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Assembly of Molecular Building Blocks into Integrated Complex Functional Molecular Systems: Structuring Matter Made to Order

Zahid Hassan,* Yannick Matt, Salma Begum, Manuel Tsotsalas, and Stefan Bräse*

In memory of Professor Viqar Uddin Ahmed

Function-inspired design of molecular building blocks for their assembly into complex systems has been an objective in engineering nanostructures and materials modulation at nanoscale. This article summarizes recent research and inspiring progress in the design/synthesis of various custom-made chiral, switchable, and highly responsive molecular building blocks for the construction of diverse covalent/noncovalent assemblies with tailored topologies, properties, and functions. Illustrating the judicious selection of building blocks, orthogonal functionalities, and innate physical/chemical properties that bring diversity and complex functions once reticulated into materials, special focus is given to their assembly into porous crystalline networks such as metal/covalent–organic frameworks (MOFs/COFs), surface-mounted frameworks (SURMOFs), metal–organic cages/rings (MOCs), cross-linked polymer gels, porous organic polymers (POPs), and related architectures that find diverse applications in life science and various other functional materials. Smart and stimuli-responsive or dynamic building blocks, once embedded into materials, can be remotely modulated by external stimuli (light, electrons, chemicals, or mechanical forces) for controlling the structure and properties, thus being applicable for dynamic photochemical and mechanochemical control in constructing new forms of matter made to order. Then, an overview of current challenges, limitations, as well as future research directions and opportunities in this field, are discussed.

The careful selection of fundamental building blocks is of utmost relevance, because diversity and complex functions of a material can arise from the innate physical/chemical properties of the founding molecular building units. By identifying the appropriate molecular building blocks (monomers, and oligomers of arene or heteroarene backbone) and employing different fabrication techniques, complex material systems can be produced with precise control over structure, properties, and functions. In this (noncomprehensive) report, we confine our discussion to the most convenient synthetic methods for preparation of the most prevalent modular organic molecules/building components, or more precisely, on rigid non-aromatic and aromatic systems, such as the linear shaped biphenyls, triphenyls and higher oligoarenes/heteroarenes (OHA), (metallo)porphyrins (PPs), trigonal planar triphenylarenes/heteroarenes (TPA), non-planar tetrahedral tetraphenylmethane (TPM) analogues, tetraphenyladamantane (TPAd), and pseudo-octahedral hexaphenyl-*p*-xylene (HPX) derivatives as shown in **Figure 1**. These molecular building blocks are tailored in such a way as to achieve thermal and chemical stability, stimuli-responsiveness, photo-switchability, and electron-conductivity for perspective applications. Illustrating these customized modular blocks, special focus is given to their assembly for the construction of various covalent/noncovalent structures including porous crystalline networks such as metal/covalent–organic frameworks (MOFs/COFs),

1. Introduction

“Auch aus Steinen, die in den Weg gelegt werden, kann man Schönes bauen”—a famous saying which can be translated as “Even the stones in one’s path can be made into something beautiful.” This excerpt relates to the fascinating journey of materials modulation and structuring matter from application perspectives that starts with the judicious selection and synthetic design of the fundamental molecular building blocks.

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surface-mounted frameworks, cross-linked polymeric gels, porous organic polymers (POPs), and related sophisticated architectures with tailored functions, as lego interlocking units can be assembled to construct an array of objects.

Organic synthesis to prepare both new and exciting customized molecules is not at all a new concept. Exploring new, milder, broader, and efficient synthetic strategies to build novel molecular structures and their mechanisms of formation have greatly fascinated chemists from the perspective of fundamental synthetic curiosity to inspiring applications. To build molecules and studying their properties is a diverse area of interest itself; however, transforming small molecular components into practically useful complex molecular systems and devices is even more challenging task beyond the limits of a single discipline that needs interdisciplinary joint research efforts. Capitalizing in design and synthetic strategies of building blocks for function-inspired molecular systems as a holistic approach, and combining insights from organic/inorganic expertise and physical/materials chemistry aided by digital twins of computing simulations have been rewarding in countless ways to open up new horizons of fundamental and practical explorations. The vital role played by building blocks in material fabrications has been the subject of a number of excellent reviews.^[1-5] This report is not to be an exhaustive display, and it is even hard to concisely cover every aspect of such a rapidly evolving research area. This article provides an overview about synthetic design of the most prevalent organic building blocks via convenient synthetic methods, and recent developments from materials application perspectives showcasing current research from our laboratories as well as others important findings in this field are highlighted. The recent developments and some landmark results discussed herein would be particularly appealing for scientists aiming to work in integrated research areas of: 1) chemical synthesis of custom-made building blocks; 2) self-assembly and materials fabrication; 3) hierarchically structured assemblies from nanoarchitecture to macrostructures; and 4) exploring advanced material applications. We hope this contribution on the design and synthetic strategies of molecular building blocks from the vantage point of their assembly into complex functional systems would be useful that inspires interdisciplinary research at the interface of chemistry, polymers, and materials. This will undoubtedly assist both the synthetic chemist and material scientists in exploration of made-to-order materials beyond the limits of a single discipline.

2. Molecular Design and Synthetic Planning of Organic Building Blocks: Tuning the Structure/Function of MOFs, Surface-Anchored MOFs, and Network Polymers

The synthetic design of coordination-driven assemblies and their numerous applications have received growing interest that have been the subject of highly inspiring articles and excellent reviews.^[1,2] MOFs and surface-anchored MOFs (SURMOFs) are crystalline hybrid materials assembled through reversible coordination bonds between appropriately functionalized organic building blocks and inorganic metal nodes (referred as secondary building units or SBU), form 1D, 2D, or 3D extended structures,



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Stefan Bräse studied in Göttingen (Germany), Bangor (U.K.), and Marseille (France), and received his Ph.D. in 1995 with Armin de Meijere in Göttingen. After postdoctoral research at Uppsala University (Jan E. Bäckvall) and the Scripps Research Institute (K. C. Nicolaou), he began his independent research career at the RWTH Aachen in 1997 (associated with Dieter Enders). In 2001, he finished his habilitation and moved to the University of Bonn as a professor for organic chemistry. Since 2003, he has been a professor at the Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT) and since 2012, also Director of the Institute of Toxicology and Genetics (ITG) at KIT. His research interests include asymmetric processes, combinatorial methods of biologically active compounds, synthesis of natural products (on solid supports), and synthetic functional materials.

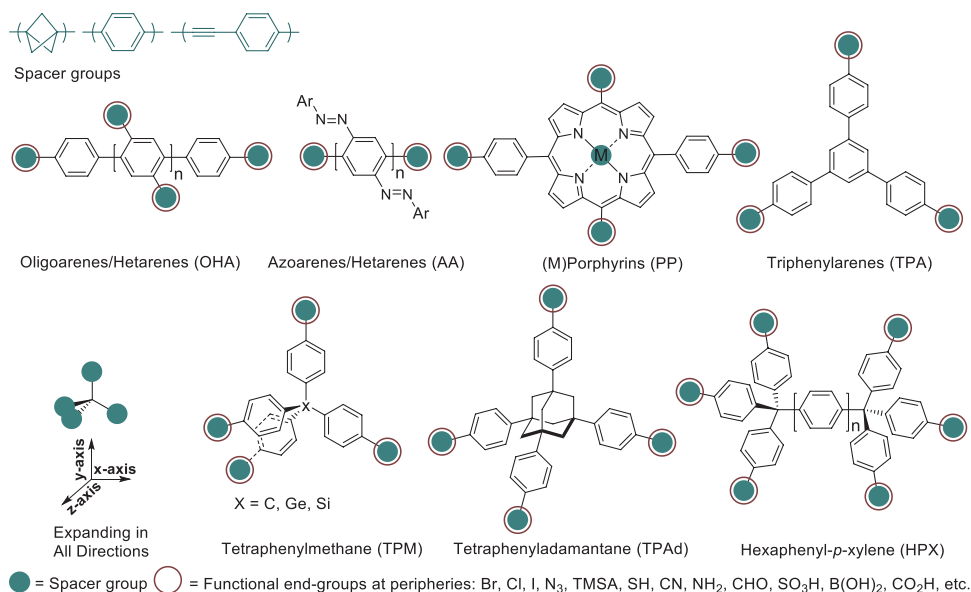


Figure 1. General representation of customized most prevalent organic building blocks used in construction of function-inspired MOFs/COFs/POPs and their post-synthetic modifications.

and find broad applications ranging from catalysis, energy materials, sensing, separation, and porous carriers to hierarchically structured materials.^[3] SBU approach to template coordination-driven reticular assemblies (inorganic metal nodes add geometrical versatility and structural regularity) has been the turning point in tuning structure and functions of diverse MOF materials. Based on the metal type, oxidation states, and coordination capabilities, various geometries of coordination-driven assemblies can be created.^[4] On the other hand, organic building blocks add structural/functional diversity; provide synthetic control on construction based on their binding strength, length, and directionality;^[5] inherent tailored chemical/physical functions to the materials;^[6] and precisely allow post-synthetic tunability.^[7] For the purpose of simplicity/consistency in this article, we have adapted a generalized term organic building blocks; however, in literature, other terms such as ligands, linker, tectons, strut, etc. also have been coined. For coordination-driven assemblies, material science community also uses multiple terminologies such as metal-organic frameworks (MOFs), porous coordination polymers (PCPs), and hybrid framework materials based on the metal-organic bonds.

Synthetic organic chemists mastered the art of modular synthesis and offer a diverse library of all conceivable molecules that could be utilized as bespoke building blocks for materials construction and later-stage fabrication. Synthesis of organic building blocks can be categorized on structural and functional basis (to engineer various structures, topologies, and porosities), aiming for materials with responsiveness, tailored conductivity, or certain bio-functions. Modular synthesis approach in design and optimization of building blocks stands in the very center and remains a powerful route to complex nanostructured materials. Modern synthetic strategies allow tying the knot between several small molecular fragments together in a single customized unit, where each fragment is intended to serve a particular purpose that make them an attractive synthon for the construction/fabrication of wide range of function-inspired materials. Milder, broader, and efficient synthetic methods combined

with versatile chemistry household-name reactions can build molecular blocks of almost any design. Most notably, aryl derivatives of boron (Suzuki–Miyaura),^[8] tin (Stille–Miyata),^[9] silicon (Hiyama),^[10] magnesium (Corriu–Kumada),^[11] and aluminum/zinc/zirconium (Negishi)^[12] are highly practical and reliable tools for carbon–carbon bond constructions that have revolutionized large-scale organic synthesis in an enormous variety of molecular shapes and sizes. Other reactions for carbon–carbon bond formation, the Mizoroki–Heck protocol^[13] to couple alkenes, Sonogashira–Tohda–Hagihara reaction to couple terminal alkynes,^[14] and Buchwald–Hartwig amination^[15] as carbon–heteroatom bond-forming useful tool, to name a few that have aided tremendously to synthesize structurally diverse arene/hetarene building blocks with the ability to modify the constitution of the spacer groups. Spacer groups are constituted to control shapes, sizes, and geometries at different length scales, ultimately the materials properties. Arene/hetarene derivatives and their extended related systems bearing carboxylic acid (COOH) or pyridyl moieties enable strong metal coordination and thus form diverse coordination-driven structures featuring intriguing properties. Adding different functional components, such as azides, alkynes, thiols, alkoxy, nitriles, and thermally labile alkoxyamine components, can covalently interconnect the molecular tectons into cross-linked covalent networks using azide–alkyne “click” reaction, photo-induced thiol–ene reaction, condensation reaction or tunable dynamic covalent approaches to tailor the molecular assemblies with novel functions.

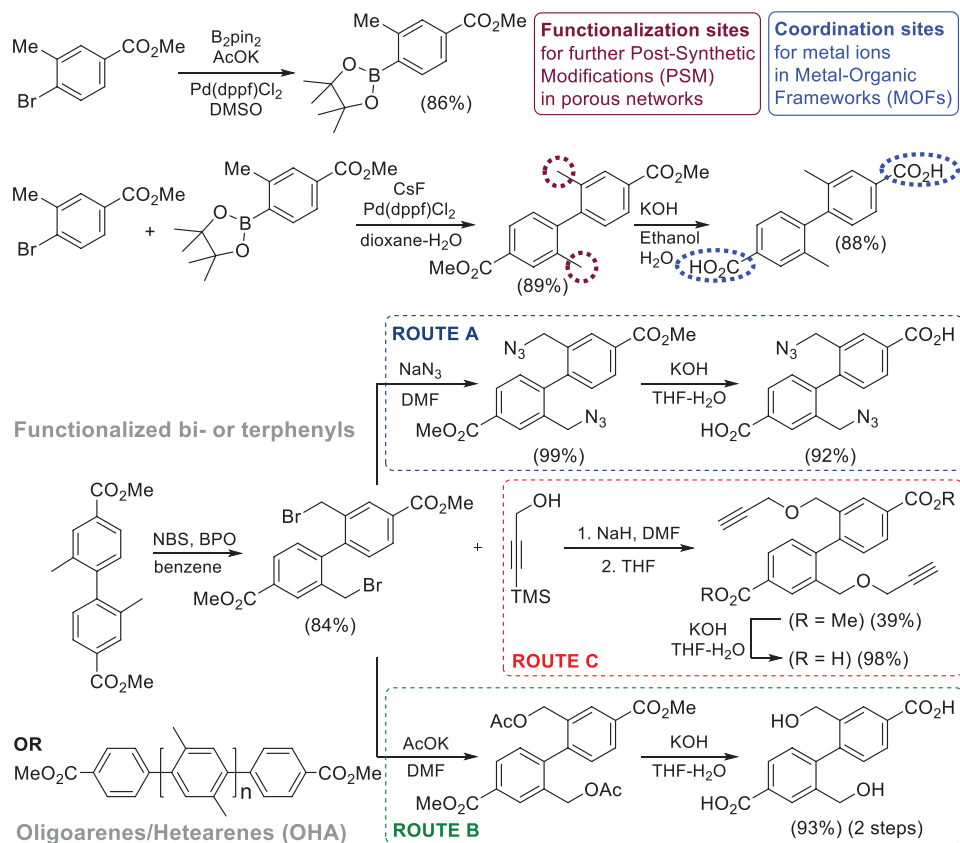
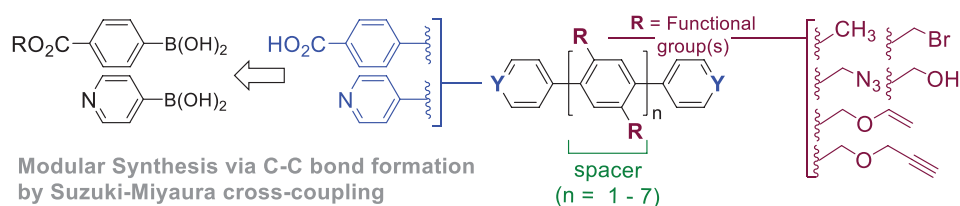
2.1. Linear Oligoarenes/Heteroarenes Bearing O/N Terminal Coordination Sites for Self-Assembly into Functional Porous Materials

1,4-Benzenedicarboxylic acid and its higher structural analogues with inserted benzene rings as spacer elements (oligoarene/heteroarenes and so on) are the most popularized organic

components that are widely incorporated in crystalline porous coordination networks such as MOFs,^[16] metal–organic nanorings/cages,^[17] and other related supermolecular assemblies.^[18] Carboxylate-functionalized arenes and pyridine-ended heteroarenes (as organic blocks) have experienced extensive explorations in the formation of coordination assemblies. In a similar way of exploiting SBU approach, the enormous variety of molecular shapes and sizes and vast range of synthetic transformations at organic cores of the MOF materials open numerous possibilities of tuning their structure and functions.^[19] Customizing the organic components at a molecular level by: 1) varying the length and constitution of the spacer groups;^[20] 2) incorporating multiple functional moieties as side-groups;^[21] and 3) by varying their geometries allows an easy tuning of both structure and functions, materials modulation at different-length scale for diverse potential applications.^[22]

For the constitution of selective carbon–carbon bonds in customized building blocks, the Suzuki–Miyaura cross-coupling

process using organoboranes is one of the widely applicable methods that offer several advantages in building of complex organic molecules. Suzuki–Miyaura cross-coupling processes are simple, scalable, high yielding, and highly selective synthetic procedures. Air- and moisture-stable commercial organoborane components in combination with organic electrophilic halides/pseudohalide can be employed under mild reaction conditions without special precautions. Hence, employing the preeminent Suzuki–Miyaura cross-coupling reaction using appropriate aromatic (or heteroaromatic) boronic acids (**Scheme 1**), coordination-capable sites such as COOH or pyridyl moieties (for the growth of networks with metal ions/clusters) can be incorporated into the molecular backbone.^[23] Multiple substitution is compatible, while in longer/higher molecular structures, by adding methyl groups into the backbone of the higher oligoarenes can assist to increase solubility and even these methyl groups at benzylic position within the core can be further used as synthetic handle by transforming into azides, alkynes, thiols,



Scheme 1. Modular synthesis of multi-functionalized organic building blocks by cross-coupling reaction used in MOFs and their post-synthetic modifications.

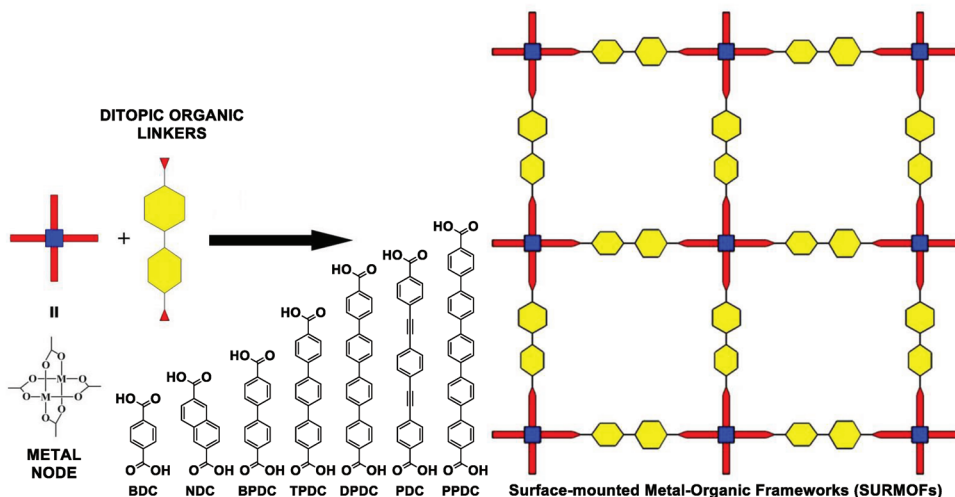


Figure 2. Structure and schematic representation of diverse ditopic modular building blocks (dicarboxylic acids) used in a series of novel isorecticular SURMOFs. Reproduced with permission.^[24] Copyright 2012, Nature Publishing Group.

and alkoxy derivatives suitable for post-synthetic modification (PSM) of the preassembled coordination systems via azide–alkyne click or photo-induced thiol–ene/yne reaction that tailor the molecular structures and functions of the assemblies.

Programming molecular structures utilizing the methods of organic synthesis supported by molecular modeling and electronic structure calculation, a series of ditopic organic molecular blocks of different length and their assembly into surface-supported isorecticular MOFs has been demonstrated (Figure 2).^[24] The choice of the elongated linkers using the same metal-node as SBU results in same topology of the material but different pore sizes. During the investigation, layer-by-layer

(LBL) liquid-phase epitaxy (LPE) approach was adopted. LBL methods, using continuous and repeated dipping and then rinsing cycle, play an important role since it allows to fabricate crystalline and highly oriented MOF layers. On suitably functionalized substrates (such as gold, silver, copper, glass, or metal oxides), monolithic crystals can be grown that direct the nucleation site, orientation, and structure of the deposited SURMOF (Figure 3).^[25] These SURMOFs are very homogeneous with respect to thickness and can be prepared with very low defect densities, thus has some important advantages compared to other MOF deposition methods (e.g., mother-solution deposition, dip coating, electrochemical growth), because it

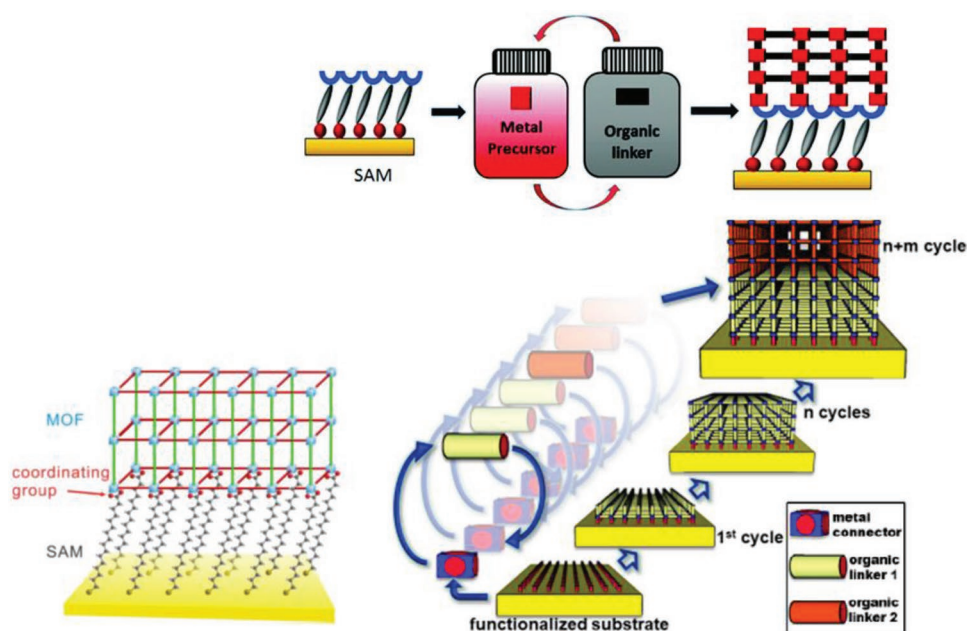


Figure 3. Schematic representation of liquid-phase epitaxy (or heteroepitaxy)/layer-by-layer SURMOF synthesis on self-assembled monolayers (SAM). Step cycles indicate repeated immersion and rinsing after each reactant exposure. The illustration shows how a MOF can become anchored onto a SAM. Reproduced with permission.^[25] Copyright 2016, Wiley-VCH.

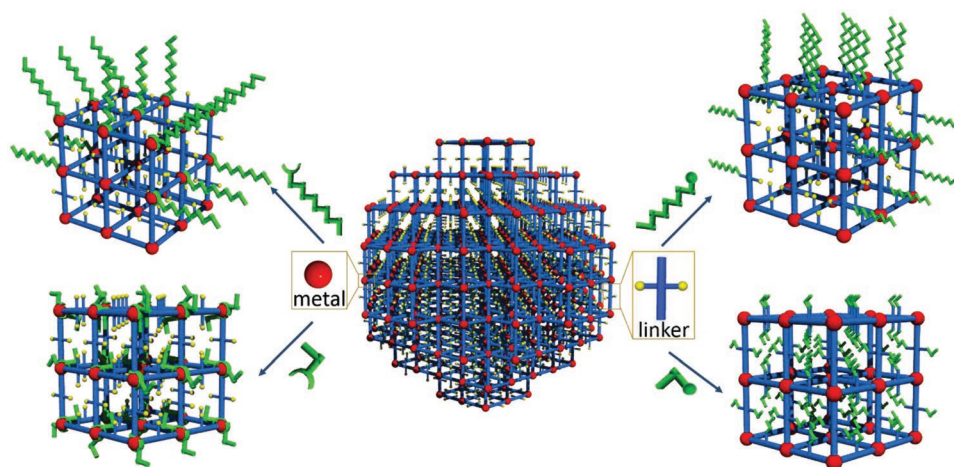


Figure 4. Illustration of MOF post-synthetic transformation on the internal surfaces (small molecules diffuse in the pores) and external surfaces (larger molecules attach to the outer surfaces). PSM via covalent bonds (right) or coordinative bonds to the metal node (left). Reproduced with permission.^[36] Copyright 2019, American Chemical Society.

allows the exact control of parameters such as the thickness and the growth orientation. Surface/interface chemistry has been the subject of previous focused reviews.^[26]

2.2. Clickable Oligo(arene) Building Blocks for MOF-Templated Hierarchically Structured Biomaterials: Post-Synthetic Polymerization Strategies

Inspired by an amazing level of control over the hierarchical organization and assembly of biomaterials, understanding of the reactions and molecular organization in confined spaces has been a long-standing aspiration. The modular approach and controlled synthesis of superstructure assemblies and their transformation at internal as well as external surfaces enable for incorporating desired functions selectively for diverse application in emerging technologies. Using mild transformation protocols, biologically relevant components such as peptides, proteins, and drugs can be immobilized into the pores, or external surfaces of the nanostructured materials for mimicking biocompatible media or interfaces to create a platform for exploration and applications in biology and bio-functions as shown in **Figure 4**.^[27]

Click components are mostly derived from alkenes and alkynes.^[28] The copper-catalyzed azide–alkyne click cycloaddition forming 1,2,3-triazoles^[29] and a multifaceted toolbox of thiol click reactions are most widely utilized and provide a reliable way of functionalization and crosslinking between molecular building block components.^[30] The possibilities of PSM via click reaction seed from building blocks, as prefunctionalized with transformable functional groups. Molecular backbone bearing azides, alkynes, or alkoxy side-groups, at least two or more, within the preassembled MOF assemblies can serve as monomers, thus enabling click cross-linking using external/guest molecules as secondary cross-linkers (CL), as the monomers are precisely organized in the MOF. Sada and co-workers introduced “Clickable MOF” based on azide-functionalized clickable building blocks.^[31] Employing customized acetylene-tagged external/guest molecules depicted in **Figure 5**,

crystal-controlled cross-linking of the preorganized azide-MOF via alkyne–azide click chemistry was successfully demonstrated. This pioneering research has opened new dimensions for hybridization of MOFs crystalline materials with soft polymers creating novel MOF composites.^[32,33] On acid treatment (hydrolysis and subsequently demetallation), the cross-linked MOFs are converted into polymer gel materials. These polymer gel materials preserve the shape of the parent MOF, represent a novel class of hierarchically structured assemblies that combine the advantages of MOFs (precisely controlled structure and enormous diversity in framework topology, high porosity) with the intrinsic behavior of polymers (soft texture, flexibility, biocompatibility, and improved stability).^[34]

Crystal-controlled polymerization via cross-linking of surface-bound azide-MOF thin films has also been investigated. The cross-linked SURMOF was converted into polymer gel materials. On acid treatment (hydrolysis and subsequently on demetallation/extraction) entirely metal-free, highly uniform, covalently bound polymer thin film, referred to as SURGEL can be fabricated (**Figure 6**).^[35] The preassembled SURMOFs can be transformed selectively at internal or external surfaces via orthogonal covalent cross-linking process with bioactive compounds, yielding SURMOF-templated polymer gels that can be tailored for biofunctions.^[36] These cross-linked polymeric materials are hierarchically structured and overcome some of the main drawbacks of the parent MOFs, for instance, their instability under physiological conditions can be overcome. Metal–organic bonds because of the chemically labile nature hardly survive, hence, release of toxic metal ions is considered a substantial issue in life sciences, whereas cross-linked polymeric materials are persistent, entirely metal-free, covalently bound assemblies and replicating the original MOF templates. Using cell culture studies/physiological conditions, various aspects of SURGEL materials for emerging bio-functions have been demonstrated depicted in **Figure 7**.

An amazing level of control over the post-synthetic transformation/molecular organization in SURMOFs-confined spaces has been achieved. On polymerization via covalent linkages, the COOH groups that formerly were coordinated to the metal

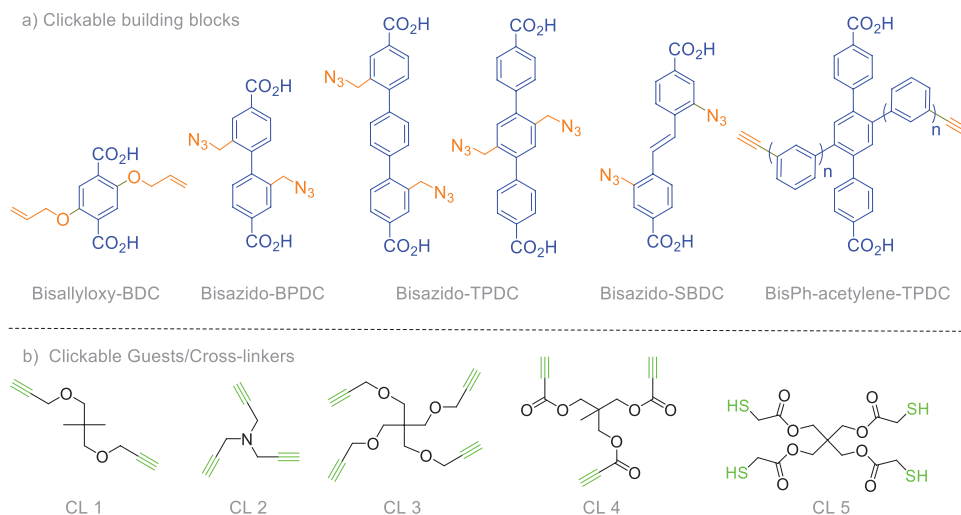


Figure 5. a) Representative clickable organic building blocks. b) Thiol or alkyne-tagged molecules can be used as guest/cross-linkers for for post-synthetic modification via click chemistry.

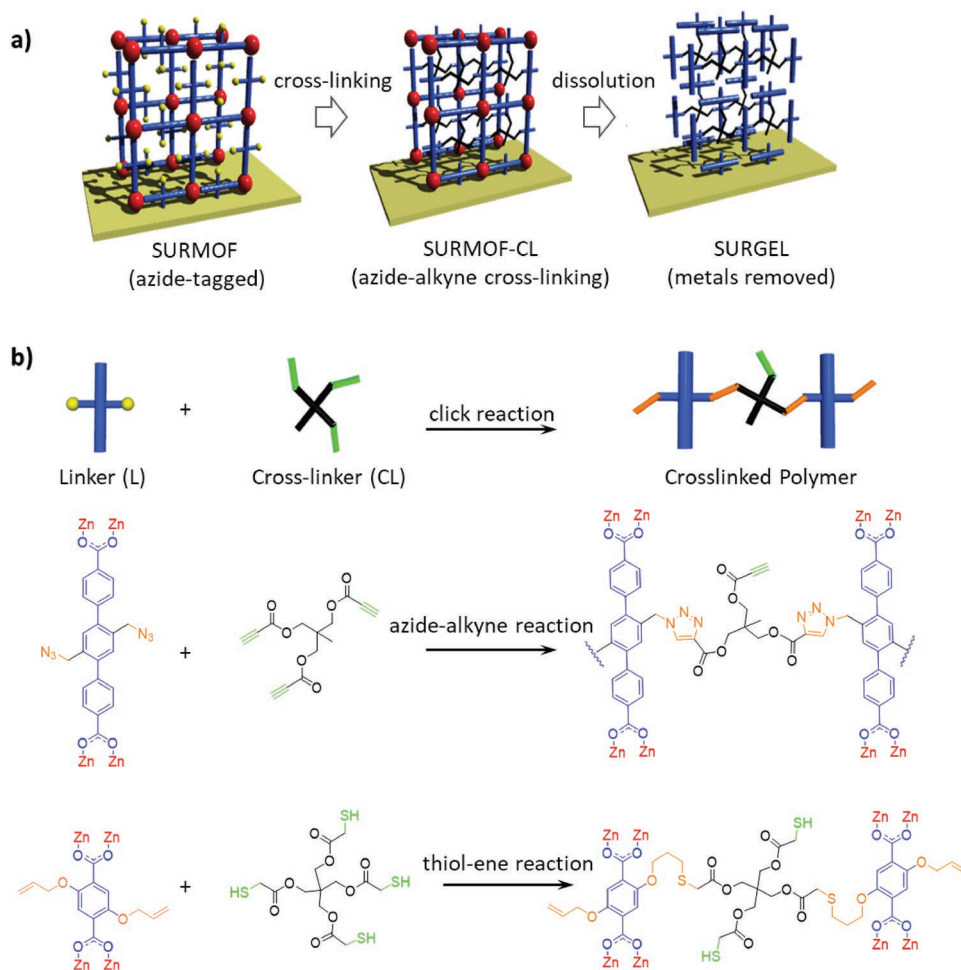


Figure 6. a) Schematic representation of the SURMOF-to-SURGEL post-synthetic polymerization process. b) Orthogonal functional sites, such as azides and alkoxy, within the linker-backbone interact with CL molecules to covalently interconnect the MOF structure via click reaction mechanisms within the preassembled MOF. Reproduced with permission.^[B5] Copyright 2013, American Chemical Society.

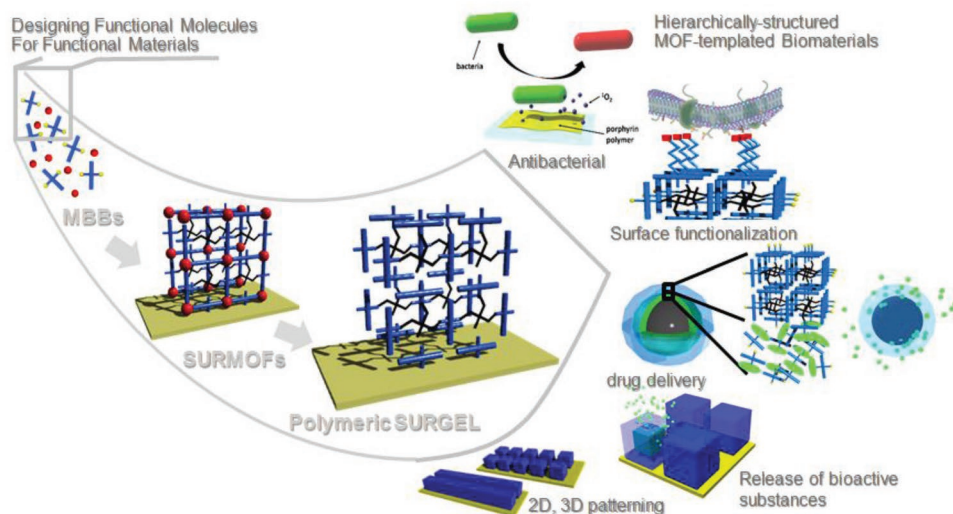


Figure 7. Function-inspired design of modular building blocks (MBBs), fundamentals and mechanism of hierarchically-structured MOF-templated biomaterials. SURMOF-to-SURGEL post-synthetic polymerization (PSP) in confined nanospaces. Reproduced with permission.^[35] Copyright 2013, American Chemical Society. Depiction of surface functionalization is adopted with permission.^[37] Copyrights 2016, Wiley-VCH. Depiction of drug delivery/release of bioactive substances^[39] and antibacterial coatings are adapted with permission.^[40] Copyright 2013 and 2018, American Chemical Society.

centers remain free for surface functionalization. Even under controlled polymerization, the remaining alkyne moieties from the cross-linking reaction could be further utilized for surface bio-functionalization by exploiting metal-free thiol–yne click reaction. As a proof-of-principle for the surface biofunctionalization of the SURGEL, attachment of short peptide sequence arginine–glycine–aspartic acid (RGD) to favor cell adhesion have been successfully demonstrated. This could enable a specific interaction with the integrin receptors of the cell membrane.^[37] The SKGSS serves as a hydrophilic factor, and the c-terminal cysteine carries the thiol moiety in its side chain that could be utilized as synthetic handle in thiol–yne-based cross-linking processes.

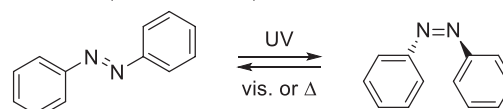
The LBL approach can also enable coating magnetic particles of different sizes with a uniform MOF shell, referred as the MagMOF system.^[38] The step-by-step use of two different building block components, bearing polymerizable alkyne/azide functionalities, allows to be selectively functionalize within the core-shell-shell system, e.g., alkyne-tagged dye molecules can be positioned via azide–alkyne click protocol.^[39] Recently azido-PP SURMOFs were prepared by employing LBL method using spray coating.^[40] Immersion into a CL solution results in covalently cross-linked PP gel via click reaction. On metal dissolution with EDTA solution, a more persistent water-stable PP polymer thin films were obtained, which exhibit potential antimicrobial activity.

2.3. Functionalized Azobiphenyls and Azoterphenyls Bearing O/N Terminal Coordination Sites for Photoresponsive Smart Materials

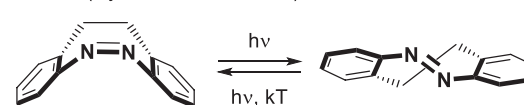
Smart materials find broad applications, ranging from photopharmacology to materials science applications such as data storages, switches, optical sensing, and molecular machines.^[41,42] Stimuli-responsive smart materials undergo

reversible conformational rearrangements, adopt new geometry and electronic states in response to physical or chemical stimuli (e.g., electric, magnetic, light or mechanical forces, electron transfer, pH, etc.).^[43] Among stimuli-responsive molecular switches, most common and widely explored are the photo-switchable azobenzenes (ABs) that contain a diaryl diazene core,^[44] diarylethenes (DAEs),^[45] and spiropyrans (SPs),^[46] which have attracted enormous interest.^[47] Stimuli-responsive components, some are depicted in **Figure 8**, have been widely

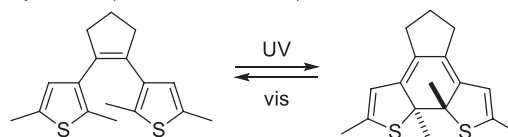
Azobenzene (ABs, *trans/cis*)



Diazocine (Cyclic ABs, *trans/cis*)



Diarylethene (DAE, *open/closed*)



Spiropyran/merocyanine (SP/MC)

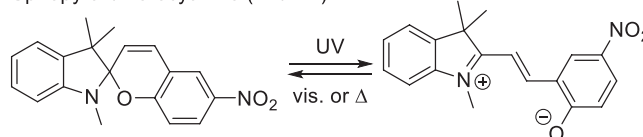


Figure 8. Most common and widely explored photoswitchable chromophores in photopharmaceuticals and smart functional materials.

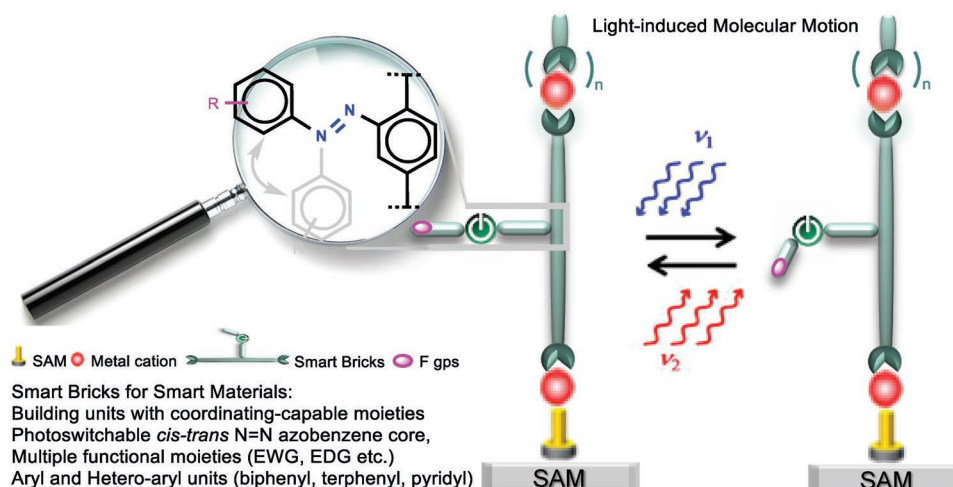


Figure 9. Depiction of photoswitchable MOF thin films and light-induced molecular motion.

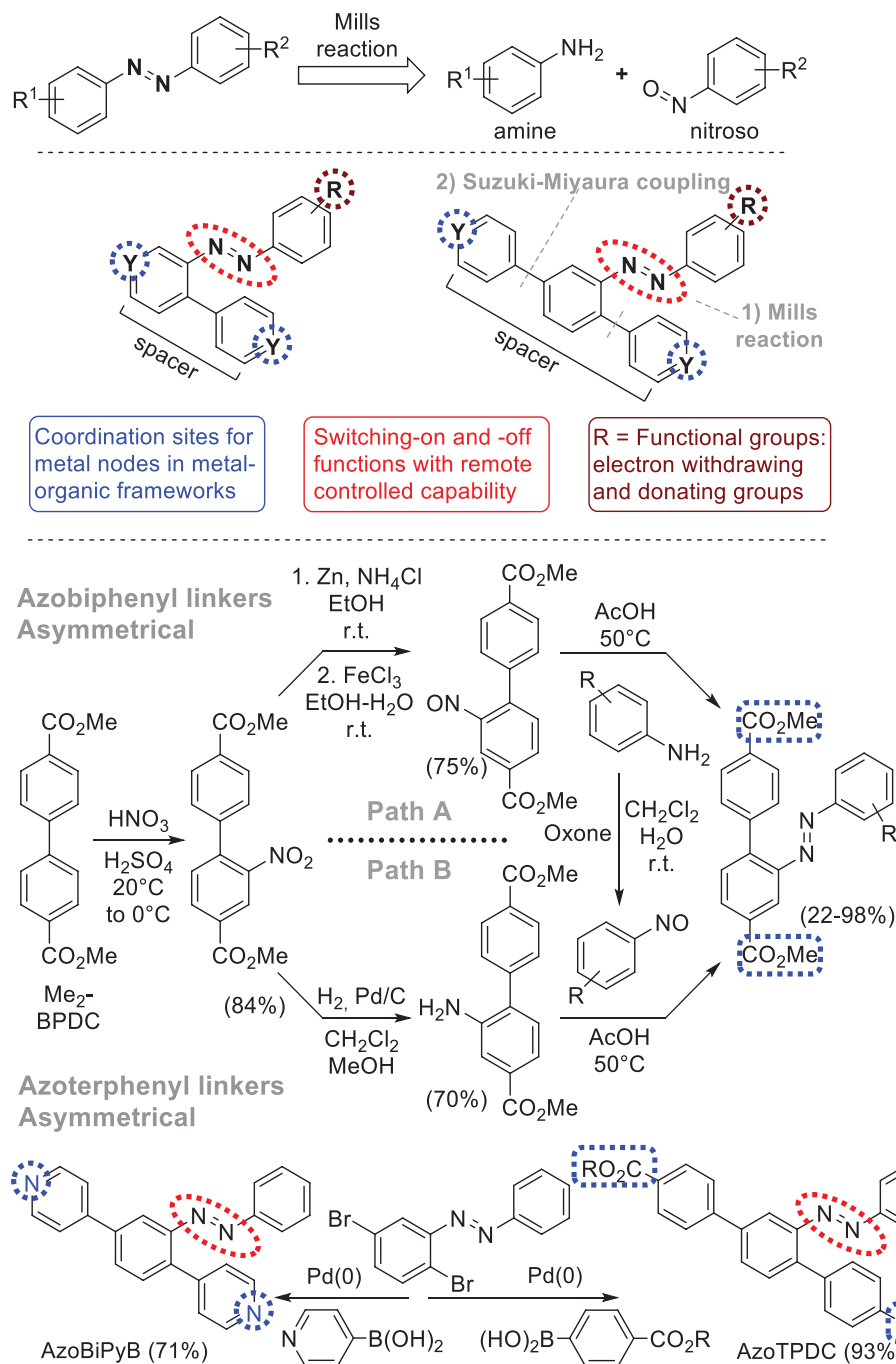
embedded into polymers,^[48] liquid crystals,^[49] porous frameworks,^[50] and molecular machines,^[51] which can be remotely controlled in a noninvasive way by using defined light for their diverse smart applications in life sciences and materials.

For the coordinative incorporation of stimuli responsive components into complex systems (either as a backbone or side-group attached to the backbone)^[52] and furthermore enabling to modulate their structure/functions by remote-controlled noninvasive process using light require special consideration.^[53] Assembling photoswitchable components into MOFs allows reversible structural transformations, a property referred as photoresponsivity.^[54] The photoinduced molecular motion results into *cis/trans* isomers of the ABs units, or making/breaking bond by irradiation of DAEs and SPs that can serve as molecular switches once assembled into MOFs materials, and can regulate the pore aperture, shape, porosity, and ultimately imparting the desired smart functions (**Figure 9**).

For the development of novel responsive thin-films materials, we focused on the modular synthesis of coordination-capable building blocks bearing the popular light-responsive AB photoswitch as side-groups.^[55] The synthesis of the photoswitchable ABs that contain a diaryl diazene ($-N=N-$) core relies on the Mills reaction.^[56] An aromatic amine and a nitrosoarene form the diazene ($-N=N-$) core (**Scheme 2**). Selective nitration of the dimethyl [1,1'-biphenyl]-4,4'-dicarboxylate and subsequent transformation to the nitroso-derivative, in a two-step/one-pot reaction (reduction by zinc, followed by oxidation with iron(III) chloride) deliver dimethyl 2-nitroso-[1,1'-biphenyl]-4,4'-dicarboxylate which on reaction with anilines in acetic acid deliver the desired dimethyl ester derivatives (the nitroso and aniline components can be exchanged, on their synthetic availability). Introducing a spacer group and to create longer backbones with three or more consecutive benzenes (for instance, carboxylate-grafted terphenyls), or pyridine-ended heteroarenes bearing a diaryl diazene ($-N=N-$) core as a side group, can be prepared in a similar way by applying a stepwise Mills/Suzuki–Miyaura cross-coupling protocol. Building blocks bearing two photoswitchable diazene ($-N=N-$) core as side groups symmetrically to the backbone can be obtained, employing the Mills reaction protocol (**Scheme 3**).

Very recently, a relatively bulkier building block *para*-terphenyldicarboxylic acid bearing two tetra-*ortho*-fluorinated ABs as side-groups has been synthesized by stepwise Mills/borylation/Suzuki–Miyaura cross-coupling reaction to exploit the advantageous photoisomerization properties with doubled density of ABs (**Scheme 3**, bottom).^[57] Hydrolysis under basic conditions affords the desired switchable building blocks in good yields.

Porous materials such as MOFs for the controlled permeation and capture/release of molecules by external stimuli such as exploiting light-induced molecular motion of ABs (photoisomerization) in a reversible manner could be utilized in engineering smart materials. Based on the incorporation of photoswitchable AB side groups, we have successfully demonstrated the preparation and fabrication of various stimuli-responsive MOFs, a promising platform to explore controlled gas permeation/transport by external stimuli. By irradiation with light of specific wavelengths, the incorporated AB photoswitches undergo reversible molecular motion (*trans* to *cis* isomerization), hence controlling the membrane's permeability and selectivity allows optically triggered dynamic molecular separation by designed nanoporous membranes (**Figure 10**).^[58] A heterobilayer SURMOF that comprises a (passive) bottom layer, acting as a container to store molecules, and a photoswitchable top layer can be fabricated.^[59] Upon irradiation with light, heterobilayer SURMOF acts as a valve that allows or prevents access to the container as depicted in **Figure 11**. To enable molecular motion and structural transition (*trans* to *cis* conformation) within the nanoporous crystalline coordination assemblies upon irradiation, and to avoid steric hindrance, the length of the organic building blocks can be adjusted.^[60] Various smart materials, including frameworks, surface-mounted hybrid systems, and thin-films have been investigated for the fundamental insights and designing functional materials.^[61,62] Coordinative integration of other photoresponsive building blocks including diarylethene (based on making/breaking bond by irradiation) has also been investigated for the construction of photoresponsive MOFs, where the porosity can be optically triggered/fabricated without structural damage to the main framework.^[63] Recently, synthesis



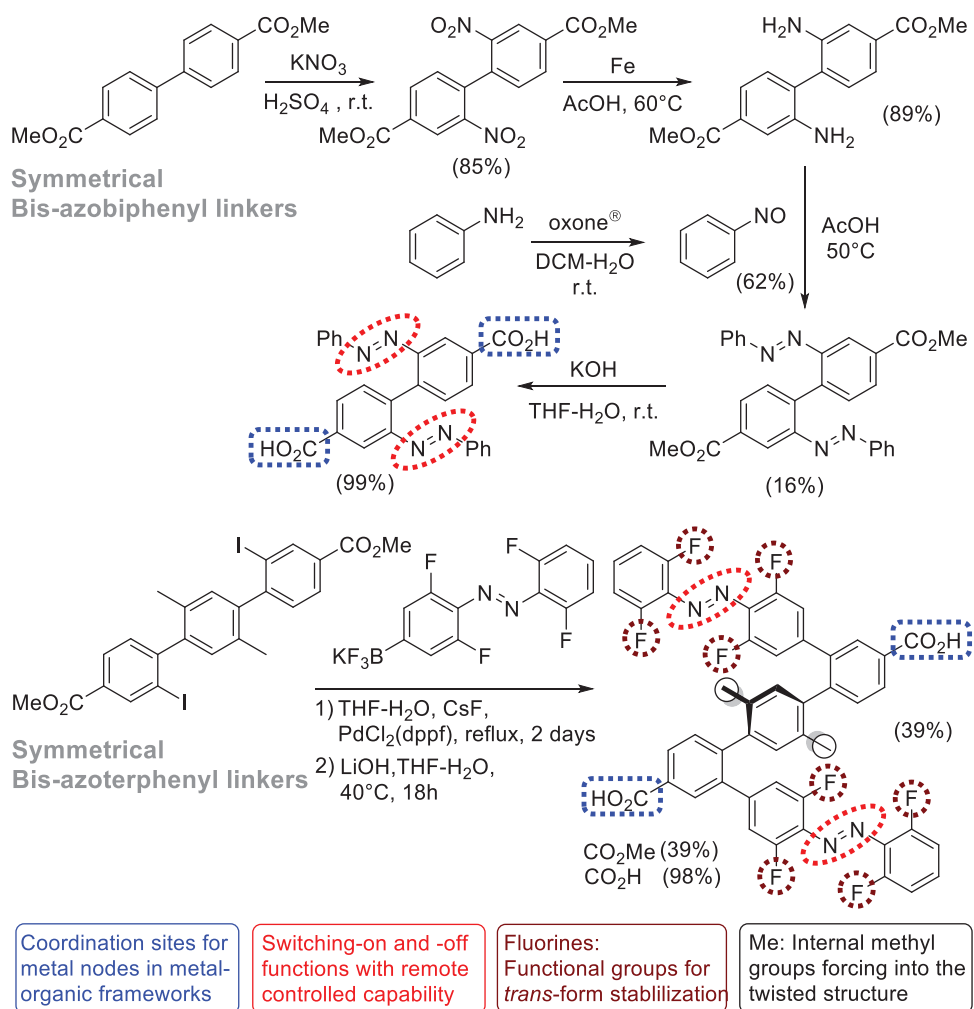
Scheme 2. Synthesis of coordination-capable biphenyl and terphenyl bearing photoswitchable diazene ($-N=N-$) core.

of novel photochromic spirocyan bearing building blocks di(pyridin-4-yl)spiro[chromene-2,2'-indoline] and di(pyridin-4-yl)-7',7'-bisp[chromene-2,2'-indoline] as well as their coordinative integration within MOFs with a strict control over photophysics, cycloreversion kinetics, and fast photoisomerization has been successfully achieved (Scheme 4).^[64]

Material modulation by insertion of photoswitchable building blocks encourages further studies for the fine tuning of smart membrane systems and advancing tailor-made materials for sensing and selective permeation/purification processes.

2.4. Functionalized PPs and Metalloporphyrins for Tuning SURMOFs Thin-Films Photoconductivity and Optoelectronic Studies

PP, a square planar aromatic macrocycle, is composed of four pyrrole units connected by methine ($=CH-$) bridges and has been extensively investigated for essential biochemical and photochemical functions in medicine, biology, and materials.^[65] Because of the rigid and planar geometry, wide spectral and electronic features, and metal-coordination capabilities,



Scheme 3. Modular synthesis of 2,2'-bis(phenyldiazenyl)-*para*-biphenyl dicarboxylic acid and tetra-*ortho*-fluoroazobenzyl-*para*-terphenyl dicarboxylic acid.

synthetic PPs and its various derivatives have been investigated for a wide range of applications, such as mimicking enzymes,^[66] photodynamic therapy (PDT),^[67] chemical sensor,^[68] molecular electronic devices,^[69] dye-sensitized solar cells,^[70] and functional systems including optical, magnetic, and light-emitting materials.^[71] Modular PPs can be prepared by employing suitable aldehydes and dipyrromethane precursors that can be selectively transformed into customized building blocks by tailoring at *meso* and β -pyrrole positions.^[72] The thermally stable macrocyclic structure and rich coordination capabilities of tetrapyrroles facilitate the tuning of physical/chemical and optoelectronic behaviors. The PP core, a tetradentate ligand, can bind/coordinate with different transition metal ions and form metalloporphyrins that constitute useful building blocks for diverse functional materials.^[73] Various PP-based molecular assemblies, utilizing covalent and noncovalent approaches, have been investigated.^[74] Customized metalloporphyrins tagged with alkyne and coordination-capable sites have been recently introduced as model molecular blocks for exploring template-directed synthesis of covalently linked PP nanorings, a new class of multiporphyrin-based novel architectures.^[75] These

coordination-based hierarchically structured large macrocycles of unprecedented dimensions are constituted of metalloporphyrins by employing well-defined molecular templates referred to as Vernier templating synthesis (**Figure 12**). For instance, the hexapyridyl modular template is accessible in two steps via 1) bromination of hexaphenyl benzene followed by 2) a sixfold Suzuki–Miyaura cross-coupling using 4-pyridineboronic acid. The template binding provides a way of locking a linear oligomer into the curved geometry of closed nanorings.

Porphyrinic 2D/3D coordination arrays or covalent assemblies have attracted considerable interest.^[76,77] We synthesized A_2B_2 -type functionalized porphyrinic blocks for the construction/fabrication of MOF films as a platform to envision their fascinating functions in a donor–acceptor system and photovoltaic performance.^[78] To identify promising chromophoric organic blocks, different substitution patterns were proposed based on computational investigations from in silico library (**Figure 13**). Various proposed A_2B_2 -type PP building blocks were synthesized by employing required suitable aldehyde and dipyrromethane precursors, and adding coordination-capable carboxylate groups to the phenyl rings at the *meso*-positions

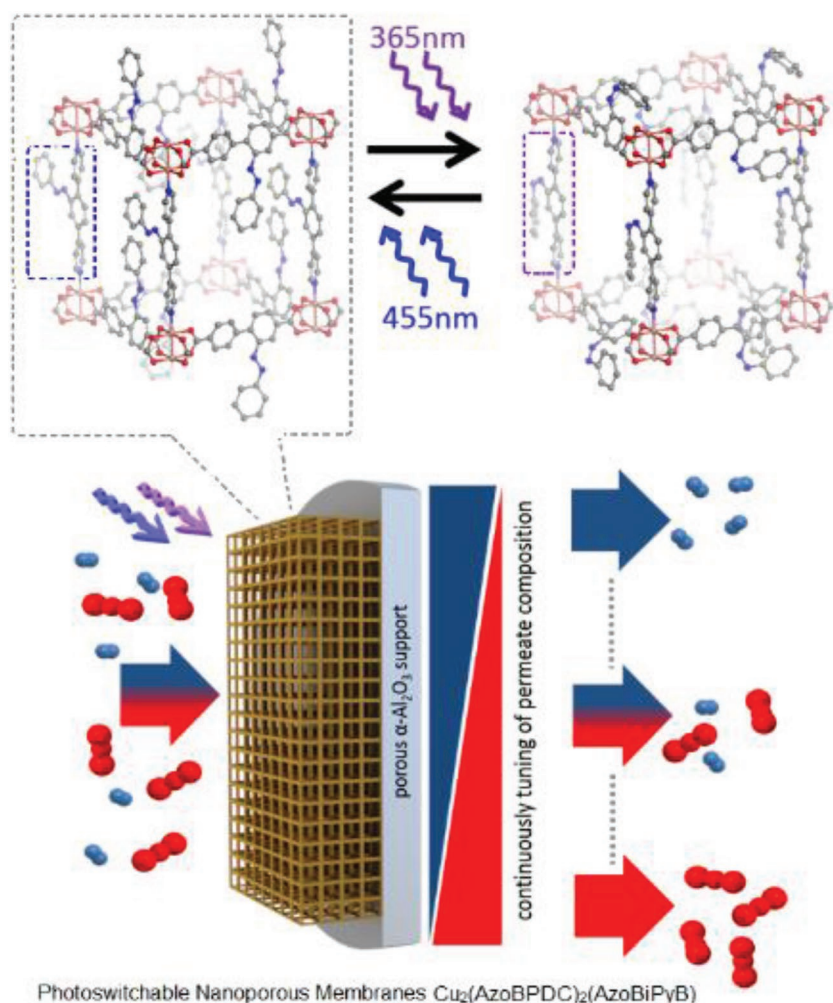


Figure 10. Depiction of a MOF nanosystem with photo-induced reversible molecular motion (*trans* to *cis* isomerization) for tunable and remotely controllable molecular selectivity. Reproduced with permission.^[58] Copyright 2016, Nature Publishing Group.

allows the use of PP chromophores for the assembly of MOFs. Regioselective halogenation at the *meso*-positions of the core, followed by subsequent metal-mediated Suzuki–Miyaura and Sonogashira cross-coupling reactions afforded the proposed PPs for their assembly to construct crystalline multi-layer SURMOF films of high optical quality. Adjusting the PP chromophore substitution pattern and consequently the MOF topology, allow to invoke band structure effects, thus increasing charge carrier mobility and allowing of indirect band gap formation. The photophysical properties can be predicted well using computational methods (in silico prediction/design of suitable PPs), thus identifying different porphyrinic linkers with different adsorption properties, allowing to bridge the so-called green gap.

Considering inorganic semiconductors, crystalline order leads to a band structure that causes drastic differences to the disordered materials, an example is the presence of an indirect band gap. In the case of organic semiconductors, since the bands are normally flat, and the band-gap therefore is direct, such effects are typically not considered. Electronic structures aided by computational values demonstrated PP arrays with a small dispersion of occupied and unoccupied bands, a consequence results in small indirect band gap.^[79] Employing LPE assembly approach, the corresponding crystalline organic semiconductors demonstrated superior photophysical properties, including unusually large charge-carrier generation efficiency and large charge-carrier mobility. Based on this novel material, a prototype

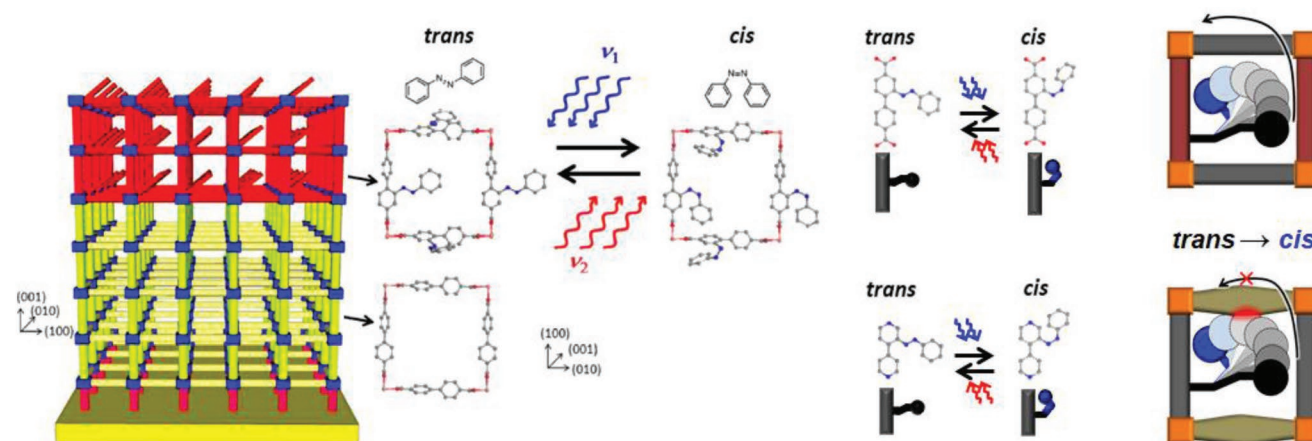
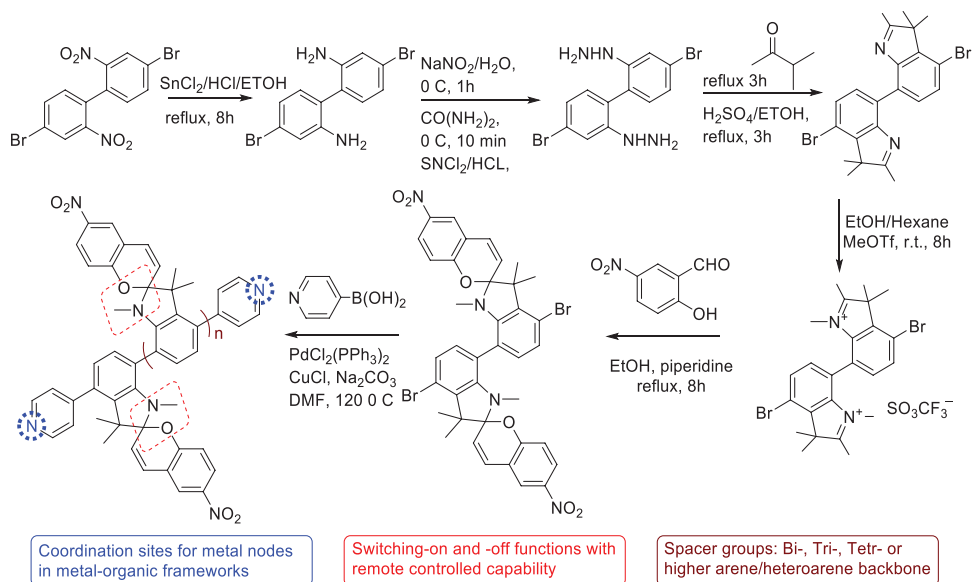


Figure 11. Depiction of a two-layered SURMOF nanosystems with photo-induced reversible molecular motion (left). Reproduced with permission.^[59] Copyright 2015, American Chemical Society. Photoswitching of two similar azobenzene-containing linkers and MOFs. The photoisomerization in MOF $\text{Cu}_2(\text{NDC})_2(\text{AzoBiPy})$ is sterically hindered (right). Reproduced with permission.^[60] Copyright 2015, The Royal Society of Chemistry.



Scheme 4. Modular synthesis of di(pyridin-4-yl)-7',7'-bispiro[chromene-2,2'-indoline] photoswitchable building blocks.

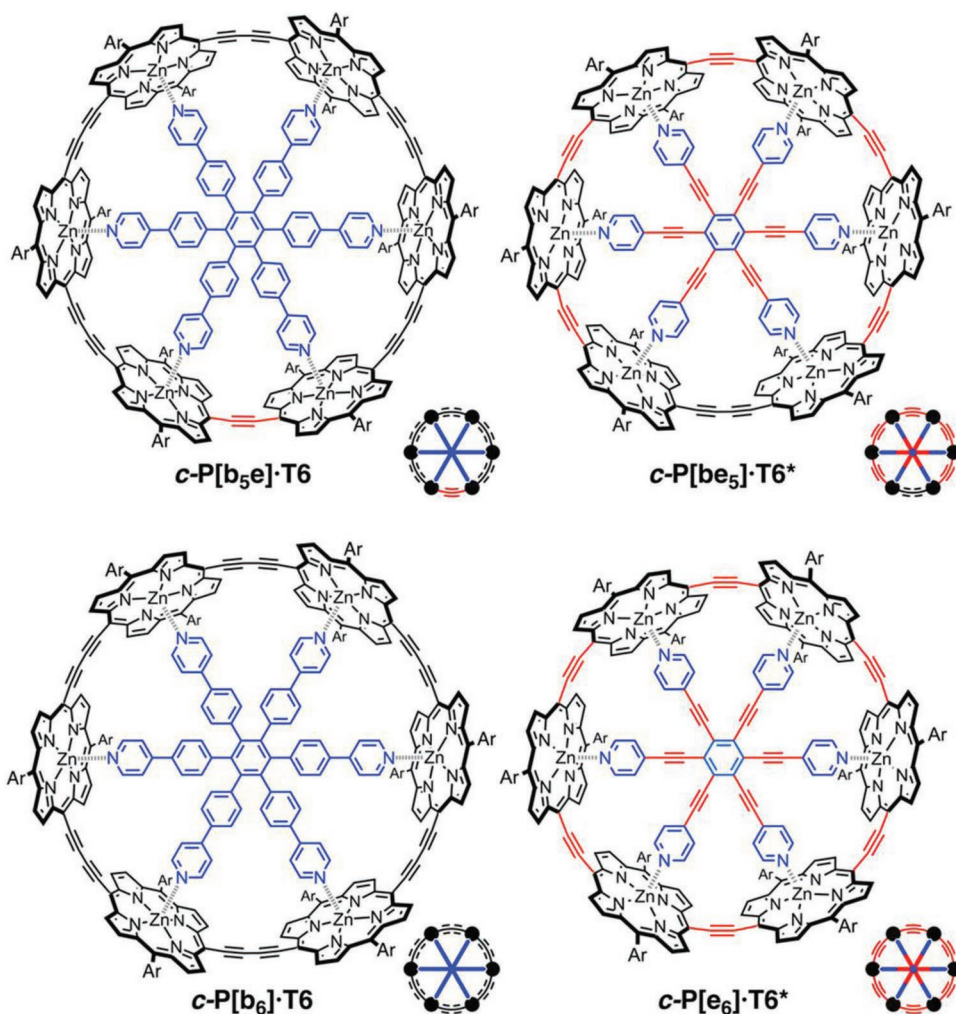


Figure 12. Molecular structures, schematic representation, and labels of the porphyrin nanorings. Reproduced with permission.^[75] Copyright 2017 and 2011, Nature Publishing Group.

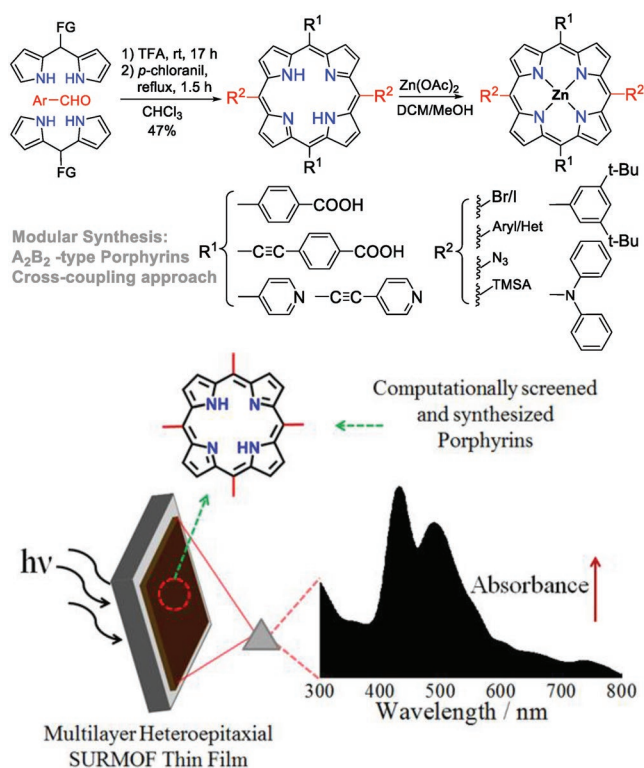


Figure 13. Synthesis and schematic representation of in silico prediction/design of suitable porphyrins for the constructions of MOF heteromultilayers. Reproduced with permission.^[78] Copyright 2019, Wiley-VCH.

organic photovoltaic device exhibits a remarkable efficiency. It was also demonstrated that the electron transport in the PP-based MOF can be further tuned. An electron donor–acceptor interactions system was designed by loading C_{60} -fullerene as guests into the pores of the PP-based MOF. In this MOF system, PP core served as an electron donor and C_{60} -fullerene worked as electron acceptor, causing a rapid charge separation (**Figure 14**). The demonstration of donor–acceptor interactions among the C_{60} guests within PP MOF could be an ideal system to investigate photoconducting properties in SURMOFs thin films.^[80] The availability of high-quality SURMOF thin films greatly simplifies the integration of chromophoric MOF materials for certain applications, including solar cells,^[81] Pd–PP-based SURMOFs with highly efficient 1D triplet exciton transport,^[82] epitaxial PP SURMOFs for all-solid-state solar cells, and photoinduced charge-carrier generation capabilities.^[83] The successful investigation of PP-based SURMOFs can be extended to phthalocyanine (PC)-based molecular systems. PCs in some regards are similar to PPs and more stable, which we hope will extend SURMOF thin-film application fields to photoelectrochemistry.

3. Tuning the Structure and Functions of Dynamic Covalent Polymer Networks: Beyond Metal–Coordination Driven Strategy

Moving away from a metal-coordination driven self-assembly strategy, organic components can be stitched together into

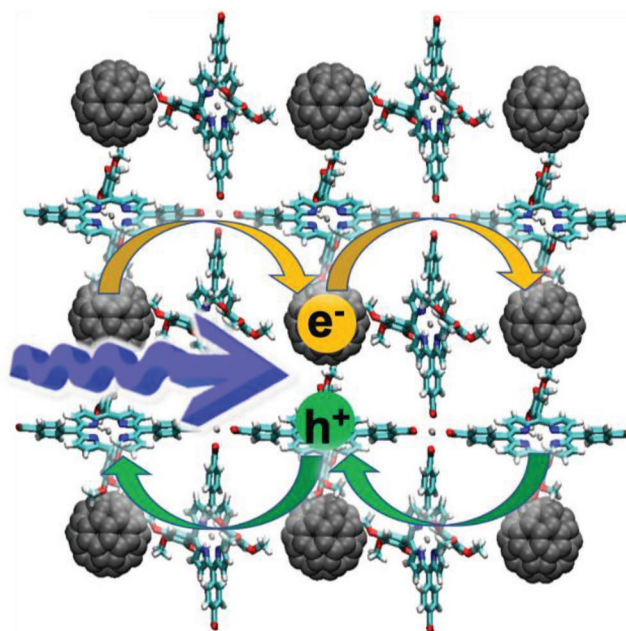


Figure 14. Sketch of the C_{60} at Zn(TPP) SURMOF. Reproduced with permission.^[80] Copyright 2019, Wiley-VCH.

extended polymeric networks via more persistent covalent linkages rather than using chemically labile metal–organic bonds that has opened up exciting new horizons of materials exploration.^[84] So far, various characteristic covalent linkages such as B–O (boronate ester),^[85] C–N (imide),^[86] C=N (imine),^[87] C=N (aromatic system, include triazine, phenazine),^[88] and B=N (borazine) covalent bond^[89] have been found suitable for the construction of architecturally and chemically stable dynamic covalent assemblies. Some representative covalent bonds reported for the construction of diverse covalent assemblies are shown in **Figure 15**. This class of designed covalent materials of low density and permanent porosity as well as high chemical/thermal stability have experienced rapid development for potential application in separation, adsorption, sensing, catalysis, and optoelectronics.^[90] In addition to the covalent linkage chemistries, the metric information of molecular building blocks (for instance, bond angles and points of extension) in trigonal or square planar, tetrahedral, hexagonal, and other geometries lead to an exceptional diversity of structures.^[91] Precisely predesigned building blocks, especially the design of angles and points of extension at the building blocks' peripheries, dictate their extended networks, pore size, shape, and functions.^[92] Molecular building blocks of planar character functionalized with polymerizable moieties result in the formation of extended 2D polymeric covalent assemblies. For instance, employing diboronic acids (taking the advantages of thermal dehydration) results into COF systems. In varying combination employing 1,4-phenylene diboronic acid, or pyren-2,7-diboronic acid and 4,4'-diphenylbutadiyne diboronic acid as coupling partners versus 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) form modular COF systems with pore size of 1.5 nm (COF-1), 2.7 nm (COF-5), hexahydroxytriphenylenepyrone-COF (3.2 nm), and 4.7 nm (hexahydroxytriphenylene-DPB COF) subsequently (**Figure 16**).^[82–89] Varying the molecular unit

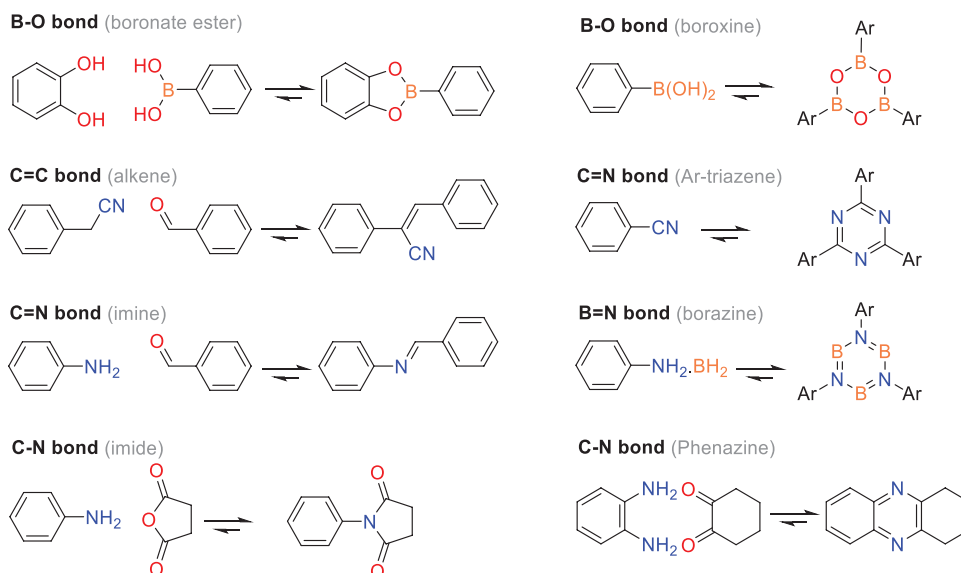


Figure 15. Common covalent linkages reported for stitching molecular building blocks in covalent framework assemblies.

size/length, such as changing from biphenyl to terphenyl and higher oligomeric backbones, or trigonal planar triphenylarenes/hetarenes and many more structurally diverse other customized organic building blocks decorated with polymerizable functional moieties have been reported for the construction of various 2D assemblies via various characteristic covalent linkages.^[82–89] Non-planar tetrahedral TPM analogues are mostly intended for the construction of 3D assemblies.

3.1. Trigonal Planar Alkoxyamine/Nitroxide Building Blocks: Tuning the Structure/Function of Dynamic Covalent Networks via Nitroxide-Exchange Reaction

Nitroxides form a class of stable free radicals, exhibit intriguing catalytic, optical, and magnetic properties that have been the subject of extensive research that find diverse applications in designing active catalyst systems, imaging agents, and engineering polymers as well as functional surfaces.^[93] Alkoxyamines derived from nitroxides, are synthetically useful building blocks, allowing the generation of C-centered radicals that can be used for nitroxide-mediated polymerization (NMP) and other nitroxide exchange processes.^[94] Like other characteristic covalent linkages, nitroxide-mediated process for the formation of reversible dynamic covalent bonds can be exploited in the covalent network formation.^[95] By the way of nitroxide-mediated reaction, a robust covalent polymer network can be obtained where the degree of covalent cross-linking can be thermodynamically controlled, hence allowing to access and dynamically adjust the materials properties.^[96] To establish the proof-of-principle, TPM-derived building block, functionalized with isoindoline moieties, was synthesized to be employed as a model. The isoindoline nitroxide moieties are strategically added that could be used against a TEMPO containing alkoxyamines in a nitroxide-exchange reaction. One of the promising features of the nitroxide-exchange process for the network polymerization is the employment of electron-paramagnetic

resonance (EPR) spectroscopy measurements that can follow the reaction progress and kinetics of the process with high sensitivity and precision. The employed nitroxides in the case of different hyperfine coupling constants can be measured with precision using electron-paramagnetic resonance (EPR) spectroscopy measurements. In case of pro-fluorescent nitroxide species, fluorescence spectroscopy measurements can be employed to track the nitroxide-exchange progress.^[97]

To fabricate a dynamic covalent polymer network, which can have a precisely tunable crosslinking degree, responsiveness to external stimuli and the capability to repair defects, we examined a distinct approach based on radical exchange reaction between defined trigonal planar molecular components of multi-spin nitroxides versus alkoxyamines. The synthetic design, especially angles and polymerizable end-groups at the building blocks' peripheries, has been crucial in forming polymer networks via multifold nitroxide exchange reaction. Triangular planar building blocks, for instance triphenylbenzene derivatives, are well-known in coordination chemistry that assemble into discrete 3D well-organized nanostructures,^[98] as well as covalent organic networks.^[99] Triphenylbenzene derivatives bearing polymerizable trialkoxyamine/isoindoline nitroxide moieties were synthesized and made way to generate dynamic covalent network polymers.^[100] The threefold trialkoxyamine molecular block can be synthesized on a multigram scale through a four-step procedure (Scheme 5 upper). The threefold triisoindoline nitroxide counterpart of the reaction can be obtained by palladium-mediated Sonogashira cross-coupling reaction by employing iodo-functionalized isoindoline nitroxide and 1,3,5-triethynylbenzene (Scheme 5 bottom).

Alkoxyamine components on thermal treatment cause C–O homolytic dissociation to generate transient C-centered radicals and persistent nitroxide (TEMPO) radicals. The transient C-centered radicals spontaneously can form new cross-linking via covalent bonds to the available isoindoline nitroxide radical species, hence enabling polymeric network structures. The mechanism of alkoxyamine and isoindoline nitroxide exchange

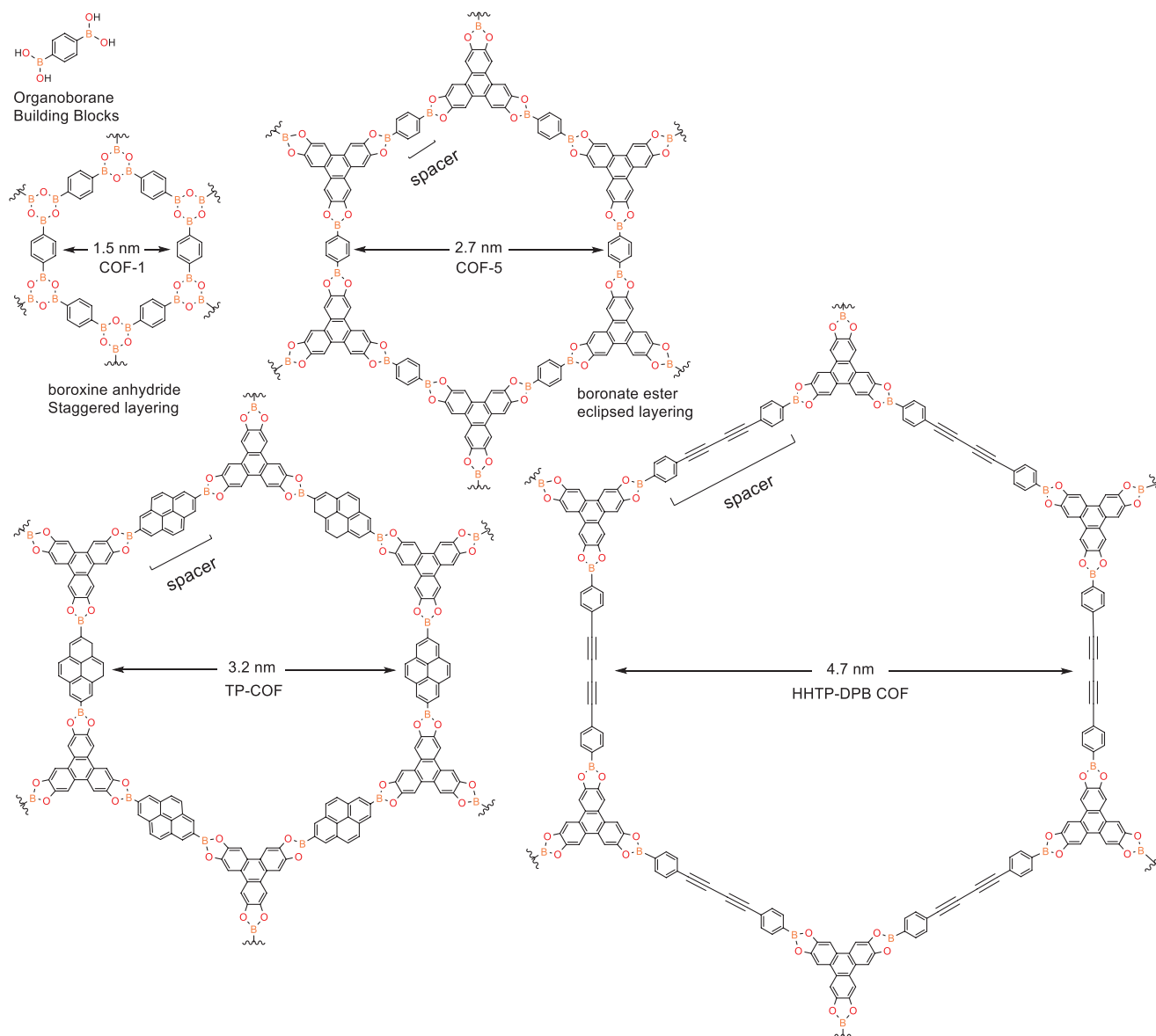


Figure 16. Representation of 2D networks built with modular organoborane building blocks.

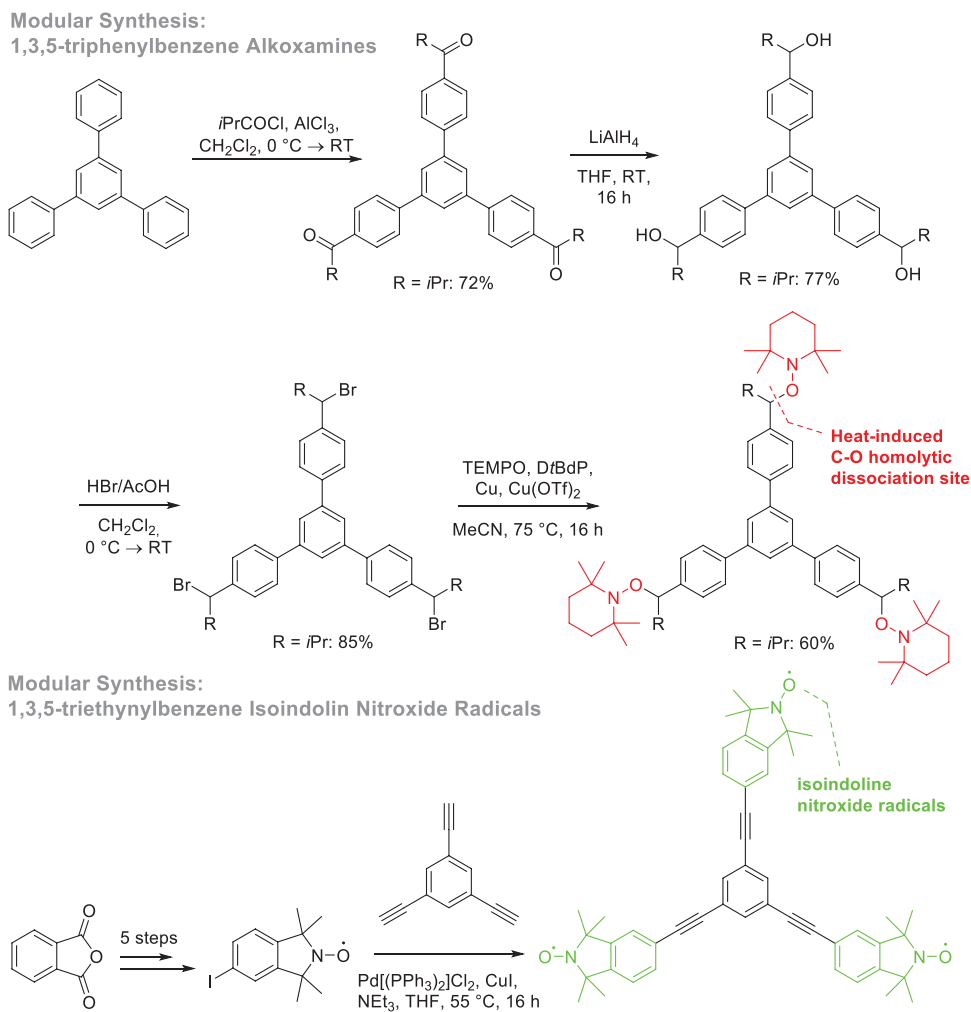
reaction and schematic representation of the dynamic covalent network formation is depicted in **Figure 17**.^[100]

Dynamic covalent networks obtained by nitroxide-exchange reaction exhibit elasticity, responsiveness, and swelling behavior on solvent impregnation. The reaction equilibrium and sol-gel-sol transitions can be reversibly tuned by thermal modulation. Adding an excess amount of TEMPO and heating it up to 100 °C shifts the equilibrium of the reaction process towards the starting components, leading to a dissolution of the polymer network allowing recovery of the starting building block components. **Figure 18** (top) represents the initial building block components in solution, the preassembled dynamic covalent networks obtained by nitroxide-exchange process (bottom, left) and the disassembled network into the building block components (bottom, left). Hence, the alkoxyamine covalent crosslinkages are shown dynamic and fully reversible in nature. The network

obtained by the nitroxide exchange reaction allows further tuning/depicts corrections of the network at molecular level. This novel dynamic covalently linked polymer network material exhibits reversibly tuneable cross-linking behavior triggered by heat and show self-healing potential. Other features, for instance, repeatedly assembly and disassembly, sol-gel-sol transitions, complete dissolution/recyclability of its building block components, make this dynamic system potential platform for certain applications such as membrane separation.

3.2. Tetrahedral Alkoxyamine/Nitroxide Building Blocks: Structuring 3D Dynamic Covalent Polymer Networks and NMP

Considering the highly dynamic nature of the nitroxide-exchange approach, combined with the choice of structurally



Scheme 5. Synthesis of trifold alkoamine and isoindolin nitroxide radical building blocks.

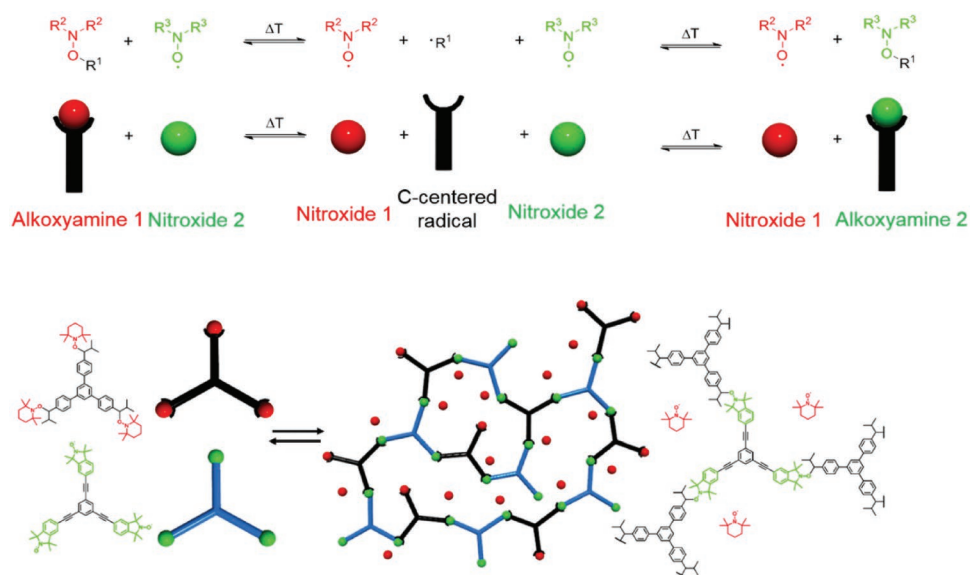


Figure 17. Schematic representation of the dynamic covalent networks via trialkoxyamines and trinitroxide molecular components. Reproduced with permission.^[100] Copyright 2019, The Royal Chemical Society.

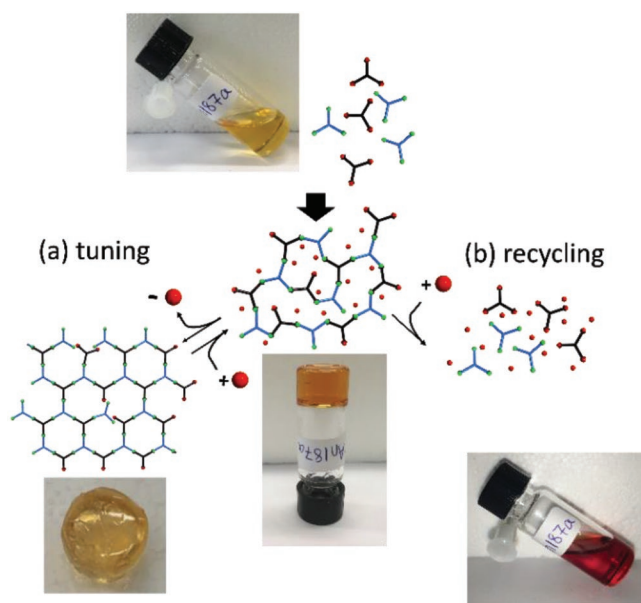


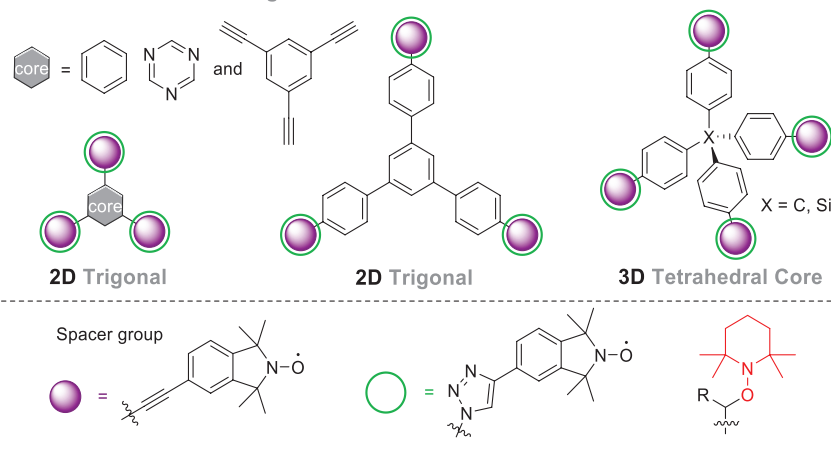
Figure 18. Dynamic and reversible equilibrium control of the nitroxide exchange reaction: Building blocks in solution before reaction (top), after gel transition on thermal treatment (bottom middle), after annealing (bottom left), and after recycling/dissolving (bottom right). Reproduced with permission.^[100] Copyright 2019, Royal Chemical Society.

diverse molecular blocks and custom-made attributes (attained by selective functionalization) including arene/heteroarenes with different spacer groups, this concept of reversible cross-linking via forming dynamic covalent bonds could be employed for the creation of highly ordered 3D superstructures. While nitroxide radicals in the pores of the framework, can work as catalytically active molecular entities. Our ability to design promising molecular blocks has significantly improved due to advances in computational screening/prediction that gives us the opportunity to systematically design/study the geometry of the potential molecular tectons and functions of the network. We have prepared various tetrahedral building blocks bearing multifold nitroxide and alkoxyamine groups as depicted in **Figure 19**, aimed to construct network materials by nitroxide exchange reaction that could be used for radical-mediated catalysis or polymerization. The alkoxyamine functional moieties within the preformed network assemblies can be exploited as dynamic bonds or a synthetic handle in the nitroxide exchange reaction. These radicals can work as potential initiator for nitroxide mediated polymerization. The upcoming section summarizes preparing various tetrahedral molecular building blocks and strategies for their assembly into diverse functional systems.

4. Tetrahedral Molecular Building Blocks: Modulating POPs and 3D Molecular Architectures

Tetrahedral molecules, being 3D building blocks, allow for the construction of sophisticated assemblies connected in all three dimensions. Since nature tends to minimize the energy of systems, building porous organic structures is a challenge due to the high surface area and the high surface energies followed by that. Therefore, avoiding the collapse of porous structures is necessary, which can be achieved by using sterically bulky and rigid, unbendable core molecules.^[101] Tetrahedral, rigid, spatial organic building blocks such as TPM, TPA_d (a cycloaliphatic hydrocarbon bearing fused cyclohexane), and pseudo-tetrahedral HPX, customized with function-capable and chemically active appropriate groups, have been intensively incorporated in molecular architectures,^[102] and find broad material applications.^[103] TPM, TPA_d, HPX, and their various structural analogues can be seen as loose (TPM, TPA_d, TPG_e, TPSi, and TPSn) or vertex-connected (HPX, NPM) tetrahedral buildings blocks, with different central elements/core allow for up to a ninefold functionalization, which can be used in the construction of complex nanostructures of high surface area and controlled porosity (**Figure 20**). The 3D tetrahedral structure of the building units imparts control over propagation/assembly process in all three dimensions.^[104] Varying the building blocks spatial geometry (ranging from 2D vs 3D atomic arrangements), their symmetry features/patterns as well as varying the number of coordination sites attached to the backbone can have a decisive role in the construction of the framework. Boom and co-workers observed the formation of coordination-polymer nanotubes by employing nonplanar 3D tetrahedral

Arene/Heteroarene 2D Trigonal versus 3D Tetrahedral Core



Dynamic Covalent Networks Modulation via Nitroxide Exchange Reaction

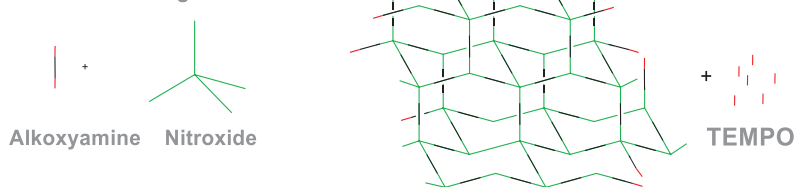
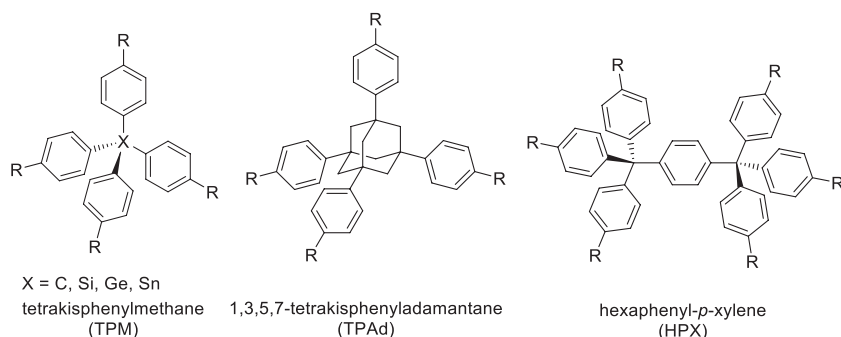


Figure 19. Structures and schematic representation of the alkoxyamines and nitroxide modular components aided by quantum chemical calculations for dynamic covalent network modulation.



R = Functional end-groups at peripheries:
 Br, I, N₃, TMSA, SH, CN, NH₂, CHO, B(OH)₂, CO₂H, etc.

Figure 20. Tetrahedral spatial organic molecular building blocks bearing customized function-capable moieties at peripheries.

building blocks whereas networks formation of nanospheres was realized utilizing 2D building blocks under similar conditions.^[105] The coordination-polymer nanotubes were predominantly formed with vinylpyridine-functionalized 3D tetrahedral TPM building blocks, while the use of the vinylpyridine-functionalized 2D planar building blocks resulted in the formation of interconnected spheres (**Figure 21**, top). Hollow molecular superstructures of novel shapes driven by metal-coordination approach were constructed by employing adamantane-based building blocks (**Figure 21**, bottom).^[106] In a similar way, for constructing/growing large

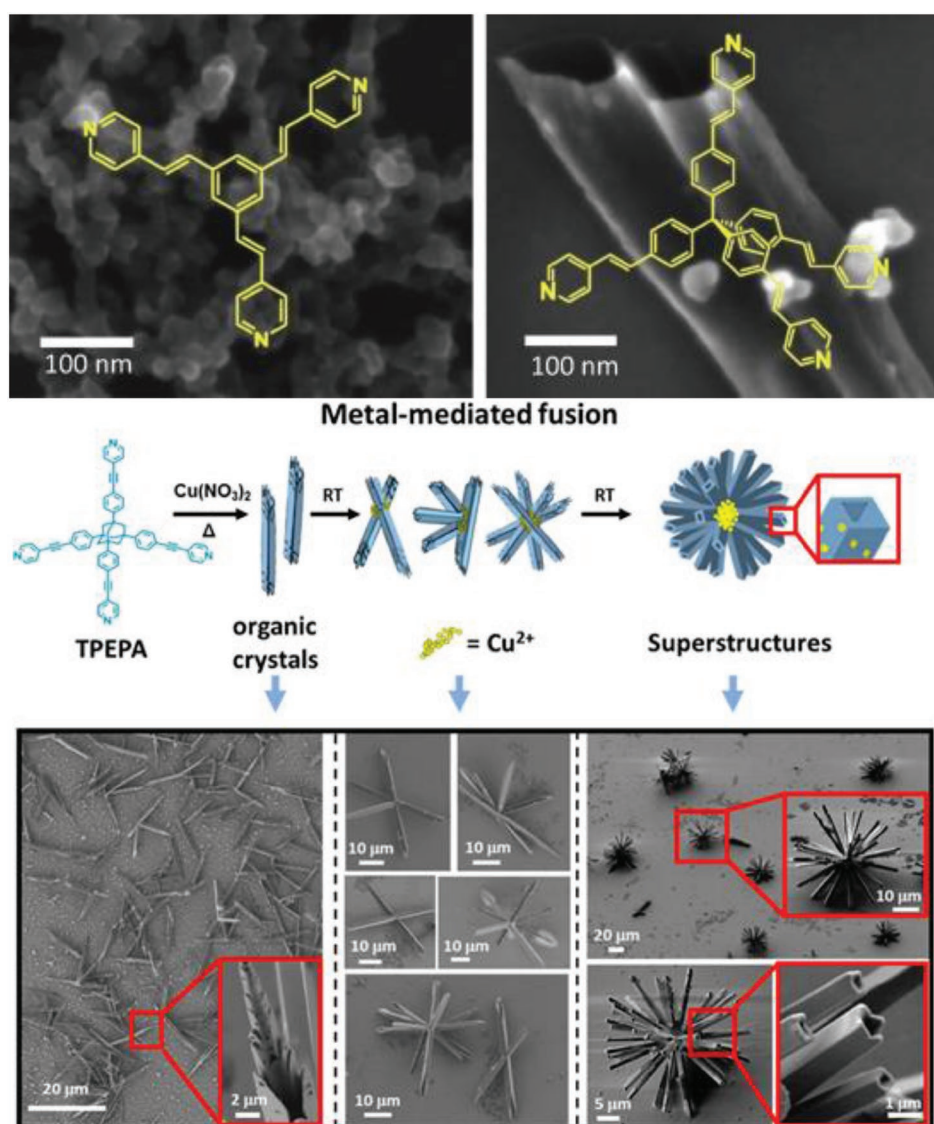


Figure 21. Ligand structure effect (2D versus 3D): Flexible and amorphous nanotubes were generated with a Pd salt and a multidentate ligand having a tetrahedral structure (upper right). In contrast, regardless of the number of metal coordination sites, ligands with a two-dimensional geometry lead to the formation of spheres and their aggregates (upper left). Reproduced with permission.^[105] Copyright 2011, Wiley-VCH. For the construction of coordination-polymer nanotubes versus networks spheres hollow crystalline molecular superstructures by varying the Adm-building blocks geometry. Reproduced with permission.^[106] Copyright 2018, American Chemical Society.

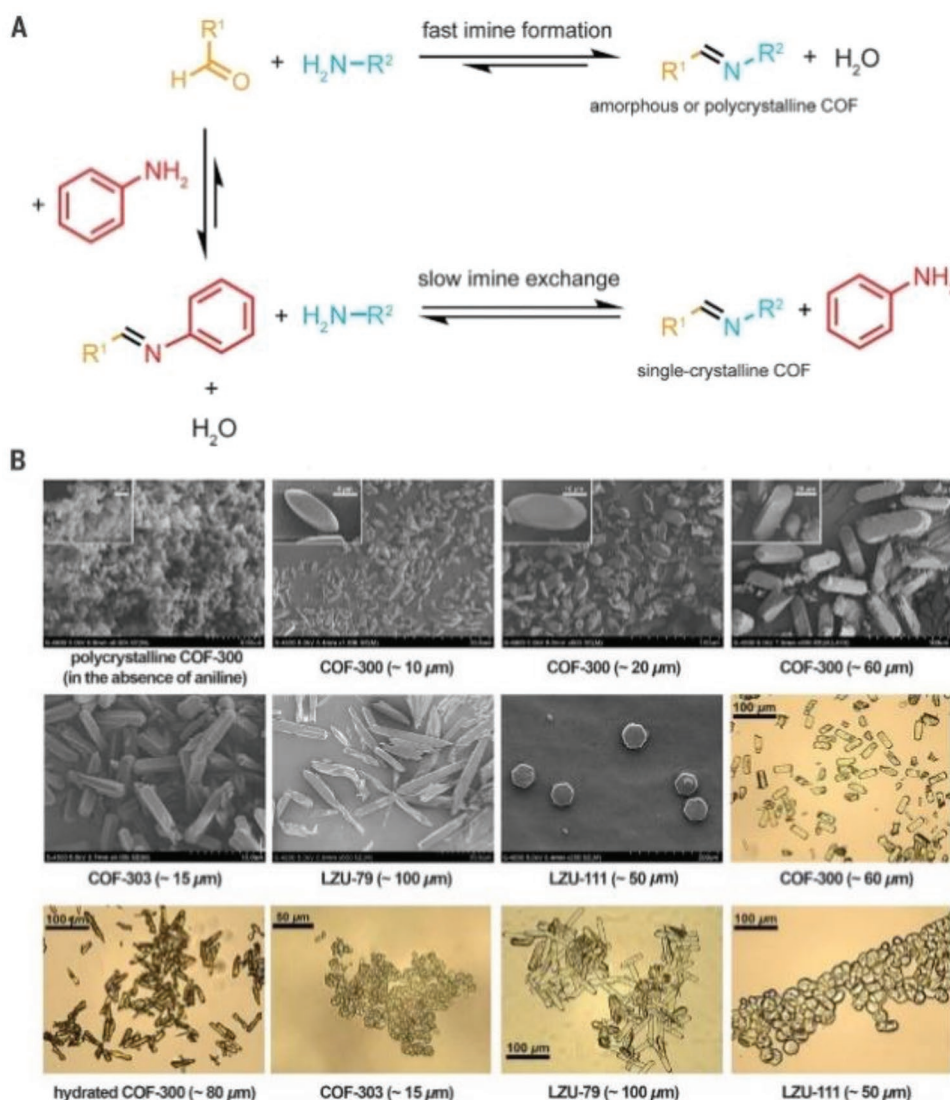


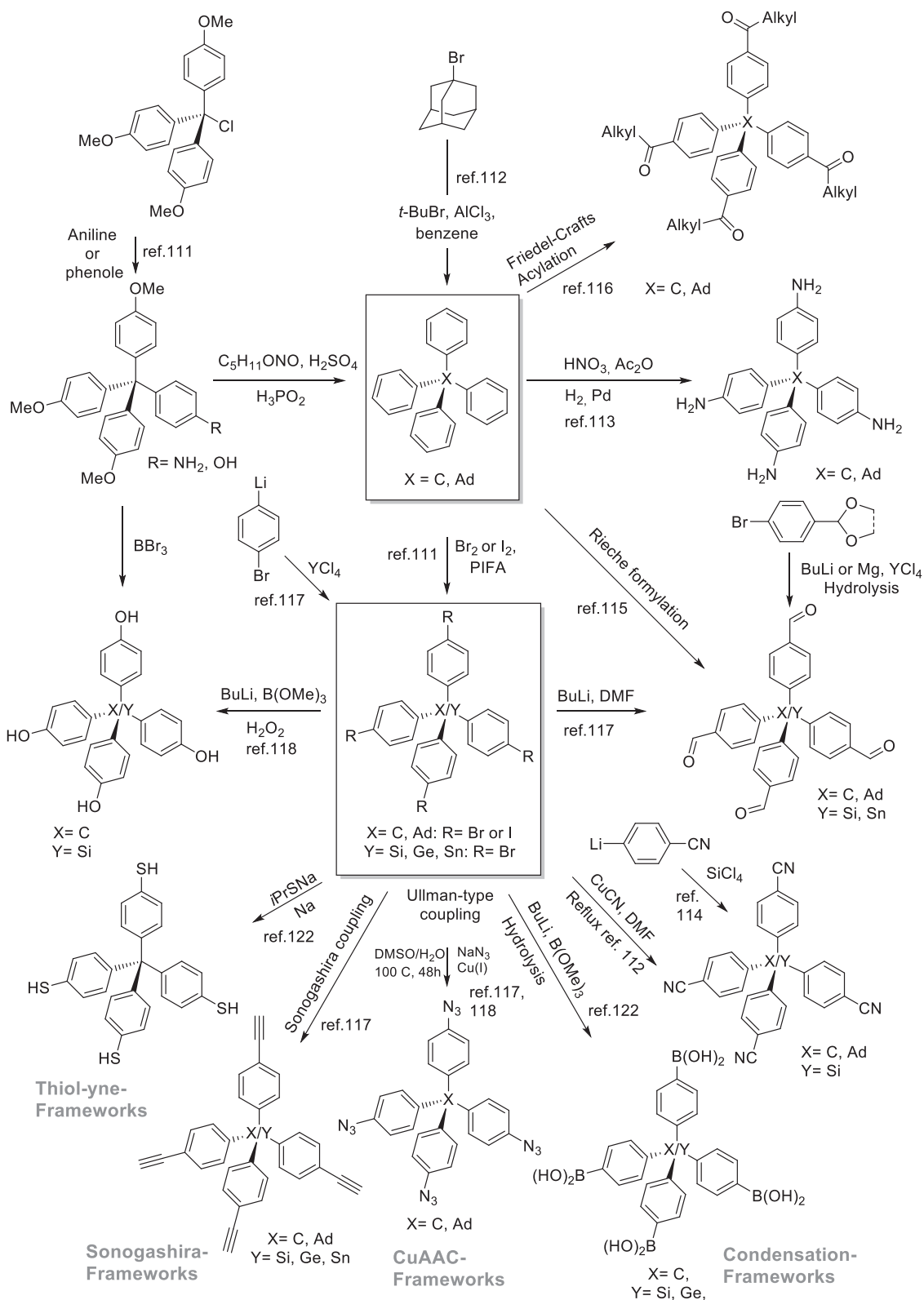
Figure 22. Crystal growth of large imine-based COFs modulated by aniline. A) In the absence of aniline, the imine-formation equilibrium is shifted toward the product, amorphous or polycrystalline COFs, whose formation is governed by fast nucleation and limited crystal growth. In the presence of aniline, the initial imine bond formation is comparably fast; however, slow imine exchange enables the growth of single-crystalline COFs. B) SEM and optical microscopy images of single-crystalline COFs. Reproduced with permission.^[107] Copyright 2018, American Association for the Advancement of Science (AAA).

single crystals of 3D chiral dynamic covalent organic frameworks (COFs), two types of 3D tetrahedral building blocks, tetraphenyl silane and tetraphenyl methane-based precursors with 3D spatial orientation, has been demonstrated (Figure 22), solving the long-standing challenge of crystallization problem in porous COFs.^[107]

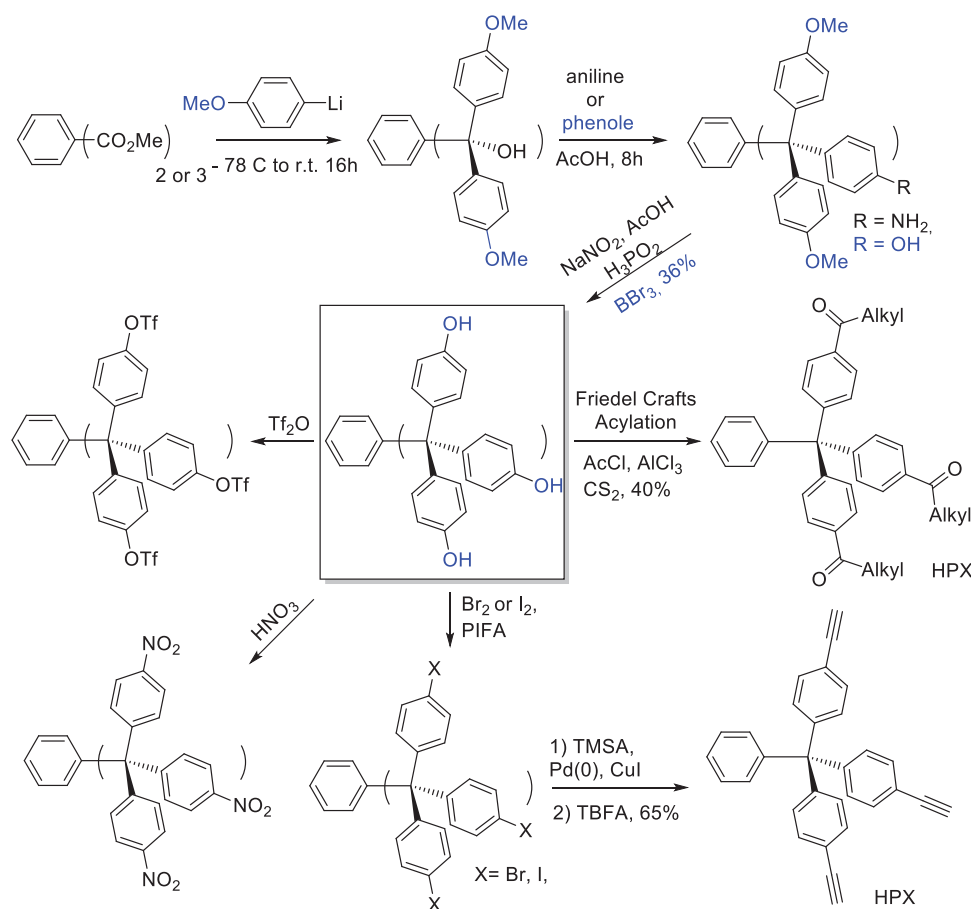
4.1. Tetrahedral TPM (C/Si/Ge/Sn) and TPAd Molecular Building Blocks: Modulating 3D Architectures

Function-inspired design of POPs, a versatile class of highly cross-linked amorphous polymers, that exhibit micropores, high and accessible surface areas, possessing hydro/thermally stable nature, has been an outstanding objective for diverse

applications.^[108] POPs are largely constructed by assembly of rigid, sterically demanding, and contorted multitopic tetrahedral TPM, TPSi, TPAd, and their various structural analogues through either hydrogen bonding or covalent bond-forming approaches including metal-mediated reactions and click chemistry approaches.^[109] One of the main advantages of these entirely organic structures is their stable nature in aqueous condition and their low densities that make them best known for gas adsorption/storage capacities.^[110] Utilizing appropriately functionalized TPM building blocks as key component in POPs, several synthetic protocols have been devised. TPM can be synthesized in a two-step reaction, by refluxing commercially available tritylchloride in aniline to afford the TPM-amine, which can be diazotized and reduced to the TPM core.^[111] This reaction can be conducted on a multigram scale



Scheme 6. Modular design and synthesis of multi-functionalized tetraphenylmethane (C/Si/Ge/Sn) and tetraphenyladamantane (TPAd) building blocks.



Scheme 7. Modular design and synthesis of multi-functionalized 1,4-ditritylbenzene and 1,3,5-tritritylbenzene derivatives.

affording high yields. Substitution of tritylchloride with its methoxy derivative, refluxing in phenol and subsequent treatment with BBr_3 leads directly to the TPM tetra-alcohol. While the TPA core is easily accessible in a single step from 1-bromoadamantane and *tert*-butyl bromide in a Friedel–Crafts-like reaction of benzene.^[112] The unsubstituted fundamental core of TPM or TPA can be further transferred into a diverse library of customized 3D tetrahedral modular building blocks such as NO_2 or NH_2 -derivatives (nitration followed by reduction),^[113] cylation,^[114] CHO (Rieche formylation),^[115] Friedel–Crafts products,^[116] and most importantly, organohalogen derivatives for versatile various metal-mediated synthetic approaches such as Suzuki–Miyaura and Sonogashira–Hagihara cross-coupling reaction.^[117] The bromo-derivatives of TPGc, TPSi, and TPSn can be accessed from 1,4-dibromobenzene and the respective tetrachlorides in a single step.^[118] The TPM or TPA core bearing halogen-functionalities represents versatile intermediates. For instance, azidation reaction of the tetrakis(4-iodophenyl)methane and adamantane derivative affords organic azides,^[119] multifold Suzuki–Miyaura and Sonogashira–Hagihara cross coupling (TMSA-tagging), leading to various attractive synthons that could be further used in click reaction to generate higher-order molecular assemblies.^[120] Optimized reaction conditions using *N,N*-dimethylethylenediamine as a ligand NaN_3 in combination with sodium ascorbate and CuI in

mixture of DMSO/ H_2O (10: 1) afforded the tetraazide in 34% yield. A selection of well-established pathways for the synthesis and selective functionalization of tetrahedral modular bricks with different substituents is summarized in **Scheme 6**. The TPA analogue of silane (TPSi) can be synthesized by the reaction of phenylmagnesium bromide with SiCl_4 or by reaction of PhLi with alkoxy silanes in one-step.^[121] Tetrakis-(thiophenol)methane (TPM-SH) can be accessed from TPM-Br in two steps including a nucleophilic substitution in dimethylacetamide followed by reduction with sodium.^[122] This protocol leads to high yields on a gram-scale synthesis under mild conditions. An analogous procedure can be applied for the synthesis of tetrakis(4-phenylboronic acid)methane and tetrakis(4-phenylboronic acid)silane having four boronic acid $-\text{B}(\text{OH})_2$ groups accessible from treating tetrakis(4-bromophenyl)methane/silane with butyllithium at -78°C in THF for 30 min, adding $\text{B}(\text{O}-i\text{-Pr})_3$, and subsequent hydrolysis with 1 M aqueous HCl.^[123] 1,4-Ditritylbenzene (HPX) and 1,3,5-tritritylbenzene (nonaphenylmesitylenes, NPM) derivatives that can be incorporated in higher molecular assemblies have been optimized on gram scales in three steps starting from either 1,4-dimethylterephthalate or trimethyl-1,3,5-benzenetricarboxylate.^[124] For HPX, similar to the synthesis of TPM, the alcohol derivatives can be synthesized while building up the core structure, which is achieved by reaction of the desired

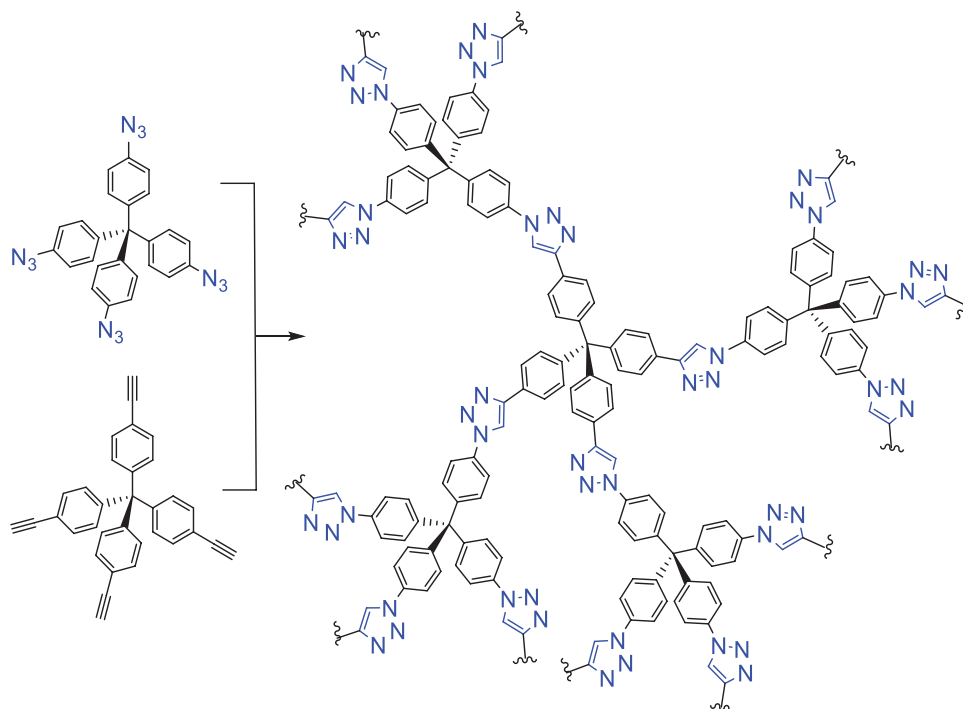


Figure 23. Design of triazole-linked POPs via click chemistry employing tetrahedral blocks bearing azides and terminal alkynes.

precursor with phenyllithium, followed by adding aniline and a subsequent diazotation/reduction step, as optimized by Benkeser et al.^[125] The HPX hexabromide derivative has been reported in excellent yield (92%) through simple bromination of the unsubstituted HPX. The hexaiodide can be obtained in moderate 55% yield where the solubility could be the possible reason of low yield. The synthesis of hydroxy functionalized core and its subsequent transformation into its triflates with triflic anhydride afforded the final product in 24% yield. The solubility of the hexa-alcohol in most commonly used organic solvents could be one of the assumed reason of the low yield. The synthetic scope of this methodology can be extended to 1,3,5-tritrylbenzen and derivatives thereof. Both, 1,4-ditrylbenzene (hexakis-substituted core) and 1,3,5-tritrylbenzene block (nonakis-substituted core), can undergo bromination, iodination, nitration, or acylation reactions (Scheme 7). These strategically designed cores can be further converted through sixfold and ninefold substitution reactions, respectively, that could be utilized in the construction of higher porous assemblies.^[126]

4.2. Multitopic Tetrahedral/Pseudo-Octahedral Organic Molecular Blocks for Higher Covalent Structures, Porous Network Assemblies, and Polymers

Based on the varying degree of chemical/thermal strength and stability of cross-linkages via covalent bond formation, various POPs can be constructed with tailored chemical/physical features for potential applications via exploiting synthetic design of the multitopic tetrahedral/pseudo-octahedral organic building blocks.

4.2.1. Synthesis and Structure/Function Relationship of 3D Frameworks via Copper-Catalyzed Azide Alkyne Cycloadditions

In 2007, Schilling et al. reported the synthesis of tetrakis(4-azidophenyl)methane and 1,3,5,7-tetrakis(4-azidophenyl)adamantane starting from the corresponding iodo-precursors. The building blocks are stable under ambient conditions, despite them violating the rule after which stable organic azides should have a ratio of carbon/oxygen atoms to nitrogen atoms above 3.^[127] Shortly after that, the Huisgen 1,3-dipolar cycloaddition reaction employing tetrahedral building blocks bearing multiple azides and/or terminal alkynes as monomers found its fascinating way into triazole-linked covalent porous organic materials (Figure 23).^[128] Cooper and co-workers in 2010 pioneered clicking tetrakis(4-azidophenyl)methane with tetrakis(4-ethynylphenyl)methane to give rise to a conjugated microporous polymer (CMP) with a Brunauer–Emmett–Teller (BET) surface area of 1128 m² g⁻¹.^[129] With slight modifications, the Nguyen and co-workers published the same material with an improved surface area of 1440 m² g⁻¹.^[130] The reported material proved to be thermally stable on heating up to 500 °C (loss of only 20 wt%) and also exhibited resistance under acidic and basic conditions. Exploring nanostructures via the synthetic design of building blocks, we deployed tetrakis(4-ethynylphenyl)methane, tetrakis(4-ethynylphenyl)adamantane, and 1,4-diazidobenzene to construct hyper-crosslinked polymers (HCPs).^[131] Compared to the earlier work of Cooper, Nguyen and their co-workers, the framework can be tuned by reacting a tetrahedral core with a linear building block. The HCP with the adamantane core was further investigated for gas uptake properties. N₂ adsorption indicated the existence of mainly micropores in the material, which has a BET surface area of 490 m² g⁻¹. Despite the similarity to the

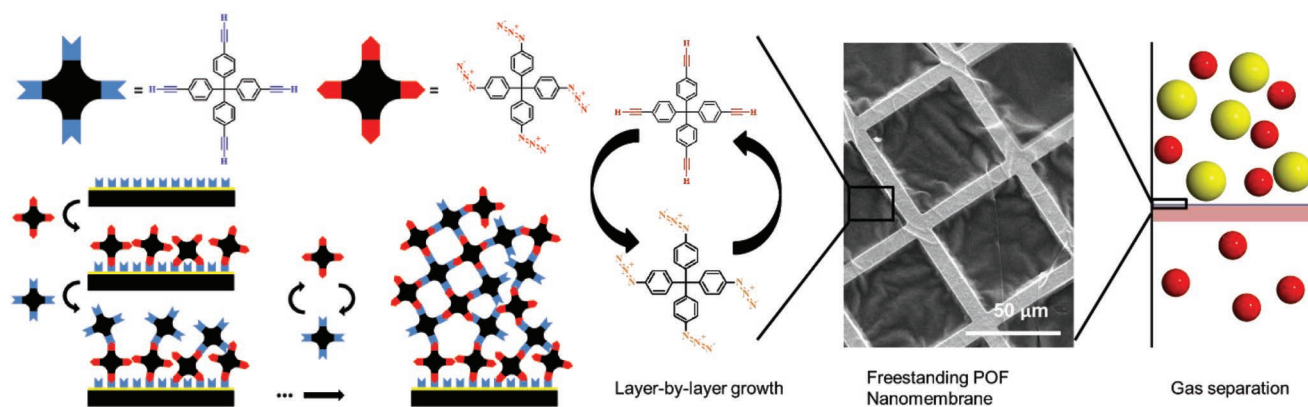


Figure 24. Molecular building blocks of the POF-system and schematic representation of their layer-by-layer synthesis on functionalized surfaces (left). Scanning electron microscope (SEM) images of the POF membrane after its transfer to a TEM grid (right). Reproduced with permission.^[132] Copyright 2014, American Chemical Society.

aforementioned material, the surface area for this combination of a tetrahedral and linear building block is much lower. Nevertheless, CO₂ adsorption shows a high efficiency of CO₂ capture even under pressure as low as 0.2 at 195 K.

Bringing POPs/POFs to practical application can sometimes be problematic in their physical manipulation due to the poor processability caused by the low solubility, which stands as a critical obstacle when synthesized as a bulk material. LBL approach of an alkyne-azide click-based porous organic framework on a sacrificial substrates can overcome this obstacle.^[132] Tetrakis(4-azidophenyl)-methane and tetrakis(4-ethynylphenyl) methane were chosen as molecular components. Self-assembled monolayer (SAM) exposing an azide or alkyne moiety was chosen, respectively. When using the alkyne-terminated SAMs, we exposed them to the azide containing building block in the presence of copper (I) catalyst. Afterward, the substrate was rinsed thoroughly and exposed to the alkyne containing building block, rinsed again, and exposed to the azide-terminated block; schematic representation is depicted in **Figure 24**. This LBL approach can be repeated and allow to control/achieve the required/desired thickness of the membrane. On dissolving the sacrificial substrate, it yields freestanding membranes. These POF membranes are highly selective in gas permeation for H₂, He, and CO₂, while retaining gases with a larger diameter like N₂, methane, and ethane (**Figure 24**, right).

Recently, employing LBL, two types of click chemistries which are orthogonal to each other, the copper-catalyzed alkyne-azide cycloaddition for the constructions of microporous nanomembranes and the light induced thiol-ene reaction subsequently for their outer surface functionalization with different molecules were explored.^[133] Contact angle measurements confirmed that microporous nanomembranes obtained through employing LBL techniques can be selectively fabricated to control their

wettability, thus strongly improving their potential in membrane application technologies.^[134] The problem of long reaction times and limited scalability of production of the freely floating POF membrane was further tackled by synthesizing thin-films and nanomembranes via light-induced thiol-ene click reaction. This technique also assist in achieving scalability of the freely floating POF membrane of about 1 nm at each cycle that was confirmed by AFM investigations and ellipsometry. The synthetic tunability of molecular building blocks, combined with processability of the resulting surface-anchored thin-films (**Figure 25**) further broaden the variability of the interfacial LBL approach.^[135]

In 2014, hexakis-substituted 1,4-ditrylbenzene as a novel rigid pseudo-octahedral building block in CuAAC was investigated for the construction of porous HCPs using different

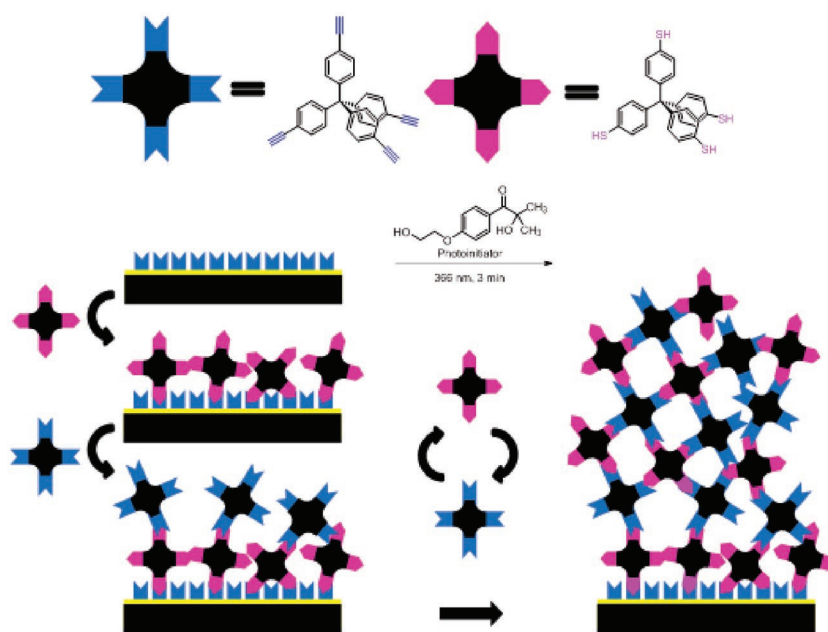
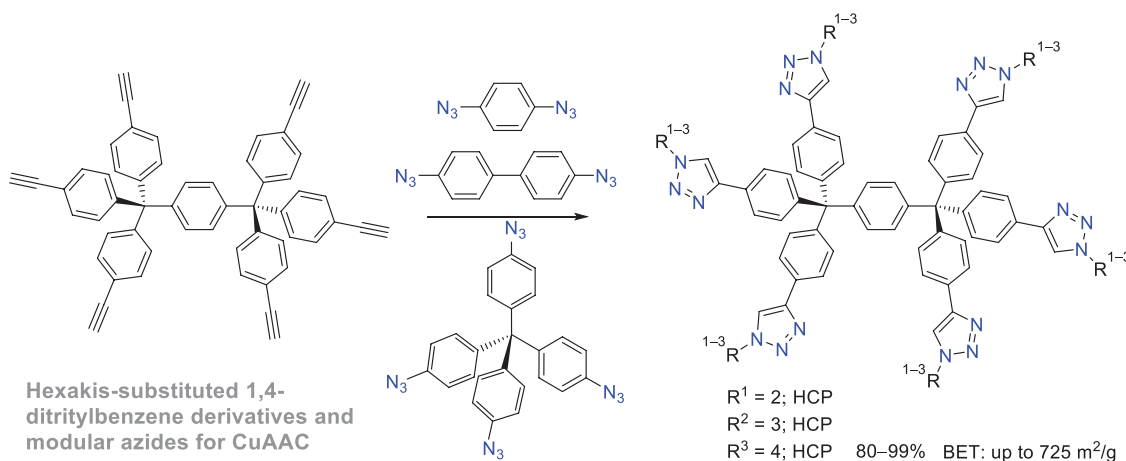


Figure 25. Molecular building blocks and schematic representation of LBL system. Reproduced with permission.^[135] Copyright 2016, Beilstein Institute for the Advancement of Chemical Sciences.



Scheme 8. Synthesis of CuAAC-based POP system using hexakis-substituted 1,4-ditriptylbenzene derivatives and various modular azides including the TPM-derivative.

azides, including the TPM derivative, which raises the complexity of the framework compared to the work of Cooper, Nguyen and their co-workers (**Scheme 8**).^[136] The porous HCPs obtained via CuAAC were insoluble in commonly used conventional solvents as well as resistant under strong acidic and basic condition. Their porosity was confirmed by sorption measurements using N₂ at 77 K. The highest BET surface area of 725 m² g⁻¹ was obtained by a combination of the TPM-azide and 1,4-ditriptylbenzene-alkyne.

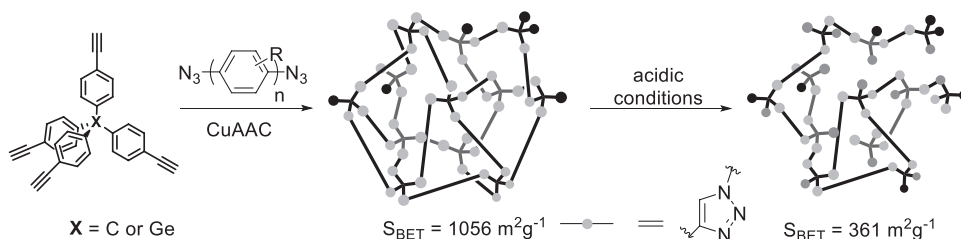
The selective incorporation of germanium as a central atom in a building block and their properties in POP systems has been rarely explored. In 2016, pioneering investigation on tetrahedral tetrakis(4-ethynylphenyl)germanium as monomer, and its incorporation into 3D frameworks via copper-catalyzed Huisgen 1,3-dipolar cycloaddition was carried out (**Scheme 9**).^[137] The presence of germanium element as component is beneficial that allows for characterization by detection via NMR spectroscopy and surface analysis methods such as XPS or ToF-SIMS for this specific nucleus. Porosity of the germanium-based POPs was further modulated under acidic conditions, hence tuning the adsorption properties. After construction of the 3D assembly, the Ge-C linkages within the preassembled framework were broken on treatment with triflic acid/iodide monochloride, consequently leading to lower BET-surface areas and total pore volume, established a new way of structuring materials with the possibility of fine-tuning their properties by chemical modification. These findings leads to the conclusion that the combination of two tetrahedral TPM cores in the CuAAC yields the highest

surface area (1440 m² g⁻¹), while lowering (employing ditopic blocks) or raising the complexity (by hexatopic blocks) seems to result in lower surface areas. Substituting the TPM-alkyne with TPGE-alkyne seems to drastically lower the surface area while simultaneously allowing for a post-synthetic tuning of the framework properties.

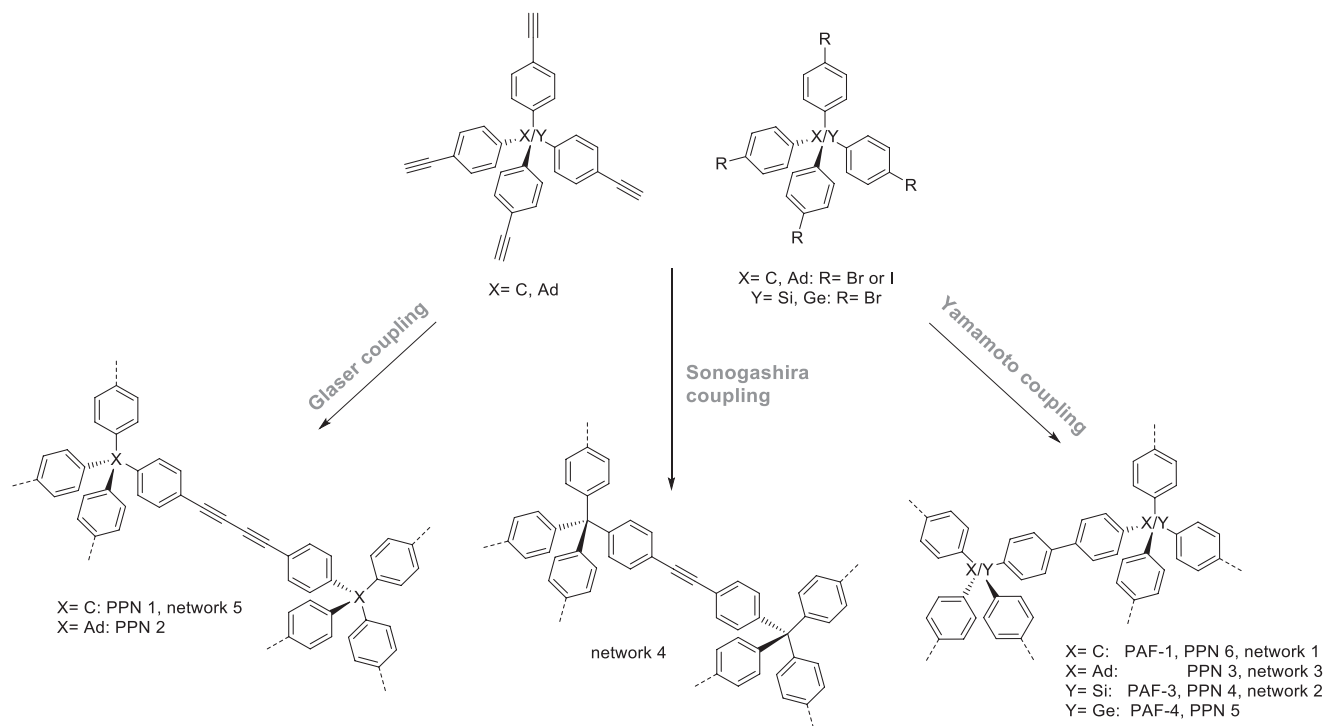
4.2.2. Synthesis and Structure–Function Relationship of 3D Frameworks via Metal-Catalyzed (Cross-)Coupling

Besides the abovementioned click-chemistry, 3D frameworks can also be synthesized in a mild way by means of metal-catalyzed coupling reactions like the Yamamoto coupling, Glaser–Hey couplings, or Sonogashira as well as Suzuki–Miyaura cross-coupling reactions (**Scheme 10**).

Yamamoto Frameworks: In 2009, Ben et al. reported the synthesis of PAF-1, which was assisted by computational design of the building blocks.^[138] They initially started from a diamond lattice, replaced one C–C bond with a phenyl ring, and calculated the BET surface area of the framework to be 1880 m² g⁻¹. When a second phenyl ring was added, the BET surface area rose up to 5640 m² g⁻¹, while the rigid building blocks should maintain the diamondoid structure of the framework. Further addition of phenyl rings gave a structure that was supposed to be mesoporous. Since microporous structures are most promising for gas storage, they chose to use TPM-Br in a Yamamoto coupling to resemble the calculated structure with two phenyl rings. Finally, they were able to produce PAF-1 with



Scheme 9. Porous organic polymers (POPs) and porosity tunability by incorporating germanium nodes tetrahedral building block.



Scheme 10. Overview over 3D frameworks generated via metal-catalyzed (cross-)coupling reactions.^[142]

a BET surface area of $5600 \text{ m}^2 \text{ g}^{-1}$ (Table 1), which was the highest for porous materials reported until then and is remarkably close to the calculated value, demonstrating the immense potential of calculation supported chemistry.

This exceptional surface area may arise from very little interpenetration in the framework due to an advantageous size ratio between monomer and pore, as suggested by theoretical calculations carried out by Martin et al.^[139] PAF-1, with its set of favorable properties became gold standard for (metal-catalyzed) porous organic frameworks for the next many years to come. Intensive research enhanced the interest in PAF-1, so that many derivatives were investigated.^[140]

After the successful synthesis of PAF-1, Cooper, Zhou, and their co-workers reported the same framework structure in 2010 and 2011 under the name “network 1” and PPN-6, respectively (Table 1). In contrast to PAF-1 and PPN-6 that were synthesized from TPM-Bromine, the Cooper’s and co-workers used TPM-Iodine as precursor for their network 1, which gave a BET surface area of just $3160 \text{ m}^2 \text{ g}^{-1}$ compared to PPN-6 ($4023 \text{ m}^2 \text{ g}^{-1}$) and PAF-1 although being isostructural, indicating a somewhat lower efficiency of iodides in the Yamamoto coupling according to the authors.^[141] In 2010, Zhou, Cooper and their co-workers further

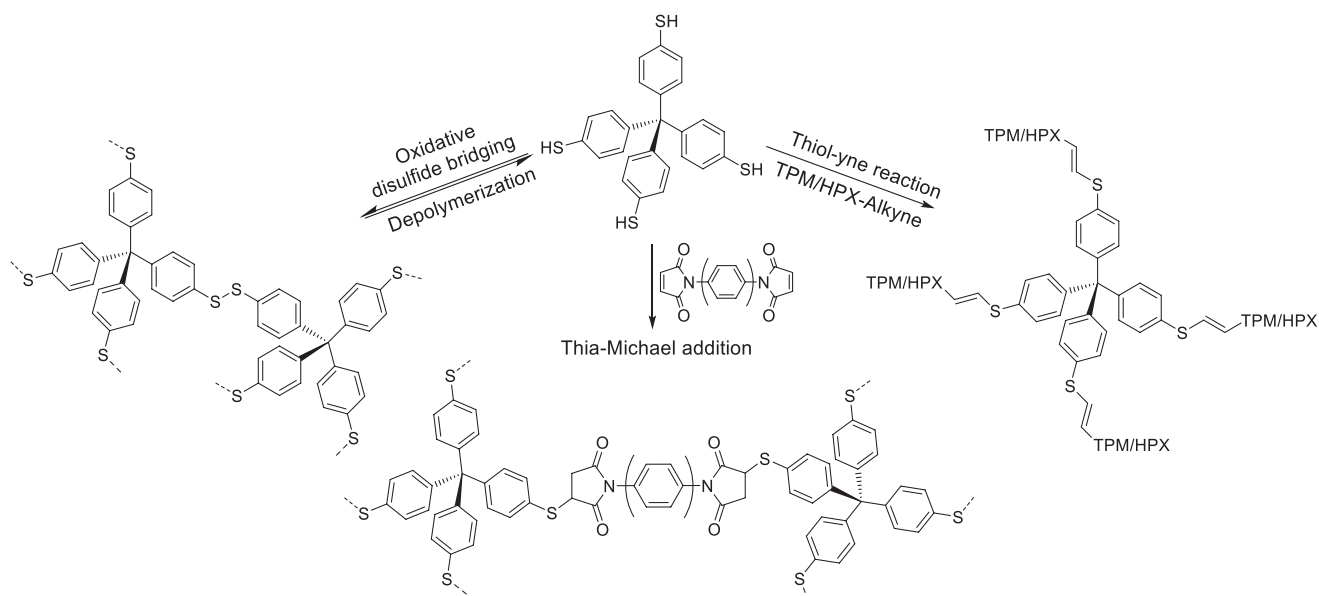
expanded their investigation on TPAAd-Br as precursor for PPN-3 ($2840 \text{ m}^2 \text{ g}^{-1}$) and network 3 ($3180 \text{ m}^2 \text{ g}^{-1}$). Initially, they measured very similar BET surface areas for their frameworks, and Zhou’s group was able to develop a new, milder procedure in 2011, which allowed a 1.5-fold increase in surface area to $4221 \text{ m}^2 \text{ g}^{-1}$ for PPN-3 (Table 1).^[142] PAF-1 derivatives with silicon or germanium as central atoms have also been reported within the same year. Yamamoto frameworks of TPSi-bromide gave network 2, PAF-3, and PPN-4 a surface areas of 1102, 2932, and $6461 \text{ m}^2 \text{ g}^{-1}$, respectively, while TPGe-bromide yielded PAF-4 ($2246 \text{ m}^2 \text{ g}^{-1}$) and PPN-5 ($4267 \text{ m}^2 \text{ g}^{-1}$) (Table 1).^[143] It is noteworthy that the optimized conditions of Zhou and co-workers gave the best surface areas compared to the competition, with PPN-4 even surpassing the surface area of PAF-1. Interestingly, these conditions were also applied for the synthesis of PPN-6 that gave a somewhat lower surface area than PAF-1.

Tuning of the properties of such frameworks can be achieved in multiple manners by manipulating the framework structure. Choosing longer building blocks leads to mesoporous structures as predicted by Ben et al. in the original publication of PAF-1. Nevertheless, such frameworks with three and four phenyl rings between the central carbon atoms have been evaluated by computational methods for their gas storage/gas separation behaviour, revealing promising results.^[144]

Presynthetic modifications include the alteration of the central structure of the building blocks as described above, when substituting carbon with adamantane, silicon, or germanium, while PSMs have been demonstrated for PPN-6 to tune CO_2 adsorption or gas-separation properties. Furthermore, frameworks containing a germanium node have been shown to undergo post-synthetic tuning, which could also be applied for the Yamamoto frameworks. Comparing these results clearly

Table 1. Overview of (cross-)coupling frameworks synthesized by different working groups, their building block motif, and surface areas.

Head 1 [units]	Qiu/Zhu	Zhou	Cooper
TPM	PAF-1 [$5600 \text{ m}^2 \text{ g}^{-1}$]	PPN-6 [$4023 \text{ m}^2 \text{ g}^{-1}$]	Network 1 [$3160 \text{ m}^2 \text{ g}^{-1}$]
TPAd	–	PPN-3 [$4221 \text{ m}^2 \text{ g}^{-1}$]	Network 3 [$3180 \text{ m}^2 \text{ g}^{-1}$]
TPSi	PAF-3 [$2932 \text{ m}^2 \text{ g}^{-1}$]	PPN-4 [$6461 \text{ m}^2 \text{ g}^{-1}$]	Network 2 [$1102 \text{ m}^2 \text{ g}^{-1}$]
TPGe	PAF-4 [$2246 \text{ m}^2 \text{ g}^{-1}$]	PPN-5 [$4267 \text{ m}^2 \text{ g}^{-1}$]	–



Scheme 11. Design and synthesis of 3D-homopolymers using TPM-thiol via: 1) oxidative disulfide bridging, 2) Thia–Michael reactions; and 3) Thiol–yne reaction.^[148,149]

demonstrates the superiority of the new procedure Zhou and co-workers introduced in most cases. Simultaneously, such tremendous deviations in several isostructural frameworks indicate that a thoroughly optimized procedure for the Yamamoto coupling seems to be the key to achieve high surface areas needed for application such as gas storage. Nevertheless, the conditions Zhou and co-workers established seem to give a very good reproducibility of the frameworks and their properties as they demonstrated for multiple batches of PPN-4.^[142]

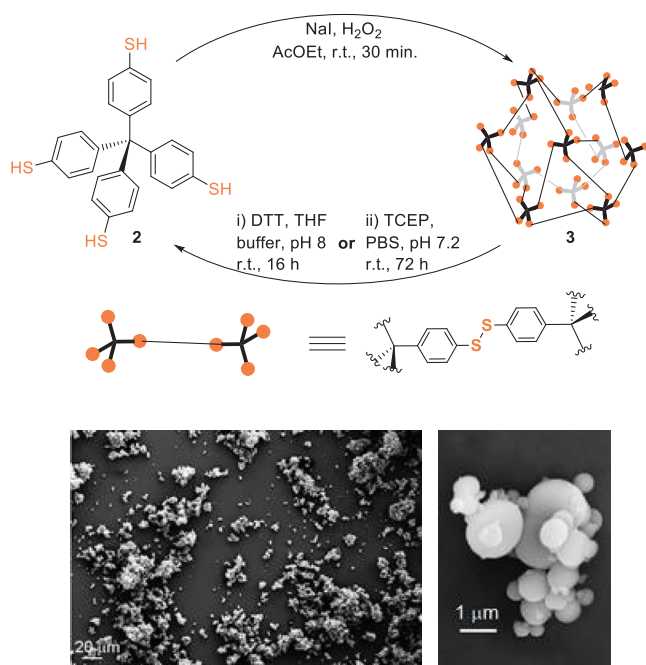
Sonogashira/Glaser–Hay/Oxidative Eglinton Frameworks: Besides the Yamamoto coupling, other metal-catalyzed couplings employing terminal alkynes can be considered for material engineering. In 2010, the groups of Cooper and Zhou independently published their results on Glaser/Eglinton frameworks.^[141] They achieved similar surface areas for their isostructural frameworks network 5 and PPN-1 with 1470 and 1249 m² g⁻¹, respectively. Alteration of the carbon center to adamantane enlarges the BET surface area to 1764 m² g⁻¹ for PPN-2, which is in accordance with the behavior of the Yamamoto frameworks (Table 1). Surface areas for the PPNs were lower than calculated theoretical values (over 5000 m² g⁻¹), partially due to interpenetration due to electronic interactions. Nevertheless, the resulting frameworks possess a high stability regarding thermal and chemical treatment and the heat of adsorption for H₂ of PPN-1 (7.59 kJ mol⁻¹) is higher than that for the well-known PAF-1 (4.6 kJ mol⁻¹). Furthermore, PPN-1 shows a fivefold to sevenfold higher selectivity for CO₂ over CH₄, which makes it a suitable candidate for gas separation.

4.2.3. Synthesis and Structure–Function Relationship of 3D Frameworks via Sulfur-Based Chemistry

To generate three-dimensional dynamic polymer covalent networks, various reactions for instance, disulfide bonds,^[145] Diels–Alder reactions,^[146] and other covalent dynamic

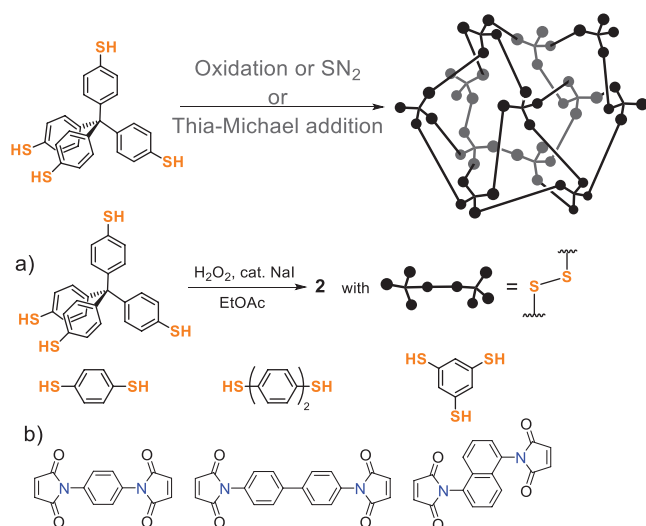
chemistries have been previously demonstrated.^[147] Disulfide bonds combine HCPs robustness with the dynamic behavior of assemblies held together, for example, by H-bonds and/or coordination bonds. This opens up new possibilities and allows rapid access to explore functional surface coatings for innovative applications. Utilizing TPM-thiol via 1) oxidative disulfide bridging; 2) nucleophilic substitution on halogenated linkers; and 3) Thia–Michael reactions allowed us the construction of 3D frameworks (**Scheme 11**).

Employing tetrahedral tetrakis(thiophenol)methane catalyzed by sodium iodide under mild conditions and short reaction times, we have demonstrated a 3D new poly(disulfide) HCP in excellent yields (**Scheme 12**).^[122] To monitor the progress of the polymerization reaction, a model study was optimized in parallel considering their insolubility issue of the generated polymer. Thiocresol was oxidized to the corresponding disulfide, and FTIR spectra confirmed appearance of the disulfide, whereas the thiol stretching band completely disappeared. The SEM analysis of the corresponding 3D homopolymer reveals spherical condensed particles (0.5–1.7 μm) with non-uniform size distribution. The 3D homopolymer exhibits no considerable porosity and a negative value for its surface area investigated on varying reaction conditions. Demonstrating the reversible character of the corresponding 3D polymer macromolecular architecture under controlled depolymerization, dithiothreitol in slightly basic conditions and tris(2-carboxyethyl)phosphine (TCEP) at neutral pH were employed. Under both the conditions, the macromolecular assemblies were disassembled into its building block components after 16 and 72 h, respectively. In a separate experiment, post-functionalization was further investigated employing a Thia–Michael reaction with maleimide. The PSM on polymer was proven through solid-state fluorescence emission spectroscopy. The degree of functionalization via PSM on the polymer was indirectly quantified taking advantage of the



Scheme 12. Formation and reduction of the dynamic/reversible polydisulfide 3D homopolymer (top), SEM pictures of the HCP (bottom). Reproduced with permission.^[122] Copyright 2014, Wiley-VCH.

depolymerization process. After the 3D homopolymer was investigated, we focused on the mixed disulfide bridging between the tetrakis(phenyl)methane core and multifunctional phenyl and biphenyl thiol building blocks by oxidation reactions that lead to different HCPs (**Scheme 13a**).^[148] As these HCPs were insoluble, only solid-state analyses for characterization were performed. IR spectroscopy revealed no stretching band relative to free thiol functional group. The elemental analysis was in accordance with the theoretical values, suggesting the formation of the desired macromolecular structure. All 3D polymers exhibit insolubility

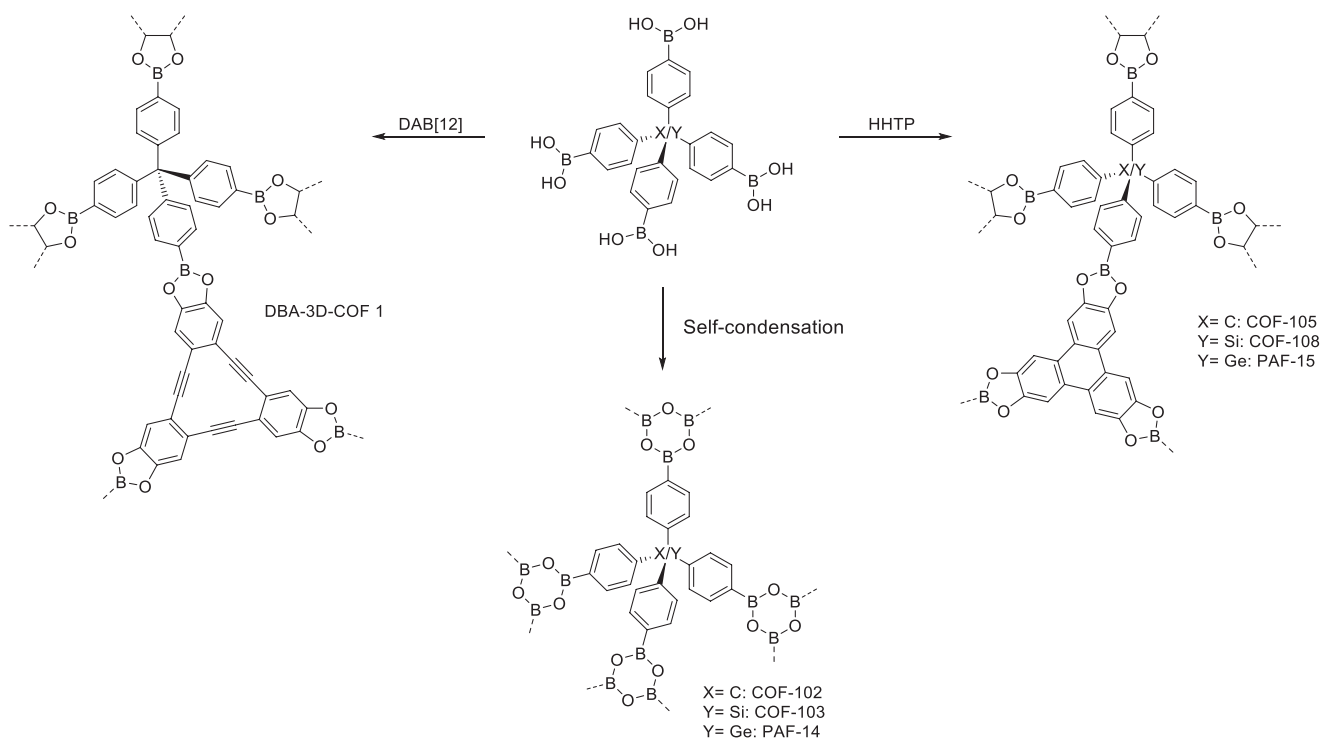


Scheme 13. Generation of 3D HCPs based on tetrakis(thiylphenyl)methane via: a) disulfide bridging, b) Thia-Michael addition and other sulfur-based chemistry.

and demonstrate a similar thermal behavior. High thermal stability of these HCPs was proven by TGA. The adsorption properties of these HCPs revealed no considerable porosity. HCPs disulfide linkages were depolymerized and the starting materials were recovered quantitatively in 20 h under basic buffered solution or with TCEP in 3 days at physiological pH, illustrating the reversible character of these new disulfide-based HCPs. These demonstrations of the polydisulfide 3D-HCPs formation and subsequent reduction of the dynamic/reversible reactions might contribute to the design of engineering new heteroatom-based HCPs materials. Despite exhibiting a very useful, fully reversible character the disulfide bridged HCPs unfortunately had no significant surface area. Therefore, other reactions involving thiols were examined, revealing that the thiol-yne reaction involving rigid TPM and HPX core structures delivered HCPs with BET-surface areas up to 650 m² g⁻¹.^[149] The Thia-Michael reaction between tetrakis(thiophenyl)methane and *N,N*-(1,4-phenylene) dimaleimide (**Scheme 13b**) was examined and yielded a framework with up to 1675 m² g⁻¹ surface area and a micro/mesoporous character, demonstrating the viability of sulfur-based chemistry for porous frameworks.

4.2.4. Synthesis and Structure-Function Relationship of 3D Frameworks via Condensation Reactions

In 2005, Yaghi and co-workers introduced the concept of COFs when they demonstrated that the thermodynamically controlled, reversible condensation of boronic acids gave highly stable, crystalline frameworks with surface areas of 711 and 1590 m² g⁻¹ for COF-1 and COF-5, respectively.^[150] This concept can not only be applied to planar building blocks, but also to their 3D equivalents successfully, as the same group demonstrated 2 years later in 2007.^[151] They were able to produce crystalline COFs by self-condensation of TBPM (TPM-boronic acid) or TBPS (TPSi-boronic acid) as well as co-condensation of both with HHTP giving boroxine COFs COF-102, COF-103 as well as boronate COFs COF-105 and COF-108, respectively (**Scheme 14**). All these materials were reported to be highly stable under thermal treatment (up to 450 °C) and have low densities. Furthermore, they feature high surface areas, with 3472 m² g⁻¹ being measured for COF-102 and even higher values calculated for COF-105 and COF-108. Especially COFs synthesized with TBPS (TPSi-boronic acid) as building block are outstanding, since COF-103 and COF-108 held the records for highest COF surface area (4210 m² g⁻¹) and lowest density for porous materials (0.17 g cm⁻³) for almost 10 years.^[152] Both records were beaten in 2016 by DBA-3D-COF 1, which is built of TPBM (TPM-boronic acid) and a dehydrobenzoannulene (DBA) yielding a structure with a surface area of 5083 m² g⁻¹ and density of 0.13 g cm⁻³.^[153] These results clearly demonstrate the immense potential of tetrahedral building blocks, based on TPM, inhibit regarding the construction of high-performance frameworks. Until now, to the best of our knowledge, the boronic acid derivative of TPad has not yet been used to generate COFs, but we suspect it to give high surface areas, since it performs similar or better than TPM-based cores in most cases. In 2012, Yuan et al. described the synthesis of TPBGe (TPGe-boronic acid), expanding the list of boronic acids with



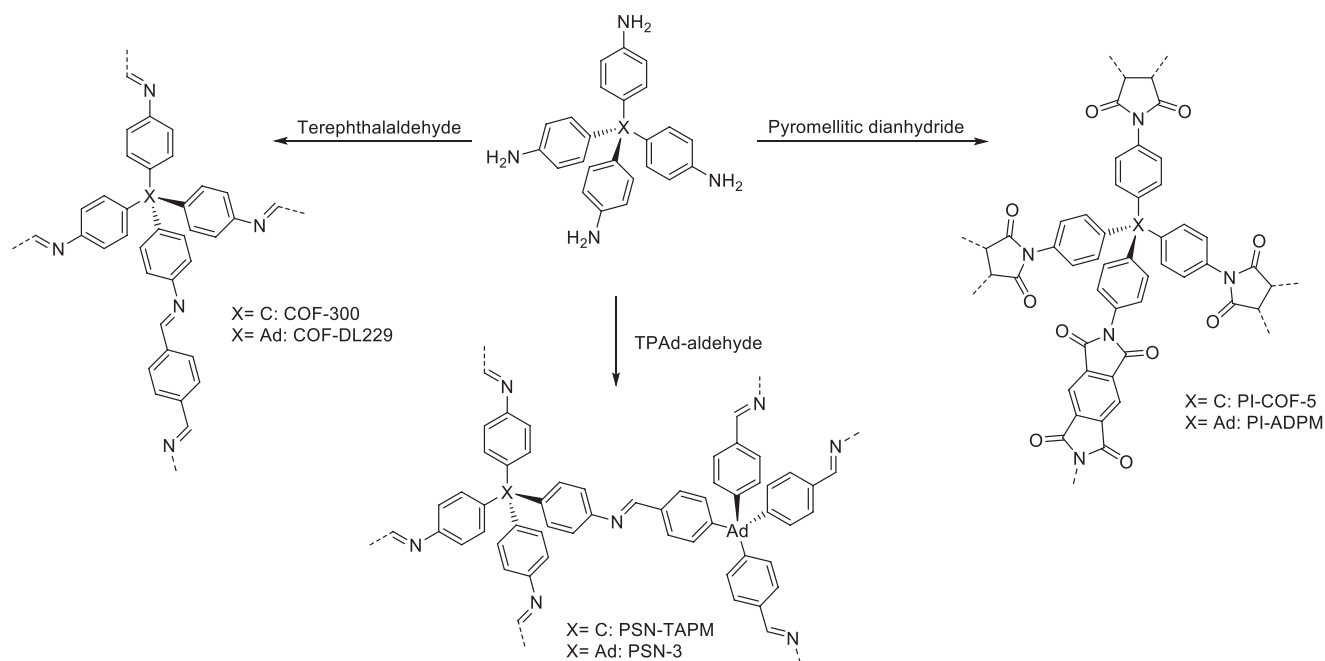
Scheme 14. Overview of framework-forming reactions of tetrakis(4-phenylboronic acid)methane, giving boroxine and boronate COFs.

different central atoms. Self-condensation of TPGe-boronic acid and co-condensation with HHTP gave the boroxine- and boronate-COFs PAF-14 and PAF-15, respectively. Although, surface areas are comparably low (1228 and 747 m^2 g^{-1}), aromatic nitro-compounds such as TNT cause a high fluorescence quenching, allowing to use them as sensors for explosives, making them highly interesting.^[154] Functionalization of such COFs include adding a monofunctional boronic acid during synthesis, truncating the framework and introducing a side group like Brucks et al. demonstrated 2013 with COF-102-tolyl doping the framework with metallocenes or nanoparticles for future applications such as catalysis or enhanced gas uptake.^[155]

Besides the condensation of boronic acids, Schiff base chemistry can be considered another synthetic approach to form porous organic frameworks. The amine-derivatives of TPM and TPA_d have been reacted with various aldehydes, sometimes even leading to crystalline frameworks as it is the case with terephthalaldehyde for COF-300 (1360 m^2 g^{-1}) and COF-DL229 (1762 m^2 g^{-1}) (Scheme 15). COF-DL229 with the adamantane core structure again seems to outperform the methane core regarding surface area, moreover it can be utilized for the effective capture of iodine, being a highly toxic fission product, with an exceptional capacity of 4.7 g g^{-1} .^[156] Reaction of TPM-amine with pyromellitic dianhydride leads to highly crystalline and thermally stable (>450 $^{\circ}\text{C}$) PI-COF-5 with a surface area of 1876 m^2 g^{-1} . According to the authors, it was the first COF to be investigated for controlled drug release, showing high drug load and a good control over the drug release.^[157] In 2013, Wang and co-workers reacted TPA_d-amine with pyromellitic dianhydride to the polyimide network PI-ADPM with a CO_2 -uptake higher than COF-5 or COF-103 and a capability of

adsorbing large amounts of organic vapors, while drug delivery has not been investigated for this framework.^[158] One year later, the same group published purely tetrahedral systems of TPA_d-aldehyde and TPM-amine (PSN-TAPM) or TPA_d-amine (PSN-3). Both are micro/mesoporous, amorphous frameworks, with high thermal stability and comparable surface areas of 763 and 865 m^2 g^{-1} , respectively. Despite the otherwise similar properties, PSN-3 and PSN-TAPM hugely differ regarding their CO_2 - and organic vapor uptake, with PSN-3 competing with the slightly better values of PI-ADPM. Thus, both seem to be promising candidates for CO_2 capture and removal of organic vapors.^[159]

We would like to add that molecular systems do not have to be limited to the abovementioned examples of building blocks. There would be diverse other structures that might share similar structural and functional features. Exploring nonconventional building blocks, from materials application perspectives, will surely lead to new inventions and advancing multifunctional efficient materials. For instance, π -stacked conjugated molecular building blocks, such as [2.2]paracyclophane (PCP), derivatives are fascinating planar chiral scaffolds that have been incorporated into π -stacked conjugated polymeric systems for chiroptical and optoelectronic properties, energy materials, and functional parylene coatings that find broad applications in novel bio- and materials science.^[160] However, unlike other arenes, PCPs have been very rarely investigated in the construction and fabrication of coordination self-assembly. In a similar way, hexakis-substituted C_{60} adducts are unique spherical scaffolds for the construction of multifunctional nanomaterials (Scheme 16).^[161] Hexakis-functionalized macrocyclic methanofullerenes can undergo metal-mediated reactions, such as click reactions,



Scheme 15. Overview of COF-forming condensation reactions based on tetrakis(4-aminophenyl)methane.

Heck, Sonogashira, and Suzuki–Miyaura cross-coupling, yield organic building blocks for higher molecular architectures. It can be anticipated that capitalizing in unconventional ambitious molecular building blocks will stimulate further research and will be scientifically rewarding in countless ways.

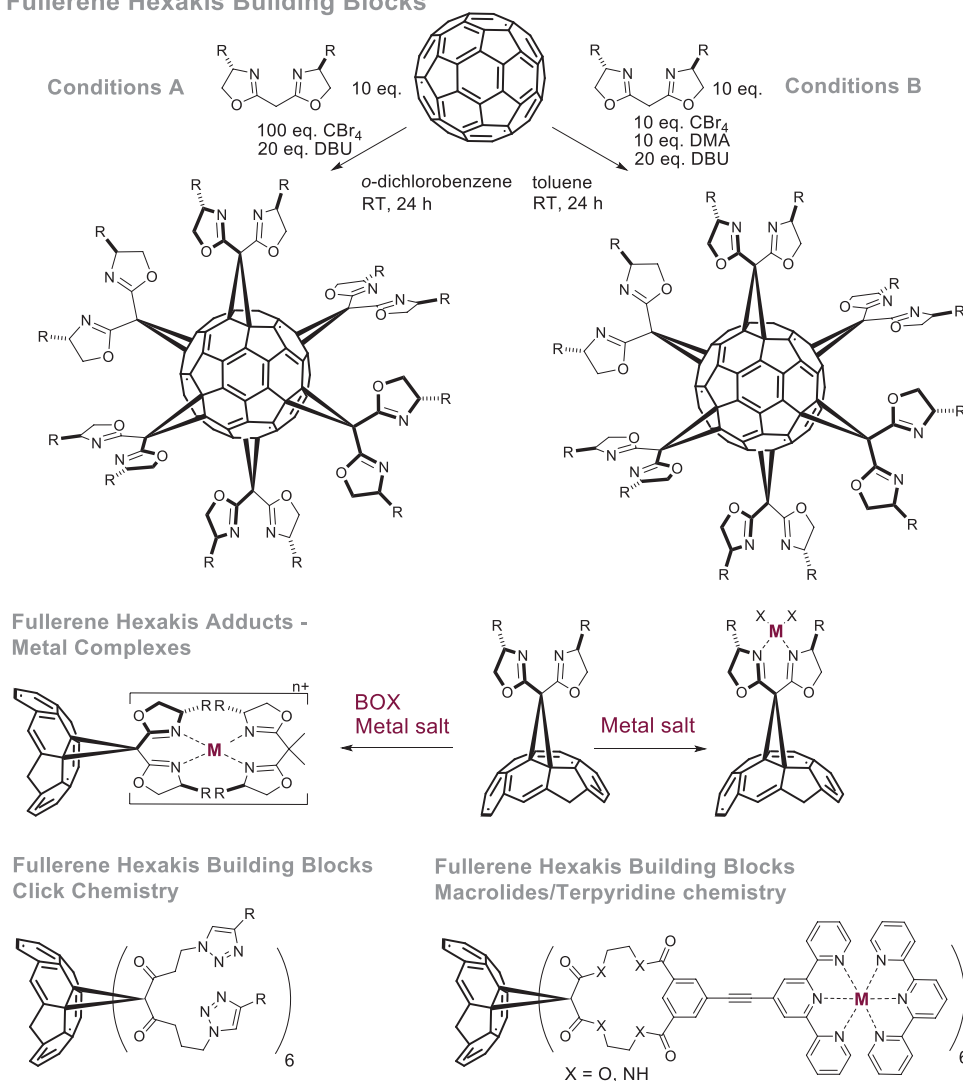
5. Conclusion and Future Perspectives

The interest in material modulation at nanoscale via synthetic design of molecular building blocks is progressing tremendously. Synthetic chemists mastered the art of modular synthesis and offer a diverse library of all conceivable molecules by combining several small molecular fragments together within a single molecular unit that could be utilized as building blocks for the construction/fabrication of wide range of function-inspired materials. Employing milder, broader, and efficient synthetic methods combined with versatile metal-mediated reactions, for instance, Suzuki–Miyaura, Stille–Migita, Hiyama, Kumada–Corriu, Negishi reaction for carbon–carbon bond formation or Mizoroki–Heck protocol to couple alkenes or Sonogashira–Hagihara to couple terminal alkynes, is practical and highly reliable tools that have revolutionized large-scale synthesis and can build molecular blocks of almost any design.

By adding characteristic features into arene/hetarene derivatives and their extended related systems such as metal-coordination capabilities, chirality, responsiveness, structural flexibility, and possibilities of post-synthetic transformation, provide useful molecular blocks for constructing various molecular structures, such as coordination-driven MOFs, surface-mounted frameworks, metal–organic cages/rings (MOCs). On the other hand, moving away from a metal-coordination strategy, organic molecular components can be assembled via covalent linkages into extended porous polymeric networks rather than using chemically labile

metal–organic bonds. Adding different functional groups to molecular building blocks, such as azides, alkynes, thiols, alkoxy, and nitriles components, can covalently interconnect the molecular tectons into crosslinked covalent networks via a wide range of synthetic reaction, including azide–alkyne click, photo-induced thiol–ene reaction, and dynamic covalent linkages to tailor the molecular assemblies with defined functions. Adding formyls, amino, nitriles, and boron components into building blocks can be exploited to form various covalent linkages such as C–N (imide), C=N (imine), and B–O (boronate ester) covalent bonds suitable for the construction of stable various 2D to 3D covalent assemblies. Molecular building blocks with distinct features, for instance, chirality, switchability, flexibility, and responsiveness to external stimuli, can also inherent such innate features once assembled into materials. We would like to emphasize on few points: 1) Synthesizing small molecules and studying their physical/chemical properties is a diverse area in itself, but assembling small molecules into practically useful functional material systems and devices is even more challenging task and beyond the limits of a single discipline. Hence, ensuing holistic approaches of interdisciplinary research by combining insights from organic/inorganic synthesis and materials chemistry aided by computational theory and simulations would be rewarding in countless ways to open up new horizons for fundamental and practical explorations. 2) The pioneering research in coordination-driven assemblies has been of fundamental understanding, predominantly mechanistic in nature. However, over the time, this has evolved from synthetic curiosity to emerging applications in materials. Along with the synthetic progress itself, theoretical simulations and prediction of optimized structures/functions have also shown inspiring progress.^[162] Implementation of multiscale theoretical simulations and advanced modeling approaches will assist to understand and select the best/optimal-performing materials. 3) In addition to many potential applications of

Fullerene Hexakis Building Blocks



Scheme 16. Representative T_h symmetrical C₆₀ at hexakis analogues employed in coordination/covalent assemblies, click, and macrolides chemistry.

coordination-driven structures and covalent porous polymers, the designer materials, such as vast library of MOFs having atomically defined pores/channels and isolation of metallic catalytic sites, shall be returned back to organic synthesis laboratories that could be exploited as heterogeneous catalysts for challenging organic reaction. Being insoluble crystalline materials, their easy recyclability, reusability, and complete recovery from the reaction products could contribute to sustainable research efforts.^[163]

4) Designing more ambitious molecular building blocks intended for multi-tasking and combining several distinct functions within a single molecular unit, for instance, dynamic interlocked building blocks,^[164] conjugated macromolecular moieties,^[165] functional capsules,^[166] π -stacked molecular components,^[167] molecular knots,^[168] buckyball- and buckybowl-based motifs for coordinative or non-coordinative incorporation into complex functional systems, will surely lead to new inventions and advancing multifunctional efficient materials.^[169]

One of our ongoing research focus, under 3DMM2O—Cluster of Excellence at Karlsruhe Institute of Technology, is to develop

molecular building blocks and their assembly into macroscopic objects that could be utilized as versatile resists or inks for 3D printing and fabrication at various length-scale exploiting light as a tool.^[170] We are looking forward to the exciting new applications that will be uncovered in the near future by sharing mutual experiences and capitalizing in interdisciplinary research efforts. A famous saying “Wer hohe Türme bauen will, muss lange am Fundament verweilen” which can be translated to “Who wants to build high towers, has to work on the foundation for a long time” relates to achieving ambitious goals of technological impact.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

functional materials, modular building blocks, molecular engineering, porous architectures, self-assembly

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- [1] a) Themed special issue on Metal–Organic Frameworks, see: H. C. Zhou, S. Kitagawa, *Chem. Soc. Rev.* **2014**, *43*, 5415. (In follow-up to the prominent themed special issue on The Pervasive Chemistry of Metal–Organic Frameworks, J. R. Long, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1213); b) Themed collection on Coordination Chemistry in the Solid State, see R. E. Morris, *Dalton Trans.* **2012**, *41*, 3867.
- [2] Special issue on Introduction to Metal–Organic Frameworks, see: H. C. Zhou, J. R. Long, O. M. Yaghi, *Chem. Rev.* **2012**, *112*, 673.
- [3] a) Themed special issue on Metal–Organic Frameworks and Porous Polymers—Current and Future Challenges, G. Maurin, C. Serre, A. Cooper, G. Férey, *Chem. Soc. Rev.* **2017**, *46*, 3104, and references therein; b) A. G. Slater, A. I. Cooper, *Science* **2015**, *348*, aaa8075, and references therein; c) H. Furukawa, K. E. Cordova, M. O’Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444; d) O. Shekhah, H. Wang, M. Paradinas, C. Ocal, B. Schüpbach, A. Terfort, D. Zacher, R. A. Fischer, C. Wöll, *Nat. Mater.* **2009**, *8*, 481.
- [4] a) S. Yuan, J. C. Qin, C. T. Lollar, H. C. Zhou, *ACS Cent. Sci.* **2018**, *4*, 440; b) M. J. Kalmutzki, N. Hanikel, O. M. Yaghi, *Sci. Adv.* **2018**, *4*, eaat9180.
- [5] a) W. Lu, Z. Wei, Z. Y. Gu, T. F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle, M. Boscha, H. C. Zhou, *Chem. Soc. Rev.* **2014**, *43*, 5561, and references therein; b) D. Zhao, D. T. Timmons, D. Yuan, H. C. Zhou, *Acc. Chem. Res.* **2011**, *44*, 123; c) Y. Bai, Y. Dou, L. H. Xie, W. Rutledge, J. R. Li, H. C. Zhou, *Chem. Soc. Rev.* **2016**, *45*, 2327; d) J. Hu, M. Zeller, A. D. Hunter, Z. Xu, *CrystEngComm* **2015**, *17*, 9254.
- [6] a) L. J. Chen, H. B. Yang, M. Shionoya, *Chem. Soc. Rev.* **2017**, *46*, 2555; b) F. A. A. Paz, J. Klinowski, S. M. F. Vilela, J. P. C. Tome, J. A. S. Cavaleiro, J. Rocha, *Chem. Soc. Rev.* **2012**, *41*, 1088; c) Z. J. Lin, J. Lu, M. Hong, R. Cao, *Chem. Soc. Rev.* **2014**, *43*, 5867.
- [7] a) Z. Wang, S. Cohen, *Chem. Soc. Rev.* **2009**, *38*, 1315, and references therein; b) S. Cohen, *Chem. Rev.* **2012**, *112*, 970; c) P. Deria, J. E. Mondloch, O. Karagiari, W. Bury, J. T. Hupp, O. K. Farha, *Chem. Soc. Rev.* **2014**, *43*, 5896, and references therein.
- [8] A. Suzuki, *Angew. Chem., Int. Ed.* **2011**, *50*, 6723.
- [9] C. C. Johansson Seechurn, M. O. Kitching, T. J. Colacot, V. Snieckus, *Angew. Chem., Int. Ed.* **2012**, *51*, 5062.
- [10] Y. Nakao, T. Hiyama, *Chem. Soc. Rev.* **2011**, *40*, 4893.
- [11] F. Chemla, F. Ferreira, A. P. Luna, L. Micouin, O. Jackowski, in *Metal-Catalyzed Cross-Coupling Reactions and More* (Eds: A. de Meijere, S. Bräse, M. Oestreich), Wiley-VCH, Weinheim, Germany **2014**.
- [12] E. Negishi, *Angew. Chem., Int. Ed.* **2011**, *50*, 6738.
- [13] J. L. Bras, J. Muzart, *Chem. Rev.* **2011**, *111*, 1170.
- [14] R. Chinchilla, C. Najera, *Chem. Rev.* **2014**, *114*, 1783.
- [15] a) J. F. Hartwig, *Nature* **2008**, *455*, 314; b) P. R. Castillo, S. L. Buchwald, *Chem. Rev.* **2016**, *116*, 12564; c) J. F. Hartwig, in *Handbook of Organopalladium Chemistry for Organic Synthesis* (Ed: A. de Meijere), John Wiley & Sons, Hoboken, NJ **2003**.
- [16] a) Y. Sun, C. Chen, P. J. Stang, *Acc. Chem. Res.* **2019**, *52*, 802, and references therein; b) S. Das, P. Heasman, T. Ben, S. Qiu, *Chem. Rev.* **2017**, *117*, 1515, and references therein.
- [17] S. Pullen, G. H. Clever, *Acc. Chem. Res.* **2018**, *51*, 3052.
- [18] Special issue on Supramolecular Chemistry in Confined Space and Organized Assemblies, see: V. Yam, M. Fujita, D. Toste, *Acc. Chem. Res.* **2018**, *51*, 9080.
- [19] O. M. Yaghi, M. J. Kalmutzki, C. S. Diercks, *Introduction to Reticular Chemistry: Metal–Organic Frameworks and Covalent Organic Frameworks*, Wiley-VCH, Weinheim, Germany **2019**.
- [20] H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gandara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O’Kee, O. Terasaki, J. F. Stoddart, O. M. Yaghi, *Science* **2012**, *336*, 1018.
- [21] a) H. Deng, C. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang, O. M. Yaghi, *Science* **2010**, *327*, 846; b) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Kee, O. M. Yaghi, *Science* **2002**, *295*, 469.
- [22] a) M. Han, D. M. Engelhard, G. H. Clever, *Chem. Soc. Rev.* **2014**, *43*, 1848; b) Y. He, B. Li, M. O’Keeffe, B. Chen, *Chem. Soc. Rev.* **2014**, *43*, 6141; c) V. Guillermin, D. Kim, J. F. Eubank, R. Luebke, X. Liu, K. Adil, M. S. Lah, M. Eddaoudi, *Chem. Soc. Rev.* **2014**, *43*, 6141.
- [23] a) S. Grosjean, Z. Hassan, C. Wöll, S. Bräse, *Eur. J. Org. Chem.* **2019**, *2019*, 1446; b) S. Grunder, J. F. Stoddart, *Chem. Commun.* **2012**, *48*, 3158; c) S. Grunder, C. Valente, A. C. Whalley, S. Sampath, J. Portmann, Y. Botros, J. F. Stoddart, *Chem. - Eur. J.* **2012**, *18*, 15632.
- [24] J. Liu, B. Lukose, O. Shekhah, H. K. Arslan, P. Weidler, H. Gliemann, S. Bräse, S. Grosjean, A. Godt, X. Feng, K. Müllen, I. B. Magdau, T. Heine, C. Wöll, *Sci. Rep.* **2012**, *2*, 921.
- [25] L. Heinke, H. Gliemann, P. Tremouilhac, C. Wöll, in *The Chemistry of Metal–Organic Frameworks: Synthesis, Characterization, and Applications* (Ed: S. Kaskel), Wiley-VCH, Weinheim, Germany **2016**, pp. 523–550.
- [26] a) J. Liu, C. Wöll, *Chem. Soc. Rev.* **2017**, *46*, 5730, and references therein; b) O. Shekhah, J. Liu, R. A. Fischer, C. Wöll, *Chem. Soc. Rev.* **2011**, *40*, 1081; c) D. Zacher, O. Shekhah, C. Wöll, R. A. Fischer, *Chem. Soc. Rev.* **2009**, *38*, 1418, and references therein.
- [27] a) J. Cui, M. P. Koevenden, M. Müllner, K. Kempe, F. Caruso, *Adv. Colloid Interface Sci.* **2014**, *207*, 14; b) A. L. Becker, A. P. R. Johnston, F. Caruso, *Small* **2010**, *6*, 1836; c) J. J. Green, J. H. Elisseeff, *Nature* **2016**, *540*, 386.
- [28] Themed special issue on Click Chemistry: Function Follows Form, see: M. G. Finn, V. V. Fokin, *Chem. Soc. Rev.* **2010**, *39*, 1231.
- [29] a) J. E. Hein, V. V. Fokin, *Chem. Soc. Rev.* **2010**, *39*, 1302; b) H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem., Int. Ed.* **2001**, *40*, 2004.
- [30] C. H. Hoyle, A. B. Lowe, C. N. Bowman, *Chem. Soc. Rev.* **2010**, *39*, 1355.
- [31] Y. Goto, H. Sato, S. Shinkai, K. Sada, *J. Am. Chem. Soc.* **2008**, *130*, 14354.
- [32] T. Kitao, Y. Zhang, S. Kitagawa, B. Wang, T. Uemura, *Chem. Soc. Rev.* **2017**, *46*, 3108, and references therein.

- [33] T. Ishiwata, Y. Furukawa, K. Sugikawa, K. Kokado, K. Sada, *J. Am. Chem. Soc.* **2013**, *135*, 5427.
- [34] a) K. Kokado, *Polym. J.* **2017**, *49*, 345; b) K. C. Bentz, S. M. Cohen, *Angew. Chem., Int. Ed.* **2018**, *57*, 14992; c) Y. Oaki, K. Sato, *J. Mater. Chem. A*, **2018**, *6*, 23197.
- [35] M. Tsotsalas, J. Liu, B. Tettmann, S. Grosjean, A. Shahnas, Z. Wang, C. Azucena, M. Addicoat, T. Heine, J. Lahann, J. Overhage, S. Bräse, H. Gliemann, C. Wöll, *J. Am. Chem. Soc.* **2014**, *136*, 8.
- [36] S. Begum, Z. Hassan, S. Bräse, C. Wöll, M. Tsotsalas, *Acc. Chem. Res.* **2019**, *52*, 1598, and references therein.
- [37] S. Schmitt, J. Hümmner, S. Kraus, A. Welle, S. Grosjean, M. H. Roos, A. Rosenhahn, S. Bräse, C. Wöll, C. L. Thedieck, M. Tsotsalas, *Adv. Funct. Mater.* **2016**, *26*, 8455.
- [38] E. Silvestre, M. Franzreb, P. G. Weidler, O. Shekhah, C. Wöll, *Adv. Funct. Mater.* **2013**, *23*, 1210.
- [39] S. Schmitt, M. Silvestre, M. Tsotsalas, A. L. Winkler, A. Shahnas, S. Grosjean, F. Laye, H. Gliemann, J. Lahann, S. Bräse, M. Franzreb, C. Wöll, *ACS Nano*. **2015**, *9*, 4219.
- [40] W. Zhou, S. Begum, Z. Wang, P. Krolla, D. Wagner, S. Bräse, C. Wöll, M. Tsotsalas, *ACS Appl. Mater. Interfaces* **2018**, *10*, 1528.
- [41] a) K. Hüll, J. Morstein, D. Trauner, *Chem. Rev.* **2018**, *118*, 10710; b) I. Tochitsky, M. A. Kienzler, E. Isacoff, R. H. Kramer, *Chem. Rev.* **2018**, *118*, 10748; c) M. V. Westphal, M. A. Schafroth, R. C. Sarott, M. A. Imhof, C. P. Bold, P. Leippe, A. Dhopeswarkar, J. M. Grandner, V. Katritch, K. Mackie, D. Trauner, E. M. Carreira, J. A. Frank, *J. Am. Chem. Soc.* **2017**, *139*, 18206; d) J. Broichhagen, J. A. Frank, D. Trauner, *Acc. Chem. Res.* **2015**, *48*, 1947; e) J. Zhang, J. Wang, H. Tian, *Mater. Horiz.* **2014**, *1*, 169.
- [42] a) L. Dong, Y. Feng, L. Wang, W. Feng, *Chem. Soc. Rev.* **2018**, *47*, 7339; b) A. Fihey, A. Perrier, W. R. Browne, D. Jacquemin, *Chem. Soc. Rev.* **2015**, *44*, 3719; c) R. Pardo, M. Zayata, D. Levy, *Chem. Soc. Rev.* **2011**, *40*, 672.
- [43] a) M. Kathan, S. Hecht, *Chem. Soc. Rev.* **2017**, *46*, 5536; b) D. Bléger, *Macromol. Chem. Phys.* **2016**, *217*, 189; c) J. Zhang, H. Tian, *Adv. Opt. Mater.* **2018**, *6*, 1701278; d) H. M. D. Bandara, S. C. Burdette, *Chem. Soc. Rev.* **2012**, *41*, 1809.
- [44] a) H. M. D. Bandara, S. C. Burdette, *Chem. Soc. Rev.* **2012**, *41*, 1809; b) E. Merino, *Chem. Soc. Rev.* **2011**, *40*, 3835, and references therein; c) R. Siewertsen, H. Neumann, B. B. Stehn, R. Herges, C. Näther, F. Renth, F. Temps, *J. Am. Chem. Soc.* **2009**, *131*, 15594; d) M. S. Maier, K. Hüll, M. Reynders, B. S. Matsuura, P. Leippe, T. Ko, L. Schäffer, D. Trauner, *J. Am. Chem. Soc.* **2019**, *141*, 17295.
- [45] M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.* **2014**, *114*, 12174.
- [46] a) L. Kortekaas, W. R. Browne, *Chem. Soc. Rev.* **2019**, *48*, 3406; b) R. Klajn, *Chem. Soc. Rev.* **2014**, *43*, 148, and references therein.
- [47] a) For details see the Special Issue: Synthetic Macromolecular Machines, D. Blegler, R. Klajn, *Macromol. Rapid Commun.* **2018**, *39*, 1700827; b) D. Trauner, *Beilstein J. Org. Chem.* **2012**, *8*, 870.
- [48] a) E. R. Draper, D. J. Adams, *Chem. Commun.* **2016**, *52*, 8196; b) T. Ube, T. Ikeda, *Angew. Chem., Int. Ed.* **2014**, *53*, 10290.
- [49] Y. Wang, Q. Li, *Adv. Mater.* **2012**, *24*, 1926.
- [50] a) S. Castellanos, F. Kapteijn, J. Gascon, *CrystEngComm* **2016**, *18*, 4006; b) R. D. Mukhopadhyay, V. K. Praveen, A. Ajayaghosh, *Mater. Horiz.* **2014**, *1*, 572; c) C. Jones, A. J. Tansell, T. L. Eason, *J. Mater. Chem. A* **2016**, *4*, 6714.
- [51] T. Muraoka, K. Kinbara, T. Aida, *Nature* **2006**, *440*, 512.
- [52] a) C. Wöll, L. Heinke, *Adv. Mater.* **2019**, *31*, 1806324, and references therein; b) A. B. Kanj, K. Müller, L. Heinke, *Macromol. Rapid Commun.* **2018**, *39*, 1700239; c) H. A. Schwartz, U. Ruschewitz, L. Heinke, *Photochem. Photobiol. Sci.* **2018**, *17*, 864.
- [53] a) J. W. Brown, B. L. Henderson, M. D. Kiesz, A. C. Whalley, W. Morris, S. Grunder, H. Deng, H. Furukawa, J. I. Zink, J. F. Stoddart, O. M. Yaghi, *Chem. Sci.* **2013**, *4*, 2858; b) J. Park, L. B. Sun, Y. P. Chen, Z. Perry, H. C. Zhou, *Angew. Chem., Int. Ed.* **2014**, *53*, 5842; c) J. Park, D. Yuan, K. T. Pham, J. Li, A. Yakovenko, H. C. Zhou, *J. Am. Chem. Soc.* **2012**, *134*, 99; d) A. Modrow, D. Zargarani, R. Herges, N. Stock, *Dalton Trans.* **2011**, *40*, 4217.
- [54] a) E. A. Dolgoplova, A. M. Rice, C. R. Martin, N. B. Shustova, *Chem. Soc. Rev.* **2018**, *47*, 4710; b) F. X. Coudert, *Chem. Mater.* **2015**, *27*, 1905; c) R. D. Mukhopadhyay, V. K. Praveen, A. Ajayaghosh, *Mater. Horiz.* **2014**, *1*, 572.
- [55] S. Grosjean, P. Hodapp, Z. Hassan, C. Wöll, S. Bräse, *Chemistry-Open* **2019**, *8*, 743.
- [56] C. Mills, *J. Chem. Soc., Trans.* **1895**, *67*, 925.
- [57] D. Mutruc, A. G. Hanssens, S. Fairman, S. Wahl, A. Zimathies, C. Knie, S. Hecht, *Angew. Chem., Int. Ed.* **2019**, *58*, 12862.
- [58] a) Z. Wang, A. Knebel, S. Grosjean, D. Wagner, S. Bräse, C. Wöll, J. Caro, L. Heinke, *Nat. Commun.* **2016**, *7*, 13872; b) J. Caro, A. Knebel, L. Heinke, S. Grosjean, C. Wöll, Z. Wang, S. Bräse, *Patent No. Ger. 16192873-4-1370*, **2016**.
- [59] L. Heinke, M. Cakici, M. Dommaschk, S. Grosjean, R. Herges, S. Bräse, C. Wöll, *ACS Nano* **2014**, *2*, 1473.
- [60] Z. Wang, L. Heinke, J. Jelic, M. Cakici, M. Dommaschk, R. J. Maurer, H. Oberhofer, S. Grosjean, R. Herges, S. Bräse, K. Reuter, C. Wöll, *Phys. Chem. Chem. Phys.* **2015**, *17*, 14582.
- [61] X. Yu, Z. Wang, M. Buchholtz, N. Füllgrabe, S. Grosjean, F. Bebensee, S. Bräse, C. Wöll, L. Heinke, *Phys. Chem. Chem. Phys.* **2015**, *17*, 22721.
- [62] a) Z. Wang, S. Grosjean, S. Bräse, L. Heinke, *ChemPhysChem* **2015**, *16*, 3779; b) K. Müller, A. Knebel, F. Zhao, D. Blager, J. Caro, L. Heinke, *Chem. - Eur. J.* **2017**, *23*, 5434; c) H. A. Schwartz, U. Ruschewitz, L. Heinke, *Photochem. Photobiol. Sci.* **2018**, *17*, 864; d) Z. Wang, K. Müller, M. Valásek, S. Grosjean, S. Bräse, C. Wöll, M. Mayor, L. Heinke, *J. Phys. Chem. C* **2018**, *122*, 19044.
- [63] B. J. Furlong, M. J. Katz, *J. Am. Chem. Soc.* **2017**, *139*, 13280.
- [64] a) E. A. Dolgoplova, V. A. Galitskiy, C. R. Martin, H. N. Gregory, B. J. Yarbrough, A. M. Rice, A. A. Berseneva, O. A. Ejegbavwo, K. S. Stephenson, P. Kittikhunnatham, S. G. Karakalos, M. D. Smith, A. B. Greytak, S. Garashchuk, N. B. Shustova, *J. Am. Chem. Soc.* **2019**, *141*, 5350; b) D. E. Williams, C. R. Martin, E. A. Dolgoplova, A. Swifton, D. C. Godfrey, O. A. Ejegbavwo, P. J. Pellechia, M. D. Smith, N. B. Shustova, *J. Am. Chem. Soc.* **2018**, *140*, 7611.
- [65] Special issue on Expanded, Contracted, and Isomeric Porphyrins, see: J. L. Sessler, Z. Gross, H. Furuta, *Chem. Rev.* **2017**, *117*, 2201.
- [66] S. L. H. Rebelo, M. Linhares, M. M. Q. Simões, A. M. S. Silva, M. G. P. M. S. Neves, J. A. S. Cavaleiro, C. Freire, *J. Catal.* **2014**, *315*, 33.
- [67] a) M. Ethirajan, Y. Chen, P. Joshi, R. K. Pandey, *Chem. Soc. Rev.* **2011**, *40*, 340; b) A. E. O'Connor, W. M. Gallagher, A. T. Byrne, *Photochem. Photobiol.* **2009**, *85*, 1053.
- [68] a) Y. Xie, J. P. Hill, R. Charvet, K. Ariga, *J. Nanosci. Nanotechnol.* **2007**, *7*, 2969; b) C. D. Natale, D. Monti, R. Paolesse, *Mater. Today* **2010**, *13*, 46.
- [69] D. Kim, A. Osuka, *J. Phys. Chem. A* **2003**, *107*, 8791.
- [70] a) C. P. Hsieh, H. P. Lu, C. L. Chiu, C. W. Lee, S. H. Chuang, C. L. Mai, W. N. Yen, S. J. Hsu, E. W. G. Diau, C. Y. Yeh, *J. Mater. Chem.* **2010**, *20*, 1127; b) S. Mathew, A. Yella, P. Gao, R. H. Baker, F. E. C. Basile, N. A. Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, M. Grätzel, *Nat. Chem.* **2014**, *6*, 242.
- [71] C. C. Guo, T. G. Ren, J. X. Song, Q. Liu, K. Luo, W. Y. Lin, G. F. Jiang, *J. Porphyr. Phthaloc.* **2005**, *9*, 830.
- [72] a) S. Hiroto, Y. Miyake, H. Shinokubo, *Chem. Rev.* **2017**, *117*, 2910, and references therein; b) V. Diév, C. W. Schlenker, K. Hanson, Q. Zhong, J. D. Zimmerman, S. R. Forrest, M. E. Thompson, *J. Org. Chem.* **2012**, *77*, 143.
- [73] M. Kielmann, M. O. Senge, *Angew. Chem., Int. Ed.* **2019**, *58*, 418.

- [74] a) T. Tanaka, A. Osuka, *Chem. Soc. Rev.* **2015**, *44*, 943; b) W. S. Li, T. Aida, *Chem. Rev.* **2009**, *109*, 6047.
- [75] a) P. S. Bols, H. L. Anderson, *Acc. Chem. Res.* **2018**, *51*, 2083, and references therein; b) M. D. Peeks, T. D. W. Claridge, H. L. Anderson, *Nature* **2017**, *541*, 200; c) A. Summerfiledm, M. Baldone, D. V. Kondratuk, H. L. Anderson, S. Whitelam, J. P. Garrahan, E. Besley, P. H. Beton, *Nat. Commun.* **2019**, *10*, 2932; d) R. Haver, L. Tejerina, H. W. Jiang, M. Rickhaus, M. Jirasek, I. Grübner, H. J. Eggimann, L. M. Herz, H. L. Anderson, *J. Am. Chem. Soc.* **2019**, *141*, 7965; e) S. Richert, J. Cremers, I. Kuprov, M. D. Peeks, H. L. Anderson, C. R. Timmel, *Nat. Commun.* **2017**, *8*, 14842; f) M. Rickhaus, A. V. Jentszsch, L. Tejerina, I. Grübner, M. Jirasek, T. D. W. Claridge, H. L. Anderson, *J. Am. Chem. Soc.* **2017**, *139*, 16502; g) M. C. O'sullivan, J. K. Sprafke, D. V. Kondratuk, C. R. Infray, T. D. W. Claridge, A. Saywell, M. O. Blunt, J. N. O'shea, P. H. Beton, M. Malfois, H. L. Anderson, *Nature* **2011**, *469*, 72.
- [76] S. Durot, J. Taesch, V. Heitz, *Chem. Rev.* **2014**, *114*, 8542.
- [77] a) S. Huh, S. J. Kim, Y. Kim, *CrystEngComm* **2016**, *18*, 345; b) W. Y. Gao, M. Chrzanowski, S. Ma, *Chem. Soc. Rev.* **2014**, *43*, 5841; c) B. J. Burnett, W. Choe, *CrystEngComm* **2012**, *14*, 3839; d) C. Zou, C. D. Wu, *Dalton Trans.* **2012**, *41*, 3879; e) L. D. DeVries, W. Choe, *J. Chem. Crystallogr.* **2009**, *39*, 229.
- [78] R. Haldar, K. Batra, S. M. Marschner, A. B. Kuc, S. Zahn, R. A. Fischer, S. Bräse, T. Heine, C. Wöll, *Chem. Eur. J.* **2019**, *25*, 7847.
- [79] J. Liu, W. Zhou, J. Liu, I. Howard, G. Kilbardam, S. Schlabach, D. Coupry, M. Addicoat, S. Yoneda, Y. Tsutui, T. Sakurai, S. Seki, Z. Wang, P. Lindemann, E. Redel, T. Heine, C. Wöll, *Angew. Chem., Int. Ed.* **2015**, *54*, 7441.
- [80] X. Liu, M. Kozłowska, T. Okkali, D. Wagner, T. Higashino, G. B. Weis, S. Marschner, Z. Fu, Q. Zhang, H. Imahori, S. Bräse, W. Wenzel, C. Wöll, L. Heinke, *Angew. Chem., Int. Ed.* **2019**, *58*, 9590.
- [81] Y. Y. Wang, S. M. Chen, R. Haldar, C. Wöll, Z. G. Gu, J. Zhang, *Adv. Mater. Interfaces* **2018**, *5*, 1800985.
- [82] M. Adams, M. Kozłowska, N. Baroni, M. Oldenburg, R. Ma, D. Busko, A. Turshatov, G. Emandi, M. O. Senge, R. Haldar, C. Wöll, G. U. Nienhaus, B. S. Richards, I. A. Howard, *ACS Appl. Mater. Interfaces* **2019**, *11*, 15688.
- [83] J. Liu, W. Zhou, J. Liu, Y. Fujimori, T. Higashino, H. Imahori, X. Jiang, J. Zhao, T. Sakurai, Y. Hattori, W. Matsuda, S. Seki, S. K. Garlapati, S. Dasgupta, E. Redel, L. Sunag, C. Wöll, *J. Mater. Chem. A* **2016**, *4*, 12739.
- [84] a) J. W. Colson, A. R. Woll, A. Mukherjee, M. P. Levendorf, E. L. Spittle, V. B. Shields, M. G. Spencer, J. Parkand, W. R. Dichtel, *Science* **2011**, *332*, 228; b) P. J. Waller, F. Gandara, O. M. Yaghi, *Acc. Chem. Res.* **2015**, *48*, 3053; c) J. Jiang, Y. Zhao, O. M. Yaghi, *J. Am. Chem. Soc.* **2016**, *138*, 3255; d) R. P. Bisbey, W. R. Dichtel, *ACS Cent. Sci.* **2017**, *3*, 533; e) N. Huang, P. Wang, D. Jiang, *Nat. Rev. Mater.* **2016**, *1*, 16068; f) S. Y. Ding, W. Wang, *Chem. Soc. Rev.* **2013**, *42*, 548.
- [85] J. R. Hunt, C. J. Doonan, J. D. LeVangie, A. P. Côté, O. M. Yaghi, *J. Am. Chem. Soc.* **2008**, *130*, 11872.
- [86] C. R. DeBlase, K. E. Silberstein, T. T. Truong, H. D. Abruña, W. R. Dichtel, *J. Am. Chem. Soc.* **2013**, *135*, 16821.
- [87] F. J. Uribe-Romo, C. J. Doonan, H. Furukawa, K. Oisaki, O. M. Yaghi, *J. Am. Chem. Soc.* **2011**, *133*, 11478.
- [88] a) P. Kuhn, M. Antonietti, A. Thomas, *Angew. Chem., Int. Ed.* **2008**, *47*, 3450; b) J. Guo, Y. Xu, S. Jin, L. Chen, T. Kaji, Y. Honsho, M. A. Addicoat, J. Kim, A. Saeki, H. Ihee, S. Seki, S. Irlé, S. Hiromoto, J. Gao, G. Jiag, *Nat. Commun.* **2013**, *4*, 2736.
- [89] K. T. Jackson, T. E. Reich, H. M. El-Kaderi, *Chem. Commun.* **2012**, *48*, 8823.
- [90] a) H. Wang, Z. Zeng, P. Xu, L. Li, G. Zeng, R. Xiao, Z. Tang, D. Huang, L. Tang, C. Lai, D. Jiang, Y. Liu, H. Yi, L. Qin, S. Ye, X. Ren, W. Tang, *Chem. Soc. Rev.* **2019**, *48*, 488; b) M. S. Lohse, T. Bein, *Adv. Funct. Mater.* **2018**, *28*, 1705553, and references therein; c) R. P. Bisbey, W. R. Dichtel, *ACS Cent. Sci.* **2017**, *3*, 533, and references therein.
- [91] a) S. J. Lyle, O. J. Waller, O. M. Yaghi, *Trends Chem.* **2019**, *1*, 172; b) S. Kandameth, K. Dey, R. Banerjee, *J. Am. Chem. Soc.* **2019**, *141*, 1807, and references therein.
- [92] S. Wuttke, D. D. Medina, J. M. Rotter, S. Begum, T. Stassin, R. Ameloot, M. Oschatz, M. Tsotsalas, *Adv. Funct. Mater.* **2018**, *28*, 1801545, and references therein.
- [93] K. A. Hansen, J. P. Blinco, *Polym. Chem.* **2018**, *9*, 1479, and references therein.
- [94] a) G. Audran, P. Brémond, S. R. A. Marque, *Chem. Commun.* **2014**, *50*, 7921; b) L. Tebben, A. Studer, *Angew. Chem., Int. Ed.* **2011**, *50*, 5034.
- [95] a) Y. Amamoto, J. Kamada, H. Otsuka, A. Takahara, K. Matyjaszewski, *Angew. Chem., Int. Ed.* **2011**, *50*, 1660; b) O. R. Cromwell, J. Chung, Z. Guan, *J. Am. Chem. Soc.* **2015**, *137*, 6492; c) C. J. Kloxin, T. F. Scott, B. J. Adzima, C. N. Bowman, *Macromolecules* **2010**, *43*, 2643; d) C. J. Kloxin, C. N. Bowman, *Chem. Soc. Rev.* **2013**, *42*, 7161.
- [96] a) W. Zou, J. Dong, Y. Luo, Q. Zhao, T. Xie, *Adv. Mater.* **2017**, *29*, 1606100; b) A. Grinthal, J. Aizenberg, *Chem. Soc. Rev.* **2013**, *42*, 7072; c) J. M. Lehn, *Angew. Chem., Int. Ed.* **2015**, *54*, 3276.
- [97] I. Wessely, V. Mugnaini, A. Bihlmeier, G. Jeschke, S. Bräse, M. Tsotsalas, *RSC Adv.* **2016**, *6*, 55715.
- [98] M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.* **2005**, *38*, 369.
- [99] a) R. L. Li, N. C. Flanders, A. M. Evans, W. Ji, I. Castano, L. X. Chen, N. C. Gianneschi, W. R. Dichtel, *Chem. Sci.* **2019**, *10*, 3796; b) M. Matsumoto, R. R. Dasari, W. Ji, C. H. Feriante, T. C. Parker, S. R. Marder, W. R. Dichtel, *J. Am. Chem. Soc.* **2017**, *139*, 4999.
- [100] Q. An, I. D. Wessely, Y. Matt, Z. Hassan, S. Bräse, M. Tsotsalas, *Polym. Chem.* **2019**, *10*, 672.
- [101] C. Weder, *Angew. Chem., Int. Ed.* **2008**, *47*, 448.
- [102] T. Muller, S. Bräse, *RSC Adv.* **2014**, *4*, 6886, and references therein.
- [103] H. Nasralla, J. C. Hierso, *Chem. Mater.* **2019**, *31*, 619.
- [104] a) S. Shankar, R. Balgley, M. Lahav, S. R. Cohen, R. P. Biro, M. E. van der Boom, *J. Am. Chem. Soc.* **2015**, *137*, 226; b) G. de-Ruiter, M. Lahav, M. E. van der Boom, *Acc. Chem. Res.* **2014**, *47*, 3407, and references therein.
- [105] R. Kaminker, R. P. Biro, M. E. van der Boom, *Angew. Chem., Int. Ed.* **2011**, *50*, 3224.
- [106] M. C. Di-Gregorio, P. Ranjan, L. Houben, L. J. W. Shimon, K. Rechav, M. Lahav, M. E. van der Boom, *J. Am. Chem. Soc.* **2018**, *140*, 9132.
- [107] T. Ma, E. A. Kapustin, S. X. Yin, L. Liang, Z. Zhou, J. Niu, L. H. Li, Y. Wang, J. Su, J. Li, X. Wang, W. D. Wang, W. Wang, J. Sun, O. M. Yaghi, *Science* **2018**, *361*, 48.
- [108] H. Bildirir, V. G. Gregoriou, A. Avgeropoulos, U. Scherf, C. L. Chochos, *Mater. Horiz.* **2017**, *4*, 546.
- [109] H. Bildirir, V. G. Gregoriou, A. Avgeropoulos, U. Scherf, C. L. Chochos, *Mater. Horiz.* **2017**, *4*, 546.
- [110] J. Germain, J. M. J. Fréchet, F. Svec, *Small* **2009**, *5*, 1098.
- [111] a) D. Su, F. M. Menger, *Tetrahedron Lett.* **1997**, *38*, 1485; b) T. Zimmermann, T. J. J. Müller, *Synthesis*, **2002**, 1157; c) I. Aujard, J. P. Baltaze, J. B. Baudin, *J. Am. Chem. Soc.* **2001**, *123*, 8177.
- [112] a) H. Newman, *Synthesis*, **1972**, 1972, 692; b) V. R. Reichert, L. J. Mathias, A. V. G. Muir, *Chem. Mater.* **1993**, *5*, 4; c) E. B. Merkushev, N. D. Simakhina, G. M. Koveshnikova, *Synthesis* **1980**, 1980, 486.
- [113] a) F. A. Neugebauer, H. Fischer, R. Bernhardt, *Chem. Ber.* **1976**, *109*, 2389; b) Q. Wei, A. Lazzeri, F. D. Cuia, M. Scalari, E. Galoppini, *Macromol. Chem. Phys.* **2004**, *205*, 2089; c) C. Shen, Z. Wang, *J. Phys. Chem. C* **2014**, *118*, 17585.

- [114] a) A. S. Cannon, T. Jian, J. Wang, J. C. Warner, *Org. Prep. Proced. Int.* **2004**, 36, 353; b) B. Blankschein, A. Schulz, A. Villinger, R. Wustrack, *ChemPlusChem* **2014**, 79, 973.
- [115] a) N. C. Duncan, B. P. Hay, E. W. Hagaman, R. Custelcean, *Tetrahedron* **2012**, 68, 53; b) M. Veith, A. Rammo, C. Kirsch, L. Khemteourian, D. Agustin, *J. Organomet. Chem.* **2004**, 689, 1546.
- [116] a) O. Plietzsch, C. I. Schilling, M. Nieger, T. Muller, S. Bräse, *Tetrahedron: Asymmetry* **2010**, 21, 1474; b) T. J. Zimmermann, O. Freundel, R. Gompfer, T. J. Müller, *Eur. J. Org. Chem.* **2000**, 2000, 3305; c) T. Islamoglu, M. G. Rabbani, H. M. El-Kaderi, *J. Mater. Chem. A* **2013**, 1, 10259.
- [117] a) C. I. Schilling, O. Plietzsch, M. Nieger, T. Muller, S. Bräse, *Eur. J. Org. Chem.* **2011**, 2011, 1743; b) B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1990**, 112, 1546.
- [118] a) Y. Yang, B. Beele, J. Blümel, *J. Am. Chem. Soc.* **2008**, 130, 3771; b) J. H. Fournier, X. Wang, J. D. Wuest, *Can. J. Chem.* **2003**, 81, 376; c) C. Pariya, Y. S. Marcos, Y. Zhang, F. R. Fronczek, A. W. Maverick, *Organometallics* **2008**, 27, 4318.
- [119] C. I. Schilling, S. Bräse, *Org. Biomol. Chem.* **2007**, 5, 3586.
- [120] a) O. Plietzsch, C. I. Schilling, M. Tolev, M. Nieger, C. Richert, T. Muller, S. Bräse, *Org. Biomol. Chem.* **2009**, 7, 4734; b) O. Altintas, T. Muller, O. Plietzsch, E. Lejeune, S. Bräse, C. B. Kowollik, *Macromol. Rapid Commun.* **2012**, 33, 977.
- [121] a) J. C. Furgal, R. M. Laine, *Bull. Chem. Soc. Jpn.* **2016**, 89, 705; b) J. K. Zareba, *Inorg. Chem. Commun.* **2017**, 86, 172.
- [122] L. Monnereau, M. Nieger, T. Muller, S. Bräse, *Adv. Funct. Mater.* **2014**, 24, 1054.
- [123] a) L. M. Wilson, A. C. Griffin, *J. Mater. Chem.* **1993**, 3, 991; b) J. H. Fournier, T. Maris, J. D. Wuest, W. Guo, E. Galoppini, *J. Am. Chem. Soc.* **2003**, 125, 1002; c) Y. Yuan, H. Ren, F. Sun, X. Jing, K. Cai, X. Zhao, Y. Wang, Y. Wei, G. Zhu, *J. Phys. Chem. C* **2012**, 116, 26431.
- [124] a) O. Plietzsch, A. Schade, A. Hafner, J. Huuskonen, K. Rissanen, M. Nieger, T. Muller, S. Bräse, *Eur. J. Org. Chem.* **2013**, 2013, 283; b) K. Peschko, A. Schade, S. B. L. Vollrath, U. Schwarz, B. Luy, C. Muhle-Goll, P. Weis, S. Bräse, *Chem. - Eur. J.* **2014**, 20, 16273.
- [125] a) R. A. Benkeser, R. B. Gosnell, W. Schroeder, *J. Am. Chem. Soc.* **1957**, 79, 2339; b) R. A. Benkeser, W. Schroeder, *J. Am. Chem. Soc.* **1958**, 80, 3314.
- [126] a) A. Singh, M. Tolev, M. Meng, K. Klenin, O. Plietzsch, C. I. Schilling, T. Muller, M. Nieger, S. Bräse, W. Wenzel, C. Richert, *Angew. Chem., Int. Ed.* **2011**, 50, 3227; b) A. Singh, M. Tolev, C. Schilling, S. Bräse, H. Griesser, C. Richert, *J. Org. Chem.* **2012**, 77, 2718; c) H. Griesser, M. Tolev, A. Singh, T. Sabirov, C. Gerlach, C. Richert, *J. Org. Chem.* **2012**, 77, 2703; d) M. Meng, C. Ahlborn, M. Bauer, O. Plietzsch, S. A. Soomro, A. Singh, T. Muller, W. Wenzel, S. Bräse, C. Richert, *ChemBioChem* **2009**, 10, 1335.
- [127] a) P. A. S. Smith, *Open Chain Nitrogen Compounds*, Benjamin, New York **1966**, p. 211; b) J. H. Boyer, R. Moriarty, B. de Darwent, P. A. S. Smith, *Chem. Eng. News* **1964**, 42, 6.
- [128] T. Muller, S. Bräse, *Angew. Chem., Int. Ed.* **2011**, 50, 11844, and references therein.
- [129] J. R. Holst, E. Stöckel, D. J. Adams, A. I. Cooper, *Macromolecules* **2010**, 43, 8531;
- [130] P. Pandey, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, M. G. Kanatzidis, J. T. Hupp, S. T. Nguyen, *J. Mater. Chem.* **2011**, 21, 1700.
- [131] O. Plietzsch, C. I. Schilling, T. Grab, S. L. Grage, A. S. Ulrich, A. Comotti, P. Sozzani, T. Muller, S. Bräse, *New J. Chem.* **2011**, 35, 1577.
- [132] P. Lindemann, M. Tsotsalas, S. Shishatskiy, V. Abetz, P. Krolla, C. Azucena, L. Monnereau, A. Beyer, A. Gölzhäuser, V. Mugnaini, H. Gliemann, S. Bräse, C. Wöll, *Chem. Mater.* **2014**, 26, 7189.
- [133] P. Lindemann, A. Schade, L. Monnereau, W. Feng, H. Gliemann, P. Levkin, S. Bräse, C. Wöll, M. Tsotsalas, *J. Mater. Chem. A* **2016**, 4, 6815.
- [134] N. A. Ahmad, C. P. Leo, A. L. Ahmad, W. K. W. Ramli, *Sep. Purif. Rev.* **2015**, 44, 109.
- [135] Q. An, Y. Hassan, X. Yan, P. Krolla-Sidenstein, T. Mohammed, M. Lang, S. Bräse, M. Tsotsalas, *Beilstein J. Org. Chem.* **2017**, 13, 558.
- [136] A. Schade, L. Monnereau, T. Muller, S. Bräse, *ChemPlusChem* **2014**, 79, 1176.
- [137] L. Monnereau, T. Muller, M. Lang, S. Bräse, *Chem. Commun.* **2016**, 52, 571.
- [138] T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu, G. Zhu, *Angew. Chem., Int. Ed.* **2009**, 48, 9457.
- [139] R. L. Martin, M. N. Shahrak, J. A. Swisher, C. M. Simon, J. P. Sculley, S. C. Zhou, B. Smit, M. Haranczyk, *J. Phys. Chem. C* **2013**, 117, 20037.
- [140] C. Pei, T. Ben, S. Qiu, *Mater. Horiz.* **2015**, 2, 11.
- [141] a) J. R. Holst, E. Stöckel, D. J. Adams, A. I. Cooper, *Macromolecules* **2010**, 43, 8531; b) W. Lu, D. Yuan, J. Sculley, D. Zhao, R. Krishna, H. C. Zhou, *J. Am. Chem. Soc.* **2011**, 133, 8126.
- [142] a) W. Lu, D. Yuan, D. Zhao, C. I. Schilling, O. Plietzsch, T. Muller, S. Bräse, J. Guenther, J. Bluemel, R. Krishna, Z. Li, H.-C. Zhou, *Chem. Mater.* **2010**, 22, 5964; b) D. Yuan, W. Lu, D. Zhao, H. C. Zhou, *Adv. Mater.* **2011**, 23, 3723.
- [143] T. Ben, C. Pei, D. Zhang, J. Xu, F. Deng, X. Jing, S. Qiu, *Energy Environ. Sci.* **2011**, 4, 3991.
- [144] a) J. Lan, D. Cao, W. Wang, T. Ben, G. Zhu, *J. Phys. Chem. Lett.* **2010**, 1, 978; b) Z. Yang, X. Peng, D. Cao, *J. Phys. Chem. C* **2013**, 117, 8353.
- [145] S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, *Angew. Chem., Int. Ed.* **2002**, 41, 898.
- [146] a) E. Trovatti, T. M. Lacerda, A. J. F. Carvalho, A. Gandini, *Adv. Mater.* **2015**, 27, 2242; b) L. M. Polgar, M. van Duin, A. A. Broekhuis, F. Picchioni, *Macromolecules* **2015**, 48, 7096.
- [147] A. Rekondo, R. Martin, A. Ruiz de Luzuriaga, G. Cabañero, H. J. Grande, I. Odriozola, *Mater. Horiz.* **2014**, 1, 237.
- [148] L. Monnereau, C. Grandclaoudon, T. Muller, S. Bräse, *RSC Adv.* **2015**, 5, 23152.
- [149] M. Lang, A. Schade, S. Bräse, *Beilstein J. Org. Chem.* **2016**, 12, 2570.
- [150] A. P. Côté, A. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O. M. Yaghi, *Science* **2005**, 310, 1166.
- [151] a) H. M. El-Kaderi, J. R. Hunt, J. L. M. Cortés, A. P. Côté, R. E. Taylor, M. O'Keeffe, O. M. Yaghi, *Science* **2007**, 316, 268; b) J. L. M. Cortes, S. S. Han, H. Furukawa, O. M. Yaghi, W. A. Goddard, *J. Phys. Chem. A* **2010**, 114, 10824.
- [152] C. S. Diercks, O. M. Yaghi, *Science* **2017**, 355, eaal1585, and references therein.
- [153] L. A. Baldwin, J. W. Crowe, D. A. Pyles, P. L. McGrier, *J. Am. Chem. Soc.* **2016**, 138, 15134.
- [154] a) Y. Yuan, H. Ren, F. Sun, X. Jian, K. Cai, X. Zhao, Y. Wang, Y. Wei, G. Zhu, *J. Phys. Chem. C* **2012**, 116, 26431; b) Y. Yuan, H. Ren, F. Sun, X. Jing, K. Cai, X. Zhao, Y. Wei, G. Zhu, *J. Mater. Chem.* **2012**, 22, 24558.
- [155] a) S. D. Brucks, D. N. Bunck, W. R. Dichtel, *Polymer* **2014**, 55, 330; b) S. B. Kalidindi, K. Yusenko, R. A. Fischer, *Chem. Commun.* **2011**, 47, 8506; c) S. B. Kalidindi, H. Oh, M. Hirscher, D. Esken, C. Wiktor, S. Turner, G. V. Tendeloo, R. A. Fischer, *Chem. - Eur. J.* **2012**, 18, 10848.
- [156] a) C. Wang, Y. Wang, R. Ge, X. Song, X. Xing, Q. Jiang, H. Lu, C. Hao, X. Guo, Y. Gao, D. Jiang, *Chem. - Eur. J.* **2018**, 24, 585; b) F. J. U. Romo, J. R. Hunt, H. Furukawa, C. Klock, M. O. Keefe, O. M. Yaghi, *J. Am. Chem. Soc.* **2009**, 131, 4570.
- [157] Q. Fand, J. Wang, S. Gu, R. B. Kaspar, Z. Zhuang, J. Zheng, H. Guo, S. Qiu, Y. Yan, *J. Am. Chem. Soc.* **2015**, 137, 8352.

- [158] C. Shen, Y. Bao, Z. Wang, *Chem. Commun.* **2013**, 49, 3321.
- [159] a) G. Li, B. Zhang, J. Yan, Z. Wang, *J. Mater. Chem. A* **2014**, 2, 18881; b) G. Li, B. Zhang, Z. Wang, *Macromol. Rapid Commun.* **2014**, 35, 971.
- [160] a) Z. Hassan, E. Spuling, D. M. Knoll, J. Lahann, S. Bräse, *Chem. Soc. Rev.* **2018**, 47, 6947; b) Z. Hassan, E. Spuling, D. M. Knoll, S. Bräse, *Angew. Chem., Int. Ed.* **2019**, unpublished.
- [161] a) W. Yan, S. M. Seifermann, P. Pierrat, S. Bräse, *Org. Biomol. Chem.* **2015**, 13, 25, and references therein; b) W. Yan, C. Rethore, S. Menning, G. B. Weiß, T. Muller, P. Pierrat, S. Bräse, *Chem. - Eur. J.* **2016**, 22, 11522; c) A. J. Inglis, P. Pierrat, T. Muller, S. Bräse, C. B. Kowollik, *Soft Matter* **2010**, 6, 82; d) P. Pierrat, S. Vanderheiden, T. Muller, S. Bräse, *Chem. Commun.* **2009**, 45, 1748; e) S. M. Seifermann, C. Rethore, T. Muller, S. Bräse, *Sci. Rep.* **2013**, 3, 2817; f) A. Giovannitti, S. M. Seifermann, A. Bihlmeier, T. Muller, F. Tpoic, K. Rissanen, M. Nieger, W. Klopper, S. Bräse, *Eur. J. Org. Chem.* **2013**, 2013, 7907; g) P. Pierrat, C. Rethore, T. Muller, S. Bräse, *Synlett* **2008**, 11, 1706.
- [162] Y. Luo, M. Ahmed, A. Schug, M. Tsotsalas, *Adv. Mater.* **2019**, 31, 1901744.
- [163] a) T. Drake, P. Ji, W. Lin, *Acc. Chem. Res.* **2018**, 51, 2129, and references therein; b) D. Yang, B. C. Gates, *ACS Catal.* **2019**, 9, 1779.
- [164] a) P. M. Bulit, A. J. Stick, S. J. Loeb, *Trends Chem.* **2019**, 1, 588; b) J. E. M. Lewis, P. D. Beer, S. L. Loeb, S. M. Goldup, *Chem. Soc. Rev.* **2017**, 46, 2577; c) V. N. Vukotic, S. J. Loeb, *Chem. Soc. Rev.* **2012**, 41, 5896, and references therein.
- [165] A. L. Kanibolotsky, N. Laurand, M. D. Dawson, G. A. Turnbull, I. D. W. Samuel, P. J. Skabara, *Acc. Chem. Res.* **2019**, 52, 1665, and references therein.
- [166] D. Zhang, T. K. Ronson, J. R. Nitschke, *Acc. Chem. Res.* **2018**, 51, 2423.
- [167] a) N. Y. Li, D. Liu, Z. G. Ren, C. Lollar, J. P. Lang, H. C. Zhou, *Inorg. Chem.* **2018**, 57, 849; b) G. S. Papaefstathiou, T. Friscic, L. R. MacGillivray, *J. Am. Chem. Soc.* **2005**, 127, 14160; c) M. Cakici, Z. G. Gu, M. Nieger, J. Burck, L. Heinke, S. Bräse, *Chem. Commun.* **2015**, 51, 4796.
- [168] a) S. D. P. Fielden, D. A. Leigh, S. L. Woltering, *Angew. Chem., Int. Ed.* **2017**, 56, 11166, and references therein; b) J. J. Danon, A. Krüger, D. A. Leigh, J. F. Lemonnier, A. J. Stephens, I. J. Vitorica-Yrezabal, S. L. Woltering, *Science*, **2017**, 355, 159.
- [169] a) A. M. Rice, E. A. Dogoplova, N. B. Shustova, *Chem. Mater.* **2017**, 29, 7054, and references therein; b) A. L. Balch, K. Winkler, *Chem. Rev.* **2016**, 116, 3812, and references therein.
- [170] M. Drost, F. Tu, L. Berger, C. Preischl, W. Zhou, H. Gliemann, C. Wöll, H. Marbach, *ACS Nano* **2018**, 12, 3825.