.1. 1 → 2 C-branched and connectivity

Hart et al. [1566–1572] reported the novel preparation of branched three-dimensional motifs comprised of polyaromatics, termed “iptycenes,” which are extended triptycenes based on bicyclo[2.2.2]octane. Their construction utilized multiple Diels–Alder transformations with bis(9,10-anthracenyl)-substituted butadiene monomer **70d**. Treatment of the highly substituted chlorobutadiene **70a** with quinone **70b** afforded the bis(triptycene) intermediate **70c**, which with diene **70d** generated dione **70e**. Transformation of the core dione moiety of **70e** to the anthracene nucleus **70f** was achieved in three-steps (NBS; LAH; DDQ); treatment of the tetrakis(triptycene) **70f** with 1,2-dichloroethene, then with Li, and subsequent Diels–Alder reaction with diene **70d** afforded an intermediate that was finally aromatized to give the superiptycene **70g**. These highly rigid superstructures possess unique molecular cavities, as evidenced by the fact that crystals of iptycene **70g** demonstrated that their cavities possessed “included” solvent molecules – a factor that affected its X-ray structure determination (Scheme 70).

Hart et al. [1573] prepared the symmetric iptycenes, *e.g.*, nonadecaipycene **71b** by the trimerization of the bicyclic vinyl halide of triptycene dimer **71a**, as well as the synthesis of the related asymmetric iptycenes, which are helically chiral and possessing a C_2 symmetry [1574] (Scheme 71). Related naphthotriptycenes [1575] and triptycene with one [1576] or



Scheme 70. Hart et al.'s [1570] basic iptycene construction.



Scheme 71. “Nonadecaptycene” (b) preparation by vinyl halide trimerization [1573,1574].

two [1577] anthracene(s) as well as angular iptycenes [1578] have also been prepared. The aryl-branched intermediates were further shown to cyclize, generating a novel series of cuppedophanes and cappedophanes that exhibited interesting molecular activities [1579–1583].

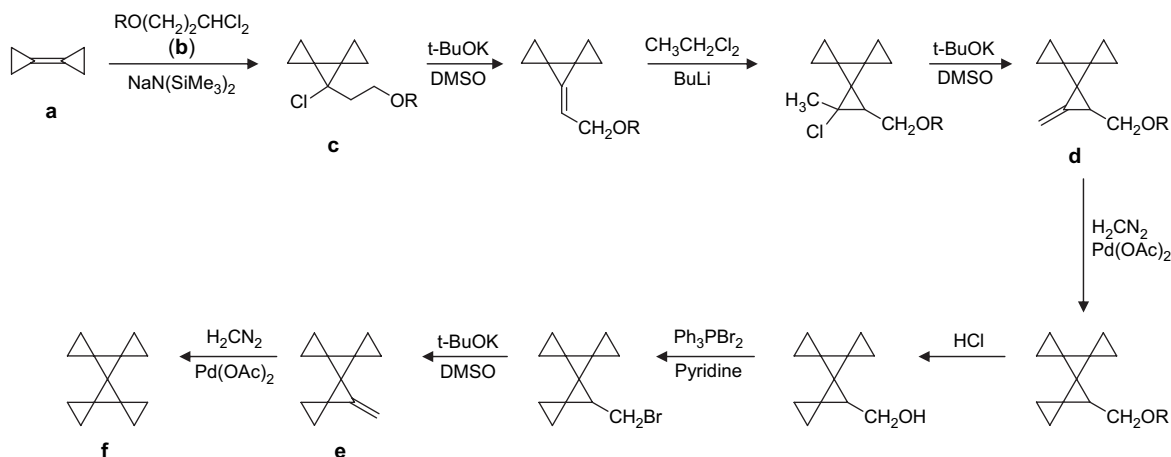
Although crystals of supertritycene [1571,1572] did not afford a structural model due to disordered solvent molecules, the structure of the crystalline 1:1 heptiptycene-chlorobenzene clathrate, in which the solvent molecules were packed in the channels between ribbons of the heptiptycene, was ascertained [1584]. The molecular geometry by Hartree–Fock [6-31G(D)] and local density methods compared well with the X-ray data.

Webster [1585] described the preparation of a water-soluble triptycene and examined the ^1H NMR chemical shift changes of various substrates due to interactions with the aromatic ring currents. For example, a D_2O solution of the triptycene and *p*-toluidine exhibited an up-field shift ($\Delta\nu = 55$ Hz) of the substrate methyl group absorption.

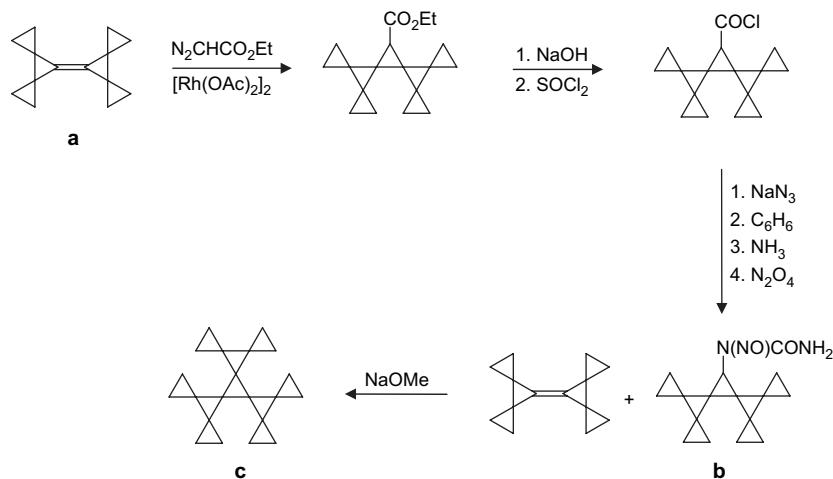
Zefirov et al. [1586] described the initial synthesis of a family of *branched* triangulanes or spiro-condensed

polycyclopropanes; an overall review has appeared [1587]. Key features of this strategy include the addition of chloromethylcarbene to methylenecyclopropanes [1588], and subsequent dehydrohalogenation. Thus, treatment of bicyclopropylidene **72a** with the chloromethylcarbene, generated from dichloride **72b**, gave the tricyclopropane **72c**. Dehydrochlorination followed by cyclopropanation (CH_3CHCl_2 , *n*-BuLi) and alkene formation (*tert*-BuOK, DMSO) generated the unsaturated ether **72d**. Alkene **72e** was converted to the desired hexakis(spirocyclopropane) (**72f**) after $\text{Pd}(\text{OAc})_2$ -mediated methyl carbene addition (CH_2N_2), acidic alcohol deprotection (HCl), bromination (Ph_3PBr_2 , pyr), and β -elimination (*tert*-BuOK, DMSO) (Scheme 72).

Preparation of other branched triangulanes with varying symmetries has also been demonstrated. A notable feature of this series of small hydrocarbon cascades is that the framework is composed entirely of quaternary, tetraalkyl-substituted carbons. This architecture closely resembles, or is at least reminiscent of, Maciejewski’s [205] proposed cascade molecule comprised of an all $1 \rightarrow 3$ C-branched interior framework (*i.e.*, without spacers between branching centers).



Scheme 72. Synthesis of branched triangulane possessing adjacent, quaternary carbon moieties [1586] (R = Me or THP).

Scheme 73. Non-iterative preparation of [10]triangulane [1589] possessing D_{3h} symmetry.

de Meijere et al. reported the preparation of symmetrical branched triangulane constructed of 10- [1589] and 14-fused [1590] cyclopropane moieties. Although the synthesis was not iterative, the structurally rigid spirocyclopropane **73c** was obtained [1589] (14%) by the reaction of nitrosoamide **73b** with bicyclopropyliene and NaOMe, which, in turn, was accessed from perspirocyclopropanated bicyclopropyliene **73a**. An unequivocal structure determination of **73c** was provided [1589] by X-ray crystallography, which demonstrated its D_{3h} molecular symmetry. The [10] Triangulane **73c** showed high thermal stability even though its thermal strain energy ($\approx 1130 \text{ KJ mol}^{-1}$) indicates it is more strained than cubane [1591,1592]. These authors speculated on the potential for a carbon network based on spiro-linked, three-membered rings. Strain energies in $[n]$ triangulanes and spirocyclopropanated cyclobutanes have been determined; comparisons of thermochemical data derived from theoretical and experimental sources have been compiled [1593]. The structures of the [15]triangulane and its dihalo derivatives have been determined by X-ray crystal analyses to possess very unique features caused, in part, by the deformation of the central dispiro[2.0.2.1]heptane unit [1590]. Alkene **73a** was also prepared (24%) in three steps from 7-cyclopropylidenedispiro[2.0.2.1]heptane or from dehalogenative coupling (82%) of 7,7-dibromo[3]triangulane. Treatment of **73a** with $CHBr_3$, followed by powdered KOH, and TEBACl in CH_2Cl_2 gave rise to (83–93%) the dibromide **74b**, which with $CuCl_2$ in THF at $-95^\circ C$ with $BuLi$ gave rise (22%) to the G3 perspirocyclopropanated bicyclopropyliene **74c** [1594]. de Meijer and co-workers have recently expanded this all-carbon series to give

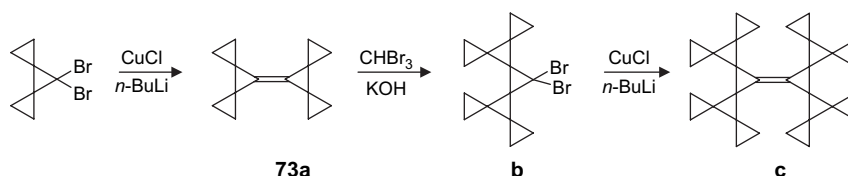
rise to novel linear and branched phospho- [1595] and cobalto- [1596] $[n]$ triangulanes, as well as $[n-2]$ triangulane dimethanols and σ - $[n]$ helicenes [1597] (Schemes 73 and 74).

Díez-Barra et al. [1598] reported the benzylation of aryl acetyl groups for the preparation of small dendritic polyketones $\{PhCOCH[CH_2(p-C_6H_4)COCH(CH_2Ph)_2]_2\}$. A crystal structure obtained for $\{(PhCH_2)_2CHCO(p-C_6H_4)COCH(CH_2Ph)_2\}$ showed the presence of aryl π -stacking in the solid state.

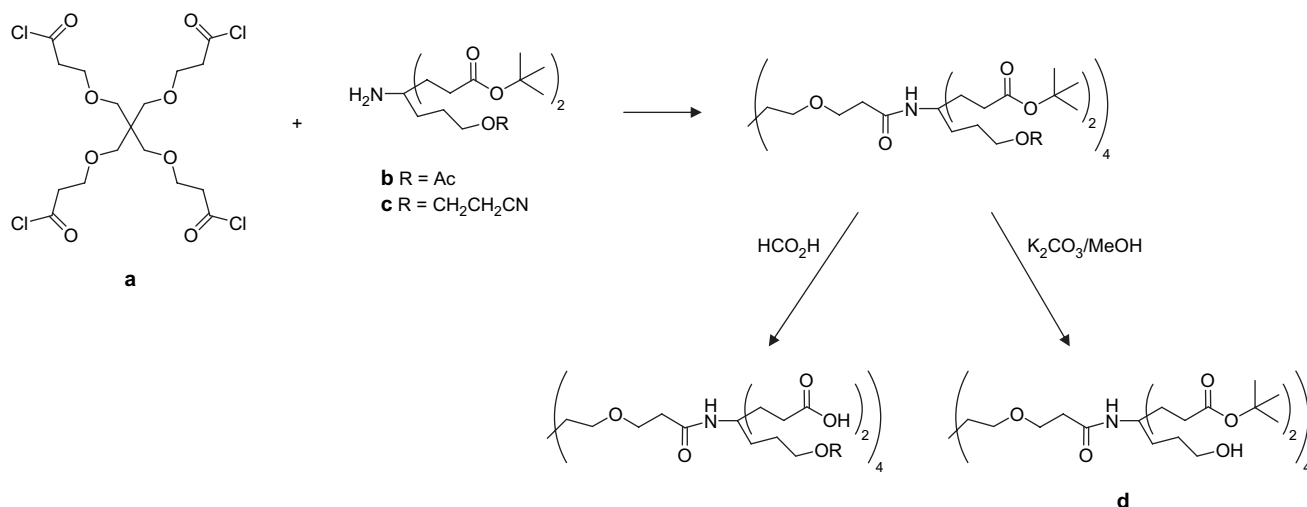
5.2. 1 \rightarrow 2 C-branched, amide-connectivity

Denkewalter et al. [6] synthesized a series of *tert*-butoxycarbonyl-protected poly(α, ϵ -L-lysine)s (see Scheme 3), the molecular models of which suggested that they were globular, dense spheres, whose molecular weight distributions were determined to be very narrow ($M_w/M_n \cong 1.0$). Since each generation in this series was synthesized in a step-wise manner, each member in the series was predicted to possess a monodisperse molecular weight.

Aharoni, Crosbey, and Walsh [1599] characterized Denkewalter's cascade macromolecules [6] by employing classical polymer techniques: viscosity determinations, photocorrelation spectroscopy, and size exclusion chromatography. It was concluded that at each tier (2 through 10), these globular polymers were, in fact, monodisperse and behaved as nondraining spheres. The purity of these molecules was not ascertained and the dense packing limits were either not realized or simply not noted, nor was the issue of chirality addressed.



Scheme 74. Synthesis of G3 perspirocyclopropanated bicyclopropyliene [1594].



Scheme 75. A simple route to internal future sites of connectivity [1600].

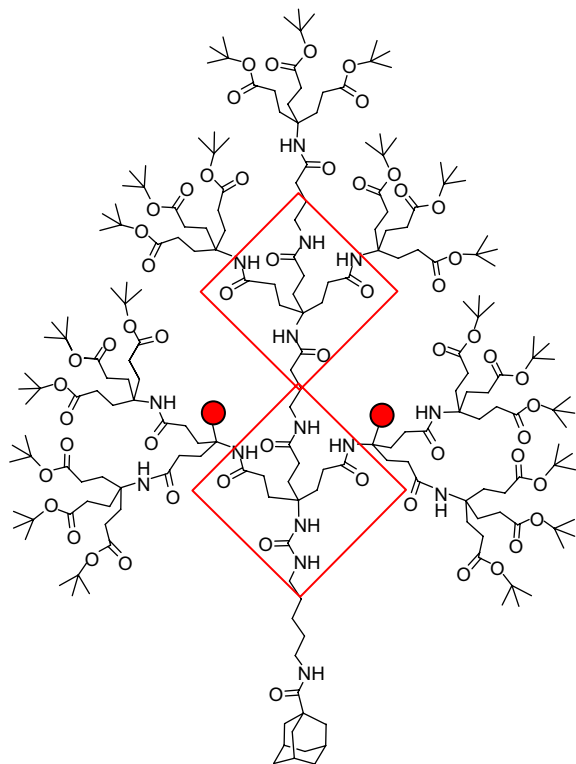
Newkome et al. [1600] have generated a simple family of 1 → 3 C branched monomers [1316,1601–1604] but during their synthesis, it was noted that at different reaction conditions the controlled formation of a variety of useful 1 → (2 + 1) C-branching products could also be prepared in high yield. For example, the initial substitution of O₂NMe with O₂NCH₂R gave rise to a simple route to ONCCR(CH₂CH₂CO₂-*t*Bu)₂ in excellent yields [1605]. But in a similar manner to the specific nucleophilic substitution on trichlorotriazine [1548], when O₂NMe is treated with activated olefins under the Michael conditions at different temperatures, the step-wise introduction of substituents can be realized in very high yields for each step. Thus at low temperatures, O₂NMe was treated with CH₂=CHCO₂CH₂Ph to give O₂NCH₂(CH₂CH₂CO₂CH₂Ph), which with CH₂=CHCO₂-*t*Bu at slightly elevated temperatures gave O₂NC[(CH₂CH₂CO₂CH₂Ph)(CH₂CH₂CO₂-*t*Bu)₂] in excellent overall yield. The selective introduction is based in the attachment of the most reactive acrylate first and at low temperatures, followed by the less reactive last, but at elevated temperatures in order to prevent scrambling *via* a retro-Michael reaction. The final reductive step – transforming the nitro moiety of the pre-dendron to the desired dendron – is generally quantitative and also circumvents the retro-Michael reaction of the final 1 → 2 or 1 → (2 + 1) C-branching monomers.

Further, a series of 1 → (2 + 1) C-branching monomers can be easily used to create a 1 → 2 branching motif while leaving a protected functional moiety for later internal activation [1600]. The initial monomers, shown in Scheme 75, can be readily attached to the four-directional core [1602] **75a** as demonstrated by treatment with **75b** (R = Ac) or **75c** (R = CH₂CH₂CN). Reaction of either product with K₂CO₃ in MeOH afforded the desired **75d**; whereas treatment with formic acid removed the *tert*-butyl groups so that further divergent growth would be possible. Using the same 1 → 2 branched monomers permitted a protected group at each tier or other 1 → 2 or 1 → 3 [1606] C-branching monomers can

be used to instill the future active site at the appropriate molecular level.

Application of the tailored assembly of 1 → 2 C-, 1 → (2 + 1) C-, and 1 → 3 C-branching monomers has been demonstrated (Fig. 10) in the step-wise construction of the conifer-shaped dendritic tree [1607].

A simple series 1 → 2 C-branched dendrons was prepared by the treatment of (SCH₂CH₂COCl)₂ with serinol to generate HSCH₂CH₂CONCH(CH₂OH)₂; the related G2 dendron and

Fig. 10. The synthesis of a simple coniferic tree *via* different monomers [1607].

different combination dendrons were synthesized and subsequently coated onto the CdS particles [1336,1337].

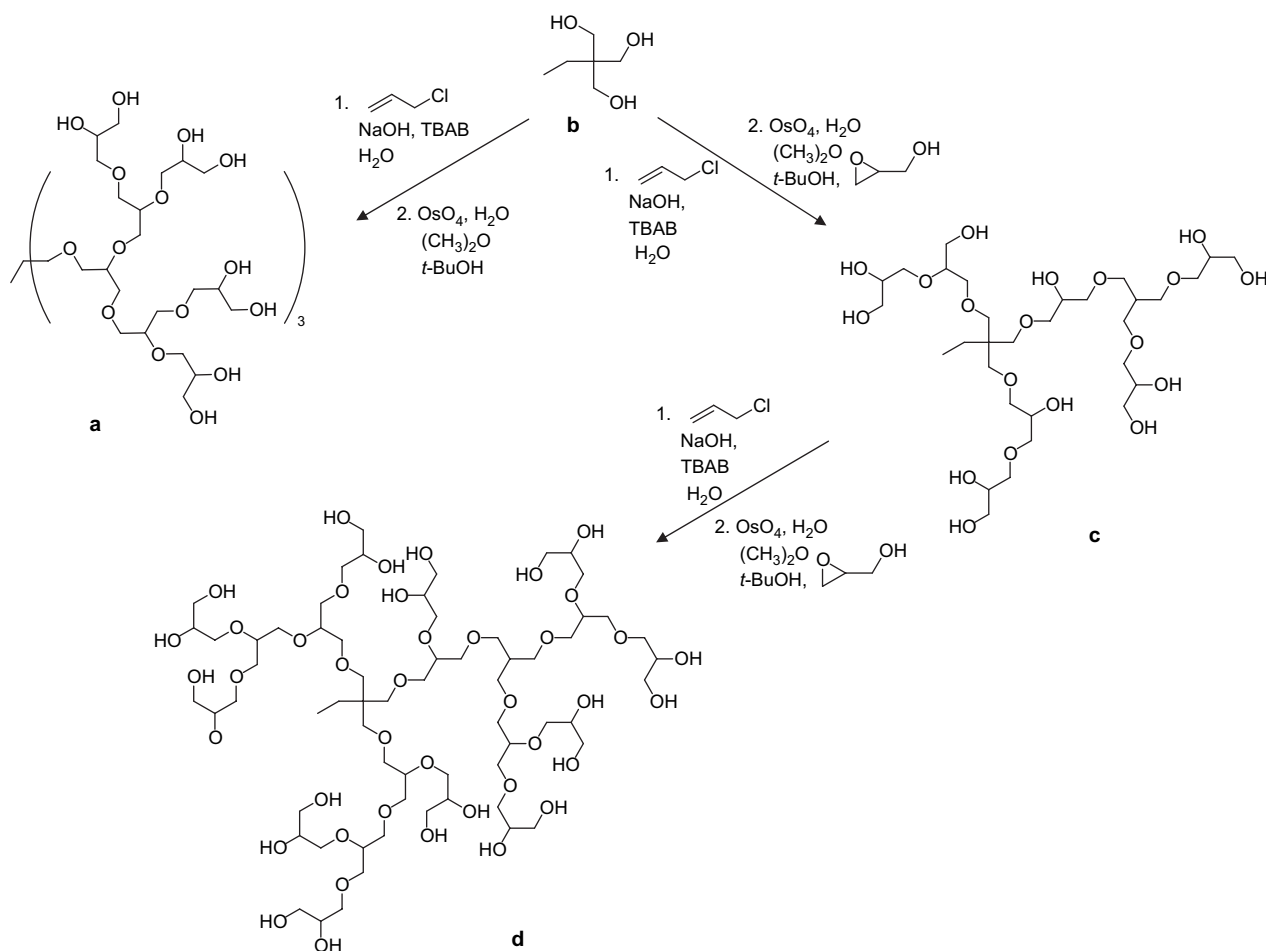
5.3. 1 → 2 C-branched, ether-connectivity

Haag et al. [1608] developed an approach to synthesize glycerol-type (pseudo)dendrimers, in which they started with tris(hydroxymethyl)ethane (**76b**). A three-fold iterative sequence of allylation (allyl chloride, TBAB, NaOH, H₂O), followed by dihydroxylation [OsO₄ (cat), *N*-methylmorpholine *N*-oxide (NMO), H₂O, acetone, *t*-BuOH] [1609] generated the dendritic G3 polyol **76a**. After one iteration of allylation and oxidation, reaction of the core with epihydroxyhydrin afforded the hyperbranched analog **76c**, which was further subjected to allylation and oxidation to yield the “pseudo-dendrimer” **76d** (Scheme 76). Notably, these water-soluble polyglycerols were accessed using aqueous reaction media for each step. Although hyperbranched construction is not the theme of this review, a recent paper by Haag et al. [1610] describing the preparation of core–shell-type dendritic architectures based on hyperbranched polyglycerol for the solubilization of hydrophobic drugs has appeared. A similar series, reported by Park et al. [1611,1612], led to the G4 and

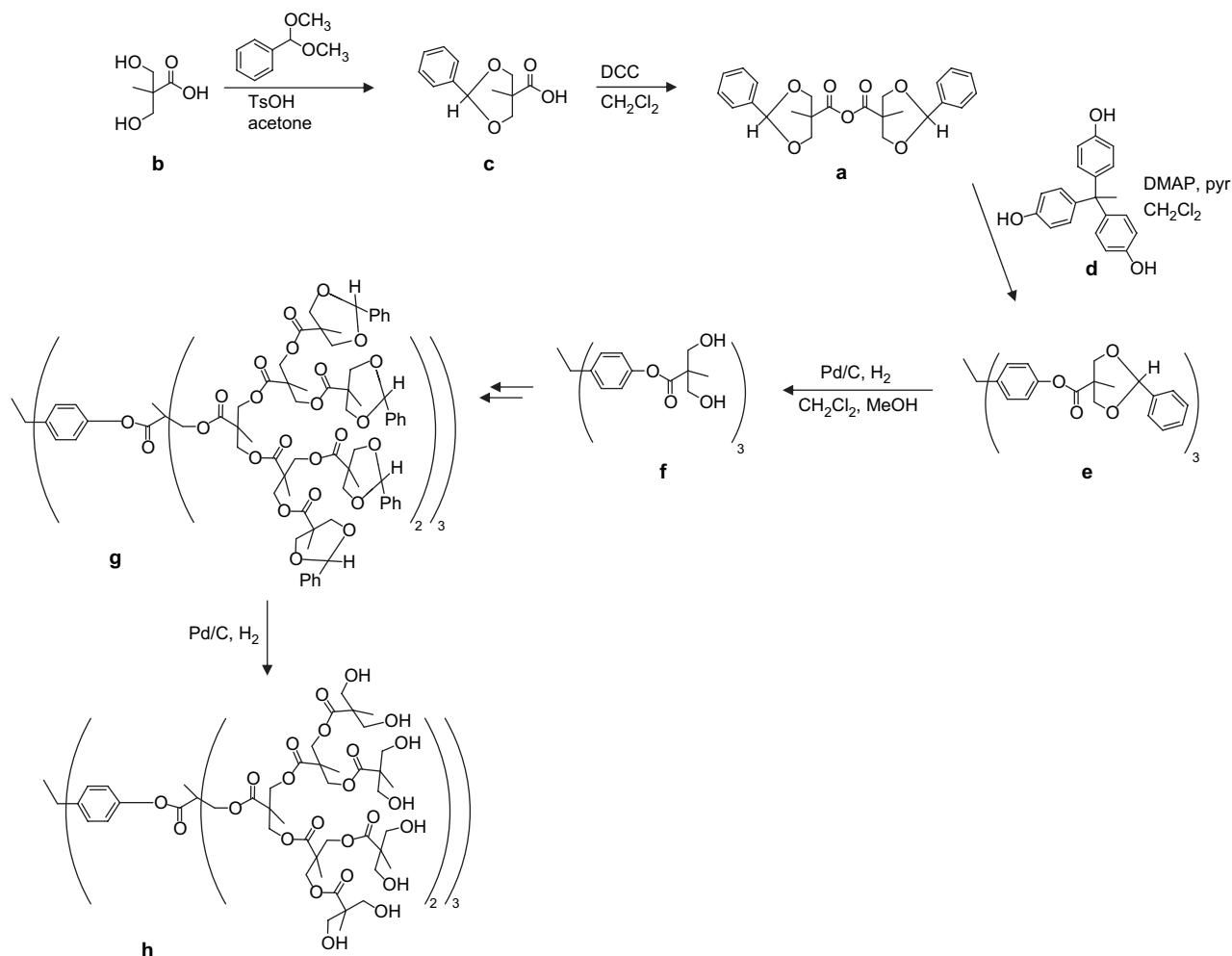
5 hydrotropic dendrimers, which were used to solubilize the poorly water-soluble paclitaxel. Deng and Zhu [1613] recently reported a macromolecular “nanotumbleweed,” which is hyperbranched relative of these dendrimers that can spontaneously break away from a surface when the polymer/surface interactions unfavorable.

5.4. 1 → 2 C-branched, ester connectivity

The use of benzylidene-2,2-bis(methoxy)propionic anhydride [1614] (**77a**) derived from 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) [1615] (**77b**) has opened a convenient pathway to a series of 1 → 2 C-branched ester-linked dendrimers [1616]. Anhydride **77a** was easily prepared in 74% yield from the benzylidene-2,2-bis(methoxy)propionic acid **77c** with DCC in CH₂Cl₂ at 25 °C for 48 h [1614]. Scheme 77 demonstrates the preparation of the key starting reagent **77a** and its subsequent reaction (DMAP) with the core **77d** to build (97%) the G1 protected dendrimer **77e**, which was easily deprotected to furnish (97%) the hexaol **77f**. Iterative treatment of the three-directional hexaol (G1, **77f**) with **77a** followed by deprotection afforded G2, then to G3, and then G4 **77g** and to the polyol **77h** in excellent overall yield. This procedure



Scheme 76. Glycerol-based architectures prepared in aqueous media [1608].



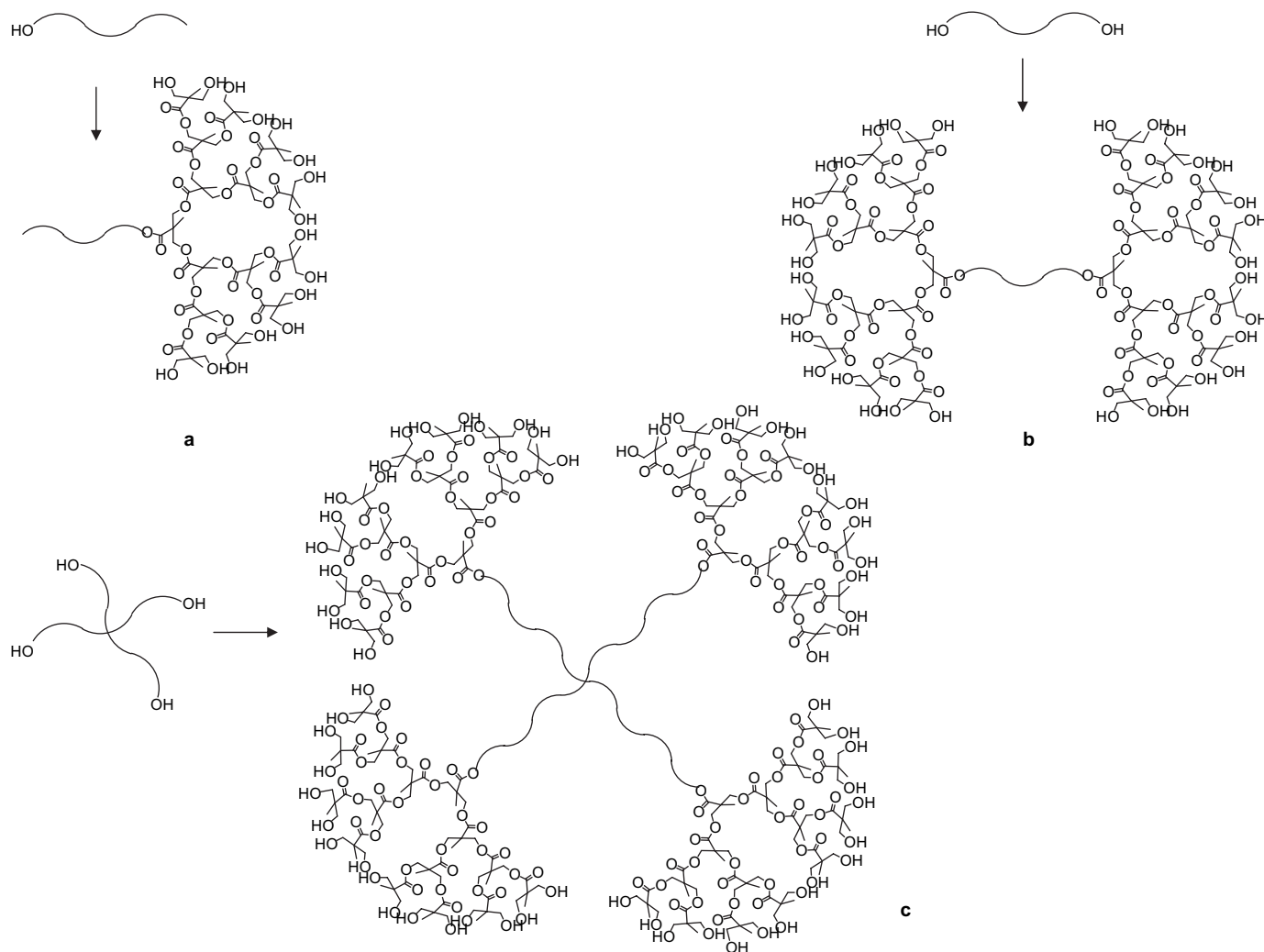
Scheme 77. Synthesis of ester connected dendrimers derived from bis-MPA [1616].

has also been utilized to generate the related one- (**78a**) [1616], two- (**78b**) [1616,1617], and four-directional motifs (**78c**) [1614,1616]. These G2 hydroxyl-terminated aliphatic dendrimers were transformed into liquid crystalline materials by the attachment of mesogens, *e.g.*, 4'-[10-(hydroxycarbonyl)decyloxy]phenyl 4-[4'-(2-(*R*)-octyloxy)-3'-nitrophenyl]-benzoate [1618] or biphenyl counterpart [1619]. Three different families of these polyester dendrimers have appeared: two sets had benzylidene termini with either a trimethylolpropane or triphenolic core and the other had an acetonide termini and triphenol core; all were characterized and their hydrodynamic radius as well as intrinsic viscosity were determined [1620]. Using either 1,1,1-tris(hydroxyphenyl)ethane or trimethylolpropane as the core, the G1 and G2 dendritic reversible addition-fragmentation chain transfer (RAFT) agents with 3-benzylsulfanylthiocarbonylsulfanylpropionic acid RAFT termini were prepared [1621]. These RAFT agents were used to prepare star polymers of poly(butyl acrylate) and polystyrene, each possessing a narrow polydispersity *via* bulk free-radical polymerization at 60 °C. The treatment of **77e** with 3-[12-(3-*tert*-butyldiphenylsilyloxy)propyl]-1,12-dicarbadodecaboranyl-1-(3-propionic acid) afforded a route

to the incorporation of carboranes within the dendritic infrastructure [1622]; the repeated heating/cooling cycles resulted in a decreasing cloud-point temperature and increased dendrimer solubility [1623]. The ToF-SIMS was used to study the dendrons, dendrimers, as well as the related hyperbranched counterparts [1624]. The synthesis and characterization of a dendron-modified regioregular poly(3-hexylthiophene) were reported in which one terminus is linked to the polyester dendron [1625]; these materials will hopefully be applicable for adhesion and light harvesting (Scheme 78).

An attractive new monomer in this series has been created [1552] from bis-MPA by first protecting the free acid moiety *via* the benzyl ester, then treatment with ethyl chlorocarbonate in the presence of Et₃N yielded the cyclic carbonate, which after crystallization was subjected to hydrolysis to afford in nearly quantitative yield the desired HO₂CCMe(CH₂O)₂C=O. These carbonates easily ring-open, when treated with amines [1626].

The amphiphilic dendritic linear copolymers, based on a monomethyl-terminated PEG (MW 5000 and 10,000 g/mol) and G3 polyester dendrons, divergently derived *via* the above procedure, were deprotected to give the desired polyol, which



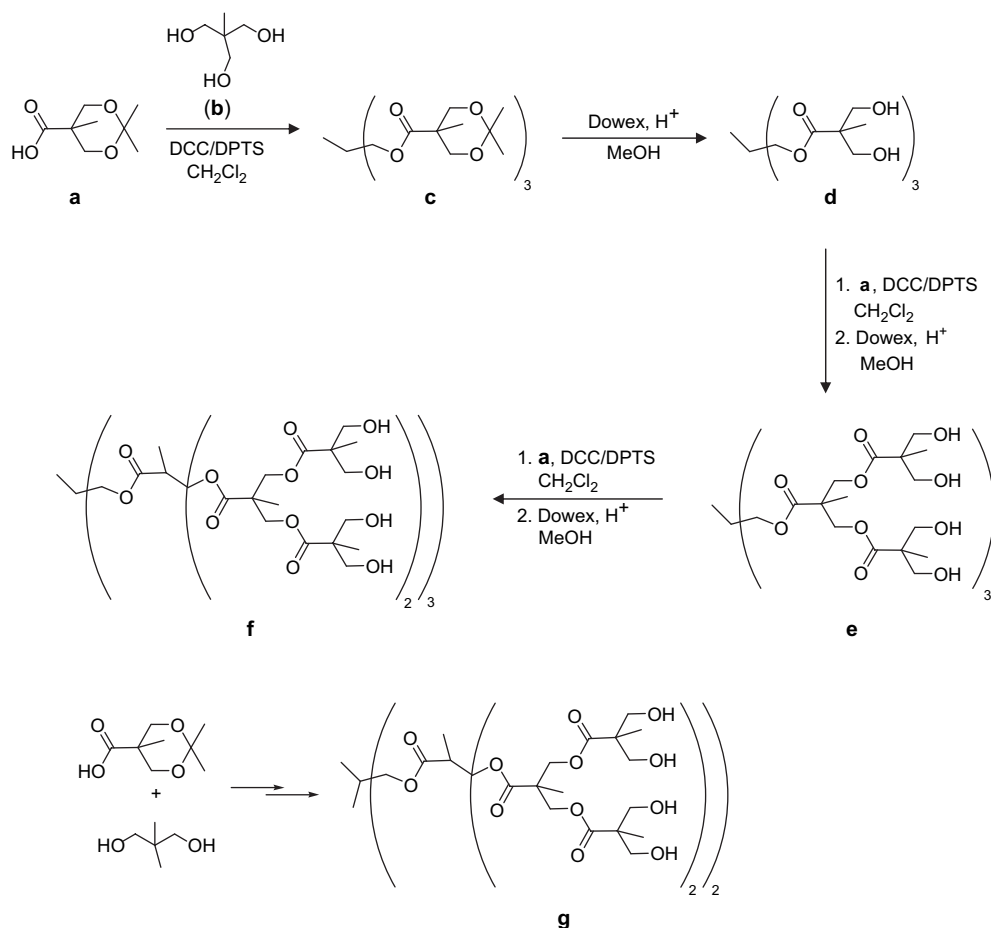
Scheme 78. One-, two-, and four-directional dendrimers with ester connectivity [1616].

was activated with 4-nitrophenyl chloroformate, then treated with 2-(2',4',6'-trimethoxyphenyl)-5-aminodioxane-1,3 [1627] to generate a tri(methoxyphenyl) surface [1628]. Micelle formation was accomplished with adding the fluorescent dye Nile red to generate a pH-responsive micellar system [1629]. In a related study [1630], after deprotection, the capping of the G1–6 dendron polyols with octanoic acid (DCC, DPTS, DMAP) gave the desired amphiphilic copolymers. The use of amphiphilic dendritic linear copolymers, based on a monomethyl-terminated PEG and G3 dendrons, derived from bis-MPA, gave rise to a structure-directing agent for organosilicates to form an oriented perforated porous lamellar morphology. Dendritic and linear block copolymers have been generated from G1–3 dendrons based on 2,2-bis(hydroxymethyl)propionic acid and poly(ϵ -caprolactone) prepared by a living ring-opening polymerization [1631]. A series of G1–4 dendronized poly(norbornene)s has been divergently prepared from 5-norbornene-2-methanol and the acetonide-protected anhydride of 2,2-bis(methylol)propionic acid [1632]; the norbornenyl dendrons were subsequently polymerized *via* a ROMP procedure by means of the Grubbs' first generation catalyst. This type of dendron was grown from a linear

polystyrene backbone then selectively detached from the polymeric support by using a $\text{Pd}(\text{OAc})_2$ catalyst under a hydrogen atmosphere; such a mode of synthesis was proposed to minimize the purification steps.

The treatment of the core tris(hydroxymethyl)ethane (**79b**) with acetonide-protected 2,2-bis(hydroxymethyl)propionic acid (**79a**) [1633–1635] using DPTS and DCC gave rise to the tris-ester **79c** in 100% yield [1617]. The acetonide moieties were removed using Dowex-50 W to afford (79%) the free G1 hexaol **79d**. The simple two-step sequence was repeated to give (80%; 93%) the G2 dodecaol **79e**, which was subsequently transformed to the G3 level **79f**. The related two-directional dendrimer (**79g**) was also created from 2,2-dimethyl-1,3-propanediol; the alternative two-directional core, 1,5-pentanediol, was utilized (Scheme 79).

The divergent construction of dendrons on a microporous resin, poly(2-hydroxyethyl methacrylate-*co*-ethylene dimethacrylate), was demonstrated [1614] by a simple three step approach; the initial reaction of the HEMA–EDMA resin with benzylidene-bis(methoxy)propionic anhydride (**77a**) terminated all of the residual surface hydroxy groups, and then the acetal moieties were selectively deprotecting with dilute

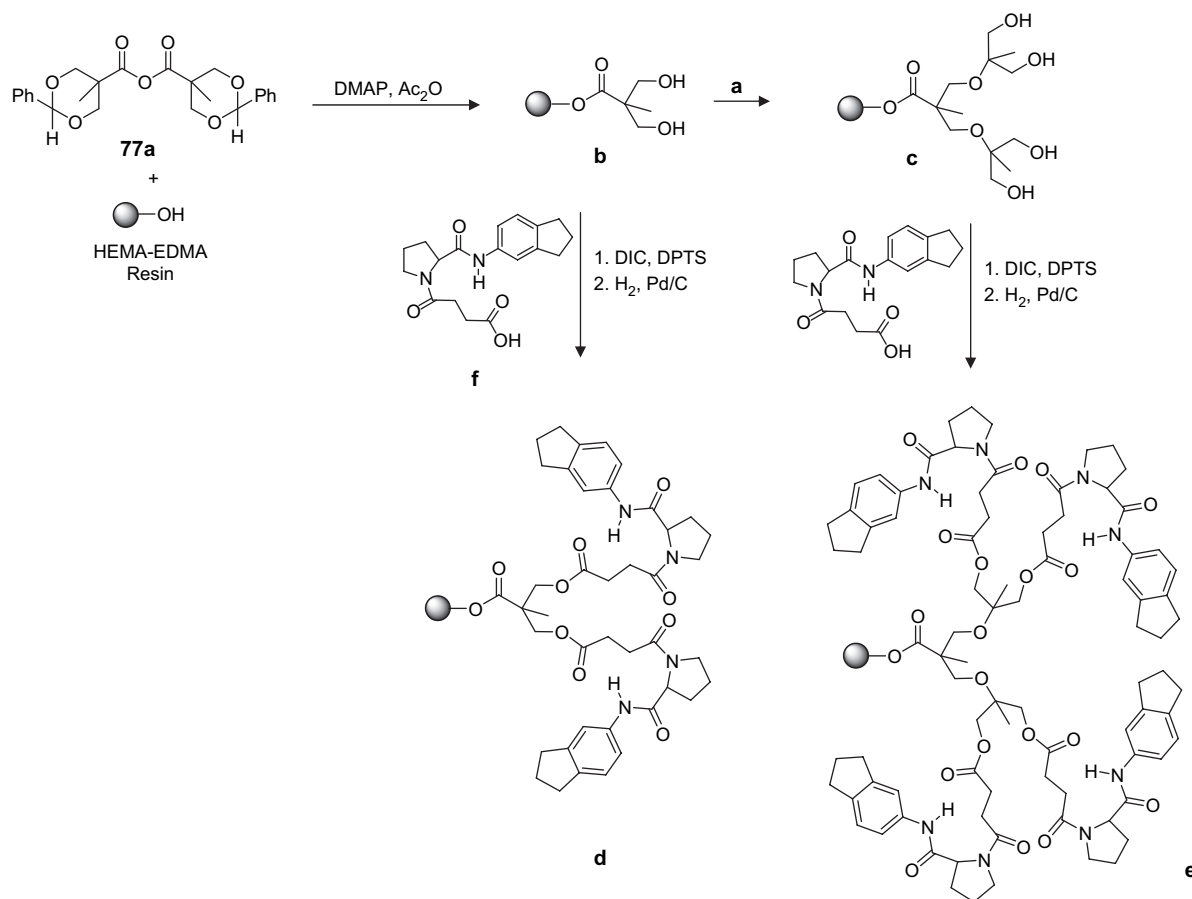


Scheme 79. The use of isopropylidene-2,2-bis(methoxy)propionic acid [1617].

sulfuric acid to give **80b** [1636]. The next tier **80b** was assembled by simple application of the sequential anhydride and hydrolysis steps; however, a convergent approach was also conducted. After surface activation (**80d** and **e**) by treatment of the alcoholic surfaces with acid **80f**, excellent enantioselectivities were achieved in the HPLC separation of racemic *N*-(3,5-dinitrobenzoyl)- α -amino acid alkyl amides (Scheme 80).

The simplicity of this family of dendrimers is exemplified by the construction of “bow-tie” hybrids that can be easily constructed and each side modified independently [1637]; several biological evaluations have recently appeared [1638]. The construction of the first half is demonstrated in the convergent synthesis of **81e** from ester **81a** in three steps. The hydroxymethyl focal moiety was treated sequentially with benzylidene-2,2-bis(methoxy)propionic anhydride [1616] **81f**, then deprotection (Pd/C, H₂) to form **81d**, followed by sequential repetition of these two-steps. Surface tailoring was accomplished by treatment of the resulting **81c** with *p*-nitrophenyl chloroorthoformate, followed by PEO–NH₂ and deprotection of the acetonide groups to generate **81f** (Scheme 81). The diversity of external functionalities offers many different synthetic combinations. The self-assembly of two complementary dendrons, generated in part by the above process, have been attached by the use of bis(adamantylurea) and glycinyurea at the focal points [1639]. Methacrylate polymeric cores

possessing these 1 \rightarrow 2 *C*-branched dendrons have been prepared and evaluated by rheological measurements, DSC, SEC, and ¹H NMR self-diffusion techniques [1640]. A similar polymer with bis-MPA dendrons was divergently constructed *via* an ATRP process [1641]. Four generations of these dendronized polymers possessing a methacrylate backbone were studied by rheology, dynamic light scattering, turbidimetry, and ¹H NMR self-diffusion procedures to afford insight to the effect of increasing hydrophilicity and molecular size on their solution properties; interestingly, these polymers showed low viscosities and Newtonian flow behavior in both aqueous and DMSO solutions [1642]. The treatment of C{CH₂O(CH₂)₂OC(=O)CMe[CH₂OC(=O)CMe(CH₂OH)₂]₂}_4 initially with maleic anhydride and followed by C₆H₅C(=S)SH, generated the desired dendritic RAFT agent possessing 16 dithiobenzoate termini [1643]. Recently, the application click chemistry has been applied to the generation of unsymmetrical dendrimers in this 1 \rightarrow 2 *C*-branched family [1644]; this methodology offers considerable diversity to the assembly process. Dendronized polymers have been synthesized by grafting dendrons onto poly(hydroxy)styrene with initially polyaliphatic esters [1645]; the surface hydroxy groups were treated with 4-pentynoic acid then capped with Fréchet-type dendrons possessing an azide focal group creating a diblock dendron attached to a polymer core. The creation of a G4

Scheme 80. Surface coatings of resins *via* ester connected dendrons [1636].

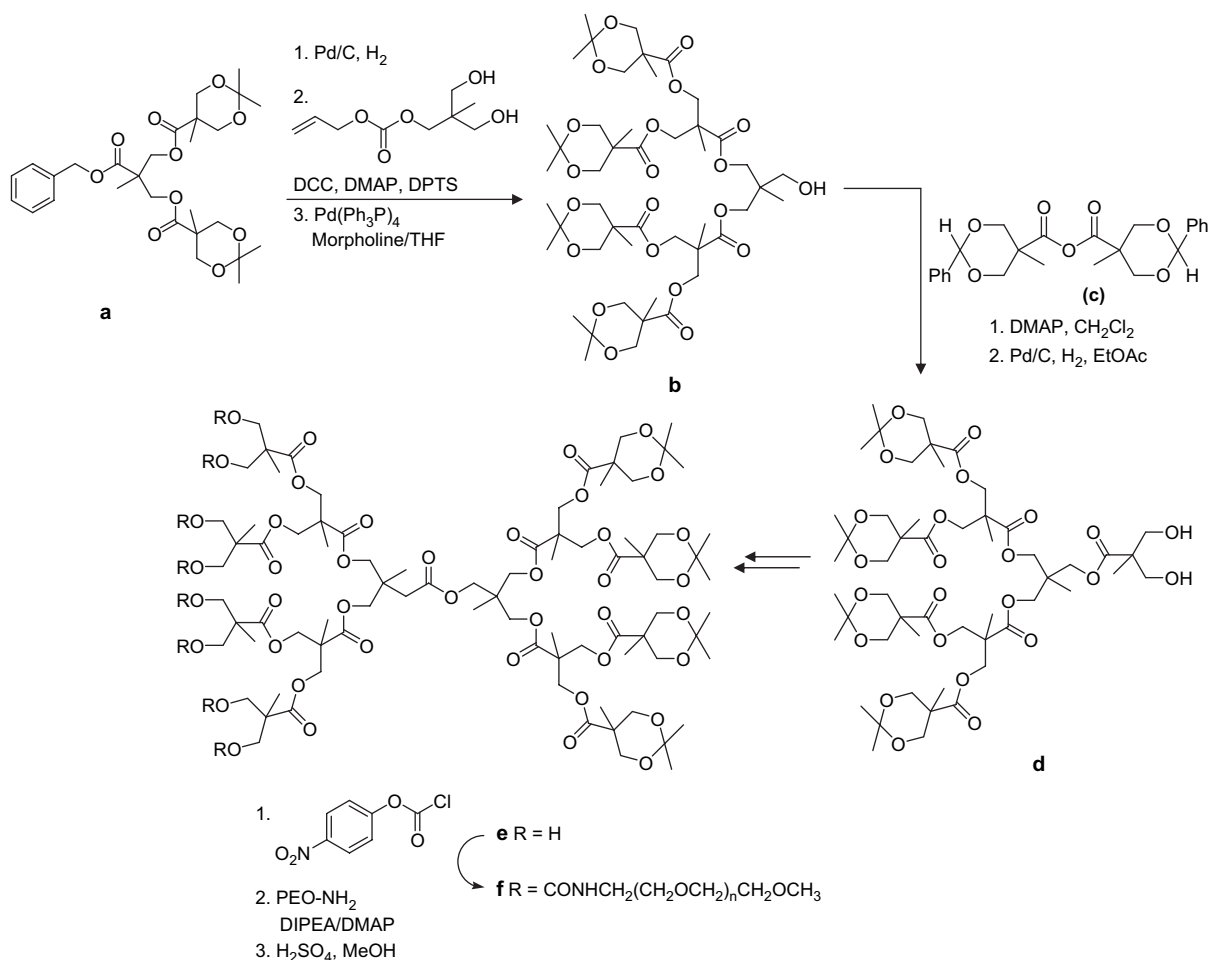
dendron possessing a methyl-PEG focal group has been prepared and then surface coated with diazonaphthoquinone moieties [1646]; it was shown to generate micelles that can release the guests upon infrared irradiation. Click chemistry has recently been used for the chemoselective and accelerated, layered approach to the 1 → 2 *C*-branched dendrimers [1536] with both ester and triazole connectivity.

Hammond et al. [1647] recently reported the construction of an amphiphilic biocompatible comb-dendritic block copolymer that can self-assemble into bilayer vesicles. These copolymers were derived from a bis-MPA-based dendron possessing a focal primary amine, followed by a ring-opening polymerization of the *N*-carboxyanhydride of γ -*n*-dodecyl-L-glutamate with this dendron, and then surface deprotection of the acetonide moieties *via* simple transesterification. They prepared the related tree-shaped macromolecular amphiphiles for nanoparticle self-assembly, based on the bis-MPA dendron, which was fashioned with a PEGED carboxylic acid exterior and the above poly(γ -*n*-dodecyl-L-glutamate) trunk [1648].

Starting from the half-protected pentaerythritol [1649] **82a**, a related Janus molecule was created [1650]. Treatment of **82a** with the protected acid **82b** using DCC and DPST, as catalyst, gave (97%) the desired diprotected **82c**, which was selectively debenzylated by catalytic hydrogenation. Gallate ethereal monodendrons [1651] **82d** were appended by the same esterification procedure. Then, removal of the acetonide protection

by mild treatment with acid gave the free terminal hydroxyl sites **82e**. The next generation was assembled by reaction with **82b**, followed by deprotection to give **82f** in high yields (Scheme 82). Beginning with such monoprotected starting materials offers a convenient route to the unsymmetrical “bow-ties.”

The dendronized hybrid dendritic and linear polymers have been created *via* either a “graft-onto” or ATRP procedure with the appropriate macromonomer [1652]. In either case, the main polymeric core was derived from acrylate units and the dendron attachments were derived from 2,2-bis(methylol)propanoic acid (bis-MPA) repeat units, as demonstrated above [1616]. The authors initially concluded that the ATRP procedure at G3 macromonomer failed whereas the “graft-onto” route was successful at that tier level; however at $G > 3$, they experienced problems associated with deprotection. They later used a 10-carbon flexible spacer and successfully polymerized the macromonomer by ATRP conditions and investigated the kinetics of this transformation [1653]. An alternative route to dendronized linear polymer was by the initial Sn(II) 2-ethylhexanoate-catalyzed polymerization of a γ -functionalized ϵ -caprolactone monomer, then the divergent construction of the dendron by hydrogenolysis was followed by anhydride **81f** with DMAP, as the acylation catalyst; up to the G4 dendron were assembled by this methodology [1654]. The organic unimolecular self-organized polymers

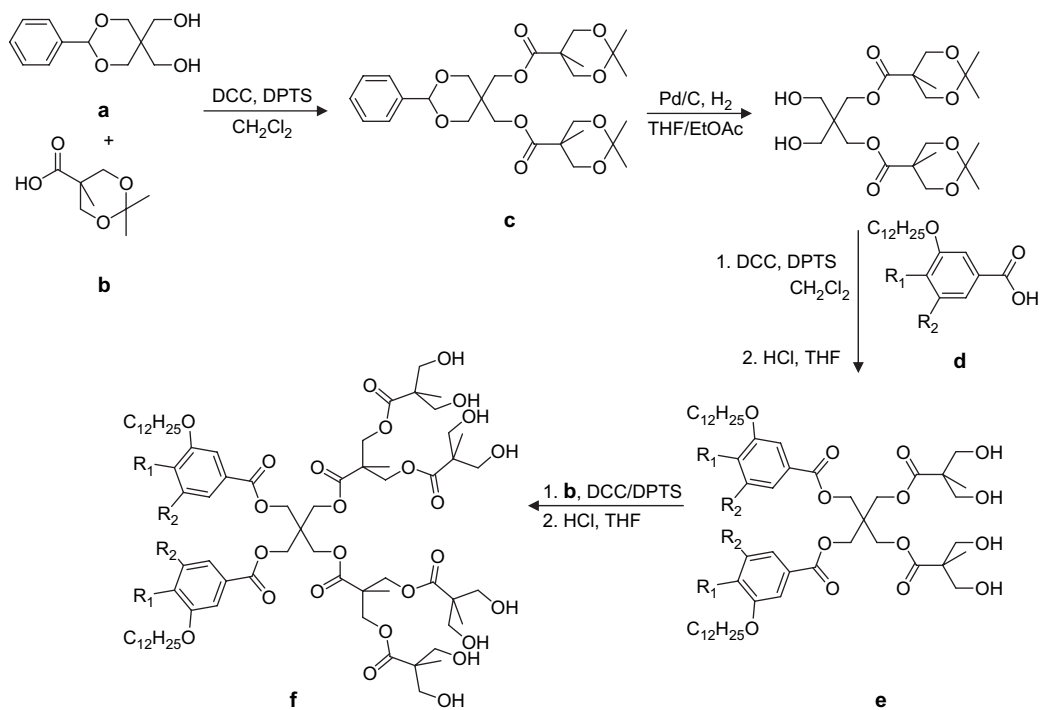


Scheme 81. Step-wise construction of “bow-tie” polyfunctional two-directional dendrimers [1637].

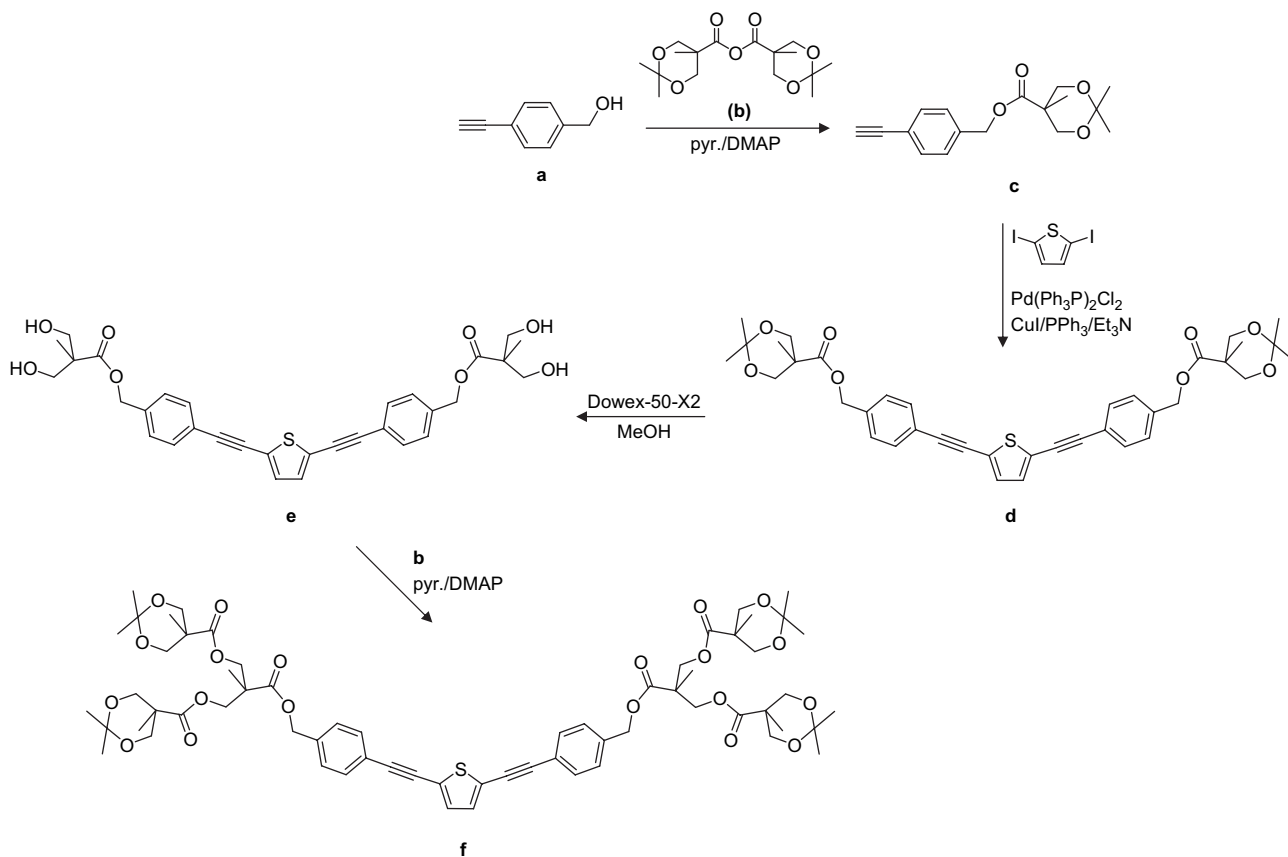
possessing the G1–3 bis-MPA dendritic core [1655] (e.g., **77d**), prepared by either tandem ring-opening or ATRP, were dispersed into thermosetting organosilicate, then thermalized to leave a latent image in the matrix [1656]. The resultant pore size mimicked the size dimensions of the polymer and provided the expected reduction in dielectric constant.

Both the free tetraphenylporphyrin, as well as its zinc complex, were used as a core to divergently generate the 2,2-bis(methylol)propionic acid-based dendrimers. The 5,10,15,20-tetrakis(4-hydroxyphenyl)-21*H*,23*H*-porphine in DMAP was treated with acetonide-2,2-bis(methoxy)propionic anhydride to generate the protected G1 dendrimer. Deprotection was conducted by simple treatment with the acidic DOWEX-50-X2 [1633] in MeOH and THF for various lengths of time (3–14 days); reiteration of this two-step procedure afforded up to G5. These bis-MPA dendrimers were shown to be much smaller than the corresponding Fréchet-type benzyl ether TPP dendrimers [1657]. The treatment of ethylenediamine with 5 equiv. of trimethylolpropane triacrylate [(CH₃CH₂C(CH₂OC(=O)CH=CH₂)₃] was carried out at 30 °C in MeOH over 6 h to afford {CH₂N[CH₂CH₂C(=O)OCH₂CEt(CH₂OC(=O)CH=CH₂)₂]₂} in unspecified yields [1658].

Dendrimers have been synthesized from the 2,5-bis(phenylethynyl)thiophene core by initially preparing 4-ethynylbenzyl alcohol (**83a**; two steps from 4-bromobenzyl alcohol with 2-methyl-3-butyne-2-ol, followed by deprotection), which was reacted with anhydride **83b** to give the dendron **83c**. The Sonogashira coupling [1659–1661] of **83c** with 2,5-diiodothiophene gave the desired protected core **83d**, then simple hydrolysis followed by the key anhydride **83b**. Up to the G4 dendrimer **83f** was created by this repetitive sequence [1662] (Scheme 83). In an related manner, the use of di[4-(hydroxymethyl)benzyl] malonate as the core, furnished the platform for the creation of the G1,2 dendrimers *via* the use of acetonide-2,2-bis(methoxy)propionic anhydride; the subsequent deprotection generated the corresponding polyols, which were capped with 2-bromoisobutyryl bromide in the presence of pyridine [1663]. In the presence of *tert*-butyl acrylate, these polyfunctional initiators were transformed (ATRP) to the corresponding poly(*tert*-butyl acrylate)s, which *via* a Bingel cyclopropanation [1664], the core was attached to C₆₀. Similarly, the hydroxy-terminated G3 dendrimer [1614], based on the tris(4-hydroxyphenyl)methane, was transformed to the polyester star-shaped polymer *via* treatment with lactide with the commercially available 1,3,4-triphenyl-4,5-dihydro-1*H*-



Scheme 82. Divergent creation of unsymmetrical “bow-ties” [1650].



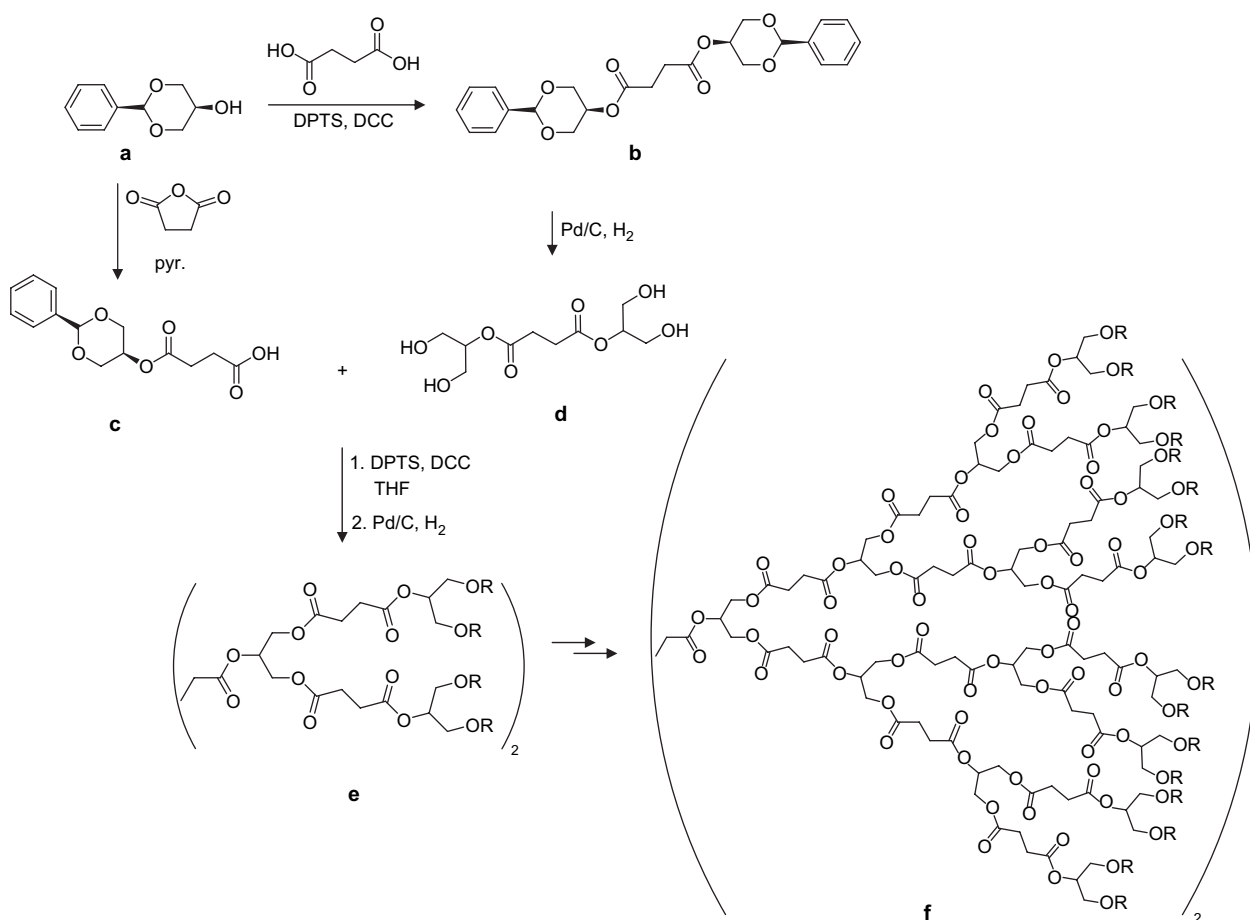
Scheme 83. Divergent synthesis of a two-directional dendrimer with a thiophene core [1662].

1,2-triazol-5-ylidene carbene [1665]; the process was applied to the formation of dendritic-linear, di-, and triblock copolymers. The dendronization up to G4 of poly(L-lysine) using **83b** has recently been reported [1666].

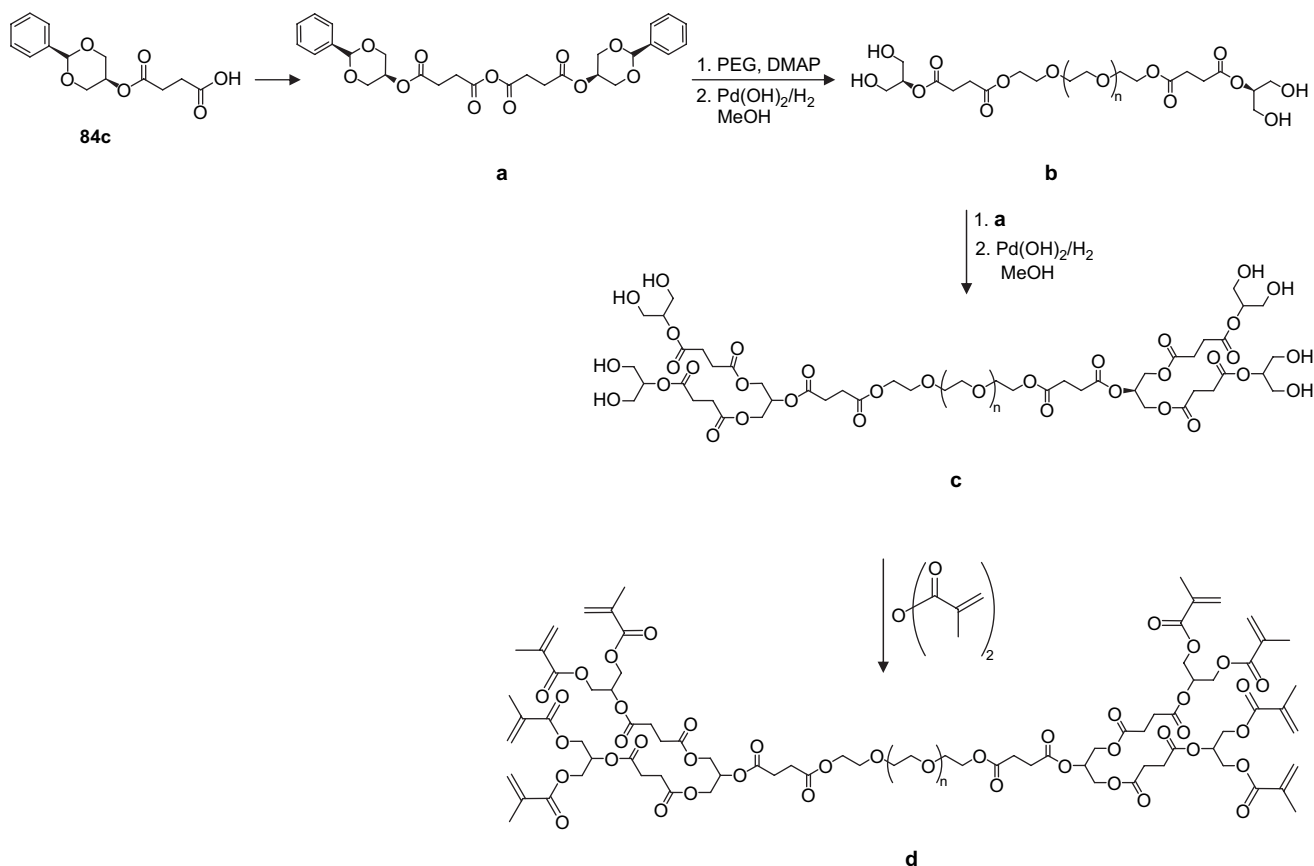
Carnahan and Grinstaff [1667] have created new avenues to biodendrimers based on a novel combination of glycerol and succinic acid to generate the key monomer **84a** and core **84c**; also see Grinstaff's review concerning polymeric biomaterials for tissue engineering [53]. Treatment of *cis*-1,3-*O*-benzylidenglycerol (**84a**) with succinic anhydride in pyridine formed (95%) the branching succinic acid mono(2-phenyl-[1,3]dioxin-5-yl) ester **84c**; whereas monomer **84a** with succinic acid in the presence of DCC and DPTS afforded (90%) the intermediary bis-acetal **84b**, which was deprotected (Pd/C, 50 psi H₂) to yield (97%) the desired tetraol core **84c**. Treatment of this core with 4 equiv. of the monomer **84c** (DCC, DPTS, THF) gave (97%) the tetraprotected G2 dendrimer **84e** (R = C₆H₅CH₂), which was deprotected (H₂, Pd/C, THF) to give (94%) the free octaol **84e** (R = H). This procedure was repeated to furnish the larger G3 and G4 species; the materials are known to be biocompatible and degradable *in vivo* to natural metabolites. Treatment of **84c** with DCC generated (95%) the corresponding anhydride **85a**, which was reacted with a PEG (3400 MW) as the core, in the presence of DMAP, followed by deprotection [Pd(OH)₂/C in H₂

(60 psi)] to generate (97%) the tetrafunctional **85b**. Repetition of this sequence using monomer **85a** afforded the G2 (**85c**)–G4 dendrimers [1668]. Treatment of these hydroxyl-terminated dendrimers (*e.g.*, **85c**) with methacrylic anhydride in the presence of DMAP gave a family of photocross-linkable dendritic gels (*e.g.*, **85d**) that were shown to possess sufficient tissue adhesive properties to seal corneal lacerations. The synthesis and properties of this type of aliphatic dendrimers possessing glycerol and various layers of succinic and adipic acids have been reported in detail [1669]. The synthesis of G4 bola-type linear-dendritic macromolecules and their application for ocular wound repair are interesting applications for biomedical purposes [1670–1676] but other application for this type of dendrimer are also useful [1677,1678] (Schemes 84 and 85).

The conventional laser-dye, 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyrane, was encapsulated into the G5 dendrimer in this family and shown to be a high-gain media for laser emission [1679]; this material demonstrated an ability to decrease the lasing threshold intensity by increasing the dye concentration. In order to demonstrate the drug delivery potential to these biodendrimers, the highly solvatochromic Reichardt's dye, as well as a poorly water-soluble anticancer drug 10-hydroxycamptothecin, were encapsulated in the carboxylated G4 poly(glycerol succinic



Scheme 84. The 1 → 2 C-branching dendrimers with ester connectivity [1667].



Scheme 85. PEGed core two-directional dendrimers with terminal cross-linking functionality [1668].

acid)s and the latter was successfully subjected to cytotoxicity assays with human breast cancer cells [1680]. In an expansion of this work [1681], the assembly formed between Reichardt's dye and a triblock polymer, derived from glycerol, succinic acid, and polyethylene glycol, [(G4) poly(glycerol-succinic acid)-OH-PEG₃₄₀₀ dendrimer] was created *via* a divergent approach by sequential esterification and hydrolysis procedures with succinic acid mono-(2-phenyl-[1,3]-dioxane-5-yl) on a PEG diol core [1668,1670]. The anticancer drug 10-hydroxycamptothecin has been encapsulated with this dendritic supra-molecular assembly [1681].

Luman and Grinstaff [1682] have synthesized an interesting family of dendritic amphiphiles that were formed by the above procedures from glycerol, succinic acid, and myristic acid. These two-directional dendritic species, similar to unsymmetrical bow-ties [1639,1650], can be generated by the convergent attachment of dendrons prepared by either the divergent or convergent approach and in a tailored manner that permits the control over the hydrophobic-to-hydrophilic ratio.

The convenient synthesis of an AB₂ building block was obtained by the reaction of benzyl acetoacetate and 2 equiv. of *tert*-butyl acrylate to generate a benzyl and di-*tert*-butyl triester **86a**, which upon catalytic reduction and decarboxylation, gave the ketodiester **86b** [1683]. Subsequent reduction with NaBH₄ gave the desired AB₂ building block **86c**. Deprotection of the ketone **86b** with formic acid, followed by EDCI/DMAP catalyzed esterification with 2 equiv. of **86c** formed G1

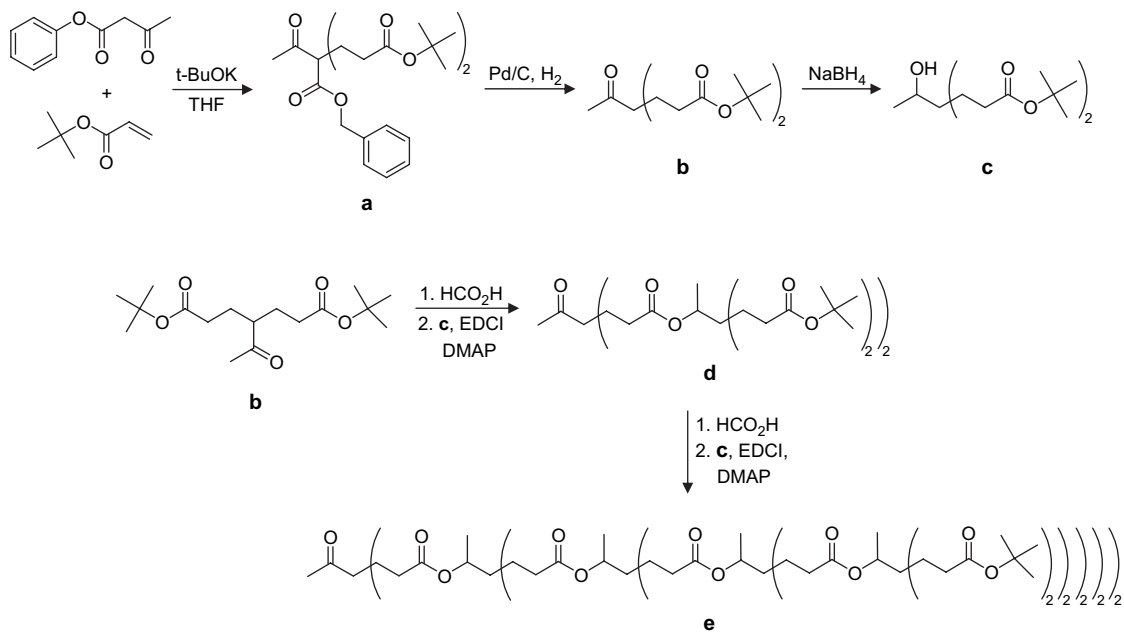
86d; repetition of the simple two-step sequence eventually gave the G4 product **86e**, possessing a novel central ketone moiety (Scheme 86).

A convenient monomer **87a** was prepared from the protected (benzyl or TBDMS) unsymmetrical 3-hydroxyacetophenone by treatment with benzyl or *tert*-butyl acrylate, allowing each end to be selectively deprotected (catalytic reduction or TBAF, respectively) or de-esterified (catalytic reduction or TFA, respectively) [1684]. Thus, the selective combinations of these reagents led to either divergent or convergent pathways to *C*-dendrimers. For example, treatment of diacid **87d** with phenol **87e** gave (65%) the tetraester **87f**, then deprotection (Pd/C, H₂) generated the corresponding tetraacid, which was treated with **87c** to give (59%) the G3 **87e** (Scheme 87).

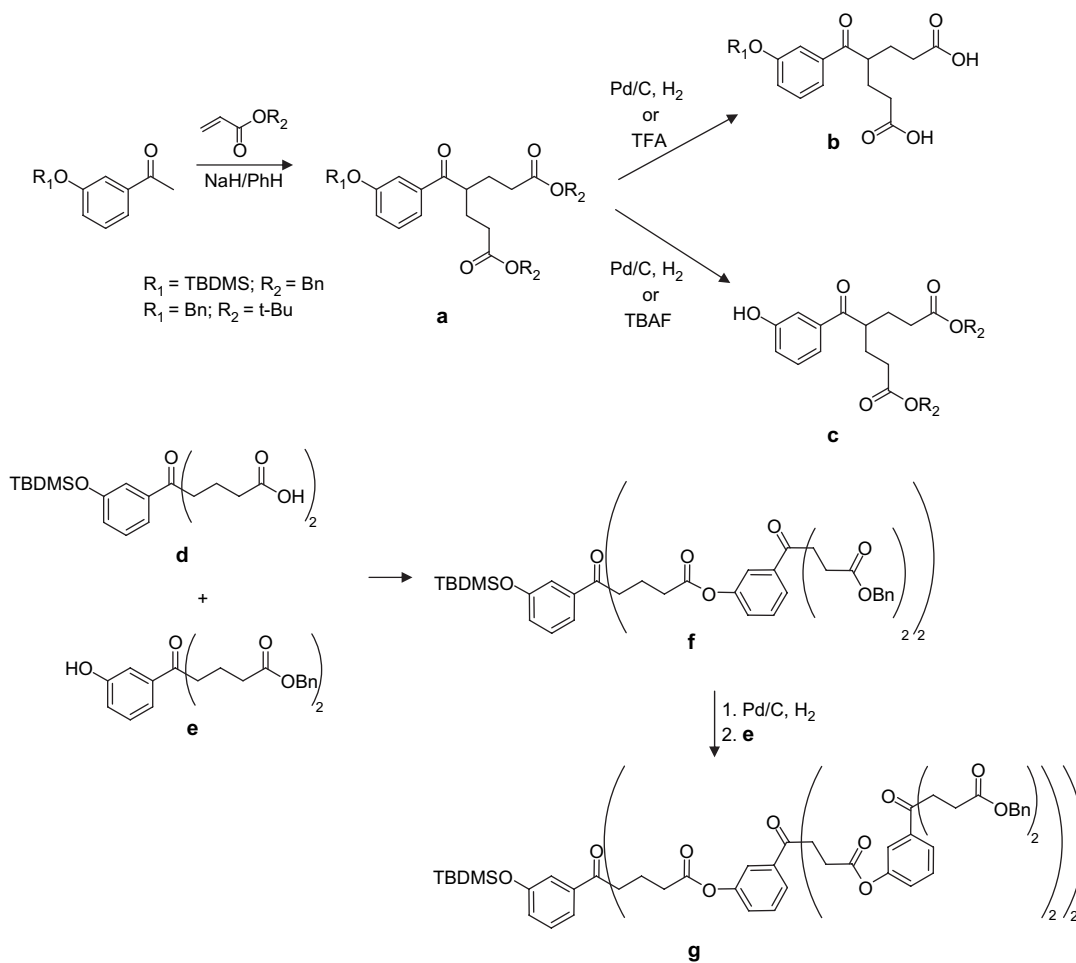
5.4.1. Dendrons with 1 → 2 *C*-branched, ester connectivity

Different cores have been utilized as the starting point for this simple protocol such as 2,2',4,4'-tetra(oxaundecanol)benzophenone (as an internal singlet oxygen sensitizer) [1685] and poly(*p*-hydroxystyrene) (high molecular weights >100,000 and water-soluble) [1686].

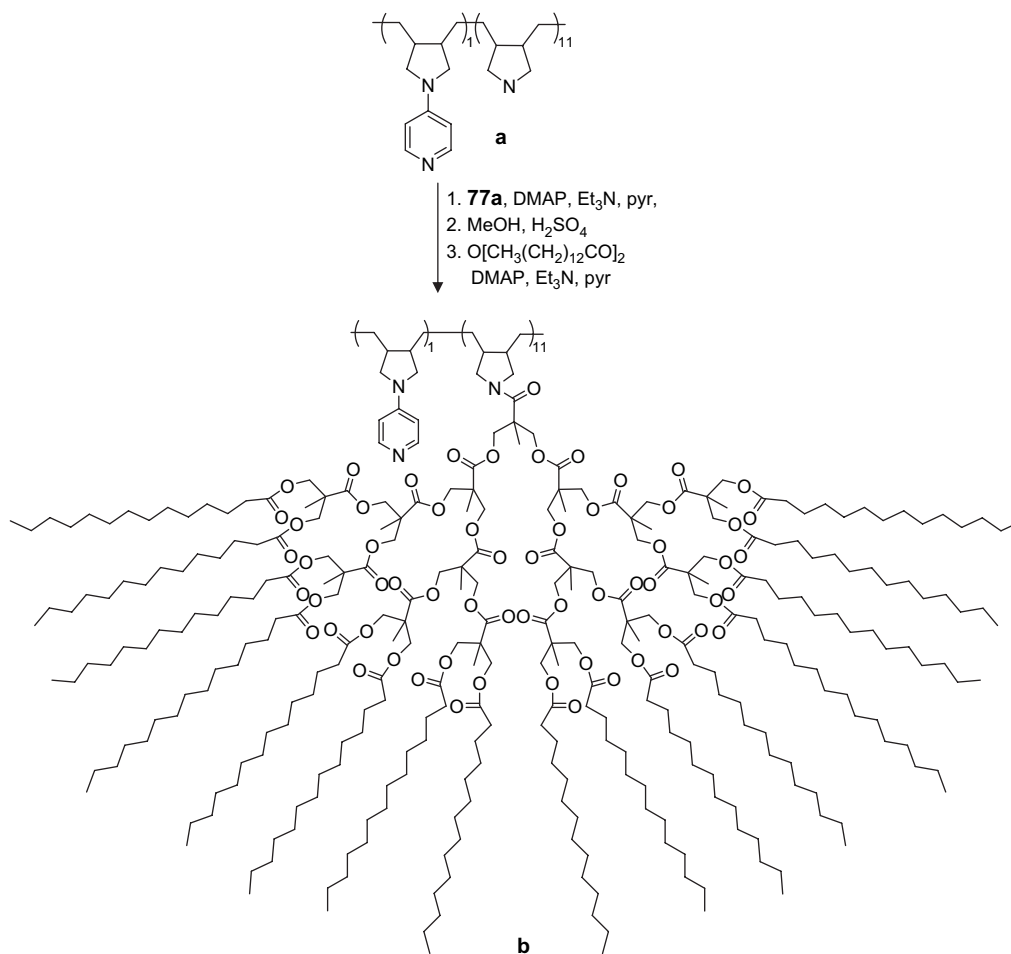
The random (1:11) cyclocopolymer [1687] core **88a** was transformed by the initial treatment with anhydride **77a** followed by hydrolysis and repetition of the sequence two additional times, followed by capping with myristic anhydride [1688]. This functionalized polymer **88b** was used to catalyze



Scheme 86. Synthesis of polyester dendrimers [1683].



Scheme 87. Synthesis of dendrimers and dendrons via a 3-hydroxyacetophenone starting material [1684].



Scheme 88. The synthesis of a dendronized cyclopolymers capable of esterification catalysis [1687].

the esterification of a tertiary alcohol with pivalic anhydride (Scheme 88).

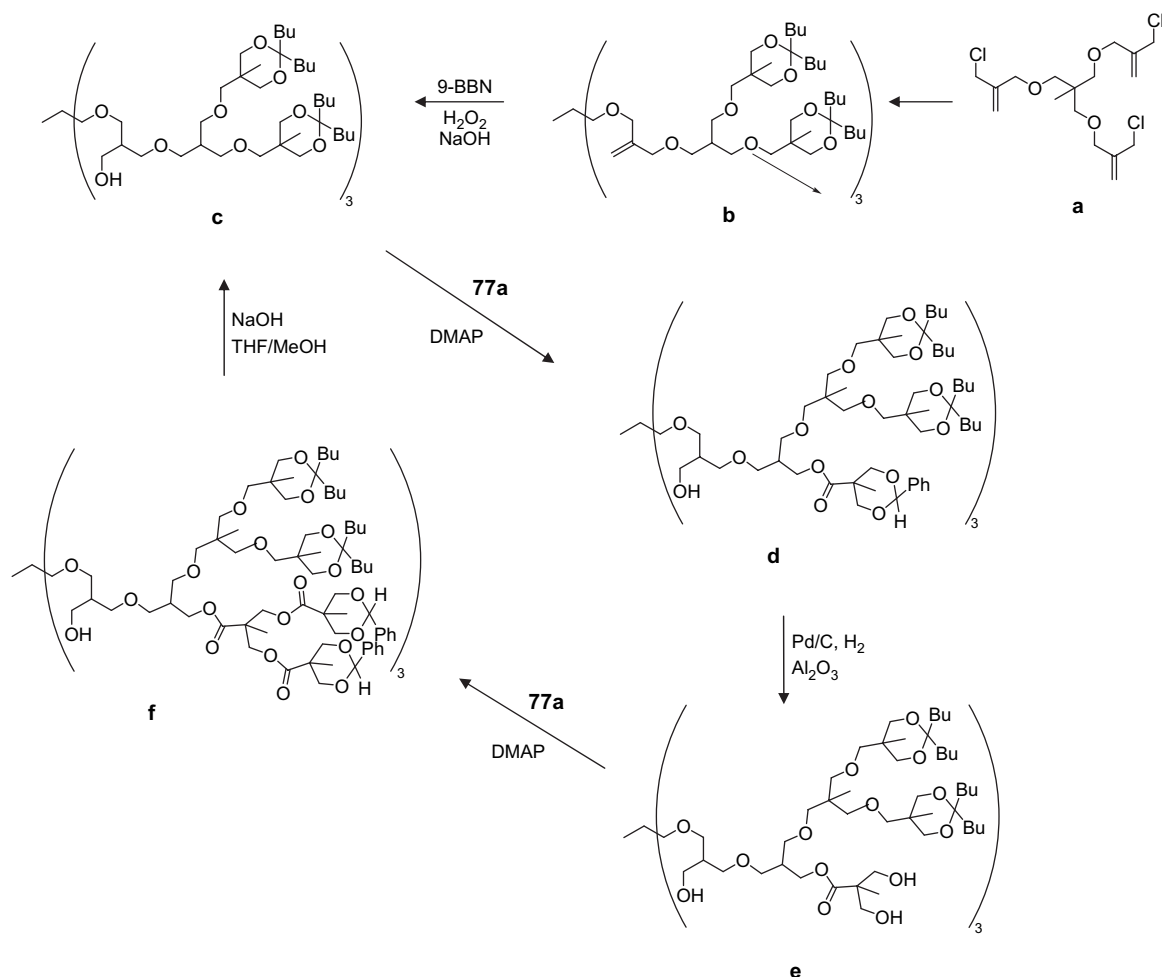
Recently, carborane-functionalized polymers were dendronized *via* a divergent procedure to incorporate 1–4G aliphatic polyesters from the polymeric core [1689]; the nitroxide-mediated polymerization of carborane-functionalized styrenic monomers gave well-defined polymers possessing a high boron content.

5.5. 1 → 2 C-branched, ester and ether connectivity

Treatment of 1,1,1-tris(hydroxymethyl)ethane with excess 3-chloro-2-chloromethyl-1-propane in DMF gave the desired triallyl core **89a**, which can be easily transformed *via* convergent methodology to **89b** [1690]. Subsequent reaction with 9-BBN followed by oxidation with hydrogen peroxide gave the internal activated primary hydroxyl moieties, as in **89c**. Reaction of these alcoholic sites with anhydride **77a** with a catalytic amount of DMAP gave **89d**, which was easily deprotected (Pd/C, H₂) to generate the hexaol **89e**. Addition of **77a** gave the next tier and repetition would give rise to the higher generations, *e.g.*, **89f**; whereas saponification regenerated the internal hydroxy groups **89c** (Scheme 89).

5.6. 1 → 2 C-branched, ether and sulfone-connectivity

Using activated aryl fluoride sites for monomer attachment, Martínez and Hay [1691,1692] constructed a series of poly-(aryl ether) dendrimers. Key fluoro-sulfide-containing phenolic monomers **90a**, prepared in three steps by the reaction of 4,4'-dichlorobenzophenone with 2 equiv. of 4-fluorothiophenol, added C₆H₅MgBr, and the acid-catalyzed carbonium ion addition to phenol were dimerized (triphosgene) to give an aryl carbonate **90b**. The carbonate moiety was then cleaved *in situ* (155–165 °C) using a metal carbonate, which essentially eliminates water formation (*e.g.*, as occurs on generation of a phenoxide using a hydroxide, as the base) as well as the need to remove the initial water from the starting material. Thus, reaction of carbonate **90b** with bis(4-fluorophenyl)sulfone (**90d**) in the presence of a CaCO₃/Cs₂CO₃ mixture yielded the G1 dendrimer **90e** by means of phenoxide (*i.e.*, **90c**) displacement of the sulfoxide-activated aryl fluoride. Oxidation (wet alumina/oxone) of the sulfide moieties to sulfones facilitated repetition of the strategy to give the G3 dendrimer **90f** (Scheme 90). Formula weights of the materials ranged from 1392 to 19,239 amu for G1–4, while measured *T*_gs increased with generation from 92 to 231 °C. The linear copoly(arylene ether sulfone) was synthesized from relatively



Scheme 89. The divergent construction within a preformed dendrimer [1690].

high molecular weight bisphenol containing two 4-fluorophenylthio moieties along with bisphenol-A and reacted with bis(4-fluorophenyl)sulfone and Cs_2CO_3 , followed by oxidation with performic acid [1692]. A relatively high molecular weight bisphenol possessing two pendent 4-fluorophenylthio groups was also transformed to a poly(arylene ether sulfone) that can also act as the dendritic core [1693].

5.7. 1 → 2 C-branched, Si(Me)₂- and thioether-connectivity

Treatment of core **91a** with allylmagnesium bromide gave the G1 intermediate **91b**, which was subsequently reacted with $\text{C}_6\text{F}_{13}\text{CH}_2\text{SiMe}_2\text{H}$ in the presence of a Pt catalyst to afford the desired fluorinated **91c** or with 1,1,2-trifluorobutyl-1-enyl-4-magnesium bromide to yield the simpler fluoro product **91d** [1694]. The related Si-branched dendrimers **91e** were also transformed by similar methods; see 1 → 2 Si- and C-branched section (Scheme 91).

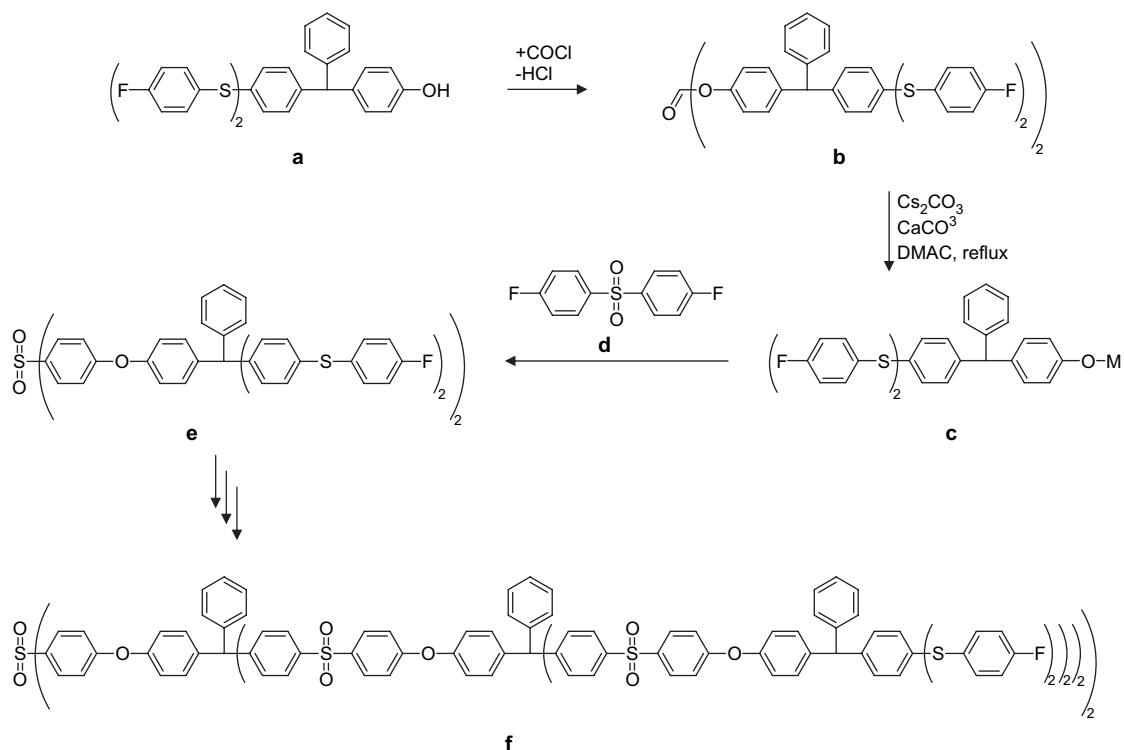
5.8. 1 → 2 Alkene-branched, alkyne-connectivity

Neckers et al. [1695] reported the synthesis of a series of dendritic enynes (“Y-enynes”) from di- (**92a**) and tri- (**92c**)

formylbenzene, which were transformed [1696] to the corresponding 2,2-dibromovinyl derivatives **92b** and **d**, respectively. These intermediates were then treated with 1-dodecyloxy-4-ethynylbenzene [1697] (**92e**) under Sonogashira coupling conditions [1660,1698] to give the desired bis-1,4- (**92f**) and tris-1,3,5- (**92g**) [2,2-bis(4-dodecyloxyphenylethynyl)ethenyl]benzenes, respectively. Both Y-enynes were highly fluorescent in solution and solid state. The extension [1699] of this process utilized 4-ethynylbenzaldehyde [1700] (**93a**) in which **92c** was reacted with **93a** in the presence of $(\text{PPh}_3)_2\text{PdCl}_2/\text{CuI}$ to generate the branched (G1) species **93b**. Subsequent treatment of **93b** with CBr_4 and PPh_3 gave (57%) **93c**. Repetition of the procedure afforded a simple route to assembly G2 (**93d**) and G3 (**93e**) in moderate yields for each conversion (Schemes 92 and 93).

5.9. 1 → 2 C-branched, carbamate-connectivity

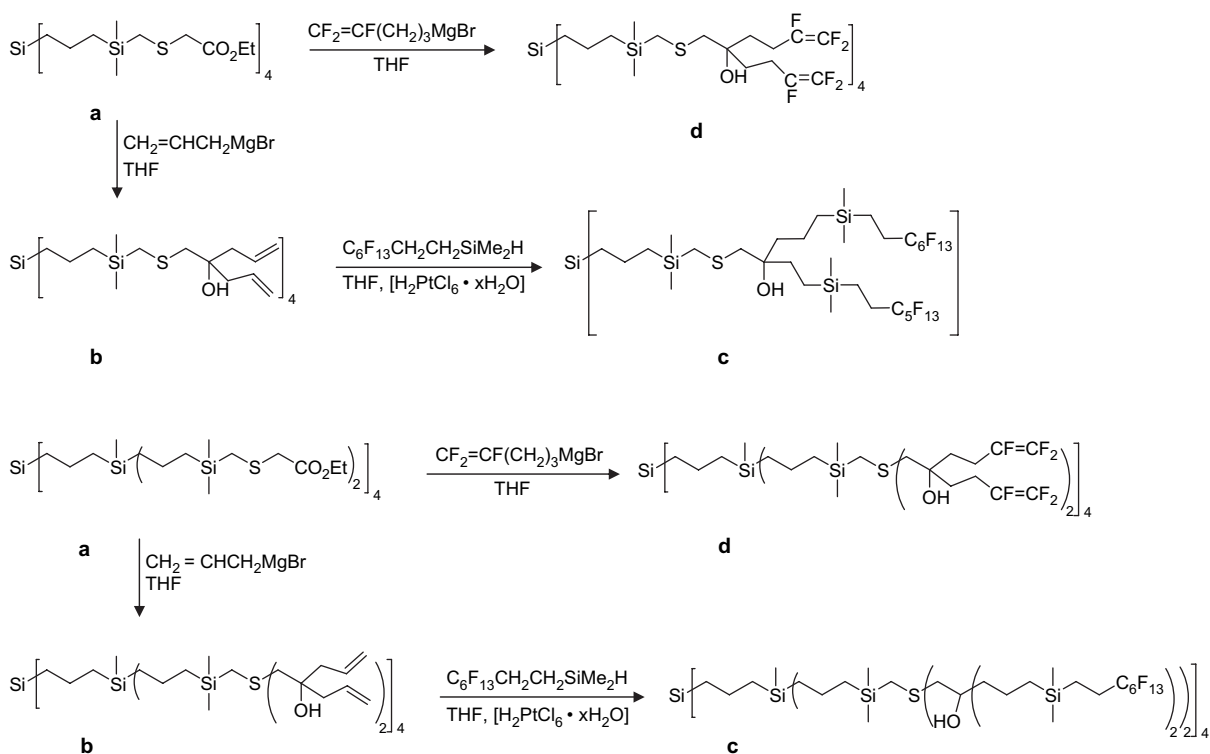
Treatment of a bifunctional PEG2000 with *p*-nitrophenyl chloroformate activated the termini, then the addition of 2-aminopropane-1,3-diol gave the desired carbamate **94a** possessing four hydroxyl end groups [1701]. A second (mono-activated) reagent was created by the monofunctionalization of similar molecular weight PEG materials by reaction



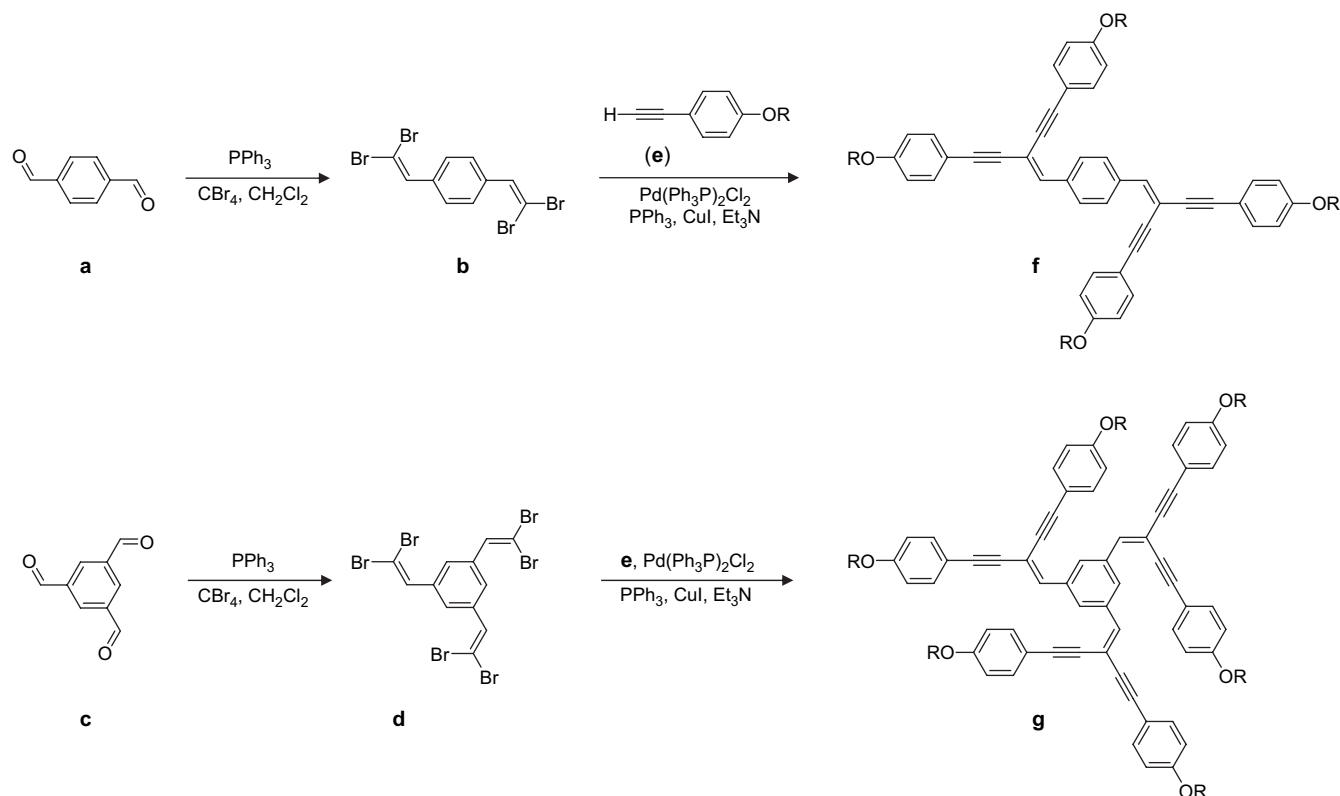
Scheme 90. Construction of fluoro-sulfide-based dendrimers [1691] via carbonate masked monomers.

with 4,4'-dimethoxytrityl chloride, followed by succinic anhydride, ion exchange and then ammonium hydroxide to generate the intermediate terminal monohydroxy end group, which was activated and amino-capped with 1,3-diaminopropane to give amine **94b**. Treatment of tetraol **94a** with *N,N'*-

disuccinimidyl carbonate then the monoamino-PEG generated the G1 pentaPEG product **94c**. Deprotection with trichloroacetic acid, activation with *N,N'*-disuccinimidyl carbonate, and lastly, treatment with 2-aminopropane-1,3-diol gave G2 octaol **94d**. These multifunctional, soluble, and biocompatible



Scheme 91. The preparation of fluorinated dendrimers possessing a Si-core and connectivity [1694].



Scheme 92. The simple synthesis of Y-enynes [1695].

polyPEGs were shown to exhibit good physicochemical properties (Scheme 94).

5.10. 1 → 2 C,N-branched, ester-connectivity

A simple procedure to dendrimers has been reported that was conducted under mild conditions and without the cumbersome protection-deprotection steps [1702]. When ethylenediamine was treated with trimethylolpropane triacrylate (**95a**) under mild conditions, it gave rise to an octaene **95b** derived from four Michael reactions [1658], which when reacted with 8 equiv. of ethylenediamine, give the octaamine **95c** [1703]. The surface amines were subsequently reacted with 24 equiv. of **95a** to generate (67.5%) the desired dendrimer possessing 48 terminal olefins **95d**, which was subsequently treated with 48 ethylenediamine affording the 48 amino-terminated surface (Scheme 95).

5.11. 1 → 2 C-branched, 1,2,3-triazole-connectivity

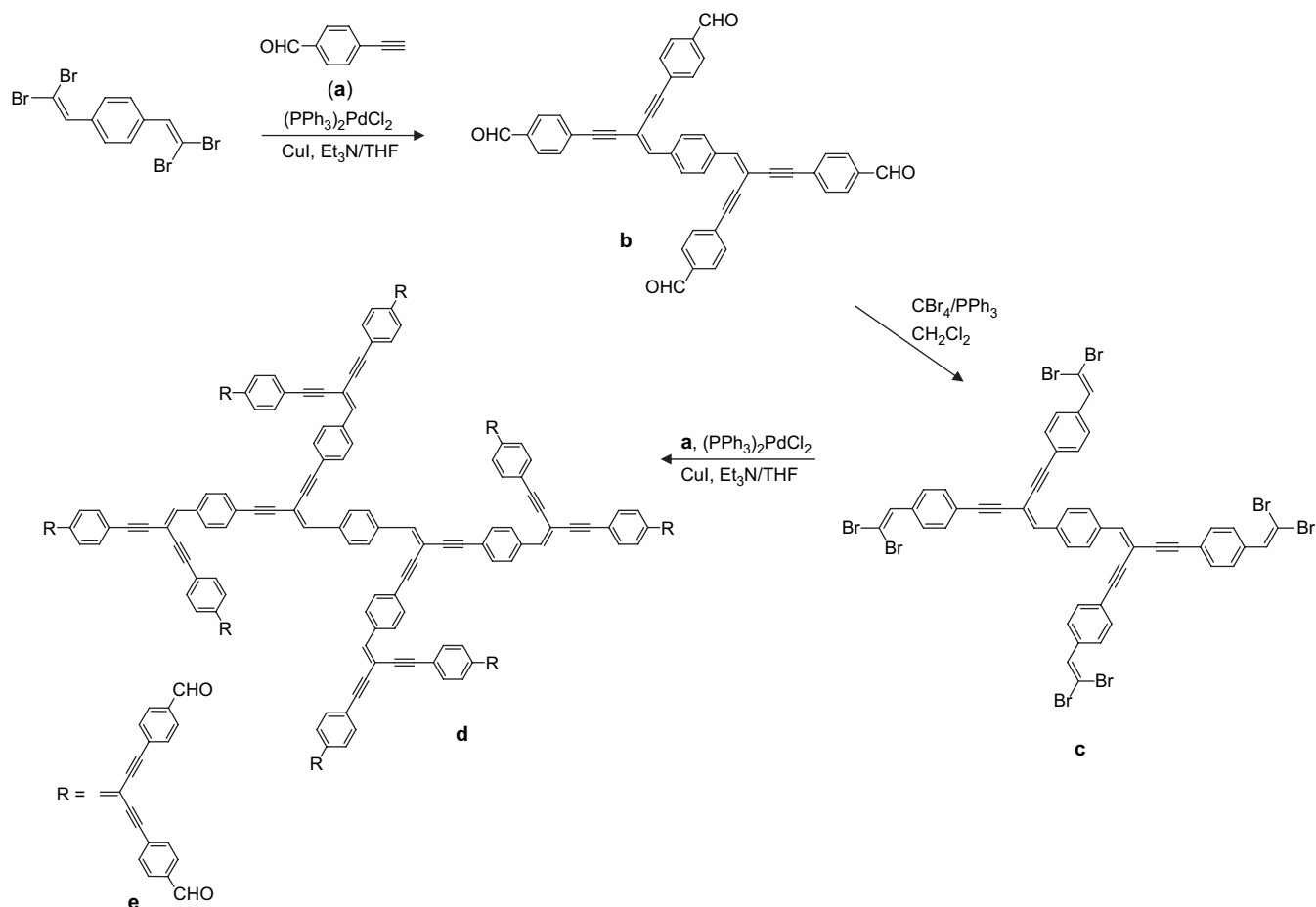
The use of click chemistry has convergently given rise to a novel family of 1 → 2 C-branched, triazole-connected dendron and dendrimers [1320]. They are only considered here because of the underlying 1 → 2 monomeric reagents, e.g., $\text{ClCH}_2\text{CH}(\text{CH}_2\text{C}\equiv\text{CH})_2$ and $\text{N}_3\text{CH}_2\text{CH}(\text{CH}_2\text{-triazoleR})_2$, depending on substituents, can be readily used in similar divergent routes.

6. 1 → 2 Si-branched

Several combinations of Si-dendrimers have appeared: the first are those that are totally composed of silicone atoms, the second are comprised, for the most part, of Si-branching centers (a carbosilane variety) and lastly are comprised of O–Si–O– branching centers (a siloxane variety). Numerous reviews have appeared that address, in part, these Si-dendrimers [1704–1720].

6.1. 1 → 2 Si-branched and connectivity

In 1995, Lambert et al. [1721,1722] reported the synthesis and X-ray crystal structure of the first dendritic polysilane $[(\text{Me}_3\text{Si})_3\text{SiSiMe}_2]_3\text{SiMe}$, in which the longest polysilane chain of 7 silicon atoms is repeated 27 times. The 2D ^{29}Si – ^{29}Si INADEQUATE NMR data have provided critical connectivity support for these structures [1723]. The construction of these polysilane dendrimers in which the structure of the G2 product was unambiguously confirmed by X-ray diffraction was later reported [1724]. The divergent procedure for the synthesis of polysilane dendrimer **96f** started with treating the core **96b** with the highly inflammable yellow crystalline silyllithium **96a**, prepared (80%) by the reaction of $\text{Hg}[\text{MeSi}(\text{SiMe}_2\text{Ph})_2]_2$ and excess Li° , to give quantitatively tetrasilane **96c**, as colorless crystals. Treatment of the latter with $\text{CF}_3\text{SO}_3\text{H}$, followed by reaction with monomer **96b**, generated (43%) the next higher level dendrimer **96d**. The



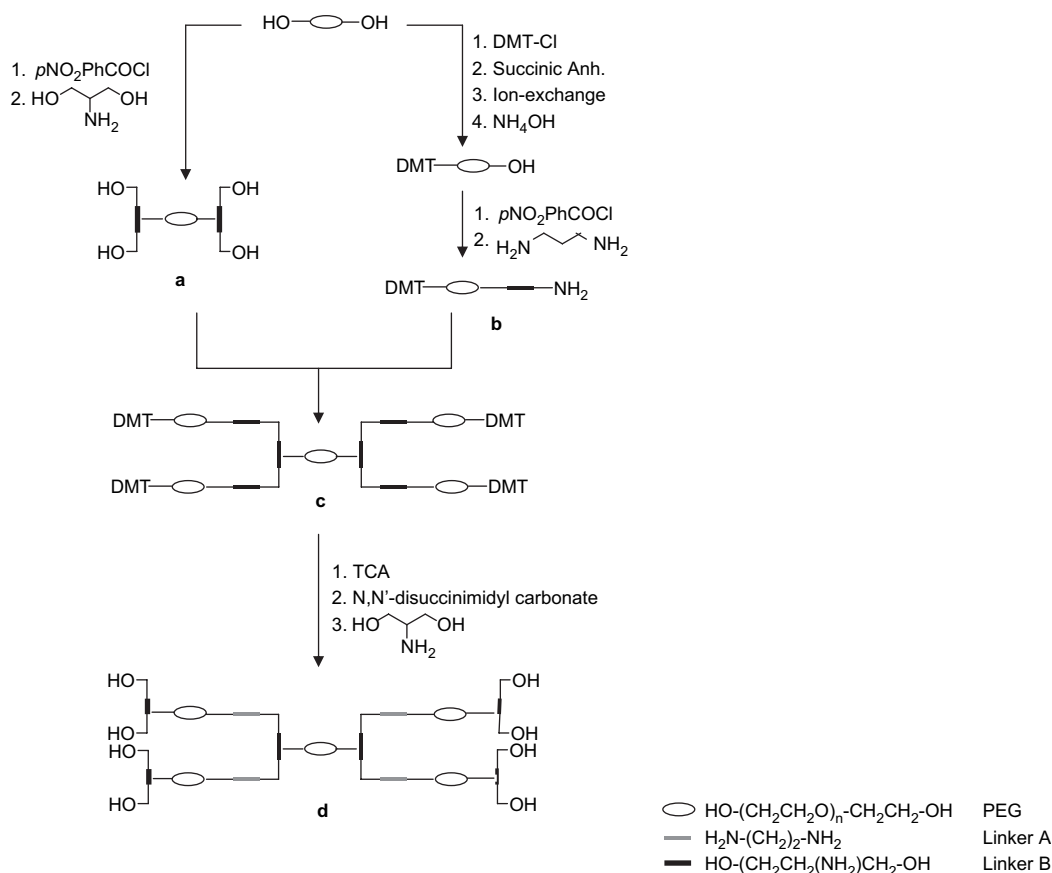
Scheme 93. The formation of larger Y-enyne dendrimers [1699].

permethylated polysilane **96f** was then prepared (29%) from tridecasilane **96d** by a similar two-step sequence utilizing $[(\text{Me}_3\text{Si})_2\text{Si}(\text{Me})\text{Li}]$ (**96e**), as the capping reagent. Lithiosilanes and their application to the synthesis of polysilane dendrimers have been reviewed [1714]. The time-resolved emission spectra of the G1 and G2 polysilane dendrimers showed two bands – the one in the UV was assigned to the emission from the excited state at the linear Si–Si chain and the one in the visible region was assigned to that of the branching point; the intramolecular energy transfer between both excited states was demonstrated by means of an emission time profile [1725]. The use of the potassium analog of **96b** $[(\text{Me}_3\text{Si})_2\text{Si}(\text{Me})\text{K}]$ with $\text{MeSi}(\text{SiCl}_2\text{Me})_3$ generated at -78° the racemic $\text{MeSi}\{\text{SiClMe}[\text{SiMe}(\text{SiMe}_3)_2]\}_3$, which with water gave a mixture of *rac-l,l* (21%) and *rac-l,u* (62%) $\text{MeSi}\{\text{Si}(\text{OH})\text{Me}[\text{SiMe}(\text{SiMe}_3)_2]\}_3$; both structures were proven by single crystal analysis [1726]. A short overview by Lambert et al. [1719] of these dendritic polysilanes has appeared and should be consulted (Scheme 96).

The treatment of $[(\text{Me}_3\text{Si})_2\text{SiMe}]_2\text{Si}(\text{Me})\text{Br}$ with lithium metal in THF afforded the desired lithium–halide exchange, then reaction with $(\text{ClMe}_2\text{Si})_2$ gave the $\{[(\text{Me}_3\text{Si})_2\text{SiMe}]_2\text{SiMeSiMe}_2\}_2$, whose structure was confirmed by a single crystal X-ray structure [1727]. Reaction of $[(\text{Me}_3\text{Si})_2\text{SiMe}]_2\text{SiHCl}$ with Na–K alloy gave rise to the oligosilane

$\{[(\text{Me}_3\text{Si})_2\text{SiMe}]_2\text{SiH}\}_2$, whose structure was also confirmed by a single crystal X-ray diffraction to possess a chain of six continuous silicon atoms [1728]. Its UV–vis spectra was also compared [1728] to $\{[(\text{Me}_3\text{Si})_2\text{SiMe}]_2\text{SiMe}\}_2$ [1729]. In a similar pathway, treatment of $[(\text{Me}_3\text{Si})_2\text{SiMeSiMe}_2]_2\text{SiMeSiMe}_2\text{Cl}$ with Na–K alloy or $[(\text{ClSiMe}_2)_2\text{SiMe}]_2$ with four $[(\text{Me}_3\text{Si})_2\text{SiMeK}]$ gave $\{[(\text{Me}_3\text{Si})_2\text{SiMeSiMe}_2]_2\text{SiMeSiMe}_2\}_2$ and $\{[(\text{Me}_3\text{Si})_2\text{SiMeSiMe}_2]_2\text{SiMe}\}_2$, respectively [1730]. Whereas $[(\text{ClSiMe}_2)_3\text{SiCl}]$ with 3 equiv. of either $[(\text{Me}_3\text{Si})_3\text{SiK}]$ or $[(\text{Me}_3\text{Si})_2\text{SiMeK}]$ [1731] gave $[(\text{Me}_3\text{Si})_3\text{SiMe}_2]_2\text{SiCl}$ or $[(\text{Me}_3\text{Si})_2\text{SiMeSiMe}_2]_2\text{SiCl}$, respectively, and $[(\text{Me}_3\text{Si})_2\text{SiMeSiMe}_2]_3\text{SiSiMe}_2\text{Cl}$, which was hydrolyzed to $[(\text{Me}_3\text{Si})_2\text{SiMeSiMe}_2]_3\text{SiSiMe}_2\text{OH}$ whose crystal structure was obtained by X-ray analysis [1732].

The first generation of dendrimer was shown by the reaction of $\text{MeSi}(\text{SiMe}_2\text{SiMeBr})_3$ with dimethylphenylsilyllithium (PhMe_2SiLi) [1733] followed by protodearylation with HBr at -78°C to afford the G1 $\text{MeSi}[\text{SiMe}_2\text{SiMe}(\text{SiMe}_2\text{Br})_2]_3$, which was cyclized to generate different novel Si-adamantanes [1734]. Similarly, the treatment of $[\text{MeSi}(\text{SiMe}_2\text{Br})_3]$ [1735] as the core, with 3 equiv. of $[(\text{PhMe}_2\text{Si})_2\text{MeSiK}]$ [1736], followed by HBr at -78°C gave (ca. 30%) a different G1 $\text{MeSi}[\text{SiMe}_2\text{SiMe}(\text{SiMe}_2\text{Br})_2]_3$. The next tier was constructed (41%) by treatment of this tribromide with 6 equiv. of $[(\text{PhMe}_2\text{Si})_2\text{MeSiK}]$ to produce the G2



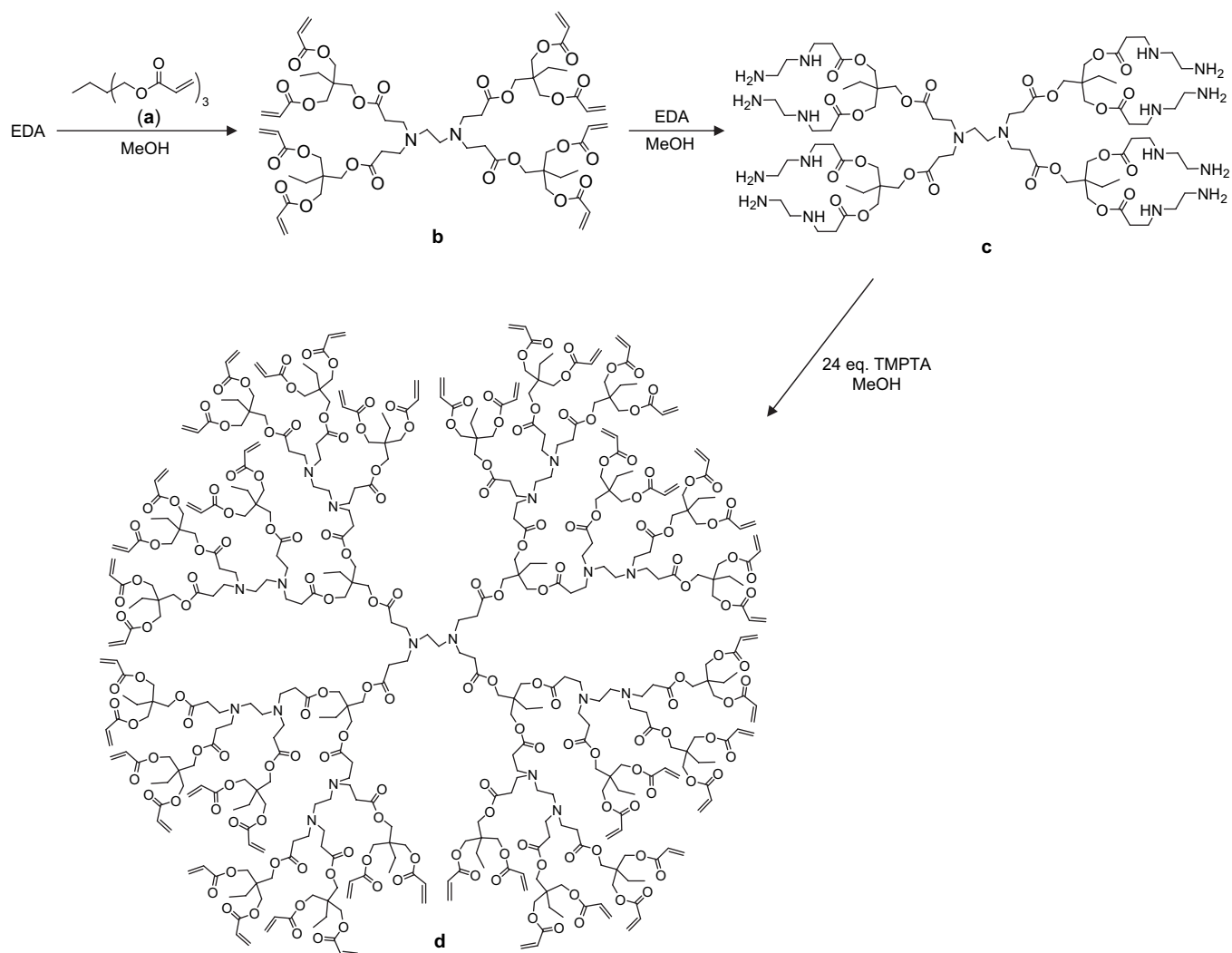
Scheme 94. MultiPEGs via a divergent step-wise procedure [1701].

$\text{MeSi}\{\text{SiMe}_2\text{SiMe}[\text{SiMe}_2\text{SiMe}(\text{SiMe}_2\text{Ph})_2]_2\}_3$. The ^{29}Si NMR has been shown to be a useful tool to study these polysilane dendrimers [1737].

6.2. 1 → 2 Si-branched and alkyl-connectivity

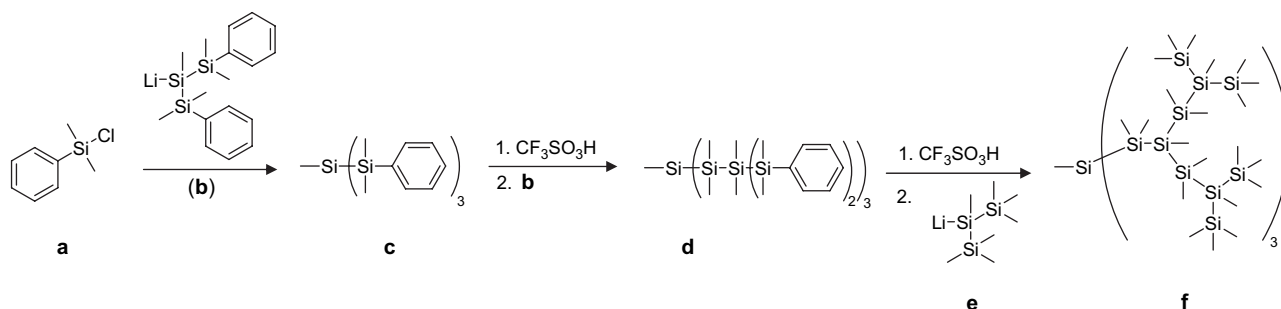
Roovers et al. [1738] synthesized a series of carbosilane dendrimers using Pt-catalyzed addition of methylchlorosilane (**97a**) to an alkene, followed by nucleophilic substitution with $\text{CH}_2=\text{CHMgBr}$ (**97d**) at the terminal dichlorosilane moieties. Thus, using $(\text{CH}_2=\text{CH})_4\text{Si}$ [1739–1742] (**97b**) as the initial tetrafunctional core, the G1 tetrakis(methylchlorosilane) **97c** was generated after the addition of 4 equiv. of **97a**. Reaction of 8 equiv. of **97d** with pentasilane **97c** generated octaolefin **97e**. Continued iterative assembly gave rise to the polyalkene **97f**, possessing a molecular weight of 6016 amu at G4 possessing 64 terminal vinyl groups (Scheme 97). These dendritic carbosilanes with 32 [1743], 64, and 128 [1740] surface Si–Cl bonds were used as coupling reagents for monodisperse poly(butadienyl)lithium. Two series of regular star polymers with molecular weights between 6400 and 72,000 amu were prepared and shown to be good models for polymeric micelles; the ratio of hydrodynamic radius over radius-of-gyration was slightly greater than $(5/3)^{1/2}$. The SANS data derived from this carbosilane series supported the tendency for enhanced spherical-like behavior with increasing

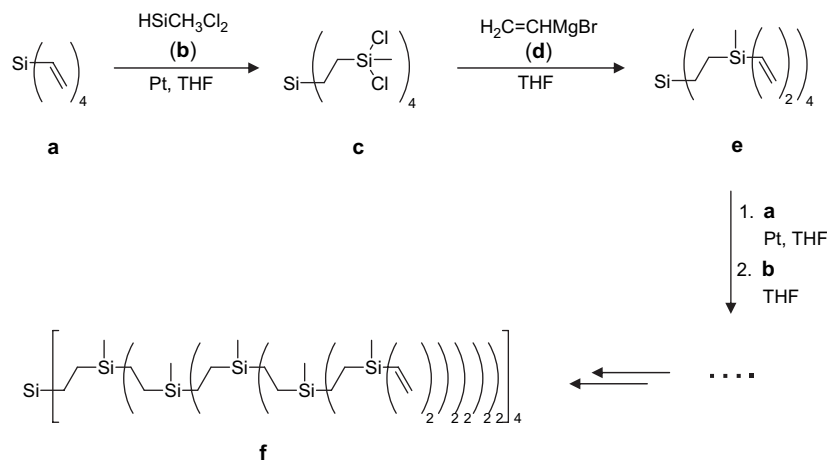
growth [1744]. Molecular force field calculations of these 1 → 2 Si branched dendrimers confirmed the general findings of other force field calculations, quantified the surface density, as well as afforded insight into the size of the encapsulated guests [1745]; yet, disagreeing with the hypothesis of dendron separation. The SANS data on Si-dendrimers with specifically labeled termini have shown that the terminal groups are concentrated near the structural periphery [1746]. In a later paper, Ozerin et al. [1747] proposed that the spatial structure of these dendrimers could be rationalized on the basis of twisted branches from the SANS data and could explain some of the earlier inconsistencies [1746]. The shape and spatial structure of these Si-dendrimers based on SANS data have been conducted within the bounds of a low-resolution model and without invoking added *a priori* information [1747]. A theoretical model of a Si-dendrimer that is immersed in a mesogenic solvent composed of Gay-Berne particles [1748] showing a different behavior resulted from simulations in different phases. A related series of polybutadiene star polymers was generated by coupling living poly(butadienyl)lithium with dendritic chlorosilane linkers [1749]; a classical MALDI-TOF MS analysis showed that with stars possessing up to 16 arms, functionality and polydispersity coincided with theory; whereas at the 32 and 64 armed level, polydispersities were less than 1.01. Reactions of these chloro-terminated carbosilane $\text{Si}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_4$ [1750–1752] or intermediates (see Scheme 28)



with $\text{LiCH}_2\text{PPh}_2$ generated the $\text{Si}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{CH}_2\text{PPh}_2)_4$ or $\text{Si}[\text{CH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{PPh}_2)_2]_2$ [1753], which were capable of facile surface metal ion complexation [1753–1758]. Treatment of the simple core $\text{Si}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_4$ with the corresponding Grignard reagent of α -bromo-3,5-dimethoxytoluene or 1-bromo-2,4-dimethoxybenzene gave $\text{Si}[\text{CH}_2\text{CH}_2\text{SiMe}_2\text{CH}_2\text{-3,5-(MeO)}_2\text{C}_6\text{H}_3]_4$ or $\text{Si}[\text{CH}_2\text{CH}_2\text{SiMe}_2\text{-2,4-(MeO)}_2\text{C}_6\text{H}_3]_4$, respectively; these structures were confirmed by single crystal X-ray analysis [1750]. The preparation of self-

assembled monolayers have incorporated the Si-dendrons *via* treating activated silica wafers with $[\text{CH}_2=\text{CH}(\text{CH}_2)_9\text{SiCl}_3]$, then MeSiHCl_2 and the platinum divinyltetramethyldisiloxane complex [1759]. After a described workup, $\text{CH}_2=\text{CHMgBr}$ was added to generate the G1 dendron, and the iterative procedure was repeated until the desired covering was accomplished. Tetravinyl silane was hydrostannated with Ph_2SnH in the presence of a Pt catalyst to generate $\text{Si}(\text{CH}_2\text{CH}_2\text{SnPh}_3)_4$, which was brominated and subsequently reduced to give



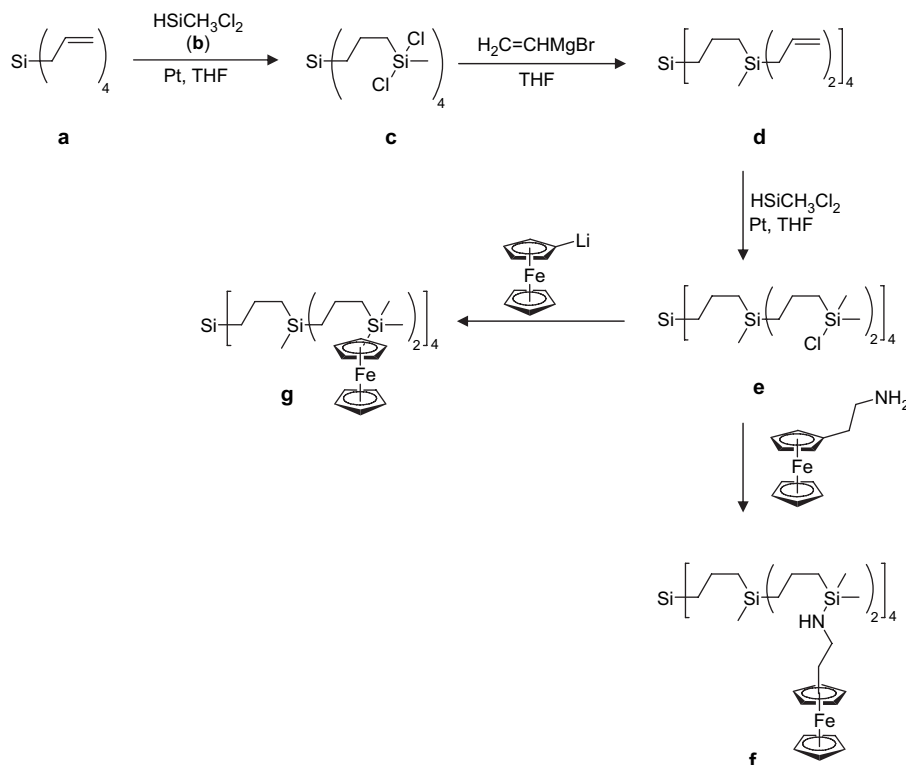


Scheme 97. Alkylsilane dendrimer construction by *Pt*-mediated silane alkenylation and vinylation [1738].

$\text{Si}(\text{CH}_2\text{CH}_2\text{SnH}_3)_4$ whose single crystal X-ray structure was ascertained [1760]; this tetrakis(2-stannylethyl)silane was further reacted with 12 equiv. of methyl acrylate in the presence of AIBN to yield $\text{Si}[\text{CH}_2\text{CH}_2\text{Sn}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})_3]_4$ [1761]. This dodecaester was subjected to numerous common transformations [1761]. The related $\text{Sn}(\text{CH}=\text{CH}_2)_4$ when being subjected to HSnPh_3 in the presence of AIBN failed to give $\text{Sn}(\text{CH}_2\text{CH}_2\text{SnPh}_3)_4$ but rather $(\text{Ph}_3\text{SnCH}_2)_2$ was isolated [1762].

Comanita and Roovers [1763] reported a modification to their protocol, which included the terminal attachment of a methyl bis(alkyl THP ether) silane monomer, greatly augmenting construction of carbosilanes with extended hydrophilic termini. These materials were proposed as useful multifunctional anionic initiators for the synthesis of dendrimer–polymer hybrids. The hydroxy-terminated G0–2 carbosilanes have been employed for the anionic polymerization of ethylene oxide; the ensuing polymers have narrow M_w distributions [1764]. The star-branched character of these polymers was confirmed by molecular weight, intrinsic viscosity, and translational diffusion data. Morris [1765] prepared the interesting cubic core, 1,3,5,7,9,11,13,15-octakis[2-(hydroxydimethylsilyl)ethyl]-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane, converting their numerous 1 → 2 branched carbosilanes (as well as 1 → 3 motifs) to their SiOH-terminated derivatives by hydrolysis of terminal SiCl groups. Dendrimers derived from this core and terminated with 16 PPh₂ moieties were treated with [Rh(acac)CO₂] to generate a catalyst that demonstrated a higher linear selectivity (14:1) than the related smaller analogs in the hydroformylation of 1-octene [1766,1767]. The molecular dynamics modeling of these (and related) dendrimers has given insight to the distance between the Si-branching sites and *P*-termini as well as the size and shape with variable temperature and solvent polarity [1768]. The crystal structure of $\text{Si}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{OH})_4$, based on a tetravinylsilane core, has been reported [1765]. Recently, a modular construction of carbosilane dendrimers, e.g., $\text{Si}[\text{CH}_2\text{CH}_2\text{SiMe}(\text{CH}_2\text{CH}_2\text{SiMe}_2(\text{CH}_2)_3(1\text{R}-1,2\text{-C}_2\text{B}_{10}\text{H}_{11}))_2]_4$, using different methodologies has been reported [1769].

Morán et al. [1770] have described utilizing a similar [1738] procedure except that allyl spacers were incorporated; their detailed reviews are available [1713,1771]. Thus, tetra(allyl)silane [1770] (**98b**), as the core, and a simple allyl Grignard reagent were utilized in the iterative construction. When silane **98b** was hydrosilylated with MeCl_2SiH (**98a**) using Pt-catalyzed conditions, the pentasilane **98c** was generated. Subsequent branching was accomplished by the reaction of octachlorosilane **98c** with $\text{CH}_2=\text{CHCH}_2\text{MgBr}$ to afford octaene **98d**, which was hydrosilylated (Me_2ClSiH) to give the capped chlorosilane **98e** [1772]. Muzaforov et al. [1773] prepared these polycarbosilane dendrimers [1774] via a successive repetitive two-step sequence consisting of an organomagnesium reagent with hydrosilylation – up to the G5 level was similarly constructed [1775]; then onto the G10 level was generated and these larger members were characterized and studied by AFM and light scattering techniques [1776]. The synthetic treatment of this polychlorosilane with either lithio- or aminoethyl-ferrocene gave the corresponding Si-dendrimers coated with ferrocenyl moieties (**98f** and **98g**, respectively), which were described as non-interacting redox centers [431,1772,1777]; for Ru(II)tris(bipyridine) peripheral units, also see [1778]. The molecular dynamics simulation of the G3 carbosilane with mesogenic functionalities, particularly $-(\text{CH}_2)_3\text{Si}(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2(\text{CH}_2)_{10}\text{C}(=\text{O})\text{O}(\text{C}_6\text{H}_4)_2\text{CN}$, has suggested that different behaviors can result based on simulations in the different phases; thus, the dendrimer can change shape from spherical to rod-like upon changing from isotropic to nematic solvents [1748]. Reaction of the G0–3 chlorosilanes (e.g., **98e**) with the phenolic product, derived from the condensation of 2-formylpyridine and 4-amino-2,5-dimethylphenol, afforded a surface possessing pyridinylimine termini, which were readily transformed to the desired Ni(II) complexes [1779,1780]; these metallodendrimers were evaluated as catalysts for the polymerization of ethylene. Likewise, surface attachments were conducted by treatment of these G1–3 chlorosilanes, initially with 4-LiC₆H₄N(SiMe₃)₂, then with [NbCp'Cl₄] (Cp' = η⁵-C₅H₄SiMe₃) in CH₂Cl₂ to give the interesting imido mononuclear niobium(V) coating



Scheme 98. Ferrocene-terminated carbosilane dendrimers [1770].

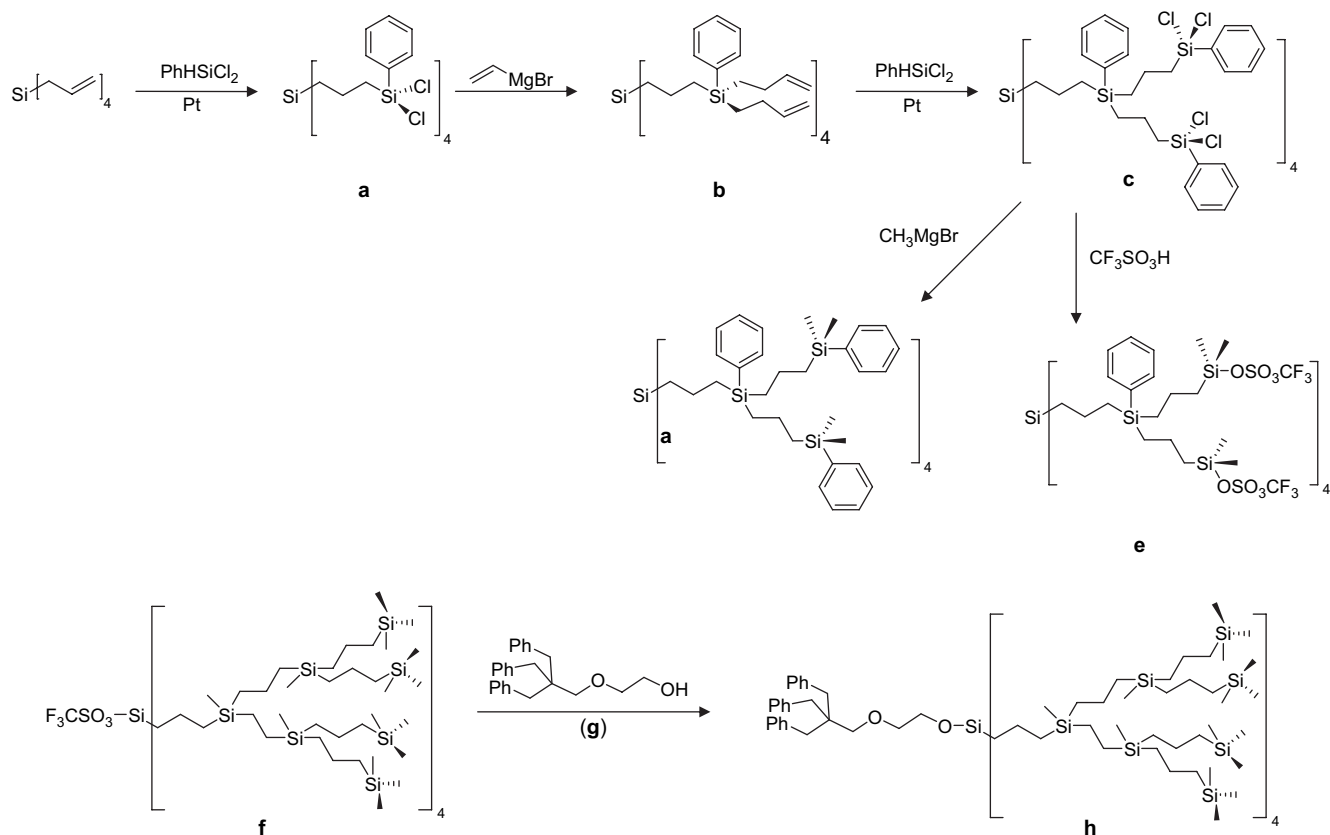
[1781]; tantalum-imido complexes were similarly prepared [1782] (Scheme 98).

Treatment of tetra(allyl)silane **98b** with PhHSiCl_2 in the presence of Karstedt's catalyst quantitatively gave **99a**, which with $\text{CH}_2=\text{CHCH}_2\text{MgBr}$ generated (70%) the octaallyl product **99b**. Its conversion into the G2 level **99c** was again quantitatively accomplished with PhHSiCl_2 , then reaction with MeMgCl led (65%) to the SiMe_2 derivative **99d**; cleavage with $\text{F}_3\text{CSO}_3\text{H}$ in toluene gave (100%) the dodeca-triflate **99e** [1783]. This simple cleavage was shown to lead to new interesting possibilities, such as the selective aryl cleavage. Dendrimer **99f** possessing a F_3CSO_3 -focal group was selectively cleaved and reacted with the triphosphine foot **99g** to yield the focally functionalized Si-dendrimer **99h** (Scheme 99). The related $\text{MeSi}(\text{CH}_2\text{CH}=\text{CH}_2)_3$, prepared from $\text{CH}_2=\text{CHCH}_2\text{-MgCl}$ and MeSiCl_3 , was treated with MeSiHCl_2 to form $\text{MeSi}[(\text{CH}_2)_3\text{SiMeCl}_2]_3$. Its reaction with $\text{CH}_2=\text{CHCH}_2\text{-MgCl}$ generated (59%) $\text{MeSi}[(\text{CH}_2)_3\text{SiMe}(\text{CH}_2\text{CH}=\text{CH}_2)_2]_3$, which was transformed to a terminal aminopropyl group by a simple two-step process using $\text{Me}_2\text{SiHOSiMe}_2(\text{CH}_2)_3\text{NH-SiMe}_3$ and a Pt catalyst, followed by washing with EtOH [1784]. A related G4 carbosilane was constructed by the above procedure [1784,1785] using diallylmethylphenylsilane, as the core possessing 32 allyl termini; the lasing emission of its cavity with encapsulated fluorescein was measured in the form of a doped dendrimer/polymer film and two opal photonic crystals [1786].

The 1 → 2 *Si*-branched, chloromethyl-terminated dendrimers have been converted to their alcohol, dimethylamino or sodium sulfonate derivatives [1787]. The water-soluble

sulfonates and poly(ammonium) salts were demonstrated to enhance the solubility of lipophilic alkyl-substituted benzene derivatives, thereby illustrating their micellar potential. An alternative approach to the introduction of surface ammonium salts was achieved by the treatment of the well-known chlorosilane-terminated G1–3 dendrimers with *N,N*-dimethylaminoethanol, followed by quaternization with MeI; these ammonium salts were susceptible to hydrolysis [1788]. The chlorosilane-terminated G1–3 dendrimers possessing surface 4-, 8-, and 16- SiMe_2Cl moieties were treated with either 3,5-($\text{Me}_2\text{NCH}_2\text{CH}_2\text{O}$) $\text{C}_6\text{H}_3\text{CH}_2\text{OH}$ or $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe-CH}_2\text{CH}_2\text{OH}$ in the presence of Et_3N to generate the different polyamine surfaces, which were readily quaternized with methyl iodide to give white solids [1789]. NMR analysis of these water-soluble, ammonium salts showed that even with a large excess of MeI and prolonged times, the yields capped at ca. 85% as a result of competitive reactions. These carbosilanes were evaluated for biocompatibility; complexation with oligonucleotides showed excellent potential for biomedical applications [1789].

Treatment of $\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{H})_4$ or $\text{Si}[\text{CH}_2\text{CH}_2\text{CH}_2\text{-SiMe}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{H})_2]_4$ (**100a**) with 1-methyl-1-vinylsila-8-crown-3 [1790] (**100b**), 1-methyl-1-vinylsila-11-crown-4 [1791] (**100c**), 2-allyloxymethyl-12-crown-4 (**100d**) or 2-allyloxymethyl-15-crown-5 [1792] gave the corresponding crown ether in near quantitative yields [1793] (Scheme 100). The related hydrosilylation of 4-allyl-2-methoxyphenol (eugenol) with these G1,2 dendrimers possessing the $-\text{SiMe}_2\text{H}$ termini generated dendrimers with the $-\text{SiMe}_2(\text{CH}_2)_3\text{-C}_6\text{H}_3(\text{OMe})(\text{OH})$ moieties [1794], which were subsequently

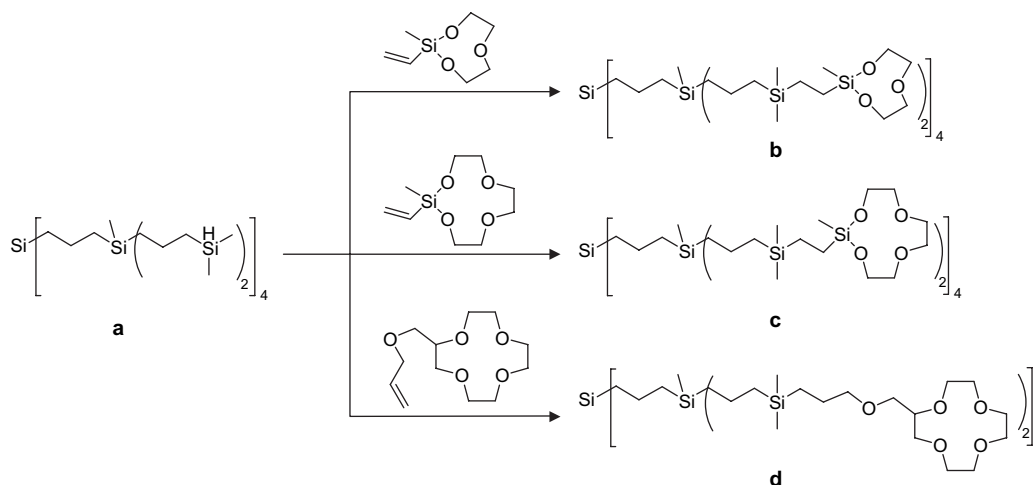


Scheme 99. Preparation of selectively cleaved Si-dendrimers [1783].

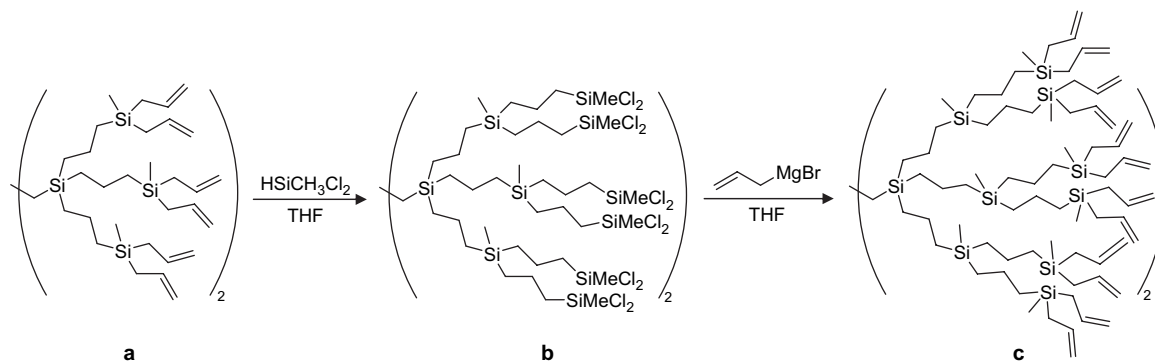
treated with [CpTiCl₃] (Cp = η⁵-C₅H₅) to provide access to cyclopentadienyl titanium surface complexes [1794–1797].

Kim et al. [1798] initially prepared up to G3 chlorosilane dendrimers whereby the G1 dodecaallyl dendrimer **101a** was subjected to Pt-mediated hydrosilylation (MeCl₂SiH) to give dodeca(dichlorosilane) **101b**, which when treated with CH₂=CHCH₂Br gave the G2 polyalkene **101c** (Scheme 101). Difficulties in obtaining the G4 carbosilane dendrimer from the G3 precursor by a hydrosilylation procedure were noted. Using similar techniques, a nearly quantitative

preparation of higher generation silane-based dendrimers possessing 64 [1799] and 96 [1800] allylic termini has been reported. Preparation of cylindrical dendrimers possessing a polycarbosilane backbone has also been advanced [1798]. The thermodynamic properties these G1–5 carbosilanes possessing allyl termini have been presented using an adiabatic vacuum calorimeter in the 6–340 K range indicating a chain-layered structure for dendritic glasses in the temperature range of 30–50 K [1801]. The temperature dependences of heat capacity of the G3,4 and G5,6 carbosilane



Scheme 100. The preparation of crown-terminated carbosilane dendrimers [1793].



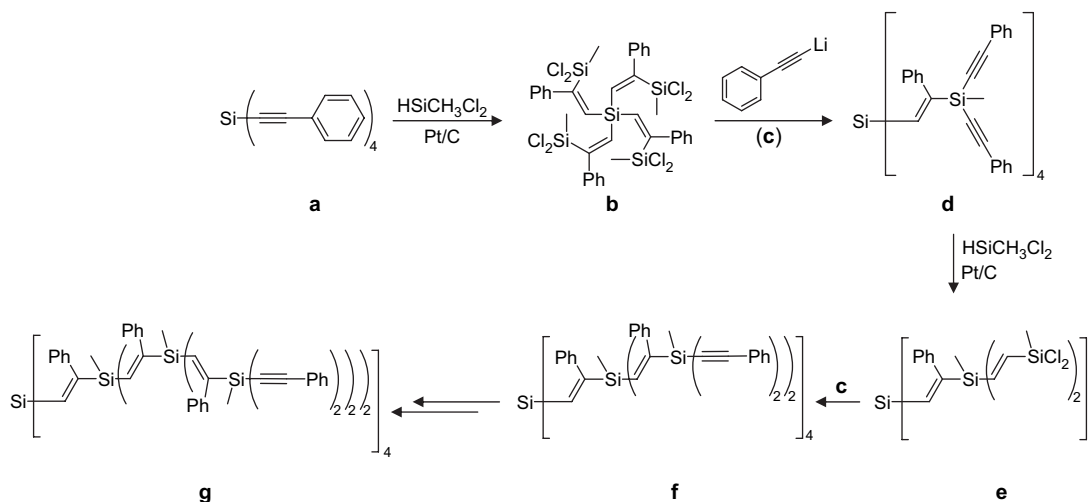
Scheme 101. Preparation of carbosilane dendrimers [1806].

dendrimers capped with butyl moieties have been ascertained in the range from 6–340 K as well as 6–600 K, respectively, by precision adiabatic vacuum and dynamic calorimetry [1802]. The coupling of modified mesogenic moieties, *e.g.*, [HSiMe₂OSiMe₂(CH₂)₁₀CO₂C₆H₄C₆H₄CN] [1803,1804], [HSiMe₂OSiMe₂(CH₂)₁₀OC₆H₄OCO₂R] [126], [HSiMe₂OSiMe₂(CH₂)₁₀OC₆H₄OH] [126], [HSiMe₂OSiMe₂(CH₂)₁₁-OC₆H₄CO₂C₆H₄CO₂C*HMeCO₂CH₂Me] [1805] to the carbosilane dendrimers possessing these allylic termini has been conducted *via* hydrosilylation in the presence of a Pt catalyst and an excess of the mesogens thereby giving rise to a series of liquid crystalline materials.

Kim et al. [1807–1810] prepared poly(unsaturated) carbosilane dendrimers by employing a modification of the standard Pt-mediated hydrosilylation–chlorosilane allylation protocol; lithium phenylacetylide was substituted for the alkylating agent. Thus, hydrosilylation of the rigid core **102a** gave tetraalkene **102b**, which was treated with lithium alkynide **102c** to afford enyne **102d**. Repetition of the sequence afforded the corresponding hexadecachloride **102e** as well as higher generation poly(enyne)s **102f** and **102g**. Defects were noted upon proceeding to the G3 poly(chlorosilane) level. The use of Me₂ClSiH also proved successful and allowed for the final capping with the acetylide. Similar lithium

phenylacetylide-based chemistry was performed on a siloxane polymer core to produce the G2 dendronized rod-shaped architecture [1811]. Kim and Ryu [1812] combined the lithium phenylacetylide protocol with that of the allyloxy-based method to generate the “double-layered” (*i.e.*, diblock architecture) dendrimers. In this series, the largest dendritic carbosilane has been reported to possess 144 phenylethynyl moieties [1813]; these constructs were derived from 1,3,5-tris(dimethylvinylsilyl)benzene and bis(phenylethynyl)methylsilyl groups. The construction of layered carbosilanes containing triple bonds on the periphery, double bonds on the (*n*-1) layer and single bonds in the (*n*-2) inner layer were prepared and characterized [1814,1815]; tailoring of the different layers has been demonstrated. The surface coating of these dendrimers was accomplished by treating diethenyl terminal intermediate (*e.g.*, **102e**) with either 4-lithio-4'-(*N*-phenyl-1-naphthylamino)benzene or *N*-(4-lithiophenyl)carbazole, followed by electrochemically deposition leading to the fabrication of OLEDs [1816] (Scheme 102).

Kim and Park [1817] further modified this protocol to include propargyl alcohol, as the alkylating agent, producing carbosilane architectures with internal, as well as external, unsaturated sites (Fig. 11); dendrimers up to G4 were reported.



Scheme 102. Kim's poly(unsaturated)carbosilanes [1807].

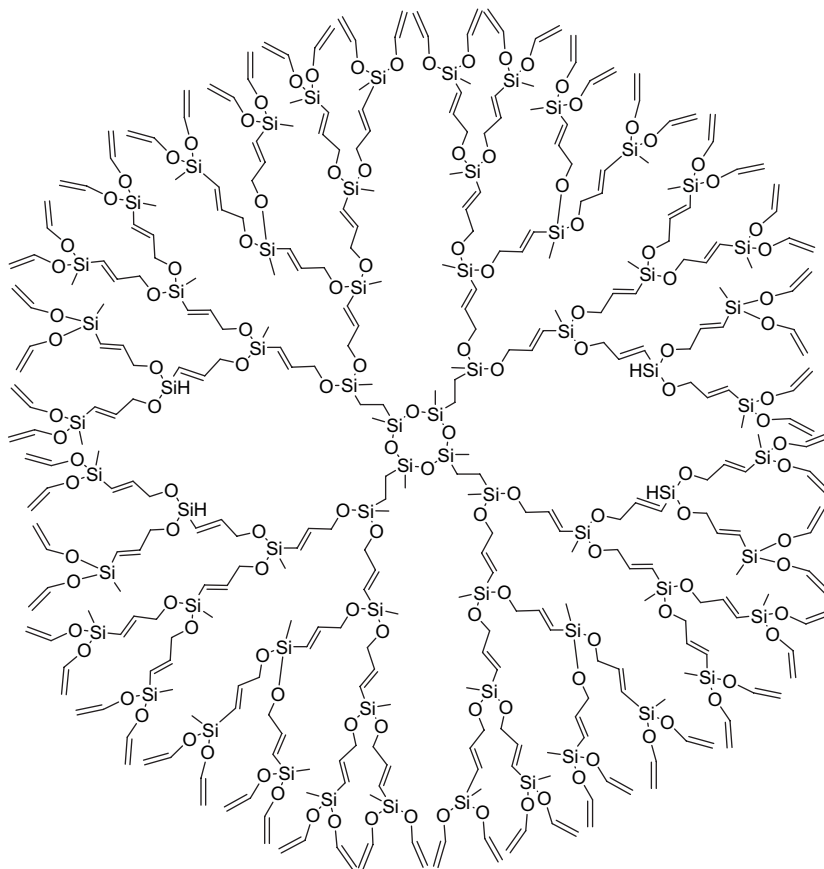


Fig. 11. Carbosilane architectures [1817].

The double-layered carbosilane dendrimers possessing 96 terminal phenylethynyl groups have been constructed by hydrosilylation and alkenylation, as well as alkynylation procedures [1818], also see [1819] for related chemistry leading to functional inner shell infrastructures. Using the dendritic core derived from this iterative hydrosilylation with dichloromethylsilane and an alcoholysis procedure using $[\text{OSiMe}(\text{CH}=\text{CH}_2)_4]$ as the core, the surface Si–Cl moieties on the G4 and G5 carbosilanes have been reacted with cholesterol [1820], *p*-pyridinepropanol [1820,1821], *p*-pyridinealdehyde [1820], 2-(2-hydroxyphenyl)benzoxazole [1822], 4-hydroxyquinoline [1823], 8-hydroxyquinoline [1822,1823], 3-hydroxy-2-methyl-4-pyrone [1822] in the presence of TMEDA, 4-methyl-5-thiazolethanol [1823], 5-thiazolethane [1823], 2-hydroxymethylantraquinone [1823], lithioferrocene (as a CO gas sensor) [1824], 4'-(6-hydroxy-1-oxohexa)-2,2':6',2''-terpyridine, then transformed to the corresponding terpyridine-platinum-pyridine complex [1825] or bis-terpyridine Ru(II) complex [1826]. Terminating these G3–5 dendrimers with anthracene has been accomplished by the reaction of Si–Cl bonded precursors with 9-hydroxymethylantraquinone in the presence of TMEDA [1820,1823] and a Diels–Alder reaction was conducted with *N*-ethylmaleimide [1827] under mild conditions. These G1–4 anthracene-coated dendrimers were similarly treated with either 1,4-benzoquinone or naphthoquinone affording the corresponding surface-coated Diels–Alder products [1828]. Treatment of the G4 carbosilane with surface

Si–Cl sites with 4-phenylazophenol [1823] gave the densely packed azobenzene coating; the surface pressure of a monolayer was measured by photoirradiation. Their results suggested that these materials can be highly efficient photo-switches at the molecular level [1829,1830]. Different carbosilanes capped with dichloride moieties were treated with 1,4-diphenylbutadiene-1,4-dianions, demonstrating an effective route to the formation of silole termini; a series of these silole-terminated dendrimers showed a green to greenish blue fluorescence.

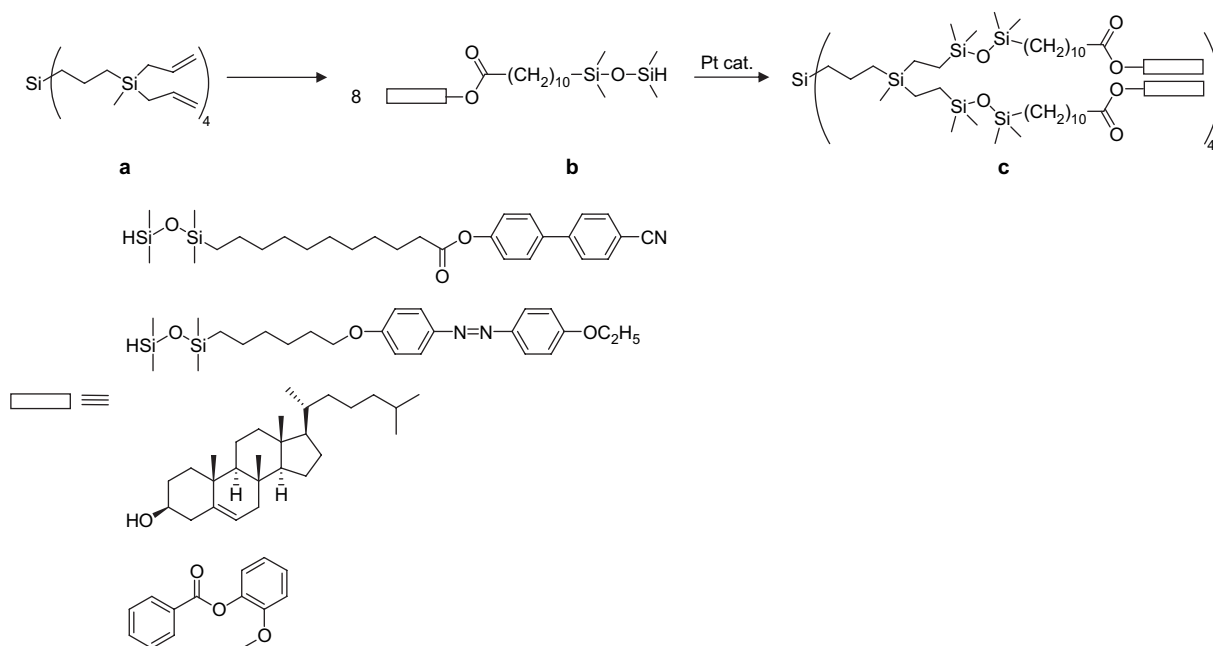
The hydroxyl-terminated carbosilanes, such as $\text{Si}\{(\text{CH}_2)_3\text{SiMe}[(\text{CH}_2)_3\text{SiMe}[(\text{CH}_2)_3\text{SiMe}[(\text{CH}_2)_3\text{OSiMe}_2(\text{CH}_2)_3\text{O}(\text{CH}_2)_2\text{OH}]_2]_2]_2\}_4$, possessing excellent amphiphilic properties have been prepared by Getmanova et al. [1831] Other synthetic routes to these carbosilane dendrimers have been explored incorporating hydroxyl moieties either at the internal [1832] or external [1833] positions. These carbosilane constructs, possessing $-\text{OSiMe}_3$ or $-\text{OSiMe}_2(\text{CH}_2)_3\text{O}(\text{CH}_2)_2\text{OH}$ termini, have been examined to evaluate their properties at the air/water interface and showed two types of wetting dependence based on the surface substituents [1834]. Three different equilibrium states for these Si-dendrimers were observed; whereas the hyperbranched counterparts of similar composition did not show the transitions and spread more like isotropic liquids [1835,1836]. Interactions of the G4 carbosilane with the hydroxy surface between two mica surfaces have been evaluated across a toluene medium by means of a surface force balance

[218]; frictional force vs. load profiles were ascertained at different shear velocities revealing marked stick-slip sliding, whereas the magnitude of the yield stress increased with longer times of contact and normal pressure, which is qualitatively different from that of the previously studied PPI dendrimers [218]. Molecular dynamics simulations have been used to investigate the effects of branching and molecular sizes as related to their structures [1746,1747,1837–1841]. The structure and intramolecular mobility of the G5 carbosilane were simulated over a wide range of temperatures demonstrating that intramolecular diffusion of the chain ends was highly temperature dependent suggesting the existence of “liquid-like” and “glassy” states for individual molecules [1842]. Kim et al. [1843] reported the conversion of the scaffoldings allylic termini to the corresponding hydroxyl moieties by hydroboration with 9-BBN. Treatment of these carbosilanes [1787,1844] with olefinic termini with $\text{HSiMe}_2\text{O-SiMe}_2(\text{CH}_2)_3\text{OCH}_2\text{C}(\text{CH}_2\text{OSiMe}_3)_3$ in the presence of a Pt catalyst [divinyltetramethyldisiloxane)platinum(0)] [1845] gave the Me_3Si -protected dendrimer, which with $\text{AcOH}/\text{MeOH}/\text{C}_6\text{H}_5\text{Me}$ gave the desired pentaerythritol (1 → 3 C-branched) coating [1833].

The synthesis of the G1 liquid-crystalline dendrimer [1846] employing carbosilane-based scaffolding with surfaces possessing mesogen modification [1847] has been described [1848]. Studies of surface mesogen modifications with 4-propylhydroxyazobenzoate [1849], cyanobiphenyl [1803,1804,1850], methoxyphenyl benzoate, methoxyundecylenate [1851,1852], cholesteryl [1846] or azobenzene [1853] of diverse G1–5 in these carbosilane dendrimers have appeared. The self-assembly of the mesogenic termini has been evaluated [1854] and diverse aspects of their liquid crystalline properties have been reported [1855–1858]. The dielectric relaxation for the

G1,2 carbosilanes with cyanobiphenyl surface functionality connected with a C5 or C11 unit reflected the mutual distortion of the dendritic scaffold at the smectic layers [1859]. The desired tetramethyldisiloxane mesogen **103a** [1848] was generated by esterification of 10-undecylenic acid chloride with an appropriate alcohol; the ester was hydrosilylated $\{[(\text{C}_8\text{H}_{17})_3\text{PhCH}_2\text{N}]_2\text{Pt}(\text{NO}_2)_4\}$ using Me_2ClSiH , and then dual hydrolysis of the mesogenic chlorosilane and additional Me_2ClSiH gave the desired mesogen **103a**. Modification of the carbosilane **103b** with mesogenic siloxane **103a** was affected by silylation (Pt catalysis) of the unsaturated termini to afford octamesogen **103c** (Scheme 103). On the basis of DSC, optical polarizing microscopy, and X-ray diffraction data, it was surmised that different smectic mesophases were formed by the different substituted dendrimers. Treatment of the G3 carbosilane with $\text{HSiMe}_2\text{OSiMe}_2(\text{CH}_2)_{10}\text{O}_2\text{CC}_6\text{H}_4\text{O}(\text{O}=\text{C})\text{OMe}$ in the presence of a Pt catalyst coated the surface, then activation of the terminal carbonate with aqueous ammonia generated the phenol, which was partially esterified with $\text{BuOC}_6\text{H}_4\text{COCl}$; the ratio of esterified to phenolic surface termini was determined by high-resolution ^1H NMR [1860]. The solution measurements of the electric birefringence (Kerr effect) as well as the dielectric polarization of the G1 $\text{Si}\{(\text{CH}_2)_3\text{SiMe}[(\text{CH}_2)_3\text{SiMe}_2\text{OSiMe}_2(\text{CH}_2)_{11}\text{CO}_2\text{-Mesogen}]_2\}_4$, in which the mesogens is $-\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_4\text{OMe}$, $(\text{C}_6\text{H}_4)_2\text{CN}$ or cholesteryl, have been conducted to ascertain the electro-optical properties of these liquid crystals [1861,1862].

This type of carbosilane architecture has also been prepared, starting with 2,4,6,8-tetramethyl-2,4,6,8-tetra vinyl-2,4,6,8-tetra-sila-1,3,5,7-tetraoxacyclooctane, $[\text{Me}(\text{CH}_2=\text{CH})\text{SiO}]_4$, as the core [1863]. Partial terminal allyl functionalization has been demonstrated by hydrosilylation—addition of didecylmethylsilane, followed by lithiation (*s*-BuLi); the internal carbanionic



Scheme 103. Alkene-terminated dendrimers [1848].

sites were shielded from intermolecular interactions that notably did not aggregate [1864]. Inclusion of photochromic termini has been accomplished by simple treatment of the hydroxy-terminated carbosilane dendrimers with 4-methoxycinnamoyl chloride [126]; these photosensitive liquid crystalline materials upon photolysis underwent a combination of *E*–*Z* photoisomerization and [2 + 2]-photocycloadditions leading to 3-dimensional networks.

Ignat'eva et al. [1865] employed a repetitive Grignard–hydrosilylation sequence for the construction of a series up to G7 of poly(allyl-terminated) carbosilanes. Thermomechanical properties were examined and the T_g was found to attain a constant value beginning at G4 and larger. The steady-state and time-resolved fluorescence experiments with related poly(allylcarbosilane)-dendrons labeled at the focal site with pyrene as the probe, has been reported [1866,1867]. The self-diffusion in CDCl₃ of these poly(allylcarbosilane)s, specifically the G5–7, has been studied over a wide-range of volume concentrations resulting in a curve for the generalized dependence of the dendrimer's self-diffusion coefficients that coincides with an analogous dependence for globular proteins in an aqueous solution [1868].

The G1 and G2 carbosilanes terminated with chloro, amino, ammonium, and sulfonic acid sodium salt moieties have been analyzed by MALDI-TOF MS by Wu and Biemann [1869], while others have introduced lactose and sialyllactose moieties [1870].

Brüning and Lang [1871] employed alternating allylmagnesium bromide and allyl alcohol additions to dichlorosilane termini to afford alternating silane-siloxane generational branching. The repetitive use of this hydrosilylation–alcoholysis protocol for the synthesis of linear, as well as branched, carbosiloxane architectures has appeared [1872]. These authors also divergently constructed a related series of dendrons derived from either Me₂Si(OCH₂CH=CH₂)₂ (to G4) or Me-Si(OCH₂CH=CH₂)₃ (to G3) as the core, by alternating treatment with HSiMeCl₂ *via* platinum-catalyzed hydrosilylation then HOCH₂CH=CH₂ with base [1873,1874]. Lang et al. [1875] have presented an efficient method to prepare carbosiloxane dendrimers with end-grafted SiH-bonds by using HOCH(Me)(CH₂)₄SiMe_{3–n}H_n, which are accessible by the hydrosilylation of MeCOCH₂CH₂CH=CH₂ with HSiMe_{3–m}Cl_m and hydrogenation with LiAlH₄. Different combinations led to the G1–3 Si-dendrimers with one to four directional cores [1875]. Surface functionalization was also possible using CH₂=CHCH₂OCH₂[15-crown-5] and CH₂=CHCH₂OCH₂[18-crown-6] [1876] or simple PEG moieties [1877].

van Koten et al. [1878] described a general method for the terminal modification of Si-Cl coated carbosilanes using organolithium or organomagnesium reagents and the development of polycationic core–shell derivatives, as phase-transfer catalysts; host–guest chemistry was described [1879].

Boysen and Lindhorst [1880] selectively protected a single saccharide alcohol moiety and elaborated the remaining hydroxyl group to construct the G1 carbosilane motif.

These types of carbosilanes have been structurally established by the use of ¹H/¹³C/²⁹Si triple resonance 3D and pulse

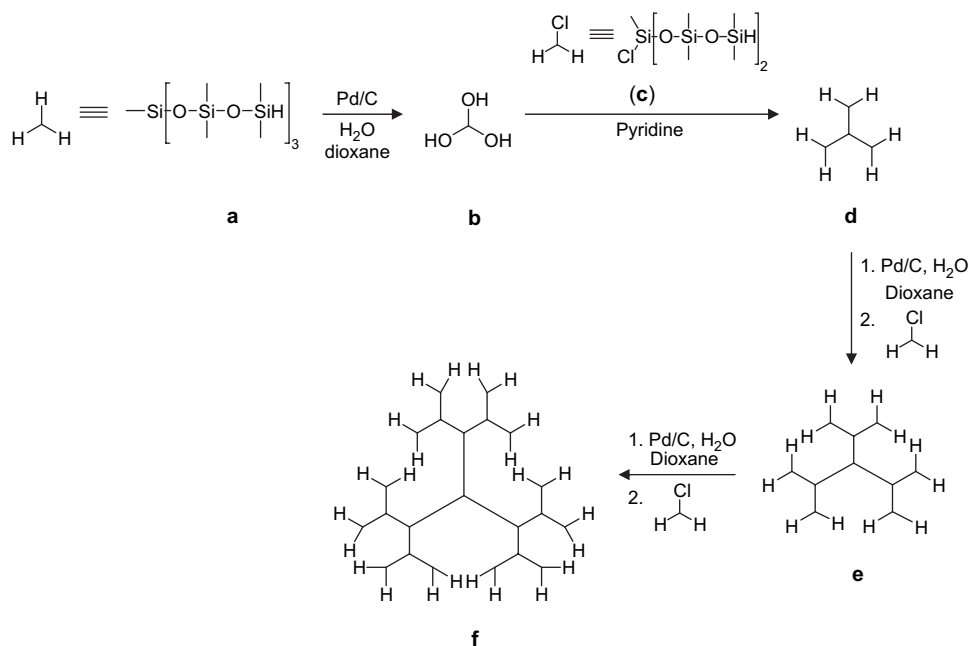
field gradient NMR techniques [1881]. This Si-dendrimer hydride core was hydrosilylated with polyfluorinated allyl ethers and monitored by ¹H and ²⁹Si NMR then characterized by atmospheric pressure chemical ionization (APCI) mass spectrometry, SAXS in C₆F₆, T_g , and TGA [1882].

Casado and Stobart [1883] created a series of 1 → 2 Si branched monomers derived from BrC₆H₄(CH₂)₃SiMe(CH₂–CH=CH₂)₂ that was adapted for sequential divergent and convergent steps to the construction of carbosilanes. The Pt-catalyzed hydrosilylation of allyl-terminated carbosilane monodendrons with the silanes {SiHMe₂[(CH₂)_nR_f]}_n, where $n = 2$, R_f = *n*-C₆F₁₃ or $n = 3$, R_f = C₆F₅, gave rise to a series of fluoro-terminated dendrons possessing the bromo focal group, *e.g.*, BrC₆H₄(CH₂)₃SiMe[(CH₂)₃SiMe₂(CH₂)_nR_f]₂, BrC₆H₄(CH₂)₃SiMe{(CH₂)₃SiMe[(CH₂)₃SiMe₂(CH₂)_nR_f]₂}, (CH₂)₃SiMe{(CH₂)₃SiMe[(CH₂)₃SiMe₂(CH₂)_nR_f]₂}, and BrC₆H₄(CH₂)₃SiMe{(CH₂)₃SiMe[(CH₂)₃SiMe₂(CH₂)_nR_f]₂]₂.

Diphenylphosphine-functionalized carbosilane dendrimers Si[(CH₂)_nSiMe₂(CH₂PPh₂)]₄ ($n = 2, 3$; G1–3) and Si[(CH₂)_nSiMe(CH₂PPh₂)]₄ ($n = 2, 3$; G1, 2) have been synthesized and utilized as ligands in the Rh-catalyzed hydroformylation of 1-octene [1884]. The Rh(I) complexes of a series of four water-soluble ligands based on the G3 PAMAM dendrimer as a core demonstrated high catalytic activity in the hydroformylation reaction of 1-octene.

Although relatively low molecular weight poly(siloxane)s were prepared through G4 [1885], Masamune et al. [1886] reported the preparation of a series of high (>10,000 amu) discrete molecular weight, Si-branching macromolecules by means of an iterative procedure utilizing two different synthetic equivalents: a trifunctional, hydrido-terminated core **104a** and a trigonal monomer **104c**. Syntheses of these two key components were accomplished by treatment of MeSiCl₃ with 3 or 2 equiv. of the siloxane oligomers, HO[Si(Me)₂O]₅Si(Me)₂H and HO[Si(Me)₂O]₃Si(Me)₂H, respectively. Repetitive Si-based transformations were used in the dendritic construction. A Pd-catalyzed silane hydroxylation of core **104a** afforded triol **104b**, which was then treated with 3 equiv. of monochloropolysiloxane **104c** to generate the hexahydrido, G1 dendrimer **104d**. Further application of the Pd-mediated hydroxylation, followed by attachment of monochloro monomer **104c** created the G2- (**104e**), and then G3- (**104f**) tiered polysiloxane dendrimers (Scheme 104).

Morikawa, Kakimoto, and Imai [1887,1888] employed a divergent methodology for the preparation of a series of siloxane-based dendrimers possessing dimethylamino, phenyl, benzyl or hydroxy peripheral moieties. Sequential tier addition involved transformation of phenylsilane termini with Br₂ to give the corresponding silyl bromide, treatment with HNET₂ to generate the silylamine moiety, and hydroxysilyl monomer displacement of the amino group. Thus, MeSi(OSiMe₂–OSiMe₂R)₃, where *R* is initially a phenyl moiety, which is subsequently converted to –Br, to –NET₂, then to –(OSiMe₂Ph), created the next tier in a simple series of displacements. Characterization by gel permeation chromatography and ¹H NMR was considered. Polydispersity indices were in



Scheme 104. Polysiloxane dendrimers [1886] via an iterative silane hydroxylation and chloride displacement.

the range of 1.30 for the phenyl-terminated G2 polysiloxane to 1.71 for the hydroxyl-terminated G3 dendrimer. The water-soluble, poly(hydrochloride) salt of the G3 dimethylsilylamine-terminated dendrimer was compared to a unimolecular micelle, as a result of structural similarities. The synthesis of multiarmed polydimethylsiloxanes has been reported and evidence for the qualitative structural transition of the molecular entities from a coil to globular structure upon increasing the number of arms was shown [1889].

The synthesis, characterization, and structure regulation of dendritic (hyperbranched) polycarbosiloxanes with a boron core have been reported for the first time [1890]. When compared to the corresponding polycarbosiloxanes of comparable molecular weight, the boron-cored materials exhibited narrower molecular weight distributions as well as a much smaller hydrodynamic radius and intrinsic viscosity.

6.3. 1 → 2 Si and C-branched, Si(Me)₂- and thioether-connectivity

The treatment of 1 → 2 Si-branched dendrimers, *e.g.*, **105a** possessing terminal carboxy moieties with allylmagnesium or 1,1,2-trifluorobut-1-enyl-4-magnesium bromide gave the 1 → 2 C-branched outer tier (**105b** or **105c**, respectively) [1694]. Subsequent reaction of **105b** with C₆F₁₃CH₂SiMe₂H with a Pt catalyst generated the desired G2 dendrimer **105d** with a fluorinated surface. The larger generation terminated esters were derived by the reaction of either Si[CH₂CH₂CH₂-SiMe(CH₂CH₂CH₂SiMe₂CH₂Cl)₂]₄ or Si{CH₂CH₂CH₂SiMe[CH₂CH₂CH₂SiMe(CH₂CH₂CH₂SiMe₂CH₂Cl)₂]₂]₄ as cores [1787], with mercaptoacetic acid, followed by esterification with EtOH and sulfuric acid, as catalyst. Although these conversions were in high yield, it was noted that reaction of

Si[CH₂CH₂CH₂Si(CH₂CH₂CH₂SiMe₂CH₂Cl)₃]₄ with mercaptoacetic acid did *not* give the desired product; there must be at least one methyl group present on the branching Si-center (Scheme 105).

6.4. 1 → 2 Si-branched and oligosilsesquioxane-connectivity

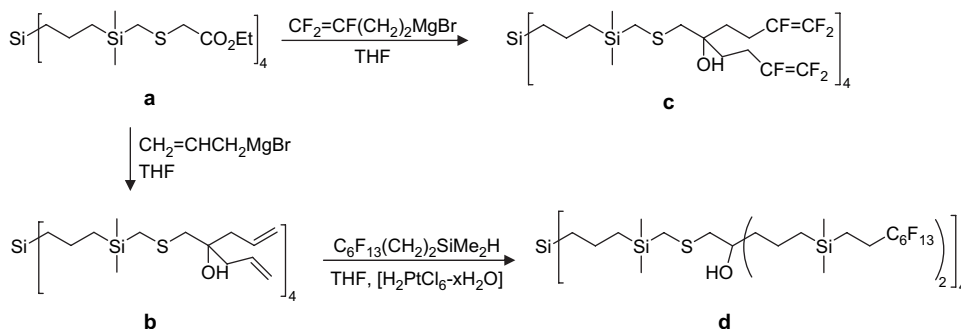
Octakis(dimethylsiloxy)silsesquioxane [(HSiMe₂)₈-Si₈O₁₂; **106a**] was reacted with 10 equiv. of silsesquioxane disilanol with a dimethylvinylsilyl group **106b** to give (83%) the branched silsesquioxane **106c** [1891]. The treatment of **106c** with 21 equiv. of chlorodimethylsilane in the presence of Et₃N in benzene at 25 °C afforded (70%) the silsesquioxane **106d**, which with 20 equiv. of **106b** in the presence of Pt catalyst for 72 h gave (63%) the idealized G2 dendritic product **106e** (Scheme 106).

Recently, a series of PEG-substituted octasilsesquioxanes was prepared [662] by the hydrosilylation of the desired unsaturated PEG with either octa(dimethylsiloxy)- or octahydrodisilsesquioxane; these would be interesting cores for dendritic growth.

7. 1 → 2 P-branched

7.1. 1 → 2 P-branched and alkyl-connectivity

DuBois et al. [1892] reported the simple construction of P-dendrimers by the free radical addition of primary phosphines to diethyl vinylphosphonate, followed by reduction (LAH) of the phosphonate intermediates to give the corresponding polyphosphines. Thus, tris-phosphine **107b**, prepared by known procedures from diphosphonate **107a** [1893,1894],



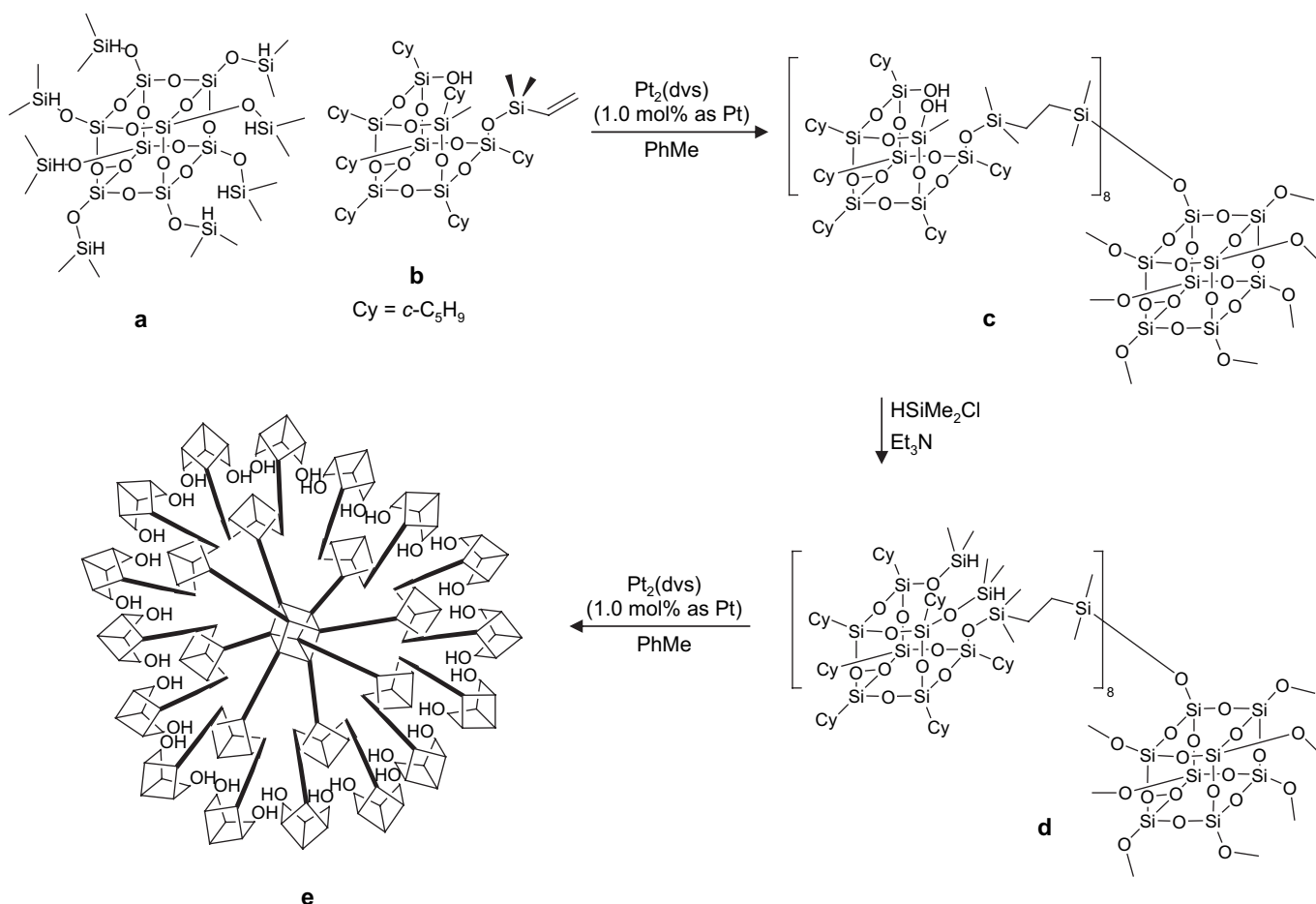
Scheme 105. Fluorinated Si-cored dendrimers [1694].

was transformed by this procedure to generate heptaphosphine **107e** or was treated with vinyl-diphenylphosphine to afford tetrakis(diphenylphosphine) **107d**. This termination procedure was also used on phosphine **107e** to give the phenyl-capped dendrimer **107f**; whereas treatment of the corresponding ethyl-terminated dendrimer **107g** with 5 equiv. of $[\text{Pd}(\text{MeCN})_4](\text{BF}_4)_2$ resulted in pentametallation. Application of this approach to *P*-dendrimers was readily applied [1892] to the creation of a tetrahedral series through the use of an appropriate four-directional silane core. Treatment of tetravinylsilane with phosphine **108a** quantitatively afforded the desired **108b**, which could

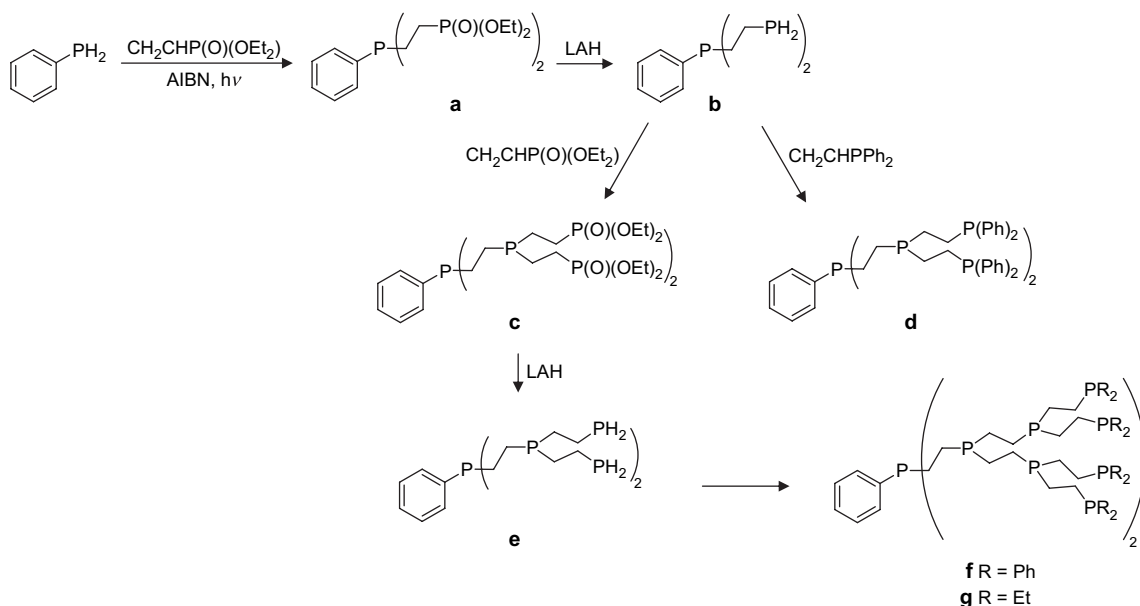
be transformed to the tetrakis(square planar palladium) complex (Schemes 107 and 108).

7.2. 1 → 2 *P*-branched and diverse-connectivity (majoral-type)

Majoral et al. [1895] reported the facile divergent synthesis of a novel series of *P*-dendrimer and has produced numerous excellent reviews delineating the multifaceted aspects of their work [110,1896–1920]. Treatment of the sodium salt of 4-hydroxybenzaldehyde **109a** with $\text{Cl}_3\text{P}=\text{S}$ gave the trialdehyde

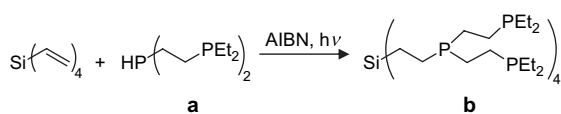


Scheme 106. The construction of a dendritic polyhedral oligosilsesquioxane [1891].

Scheme 107. DuBois et al. [1892] prepared *P*-based dendrimers for metal complexation.

109b, which was reacted with 3 equiv. of the hydrazine derivative **109c** to quantitatively afford the G1 dendrimer **109d** possessing six P-Cl bonds juxtaposed for repetition of the sequence. The G2–4 (e.g., **109e**) dendrimers were constructed *via* this simple iterative sequence. Key features of this sequence were that no protection–deprotection procedures were required and that the only by-products were NaCl and water assuming quantitative transformations. In a subsequent paper [1921], expansion of these *P*-dendrimers to the G5–7 possessing up to 384 functional groups (G7; 94,146 amu) was reported in which the long branches were composed of [–P(S)OC₆H₄CH=NNMeP(S)]-linkages introducing a semi-rigid component [–OC₆H₄CH=NNMeP(S)–] into the infrastructure [1922]. Facile functional group manipulation at the periphery permitted the attachment of α,β -unsaturated ketones, crown ethers, and alcohols. Treatment of the PCl₂ moieties with bis(allyl)amine afforded the monosubstituted termini [*i.e.*, –P(Cl)N(CH₂CH=CH₂)₂]. The surface-incorporated crown ethers interestingly acted as “shields” with respect to attempted imine hydrolysis [THF, H₂O (4:1), 25 °C, 48 h]. Spectral evidence for the structure included ³¹P NMR; in which no overlapping resonances (³¹P NMR) were observed until G4. These neutral G1–4 *P*-dendrimers possessing terminal aldehyde moieties have also been characterized by MALDI-TOF MS [1923]; typical fragmentations and formation of new bonds were shown to involve N–N cleavage, imine metathesis, and the reaction of aldehyde

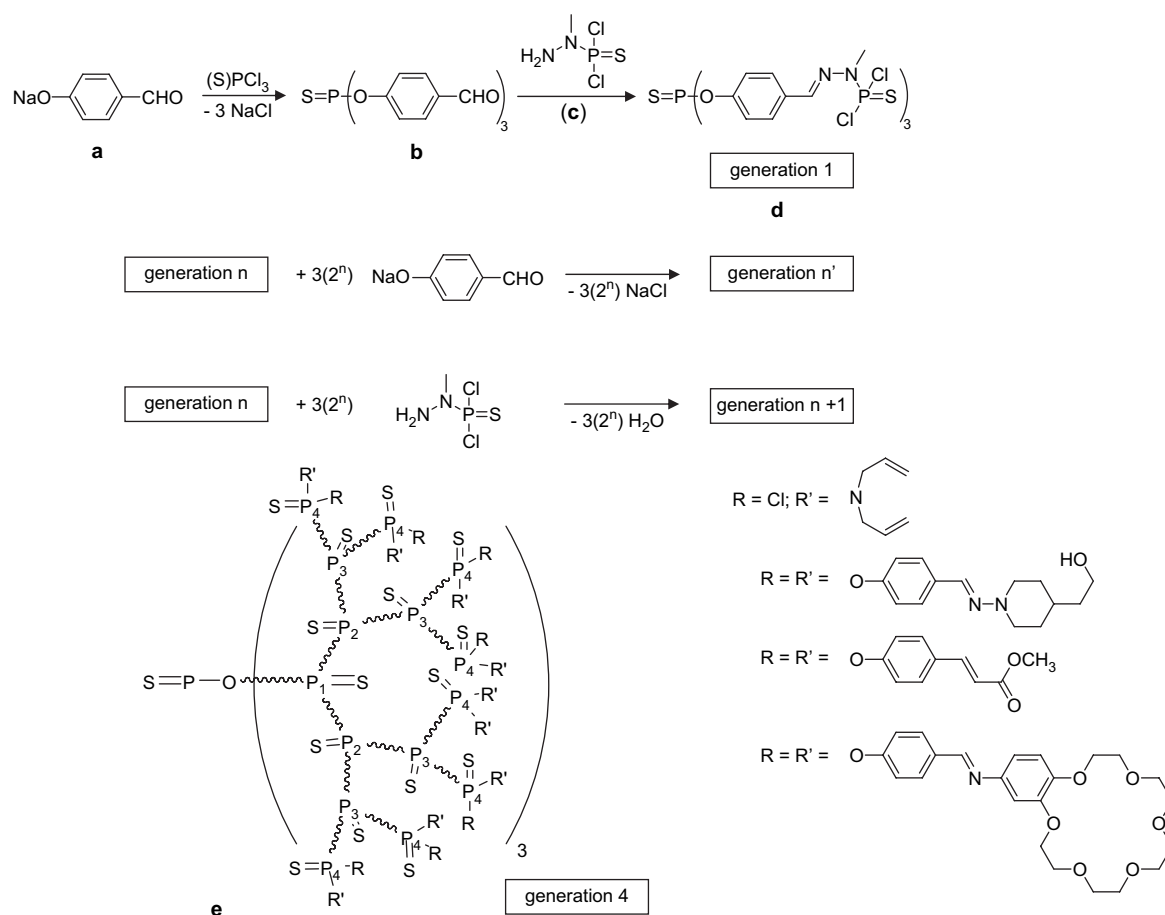
groups with internal imino groups. The aldehydic-terminated G0–4 *P*-dendrimers were easily reacted with either Girard-P [H₂NNHCOCH₂(Py)⁺, Cl[–]] or Girard-T (H₂NNHCOCH₂-N⁺Me₃, Cl[–]) reagents to create hydrogels and microscopic fibers that formed *via* the salt-induced self-assembly of the resultant water-soluble polycationic *P*-dendrimers [1924,1925]. Incorporation of different cores has been demonstrated [1926], thus the use of an octasubstituted phthalocyanine was but one option derived from the known [1927] octaformylphthalocyanine. Introduction of other semi-rigid components into the infrastructure was accomplished by the nucleophilic substitution of the –P(S)Cl₂ termini with 4-hydroxy-3-methoxycinnamaldehyde and then the subsequent condensation of the new –CHO end-groups with dichlorophosphorhydrazide [H₂NNMeP(S)Cl₂] affording an extended, semi-rigid linkages [–OC₆H₃(OMe)CH=CHCH=NNMeP(S)–] and *P*-dendrimers up to G5 [1922]. The first linear multiphosphazene possessing five different side groups has been constructed and then transformed into a dendritic structure [1928]. Majoral et al. [1929] reported a macrocycle **110a** possessing a flexible but nearly planar structure, as well as potentially existing as five diastereoisomers. In order to ascertain the presence of these isomers, **110a** was reacted with Ph₂P(C₆H₄CHO) (**110b**), but there was no evidence for the isomers. The grafting of {[MeO₂CC₆H₄O]₂P(=S)N=PPh₂C₆H₄O]₂P(=S)NMeNH₂} [1928] (**110c**) on the four aldehydic moieties *via* the formation of new hydrazone connections gave a dendronized macrocycle [1929] **110d**, which showed the existence of the diastereoisomers. Thus, it was suggested [1926] that the attachment of dendrons could act as molecular amplifiers of local hidden infrastructure anomalies [1930]. The synthesis of the G > 10 phosphino-capped *P*-dendrimers possessing >3000 phosphino termini [1931–1933] was demonstrated; these phosphino end groups were coated with [G5] P → Fe(CO)₄, [G4] P → W(CO)₅, and

Scheme 108. Free radical mediated construction [1892] of mixed *Si/P*-based dendrimers.

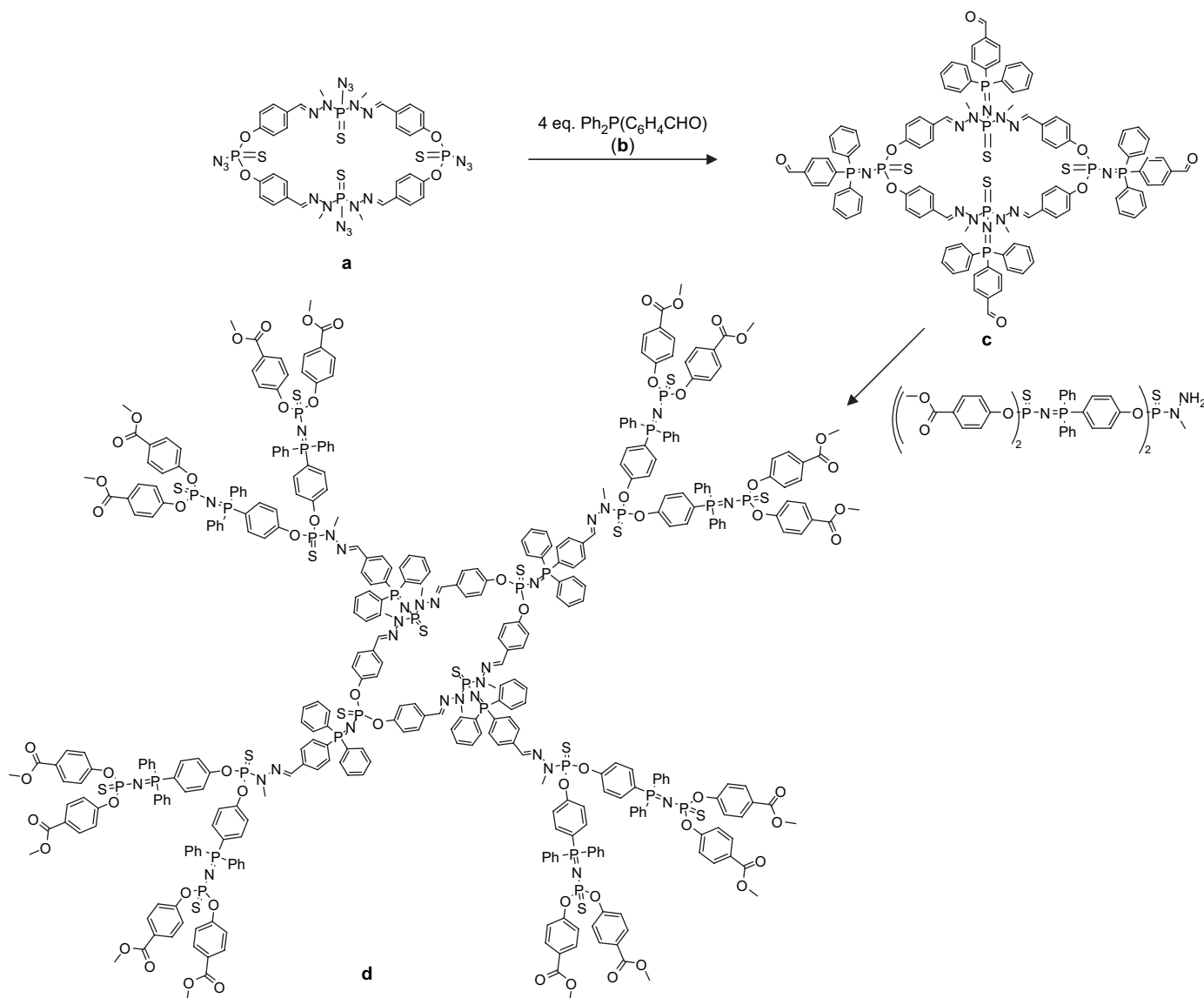
[G10] P → AuCl moieties [1934]. The use of other metals, *e.g.* Pd(II), Pt(II), and Rh(I), in this type of surface metal coating has appeared [1935] as well as Ru(II) [1936] and *via* the $-\text{N}(\text{CH}_2\text{PPh}_2)_2$ surface coating. Alternatively, Pd(II) complexes of diverse β - and γ -iminophosphines have been prepared on the surface of these P-dendrimers [1937]. The use of a G2 (see [1938] for the G4) thiol-terminated dendrimer afforded access to the attachment of an azazirconacyclopentane moiety [1939]; alternatively, a formal [3 + 2]-cycloaddition between surface aldehydic groups and 2-phosphino-1-zirconaindene gave rise to stable anionic, zwitterionic, surface zirconocene complexes [1940]. Mesostructural hybrid materials have been assembled by the use of $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}]$ clusters with small 1 → (3 + 2) dendrons possessing both a S=P focal moiety and six terminal carboxylic acid groups [1941]. The incorporation of a ferrocene core has been accomplished utilizing two-electron withdrawing P=N–P=S linkages thus altering its electrochemical properties; these substituents were capable of complexing group 11 metals [1942]. A series of related P-dendrimers possessing ferrocenyl moieties within the branches has also been reported by means of a 1,1'-disubstituted ferrocene building block [1943]. The polycationic or neutral G1–3 dendrons bearing amino end groups and a vinylic focal group as well as polyanionic or neutral G1–3 dendrons with carboxylic termini; the careful assembly *via* a convergent

type permitted a novel layer-by-layer construction, including a silica surface [1944] (Schemes 109 and 110).

The synthesis and spectral details of the $G < 3$ P-dendrimers based on a cyclotriphosphazene core $[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{CHO})_6]$ [1945,1946], and step-wise construction with methylhydrazine, followed by either Ph_2PCl or chlorodiazaphospholane and then capping the terminal aminophosphino moieties with $\text{N}_3\text{P}(\text{S})(\text{OC}_6\text{H}_4\text{CHO})_2$, have been reported [1947]. The simple procedures led to a spherical surface bearing electrophilic or nucleophilic reactive moieties, such as aldehydes, hydrazones, and aminophosphines. Small P-based dendrimers, possessing peripheral aldehyde, amine, phenoxy, phosphine or P–Cl moieties and starting from $\{(\text{S})\text{P}[\text{N}(\text{Me})-\text{NH}_2]_3\}$, have also been reported [1948]. Additional notable chemistry of interest associated with these novel dendrimers includes [1717,1916,1933,1949–1952]: phosphate-, phosphite-, ylide-, and phosphonate-surface groups [1953]; use of the Horner–Wadsworth–Emmons reaction to generate α,β -unsaturated and amino acid surfaces [1954]; dipole moment measurements [1955]; phosphoryl group chemistry [reiteration of aldehyde and P(O)Cl₂ end groups] and capping with different surface moieties: α,β -unsaturated esters, crown ethers, chiral phosphine sulfides, and diallylamine [1956]; chemoselective polyalkylations and the introduction of charged layers [1957]; chiroptical properties of stereogenically



Scheme 109. A series of neutral pentavalent P-based dendrimers [1895].



Scheme 110. Attachment of a bulky dendron to ascertain topological differences [1929].

terminated materials [1958]; coating of the surface with tetraazamacrocycles [1959]; incorporation of internal $\text{P}=\text{N}-\text{P}=\text{S}$ linkages permitting regiospecific grafting of isothiocyanate, aldehyde and primary amine derivatives, postconstruction [1960]; chemoselective internal infrastructure functionalization [1961]; X-ray diffraction studies [1955]; X-ray photoelectron spectroscopy [1962]; layer-block construction with regular alternation of repeat units $[\text{RP}(\text{S})/\text{RP}(\text{O})]$ [1963]; incorporation of a central 2,6-disubstituted pyridine moiety [1951]; steady-state fluorescence spectra and the decay of excitation of a *P*-dendrimer possessing 12 internal pyrene-labels dissolved in diverse solvents [1964]; a combined TSC and DDS study permitting insight into temperature and frequency dependence of β -relaxation [1965–1967]; IR [1968] and Raman spectra [1969–1978]; temperature-modulated calorimetry and standard differential scanning calorimetric techniques with G1–5 *P*-dendrimers possessing a strong $\text{P}=\text{S}$ dipole [1979]; the thermostimulated currents and broadband

dielectric spectroscopy of G1–5 *P*-dendrimers as related to fractal architecture and surface functionalization [1980]; and Raman spectra of G0–10 *P*-dendrimers possessing aldehydic termini [1981]. Thermal stability of different families of these *P*-dendrimers has been studied, and depending on the structural composition, up to 70% of the initial mass was retained at 1000 °C [1982]. The synthesis and supramolecular auto assembly of catanionic, low generation, *P*-dendrimers mimicking multisite analogs of galactosylceramide have been reported [1983,1984]. The advent of “dendrilsides” for accurate, reliable, and cost effective DNA assays has been described; these dendrilsides are still active after 3–5 months of storage at ambient temperature [1985,1986]. “Dendrilsides,” which are stable, reusable, and highly sensitive DNA chips [1908], have added a novel addition to this exotic and utilitarian Majoral family of *P*-dendrimers. Interestingly, the formation of nanoscopic fluorescent *P*-dendrimers possessing up to 96 two-photon chromophores exhibited a very large

two-photon absorption cross-section and they were suggested to be an organic alternative to quantum dots or “nanodots” [1987,1988]. The initial studies directed to using these Majoral dendrimers, as biosensors for DNA microarrays and microchips, are being evaluated in medicinal, forensic, and environmental analyses [1989]. A new device based on 4×4 matrix micro-machined resonating piezoelectric membranes used as DNA–DNA hybridization biosensor has been developed [1990].

The crystal structure of $S=P(O-p-C_6H_4-CH=NNMe-POCl_2)_3$, a convenient core, was determined [1963]. The use of a tetraphosphorus macrocyclic core possessing the bulky *P*-dendrons afforded evidence for the first time of the amplification of topological differences in the core as shown by ^{31}P NMR [1930].

Additional reports include hybrid materials [1991–1995], redox-active [1992,1996,1997], and multidentate systems derived from divergently generated dendrons [1998]. These *P*-based dendrimers have been terminated by conjugated bi-thiophene moieties affording electroactive materials, as demonstrated by cyclic voltammetry, electronic absorption spectra, supporting the formation of polydendrimers *via* intermolecular bond formation [1999]. The introduction of an *N,N*-disubstituted end-groups [2000–2002] permitted the use of Schiff base chemistry to introduce carbohydrates [2003], carboxylic acid and boronic acid functionality onto the dendritic surface. *N*-Thiophosphorylated [$R_3P=N-P(S)R_2'$] and *N*-phosphorylated [$R_3P=N-P(O)R_2'$] iminophosphoranes have been reported as models for dendrimer construction [2004]. The catalytic activity of a series of the G1–3 *P*-dendrimers coated with *N*-[(1*E*)-pyridin-2-ylethylene]-aniline was evaluated to ascertain their ability to stabilize copper by means of the presence of this bidentate chelators [2005]. The catalytic activity was demonstrated for simple *O*-arylations as well as the *N*-arylation and vinylation of pyrazole thus supporting a strong dendritic effect with these coated *P*-dendrimers. Different families of these *P*-dendrimers having chiral ferrocene moieties specifically located within the shell of the dendrimer have been synthesized [2006]; their electrochemical and chiroptical properties have been shown.

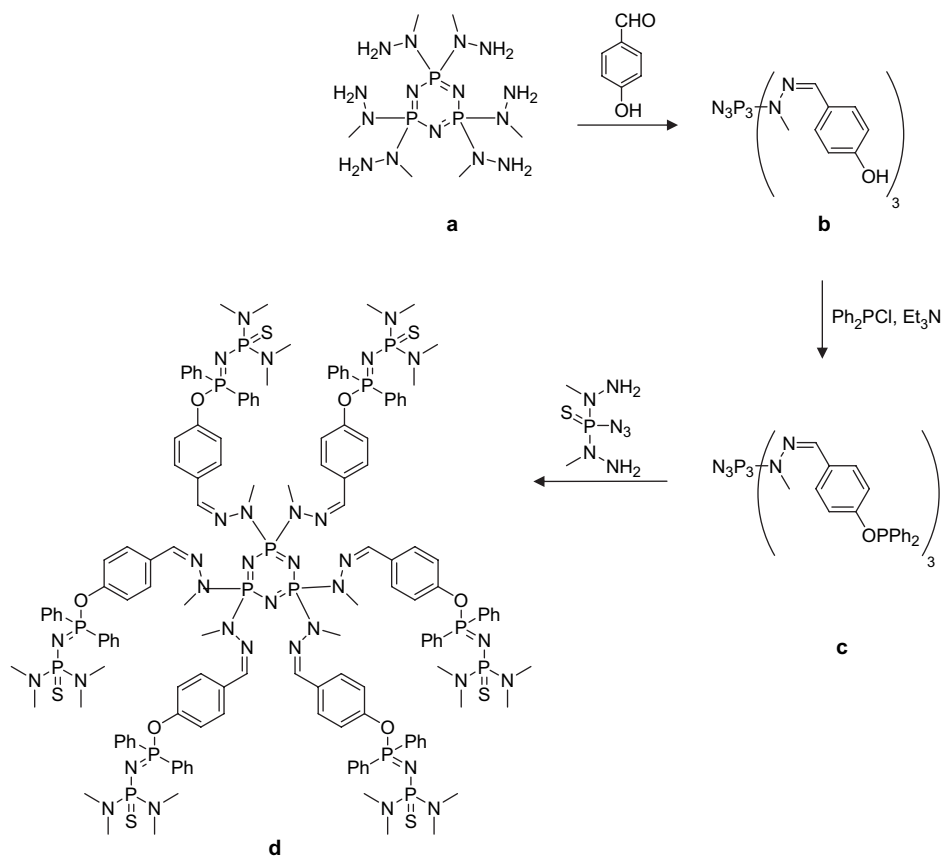
Schmid et al. [2007,2008] used thiol-terminated, G4 Majoral-type dendrimers as matrices for perfect crystal growth of Au_{55} clusters that coalesced into “well-formed” microcrystals (Au_{55})_{*n*}; the role of the dendrimer was proposed to remove the phosphine and chloride ligands and to act as an ideal matrix for perfect crystal growth. The divergent construction of *P*-dendrons has afforded a simple method to convergently combine these dendrons in order to generate surface-block, layer-block, layered surface-block, or segment-block dendrimers – all from the original dendron [2009]. An alternate approach to the growth of a second dendritic wedge on the core of a first dendron is a slightly more difficult route to the generation of diblock *P*-dendrimers but provides an expanded methodology to tailored materials [2010]. The incorporation of a hydrolyzable $Si(OEt)_3$ moiety at the critical focal point has been prepared, thus permitting its inclusion

in dendrimer (dendron)-silica xerogels; this dendron remained intact during the sol–gel process [2011]. The smallest 1,2,3,4-heterohexatriene studied by the Majoral group is that of $H_2C=CHP(Ph)_2=NP(OPh)_2=O$ [2012], which was synthesized in quantitative yield from diphenylvinylphosphine and diphenylphosphoryl azide [2009].

Since surface functionalization of dendrimers is generally the easiest of structural modifications possible, the introduction of tetrathiafulvalene (TTF) on the surface and subsequent modification of electrodes [1996] and electroconductivity [2013] have been demonstrated. The incorporation of surface pyridinium chloride moieties afforded examples of water-soluble, pH independent *P*-dendrimers that can act as gelators in water, permitting the incorporation of various organic and organometallic guests under very mild conditions [2014]. Surface functionalization with various primary and secondary amine, alcohol, glycol, and azide groups was readily achieved by thioacylation involving dithioester end groups and various functionalized amines [2015]. When this procedure used *S*-benzyl-4-hydroxydithiobenzoate to functionalize the surface of the dendritic precursor bearing $SPCl_2$ termini, a dodecafunctional *P*-containing dendritic reversible addition–fragmentation chain transfer (RAFT) agent was synthesized [2016]. Introduction of bis-phosphine [2017] or imine-phosphine [2003,2018] moieties permitted access to the metallodendrimers that proved to be efficient and recoverable. The G3 *P*-dendrimer based on $[-OC_6H_4CH=NNMeP(S)-]$ connectivity possessing 24 chiral iminophosphine termini was derived from (2*S*)-2-amino-1-(diphenylphosphinyl)-3-methylbutane [2019]. The surface functionalization of a supramolecular auto-assembly afforded a water-soluble cationic *P*-containing dendrimers of low generation possessing multi-site analogs of galactosylceramide (Gal β_1 cer) [1983,1984]; the goal is the “blocking [of] HIV infection prior to the entry of the virus into human cells.” A novel two-directional core has been used to divergently build their *P*-dendritic infrastructure with the design of water-soluble two-photon markers from lipophilic two-photon fluorophores leading to *in vivo* imaging possibilities [2020].

Internal differentiation within a dendrimer superstructure has been very limited since it must incorporate predetermined lability, thus Majoral et al. elegantly addressed this by the grafting of allyl and pyrene derivatives *inside* the dendrimers during construction [2021] by capitalizing on selectivity of the reaction of amines and hydrazides with only one Cl on each of the $P(S)Cl_2$ or $P(O)Cl_2$ end groups.

Majoral et al. [1932,2022] demonstrated the versatility of cyclotriphosphazene **111a** as a starting core, which was obtained in high yields by the treatment of hexachlorocyclotriphosphazene with methylhydrazine. Hexamine **111a** was initially condensed with *p*-hydroxybenzaldehyde hexaphenol **111b**, and then that product was treated with PPh_2Cl to give the corresponding hexadiphenylphosphine **111c**. Reaction of **111c** with azidophosphodihydrazide [2023] yielded the 12-amino-terminated dendrimer **111d**, which was fully characterized by ^{31}P NMR. Similar chemistry has been employed for the synthesis of “bowl-shaped” dendrimers through G8



Scheme 111. Dendrimer construction using a cyclotriphosphazene core [2022].

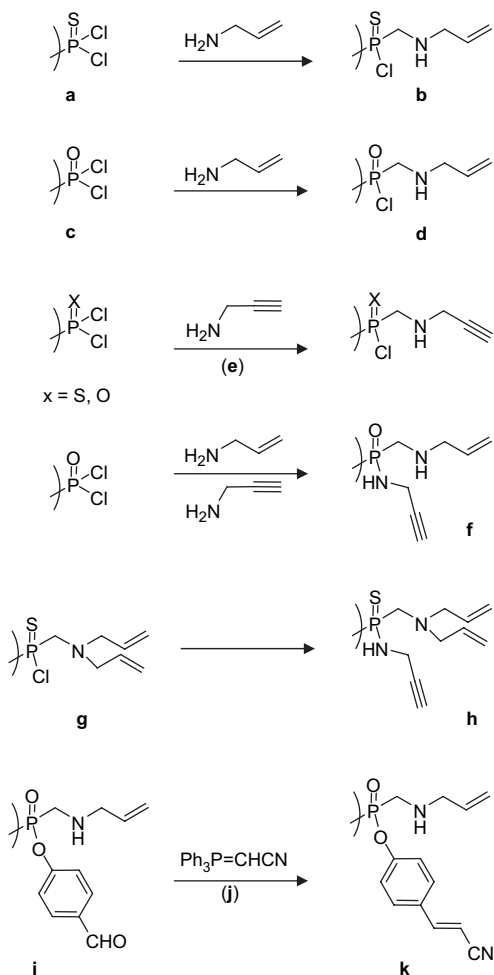
possessing a purported 1536 surface aldehyde moieties [2024] (Scheme 111).

A family of poly(organophosphazenes) possessing ethyleneoxy side-chains has been reported for investigation of solid electrolyte properties [2025].

Majoral et al. [2026] reported the tri- and tetrafunctionalization at the terminal units of their *P*-based dendrimers. The introduction of multiple substituents at each chain end [$P(S)Cl_2$ or $P(O)Cl_2$] was predicated on quantitative and selective monosubstitution at each terminus prior to the observation of disubstitution. Thus, reaction of the dichlorothiophosphoryl moieties **112a** with 1 equiv. each of allyl amine afforded the trifunctional chlorophosphoryl amido alkene **112b**. Reaction of dichlorooxaphosphoryl termini **112c** proceeded with similar selectivity to give the desired monoalkene **112d**, while similar reactivity was observed when propargyl amine (e.g., **112e**) was used instead of allyl amine. Treatment with 1 equiv. of allyl amine, followed by 1 equiv. of propargyl amine, yielded the desired ene-yne moiety **112f**. Attempts to react excess bis(allyl)amine in order to obtain the tetraalkene only gave the monosubstituted product **112g**, which was further treated with propargyl amine to afford the diene-yne **112h**. Nitrile surface groups were also introduced by the Wittig reaction of phosphate aldehyde **112i** with nitrile **112j** to give ene-nitrile **112k** (Scheme 112).

Majoral et al. [2027] modified the termini of these *P*-based dendrimers such as that shown in Scheme 109: benzaldehyde-coated dendrimers were reacted with various amine- and

hydrazine-based reagents, such as hydrazine, methylhydrazine, 1-amino-4-(2-hydroxyethyl)piperazine, fluorenone hydrazone, and 4-aminobenzo-15-crown-5. Wittig transformations affording α,β -unsubstituted ketone and nitrile termini were effected by reaction with (acetylmethylene)- or (cyanomethylene)-triphenylphosphorane, respectively; and finally, exhaustive substitution of $P(S)Cl_2$ termini was achieved by treatment with allyl amine, propargyl amine or *N*-(trimethylsilyl)imidazole. Selective internal *S*-alkylation of a $[P=N-P(S)]$ group by treatment with CF_3SO_3Me , followed by $P(NMe_2)_3$ produced the highly reactive internal $P=N-P$ moieties [2028]. The addition of $N_3P(S)(OC_6H_4CHO)_2$ generated an excellent starting point for the branched construction of the infrastructure. The preparation of G1–5 thiophosphate-based dendrimers, predicated on phosphorylation of propanediol derivatives and reaction with elemental sulfur, has been reported [2029]. The hemotoxicity and cytotoxicity of the water-soluble, G5 thiophosphate dendrimer have been ascertained as well as their impact on the growth of nucleated Chinese hamster ovary cells; their interaction with erythrocyte membrane proteins triggered eicnocyctosis and increased erythrocyte membrane stability as well as its thermal stability [2030]. Preliminary studies have shown that *P*-dendrimers possessing *N,N*-diethylethylenediamine hydrochloride on the surface, showed moderate cytotoxicity toward HeLa, HEK 293, and HUVEC cells in a standard MTT assay in serum-containing medium, generally lower than lipofection [2031].



Scheme 112. Surface functionalization of dichlorophosphoryl termini [2026].

Hollow microcapsules composed of poly(styrenesulfonate) [PSS] and the G4 PAMAM were previously prepared [1251]. Vinogradova et al. prepared polyelectrolyte *P*-dendrimer multilayer microcapsules by alternating poly(styrenesulfonate) and positively charged G4 dendrimer or alternating poly(allylamine hydrochloride) with the negatively charged G4 dendrimer [2032].

An “orthogonal coupling strategy,” generally applied to the convergent route to dendrimers, has been utilized in a simple divergent pathway [2033], in which two key AB₂ monomers were utilized: (1) 2 equiv. of NaCC₆H₄PPh₂ [2034] were reacted first with P(S)Cl₃ to give ClP(S)(OC₆H₄PPh₂)₂, then with MeHNH₂ to afford H₂NNMeP(S)(OC₆H₄PPh₂)₂ (**113b**) and (2) [N₃P(S)(OC₆H₄CHO)₂] (**113d**), previously prepared [2023]. Starting with (S)P(OC₆H₄CHO)₃ (**113a**), as the core, treatment with 3 equiv. of **113b** generated G1 **113c**, then the Staudinger reaction [1947,2000,2009] with 6 equiv. of **113d** gave G2 **113e**. The G4 *P*-dendrimer **113g** was thus made in a one-pot synthesis with quantitative conversions — no need for the deprotection and no cumbersome by-products [2035]. The use of the related azido[3,5-bis(borane-diphenylphosphino)phenoxy](phenoxy)thiophosphate, {N₃P(=S)(OC₆H₅)[OC₆H₃(PPh₂·BH₃)₂]}, has been reported [2036]; it was initially treated with PPh₃, followed by removal of the

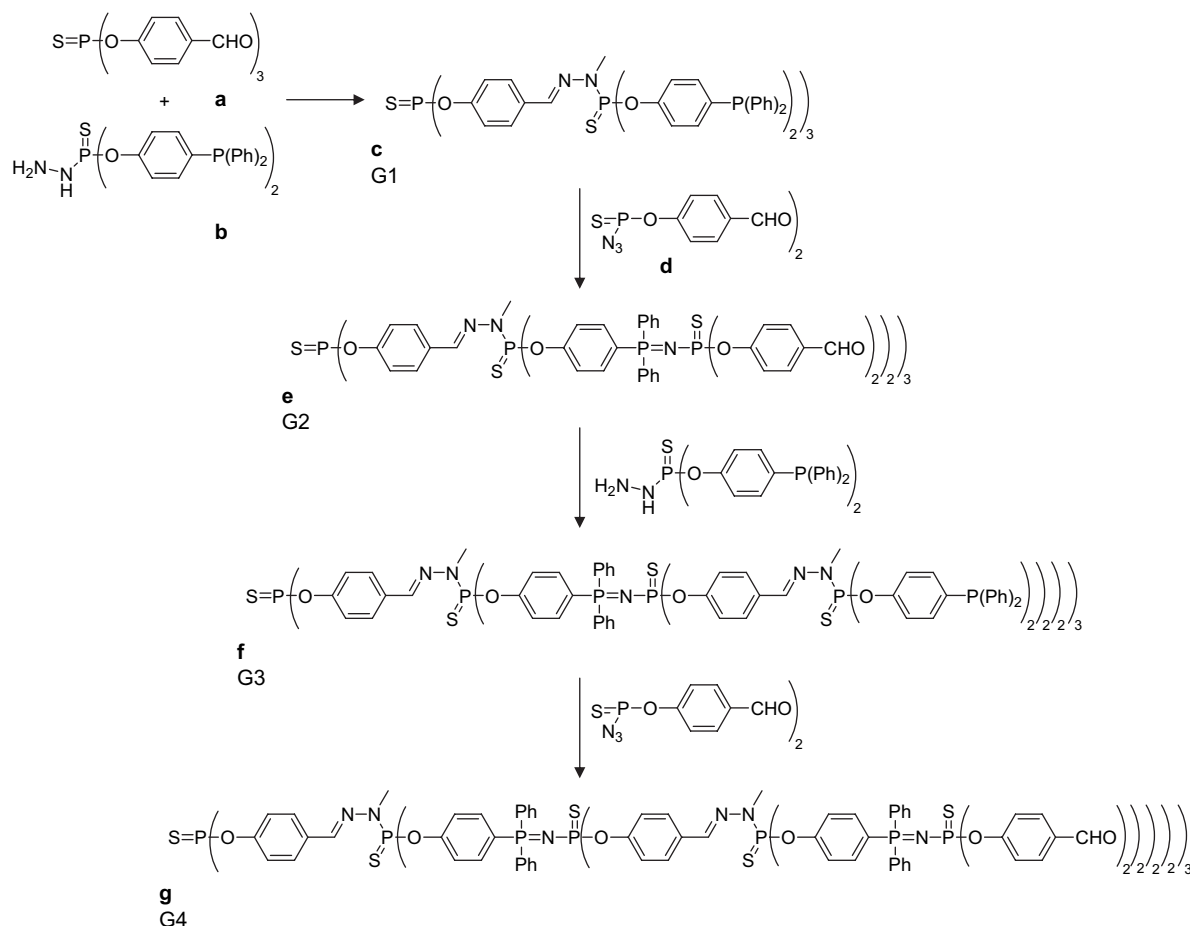
borane protection group to generate {Ph₃P=NP(=S)(OC₆H₅)[OC₆H₃(PPh₂)₂]}, which when treated with 2 equiv. of the above azide formed the desired —P(PPh₂)=NP(=S)(OC₆H₅)[OC₆H₃(PPh₂·BH₃)₂] termini. The specific insertion of azobenzene derivatives at different generations, both internally and on the surface, has been reported [2037]; irradiation at 350 nm induced isomerization of these azobenzene groups from the *E* to *Z* form irrespective of location. A novel synthetic strategy to generate related linear, hyperbranched, and dendritic *P*-polymers as well as a comparative study of their physical properties has been presented [2038] (Scheme 113).

A family of *P*-dendrimers using an octaaldehydic metal-free phthalocyanine core was divergently constructed [2028] using >G5 dendrons possessing an organic soluble surface functionality, which was transformed into water-soluble ammonium groups [1926,2039]. Five different generations of the water-soluble *P*-dendrimers, based on a hexasubstituted cyclophosphazene core, had previously been examined as transfection agents of the luciferase gene within 3T3 cells [2040], of which, those possessing ammonium surfaces in the G3–5 size range were more efficient.

The attachment of a pesticide (fipronil) to the surface of Majoral’s dendrimers by means of a very sensitive imine connection has been accomplished and demonstrated to be released by simple hydrolysis *via* Route A [2041]. The rate of release was shown to be faster for the G4 dendrimer **114c** (37% after 35 days) than that of G1 (**114b**) (12%). An alternative hydrolysis Route B occurred at the unexpected P-OAR connection (Scheme 114).

The *P*-dendrimers possessing perfluoroalkyl surfaces were reported to be soluble in chlorofluorocarbons and with either guanidinium or pyridinium surfaces instilled hydrophilic properties [1982].

A series of selenophosphate dendrimers has been created [2042] by treatment of Se=P[O(CH₂)₃OH]₃ (**115a**) with a slight excess of the Et₂NP[O(CH₂)₄OAc]₂ (**115b**) in the presence of tetrazole to generate an intermediate and ethylammonium salt of tetrazole; treatment of this initial adduct with pyridine and black selenium afforded (94%) the desired dendrimer possessing an acetate surface that was subsequently cleaved with K₂CO₃ in MeOH to quantitatively generate the corresponding polyol **115c**. The sequence was repeated to afford (98%) the G2 polyol **115d**. The next two tiers were formed in the same repetitive manner in 70% and 52% yields, respectively. Treatment of the G3 selenophosphate dendrimer **115e** with *tert*-BuO₂SiMe₃ in CH₂Cl₂ for 75 h gave (96%) the corresponding water-soluble phosphate analog **115f** [2042]. In the synthesis of *P*-dendrimers possessing different (P=Se, P=O, and P=S) branching units in the same molecule, *e.g.*, {[[[(AcO(CH₂)₅)₂]₂P(=O)(CH₂)₄]₂P(=S)(CH₂)₅]₃P(=Se)}], the application of *t*-butylperoxy-trimethylsilane, as a selective oxidant of phosphite to phosphate, was demonstrated with the retention of the sensitive P=S and P=Se moieties [2043]. Synthesis of water-soluble, polyanionic conjugates of these G1,2 thiophosphate dendrimers with acyclovir has been reported to be potential antiviral prodrug candidate [2044] (Scheme 115).

Scheme 113. Divergent “orthogonal coupling system” to *P*-dendrimers [2033].

Phosphitylation of tris(5-hydroxypentyl)boranophosphate, $\text{H}_3\text{B} \leftarrow \text{P}[\text{O}(\text{CH}_2)_5\text{OH}]_2$, with the phosphoramidite $\{\text{Et}_2\text{NP}[\text{O}(\text{CH}_2)_5\text{OAc}]_2\}$ in the presence of tetrazole in CH_2Cl_2 followed by borane-methyl sulfide cleanly gave (93%) the G1 dendritic boranophosphotriester $\{\text{H}_3\text{B} \leftarrow \text{P}[\text{O}(\text{CH}_2)_5\text{OP}(\rightarrow\text{BH}_3)[\text{O}(\text{CH}_2)_5\text{OAc}]_2\}_2$ (**3P₄B₄**) [2045]. Cleavage of the acetate groups was accomplished with saturated K_2CO_3 in MeOH, then repetition of this simple sequence gave G2 (**3P₁₀B₁₀**; 90%), G3 (**3P₂₂B₂₂**; 82%), and then G4 (**3P₄₆B₄₆**; 59%). Removal of the BH_3 was conducted by the treatment of the boranophosphotriester with Et_3N at 80°C affording the corresponding air-sensitive labile phosphite dendrimers [2045].

7.3. 1 → 2 *P*- and 1 → 2 pyridinyl-branched and -connectivity

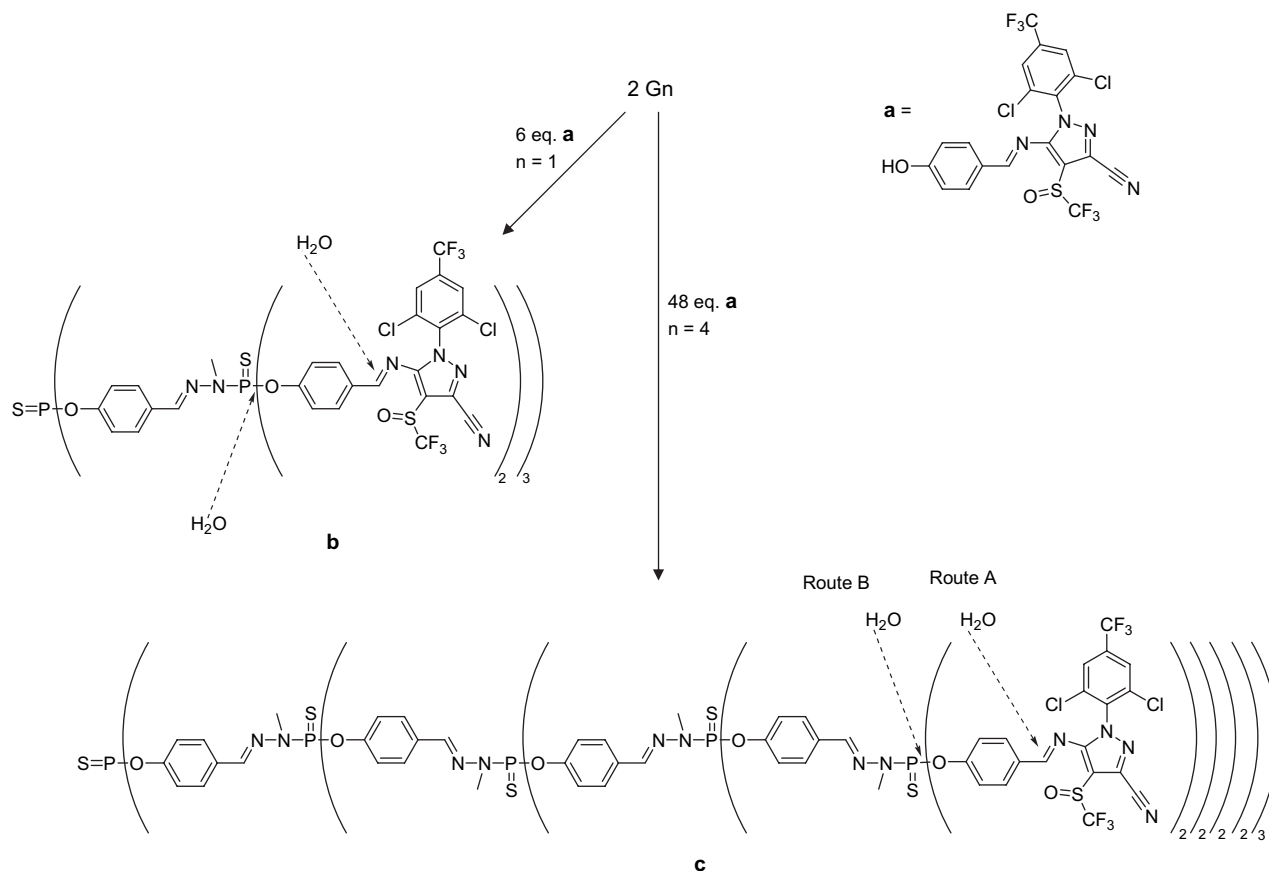
The treatment of 4-bromo-2,6-disubstituted-pyridine, initially with *n*-butyllithium, generated the intermediate lithio-derivative, which was added to 1,2-bis(dichlorophosphino)ethane to afford the desired 1,2-bis{[2',6'-di(substituted)pyridinyl]phosphine}ethane in *ca.* 20–30% yield [2046].

8. 1 → 2 Calix[4]arenyl-branched

8.1. 1 → 2 Calix[4]arenyl-branched, amide-connectivity

The synthesis of the two key monomers, **116c** and **116f**, was accomplished from the readily available calix[4]arene **116a**, which when treated with 2.1 equiv. of ethyl bromoacetate gave the desired diether **116b**. Partial saponification of **116b** with KOH in acetone followed by nitration gave (80%) the monoacid **116c** that is readily converted into the corresponding acyl chloride **116d**. The second monomer was derived from **116b** upon nitration [2047] and subsequent quantitative reduction generated the desired diamine **116f**, which with 2 equiv. of acyl chloride **116d** gave (60%) trimer **116g** as confirmed by its X-ray crystal structure. Hydrogenation of this tetraester **116g** gave the tetraamine **116h**, which with 4 equiv. of acyl chloride **116d** generated (27%) the dendritic G2 heptacalix[4]arene (not shown) [2048]. A review of dendritic calix[4]arenes and thiacalix[4]arenes has recently appeared [2049] (Scheme 116).

Thiacalix[4]arenes have also been introduced as the alternating core, which is reacted with an aminocalixarene to assemble the first stages of calixarene-based dendritic structures [2050].



Scheme 114. Location for hydrolysis and fibronil imine termini [2041].

Böhmer et al. [2051] have initiated a self-sorting process of different tri- and tetrathiaureas to self-assemble dendritic structures possessing calix[4]arenes with different rim substituents.

8.2. 1 → 2 Calix[4]arenyl-branched, ether- and ether-connectivity

Monomer **117a**, previously prepared by Reinhoudt et al. [2052], was reduced (NaBH_4) to the alcohol, **117b**, or hydrolyzed ($\text{Me}_4\text{N}^+ \text{OH}^-$) to the bis-free-acid **117c**, which was subsequently esterification (DCC/DMAP) with 2 equiv. of **117b** to give (91%) the desired G1 dendron **117d** [2053]. Although both divergent and convergent routes were considered, because of the difficulties associated with the selective hydrolysis of the different ester moieties, the convergent route was selected for the creation of the G2 dendron. The specific reduction of **117d** gave the corresponding alcohol, which was treated with the bis-acid **117c** affording (88%) the desired product (Scheme 117).

9. 1 → 2 B-branched, pyridinyl-connectivity

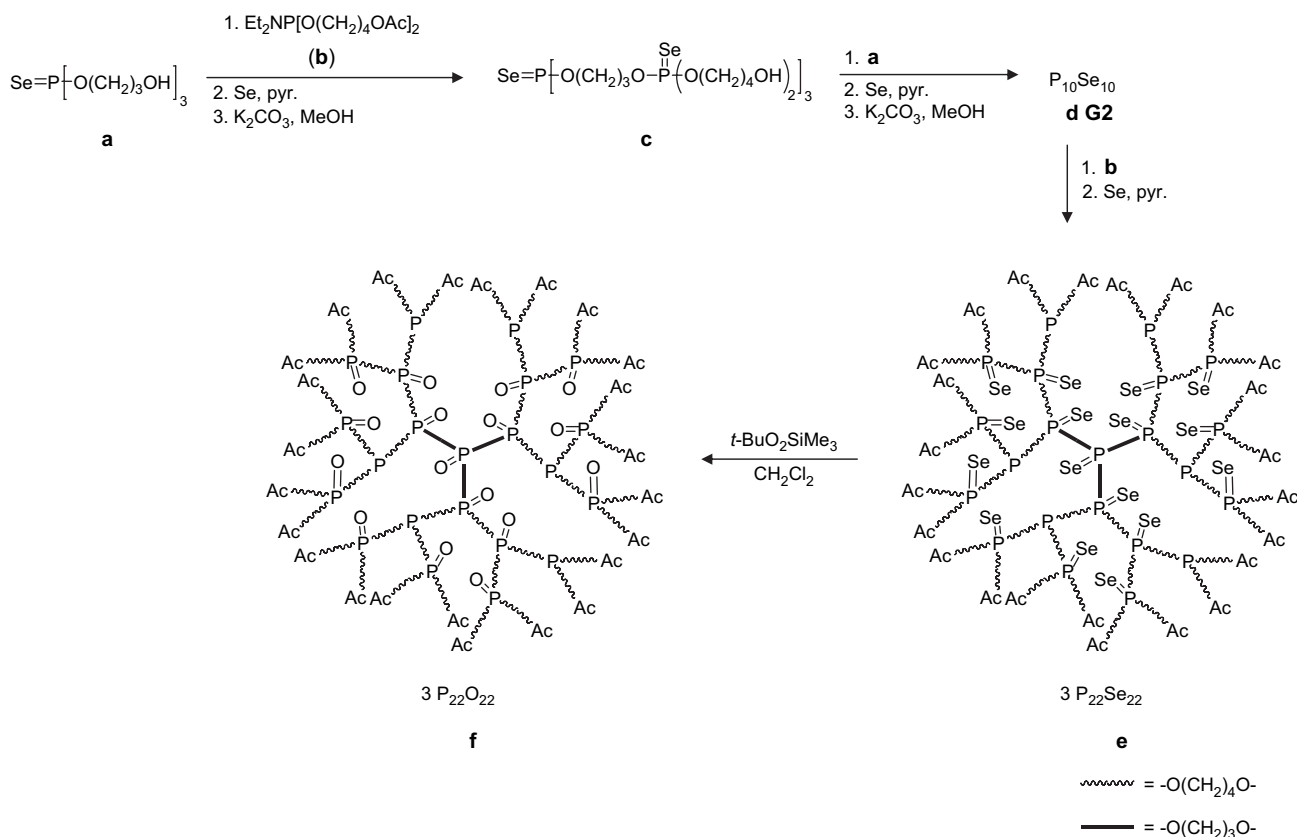
The novel assembly of boron–nitrogen bonds has led to the formation of two- and three-directional dendrimers based on 1,4-bis- or 1,3,5-tris(bromoboryl)benzene with 2 or 3 equiv. of 4,4'-bis(but-3'-enyl)-2,2'-bipyridine affording the

corresponding 2,2'-bipyridinylboronium cations in nearly quantitative yields [2054]. The terminal olefins, as shown in the dendron **118a**, can be treated with $\text{HSiEt}_3/\text{BBr}_3$ to hydroborate the unsaturated center generating **118b**, then its treatment with bipyridine afforded the next generation **118c**. Although the procedure was not pursued to higher generations, the process is certainly amenable to such growth (Scheme 118).

10. Theoretical aspect as related to 1 → 2 branched dendrimers

de Gennes and Hervet [1522] statistically found that these cauliflower-like polymers [24] (nee dendrimers) exhibited restricted idealized growth; this phenomenon is also known as “dense packing”, when the number of generations $m = m_1$, where $m_1 \cong 2.88 (\ln P + 1.5)$. This relates in space to the limiting radius R_1 , which increases linearly with P monomers. Below this limit, the radius $R(M)$ of the dendrimer, when plotted as a function of molecular weight (M), should increase ($m^{0.2}$); above this limit ($R > R_1$), compact structures ($R \approx M^{0.33}$) should result.

Murat and Grest [555] performed a molecular dynamics study of dendrimers using a coarse-grained model in varying quality solvents. The dendrimers were found to possess a space filling, or compact, structure under all solvent conditions, and the radius-of-gyration was proportional to the number of



Scheme 115. The synthesis of selenophosphate dendrimers [2042].

monomers (*i.e.*, $R_G \propto N^{1/3}$). Higher generation dendrimer density profiles, under diverse solvent conditions, showed core regions possessing high density, probably due to back-folding of the outer segments. At maximum size, density was nearly uniform throughout, while for low generations ($0 \leq g \leq 4$) higher density was found to be localized near the surface, or termini; this is in agreement with the earlier studies [539,1161]. Giupponi and Buzza [544] have recalculated the radius-of-gyration, the form factor, and the intramolecular density profile for G1–8 dendrimers and have shown that their data qualitatively fit the earlier work [539], suggesting that the error due to detailed balance violation was much smaller for self-avoiding dendrimers.

Using Gaussian monomer–monomer interactions, Hammouda determined the structure factors, $P(q)$, for regular dendritic gels [2055] and two-dimensional tetrafunctional networks [2056]; structural considerations included intrabranched self- and cross-correlations, as well as interbranch correlations.

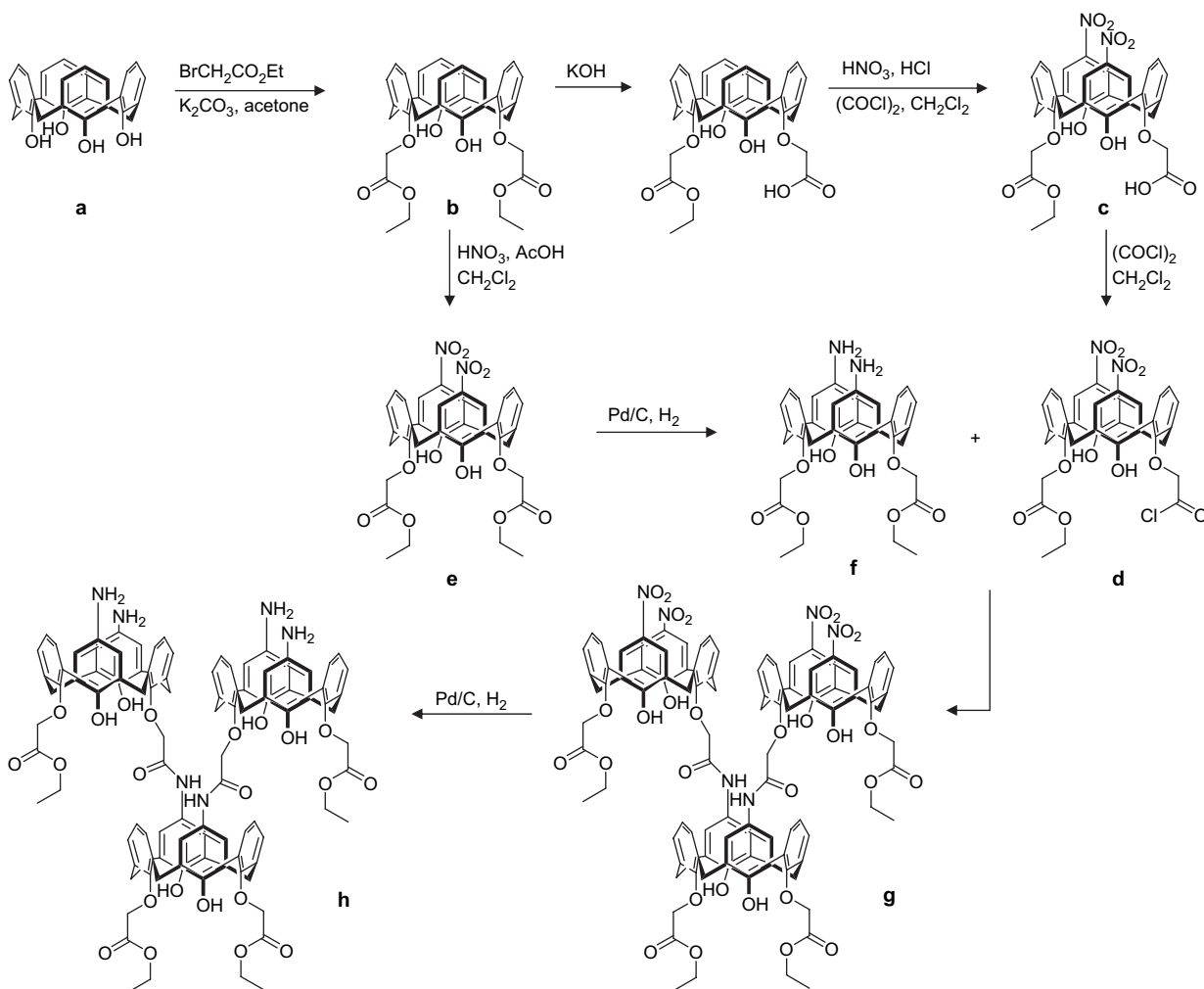
La Ferla [2057] examined dendrimers using the extended Rouse–Zimm discrete hydrodynamic model. Pertinent dynamic parameters were studied on the basis of criteria, such as local stiffness, topology, and generation. Good agreement with previous results [589] was found with respect to moderate local increases in stiffness, accounting for dendritic molecular dimensions and intrinsic viscosity.

By Monte Carlo calculations, Mansfield [1162] investigated the segregation of individual branches at equilibrium. It was postulated that in solutions of the highest attainable generation

in poor solvents or in neat dendritic fluids, branch segregation disappears. Fractal dimensions for dendrimers were ascertained to be in the 2.4–2.8 range. Chen et al. [2058,2059] reported the results of Monte Carlo simulations on 1 → 2 branched dendrimers. The size of these branched macromolecules, in the scaling regime, was ascertained to be proportional to $(P_g)^{1-\nu}N^{2\nu-1}$, where P is the number of spacer bonds, g the generation, N the total number of monomers, and ν the scaling exponent. The scaling exponent was found to have a similar value to that of linear polymers. Physical properties in the high-concentration regime, where the scaling law is not valid, were discussed.

Mansfield [2060] examined the molecular weight distributions of imperfect dendrimers and their relationship to hyperbranched materials. Fourier analysis of these distributions revealed that essentially monodisperse molecular weight ranges could be obtained for divergent growth if, at the early stages of growth, perfection is or nearly maintained, while later generations inevitably possess arbitrary amounts of defects. This hypothesis has been observed for the one-step preparation (melt polymerization at 210 °C of *N*-acryloyl-1,2-diaminoethane·HCl) of PAMAM-like dendrimers [500].

These dendrimers have been subjected [2061] to two different fractal analyses [2062,2063]: (a) $A \approx \sigma^{(2-D)/2}$, where A is the surface area accessible to probe spheres of cross-sectional area, σ , and D is the surface fractal dimension that quantifies the degree-of-surface-irregularity, and (b) $A \approx d^D$, where d is the object size. Both methods give nearly identical results



Scheme 116. Preparation of the key monomers and their pathway to a dendritic heptacalix[4]arene [2048].

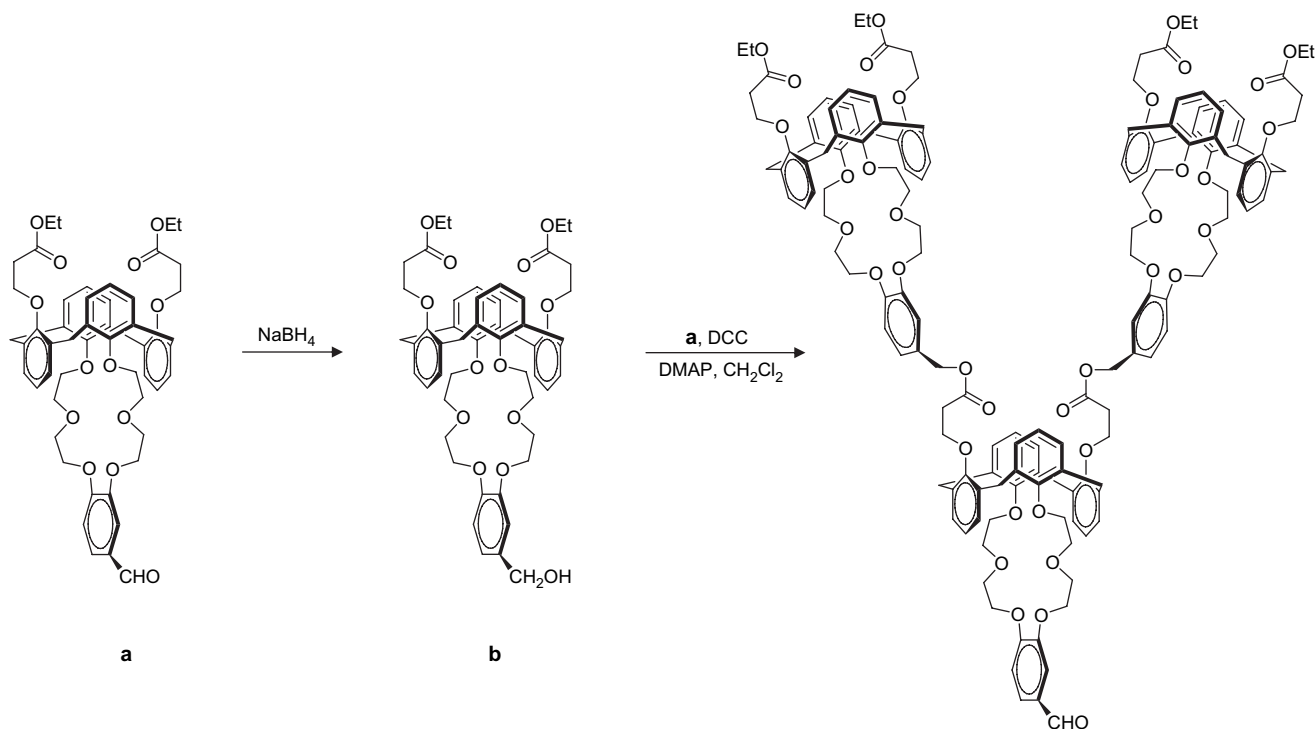
with $D = 2.41 \pm 0.04$ with a correlation coefficient of 0.988 and 2.42 ± 0.07 (0.998), respectively. Essentially, the dendrimers at larger generations are porous structures but possess normally rough surfaces.

Traditional spline cutoffs for long-range coulombic and van der Waals interactions can lead to serious distortion in large dendritic structures; the adjustment of cutoff parameters has led to an improvement in shape considerations [2064] when using common computational methods found, *e.g.*, in CHARMM and AMBER.

Boris and Rubinstein [2065], employing a self-consistent mean field model for dendrimers, examined the dense-core vs. dense-shell models. Their data showed that for flexible dendrimers, the cores are dense, not hollow, and the density decreases progressing outward toward the surface. This is consistent with previous pertinent simulations [539,555,589,1161]. The authors noted that flexible spacers distribute density thus facilitating construction of larger species, by pushing the dense-packing limitations to higher generations — a phenomenon that has been addressed and demonstrated by Moore et al. [2066] by means of his SYNDROME construction approach [2067]. Also, the Flory

theory was described for the correspondence of dendrimer size to that of generation.

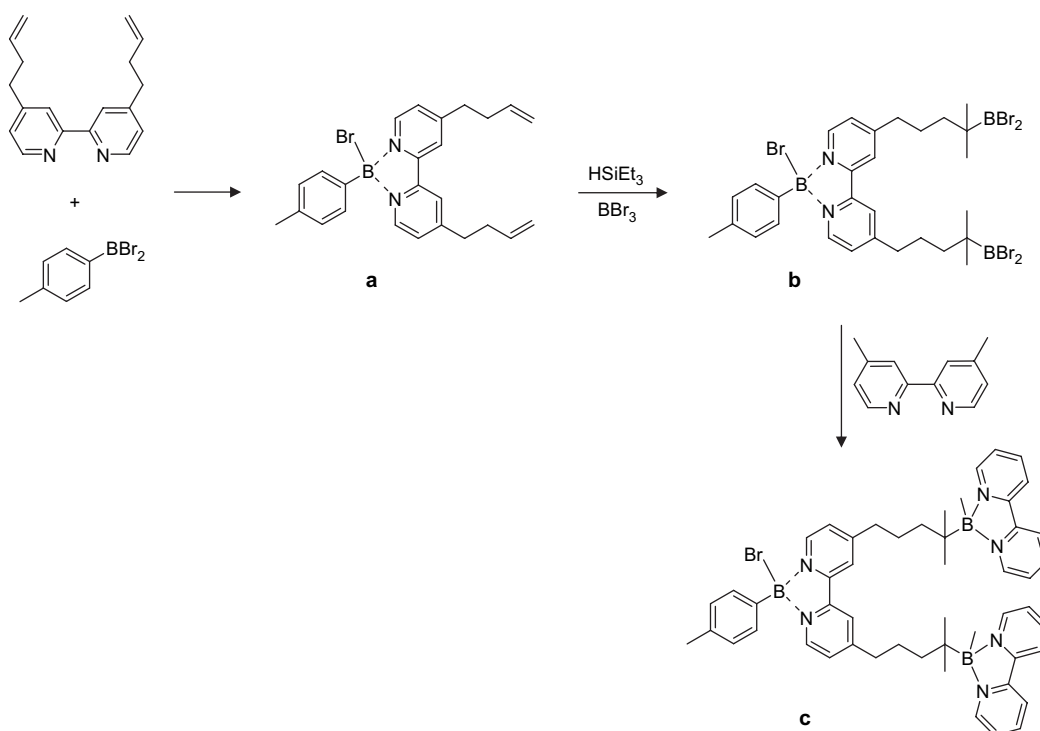
Mansfield [540,2068] studied flexible, model dendrimers and their surface adsorption characteristics. Computer simulations of lattice model dendrimers were analyzed for their interaction with an adsorbing planar surface. It was observed that for an increase in interaction strength (A), the dendrimer flattened and spreading occurred. For low dendrimer generation and high A , most of the dendrimer components can access and contact the surface due to the ease of molecular deformation; at high generations, a smaller percentage of the overall dendrimer had access the surface due to decreased deformability. Different adsorption states were observed; thus, a tridendron-based dendrimer either completely adhered to the surface (S_3 state) or two of the dendron components were adsorbed and the third was arranged more perpendicular to the surface plane (S_2 state). These simulation techniques were noted [2069] to have violated detailed balance, thus the ensuing errors were sizeable for dendrimers without excluded volumes. The technique was modified [541] to satisfy the “detailed balance problem” and reported on dendrimers as high as G11.



Scheme 117. Synthesis of calix[4]crown dendrons [2053].

In general, there have been numerous theoretical papers that have addressed different 1 \rightarrow 2 branched dendrimers but have not considered a specific dendritic family by molecular structure, which have been included above under the specific chemical structure. Thus, while not a comprehensive

listing, many of the papers are compiled in this section under the specific type of study using Monte Carlo [537,539–541,543–546,2069–2075], molecular dynamics simulations [546,2076–2078], Langevin dynamics simulations [555], Brownian dynamics simulations [557,564,2079–2081],



Scheme 118. Methodology to B-N-containing dendrimers [2054].

Rouse dynamics [560,564,2082–2085], Zimm-type model [590,2084], dissipative particle dynamics method [2086], Gaussian self-consistent approach [2087], PM3 semiempirical MO method [2088], cascade theory [2089], unified lattice theory [2090], and one should also see the references in these citations. There has been a recent highlight [80] of these studies as well.

These theoretical studies have been directed to particular topics, such as: glass transitions [2078,2091–2093], terminal group modifications on the solution properties [2077], shear flow [2079], extensional and hydrodynamic interactions [2094], modeling the rheology [2095,2096], kinetic and Monte Carlo modeling [2070,2071,2097–2102], Wiener and hyper-Wiener number [2080,2103–2113], microphase boundaries and chain conformations [2114], phase boundaries [2115], proton binding characteristics of branching polyelectrolytes [2116], dimension indices of surfaces *via* TOPO and GEPOL [2117], intrinsic viscosity calculations [2118–2120], exciton migration dynamics in dendritic molecules [2121,2122], polarizabilities [2123–2126], third-order nonlinear optical properties [2127], simulations for drug delivery [2072], molecular conductance of dendritic wire [2128], simulation with block polynomials [2129], molecular topology [2112, 2130], phase behaviors *via* simulations [594,596,2131–2133], linear absorption spectra [2134], vectorial cascade theory [2089], proton to metal-ion binding equilibria [1153], diffusion and internal trapping within a dendrimer [2135], radial size *vs.* solvents [2136], elongational flow [2081], excluded volume [2075,2137,2138], dynamics of neutral and charged dendrimers [557], effective interactions between dendrimers [546], the effect of solvents [545], relaxation effects [2085], amphiphilic co-dendrimers [543], radius-of-gyration [564,2139,2140], dendritic forest or brush [2141], spin dynamic of magnetic dendrimers [2142], light harvesting in dendrimers [2143], entanglement transitions [2144], size exclusion chromatography [2089], hydrodynamic homology [2145], topological effects in electron transfer [2146], swelling and collapse of neutral dendrimers [564], electron dynamic in dendrimers [2147], asymmetric dendrimers [2148], radial dimensions of starburst polymers based on the Edwards model of linear homopolymers [1047], and asphericity of star polymers [1819]. The conformation of polyelectrolyte dendrimers for different generations, spacer lengths, charge distributions, and ionic strength has been studied using a molecular dynamics and mean field theory approach to explicitly account for the free ions [1920].

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