CHAPTER 6

Hydrogen Bonding Donor–Acceptor Carbon Nanostructures

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6.1 Introduction

The success of Nature to convert inexpensive, nonpolluting and inexhaustible sunlight into energy has stimulated the investigation on the natural photo-synthesis in order to emulate it. The photosynthetic process starts with the absorption of light by plants and bacteria and continues with cascades of energy- (ET) and electron- (eT) transfer events. This complex process results in the conversion of CO_2 and H_2O into glucose and energy (ATP).[1] Energy- and electron-transfer processes are also key events in molecular-scale optoelectronics (for instance in plastic solar cells), photonics, sensors and some other emerging areas of nanoscience and nanotechnology.[2]

A remarkable feature is that in Nature, all these events are produced in a rigid matrix and, hence, in a well-ordered media of supramolecular ensembles. Whereas a precise control on the structure as well as on the function of the materials created from molecular components can be efficiently achieved by using the vast tools of covalent chemistry, to reach a similar control with supramolecular principles involves a higher degree of complexity. To face this challenge, *Mother Nature* provides excellent and plentiful examples of nano-metric multifunctional materials in which size, shape and function are regulated

by noncovalent interactions.[3] The noncovalent forces used to create multi-molecular arrays comprise ion–ion, ion–dipole, dipole–dipole, π–π stacking and, finally, hydrogen bonds. Using these weak interactions, whose binding energies range from a few kJ mol^{-1} to several hundred of kJ mol^{-1}, supramolecular growth is driven by thermodynamic forces or is the result of kinetic processes.[4]

The binding energies of hydrogen-bonding interactions, which can reach up to 120 kJ mol^{-1}, have prompted their use as a versatile supramolecular methodology. It has been demonstrated that H-bonding specificity and directionality governs the 3D structures in novel chemical and biological systems.[5] Nonetheless, and due to the characteristic weakness of a single H bond, to create stable architectures an array of multiple H bonds or the combination of H bonds with additional supramolecular interactions, such as hydrophobic or electrostatic forces, is necessary (Figures 6.1a and b).[6] Whereas association constant (K_a) values of ~ 10 M^{-1} are achieved in the simplest DH•A arrays, built upon one H donor (DH) and one H acceptor (A) site, K_a values as large as 10^2–10^3 M^{-1} are determined for triple H-bonding motifs (see Figure 6.1c).[7] Remarkably, Meijer *et al.* have demonstrated that the concurrence of H bonds together with four attractive secondary interactions in 2-ureido-4-pyrimidinones (UP) shed extraordinary high K_a values, higher than 10^7 M^{-1} (see Figure 6.1d).[8]

A major goal in the field of *supramolecular chemistry* is the search for new artificial photosynthetic models, in which biomimetic principles can be used for their implementation in molecular electronic devices. Thus, such biomimetic models should fulfill the following requisites: i) the presence of an electron donor (D) connected to an electron acceptor (A); ii) the ability of one of the components to absorb visible light, thus acting as an antenna, and iii) an organisational principle that controls their electronic interactions (and therefore the rates and yields of eT).[1] The structural and electronic features of fullerenes and carbon nanotubes (*i.e.* their extended and delocalised π-electron system and their good electron-acceptor properties) offer new possibilities in the quest for biomimetical model systems as well as in the construction of photoactive devices.[9]
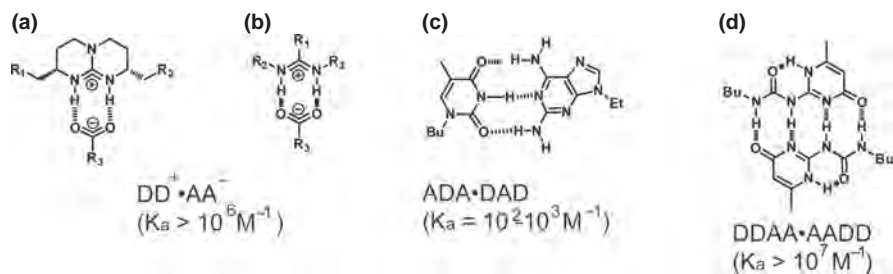

(a)

DD$^+$•AA$^-$
($K_a > 10^6$ M^{-1})

(b)

(c)

ADA•DAD
($K_a = 10^2$–10^3 M^{-1})

(d)

DDAA•AADD
($K_a > 10^7$ M^{-1})

Figure 6.1 K_a values for different H-bonding motifs (measured in toluene/DMSO (99/1) for (a) and (b) and in CHCl$_3$ for (c) and (d)).

Despite the importance of noncovalent motifs, and in particular H-bonding in the design of supramolecular architectures, their application to nanoscale carbon-based materials, such as fullerenes and carbon nanotubes, has been largely neglected. Only recently the combination of such family of compounds and noncovalent motifs started to develop into an interdisciplinary field.[10] In particular, we and others became interested in applying such weak inter-molecular forces as a mean to modulate fullerene-based architectures and to control their function.[11]

The aim of the present chapter is three-fold: i) showing that electronic com-munication in C_{60}-based donor–acceptor ensembles – connected through hydro-gen bonds – is at least as efficient as that found in covalently connected systems, ii) sketching that hydrogen-bonding fullerene chemistry is a versatile concept to construct supramolecular polymers with exciting and singular features, and, iii) highlighting the remarkable contribution of H-bond interactions in noncovalently bonded carbon-nanotube-based donor–acceptor supramolecular architectures.

6.2   Hydrogen-Bonded $C_{60}\bullet$Donor ($C_{60}\bullet$D) Ensembles

It is well established that a thermodynamically driven charge separation (CS) process is generated by light irradiation in electron-donor–electron-acceptor ensembles.[12] In C_{60}-based derivatives, such charge-separated radical-ion pairs generated upon irradiation show lifetimes ranging from picoseconds to sec-onds. Most of these donor–acceptor compositions are based on covalent lin-kages between donor and acceptor units. However, much less is known about H-bonded model systems,[13] and only recently, examples of H-bonded orga-nofullerene diads have been reported. Such noncovalent $C_{60}\bullet$D conjugates will be summarised next attending to their electron-donor moiety nature.

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6.2.1   H-Bonding Interfaced Metallomacrocycles$\bullet C_{60}$ Diads

To the best of our knowledge, the first H-bonded interfaced $C_{60}\bullet$D diad (1) was reported in 2002 by Guldi, Torres, Prato *et al.*,[14] using a zinc phtalocyanine as electron-donor moiety (Figure 6.2). In this pseudorotaxane-like complex, the corresponding radical-ion pair species (*i.e.* $C_{60}{}^{\bullet-}\bullet$ZnPc$^+$) evolve as a product of an efficient intracomplex electron-transfer starting from the excited state of the ZnPc fragment. Interestingly, the reported lifetime was in the range of micro-seconds. This value is three orders of magnitude higher than that reported for the related covalently bonded C_{60}–ZnP diads.[15]

The similarity of porphyrins (P) with natural electron-donor centres has made this kind of electroactive chromophore the main choice for the pre-paration of a wide variety of covalent C_{60}–P diads.[16] However, in recent years, several H-bonded $C_{60}\bullet$P diads have been extensively investigated as an alter-native to the covalent models. For example, Takata, Ito *et al.* reported on a rotaxane-like $C_{60}\bullet$ZnP supramolecular diad (2a) (Figure 6.3).[17] Laser irradia-tion on such a composition induced a charge-separation process that
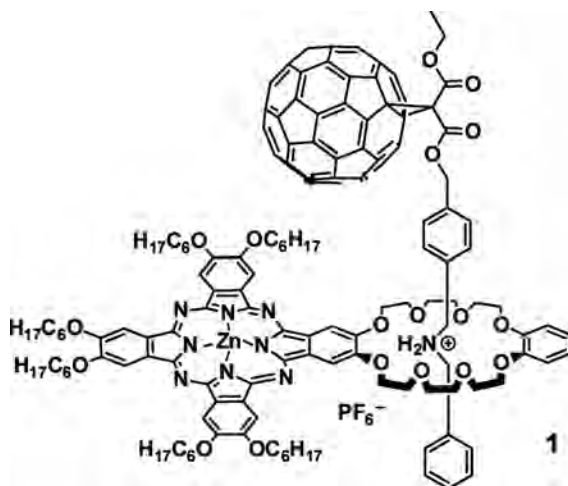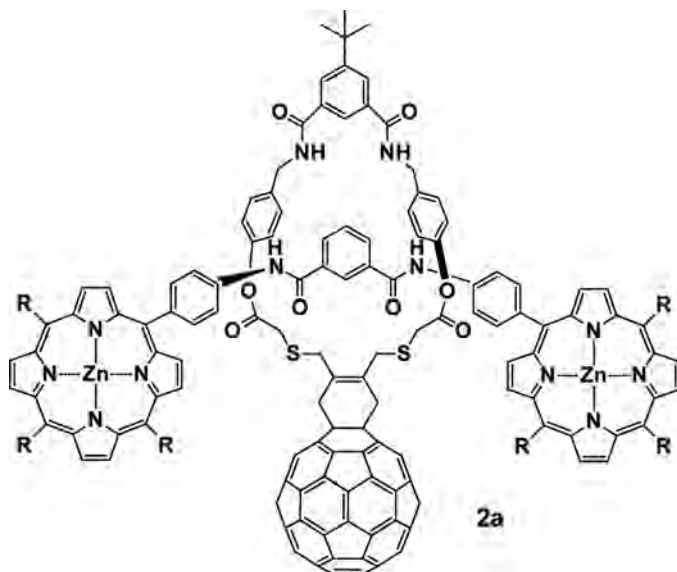
Figure 6.2   H-bonded C_{60}•ZnPc diad **1**.

Figure 6.3   Rotaxane-like C_{60}•ZnP supramolecular diad **2a**.

commences with the initial photoexcitation of the ZnP moieties and that yields the C_{60} $^{\cdot -}$•ZnP^{+} radical-ion pair whose lifetime (180 ns) is comparable to those reported for some other covalently linked C_{60}–P diads ($\tau_{CS} = 770$ ns).[18]

The same authors have also reported on the synthesis and photophysical study of a series of C_{60}-based rotaxanes (**2b** and **c**) in which the length of the axle has been systematically modified (Figure 6.4).[19] A photoinduced

electron-transfer process takes place after laser irradiation thus generating the corresponding radical-ion pair. Interestingly, the rate constants and the quantum yields of the radical-ion pairs decrease with the length of the axle. However, they are not sensitive to solvent polarity. In addition, the lifetime of the charge-separated (CS) state increases from 250 ns for **2b** to 650 ns for **2c**. The axle length also conditions the excited state from which the radical-ion pair is formed. Thus, for **2a** this CS state is formed *via* the singlet excited state of the P moiety, whereas in the case of **2c** the CS state is formed through the triplet state. All these phenomena clearly point to a through-space eT mechanism in such ensembles.
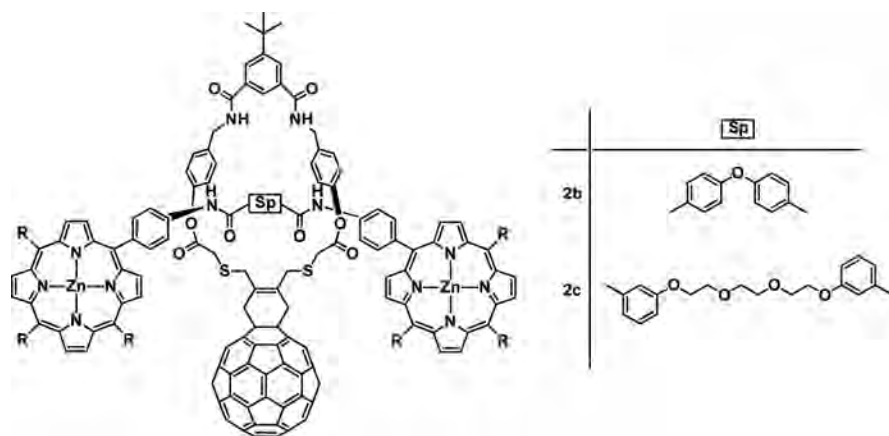

Figure 6.4   Structures of rotaxane-like $C_{60} \bullet ZnP$ supramolecular diads **2b** and **c**.

Following the end-capping methodology, Takata *et al.* have reported the synthesis of rotaxane ensembles **3** in which the [60]fullerene cage makes up the axle of the supramolecular structure.[20] In [2]rotaxane **3**, the acceleration of the end-capping process, which enhances its overall efficiency, has been ascribed to an attractive interaction between the two chromophores, *i.e.* C_{60} and ZnP (Figure 6.5).

Other hydrogen-bonding motifs have yielded remarkably stable supramolecular hybrids. For example, the two-point amidinium-carboxylate binding motif proved to form stable aggregates ($K_a = 10^5$, *i.e.* 10^7 M^{-1}) due to the synergy of hydrogen bonds and electrostatic interactions.[21] In addition, the potential of the Hamilton-receptor/cyanuric acid has been established in a series of porphyrin (free base, Zn, Sn)•fullerene systems, where a fine tuning of the strength of the complexation and control of the electronic coupling was observed.[22]

The so-called "two-point" binding strategy is a very successful methodology to assemble fullerenes and porphyrins. First used by D'Souza, Ito and coworkers, this methodology involves axial coordination of the Zn atom from the P and H-bonding interactions.[23] Following this strategy, highly stable
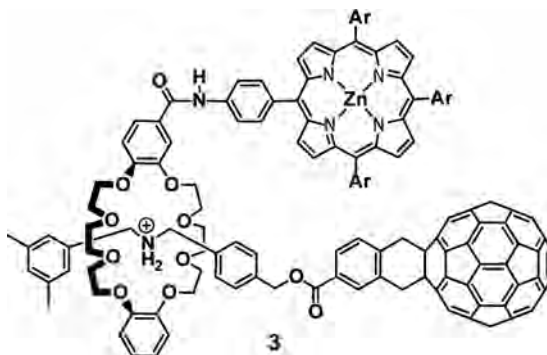
Figure 6.5   End-capped $C_{60} \bullet ZnP$ rotaxane diad **3**.

supramolecular $C_{60} \bullet ZnP$ complexes (**4**) (Figure 6.6), led to the creation of well-defined distanced and oriented noncovalent ensembles.[24] Time-resolved emission and nanosecond transient absorption studies have revealed efficient charge-separation processes, with rates of 6.3×10^7 and 3.1×10^9 s^{-1} in **4a** and **4b**, respectively.
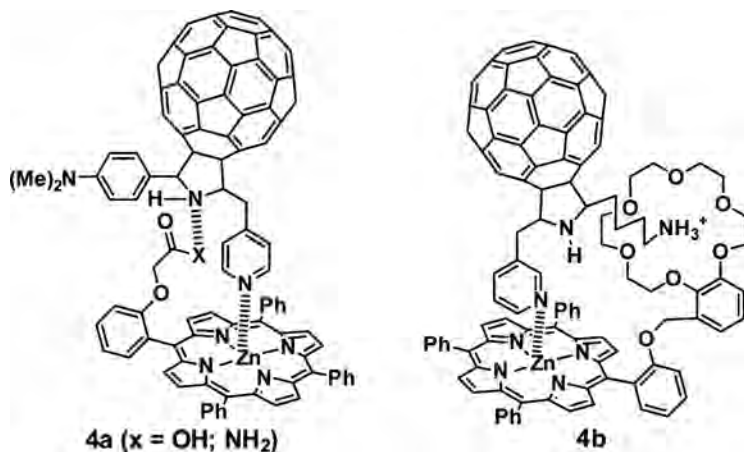

Figure 6.6   "Two-point" assembled $C_{60} \bullet ZnP$ compositions.

The effect of different noncovalent forces (axial ligation or π–π interactions) on the photophysical properties of "two-point" bound supramolecular $C_{60} \bullet ZnP$ compositions, have recently been reported by the same authors.[23,25] The different fullerene hosts (**5a,b**) and porphyrin guests (**6a–c**) are depicted in Figure 6.7. In all these "two-point" ensembles, and regardless of the type of noncovalent bonds, an electron-transfer process induced by light is observed. These eT events give rise to radical pairs with lifetimes ranging from 50, *i.e.* 500 ns depending upon the host and the guest. In the case of P-crown ether **6a**,
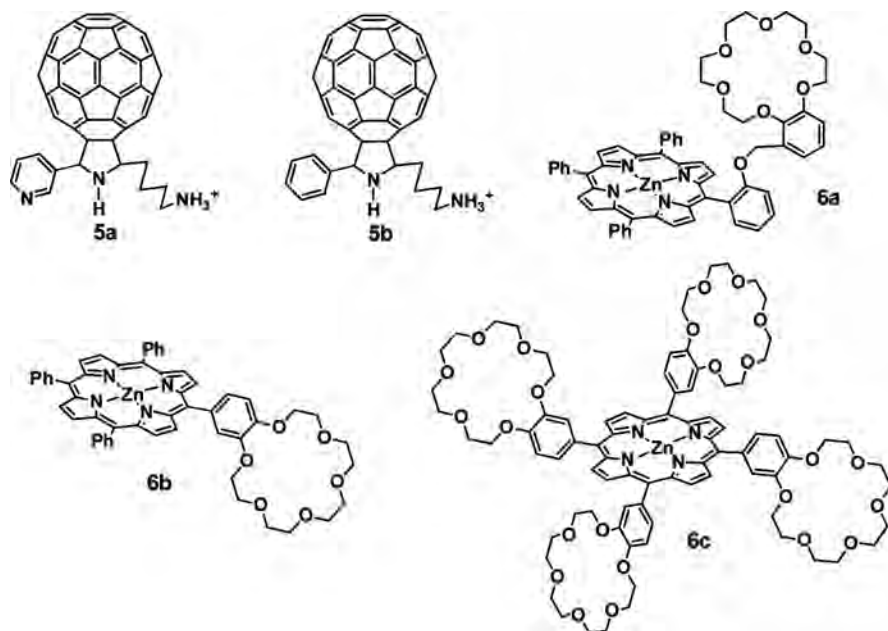
Figure 6.7   Structure of the C_{60}-hosts (**5a** and **b**) and porphyrin guests (**6a–c**) used to create "two-point" supramolecular conjugates.

longer lifetimes are detected for the corresponding CS states independently of the C_{60} host used.

Gathering C_{60} with a porphyrin moiety to form array **7a** showed a remarkable impact on the lifetime of the photogenerated radical-ion pair. Thus, the lifetime of the radical-ion pair in **7a**, in which C_{60} and ZnP are tethered by means of a guanosine–cytidine scaffold[26b] – one of the Watson–Crick pairs – is 2.02 µs. The beneficial effect of the H bonds, as a part of the whole bond framework, stems from the fact that this value is higher than those reported for related covalently linked C_{60}–ZnP diad.[26] However, when the ZnP is replaced by a phthalocyanine, a highly stabilised complex **7b** is formed, for which a binding constant of 2.6×10^6 M^{-1} (*vs.* 5.1×10^4 for **7a**) was determined.[26c] This stability, is justified by additional π–π and charge-transfer interactions in the Pc-based system (Figure 6.8).

Nierengarten's and Soladié's groups described the synthesis of supramolecular cup-and-ball C_{60}-P conjugates (**10** in Scheme 6.1) by direct mixing of P-crown ethers **8** and C_{60}-ammonium host **9**.[27] In conjugates **10**, two different noncovalent interactions, ammonium-crown ether and π–π stacking between the fullerene surface and the planar P, exert a dramatic effect on the recognition interaction between the two redox centres. The K_a value, obtained by fluorescence titration, for conjugate **10** was of 375 000 M^{-1}. This value is two orders of magnitude higher than those reported for related ammonium-crown ether complexes formed by using **8** with some other crown ether receptors.[28] Interestingly, the NMR
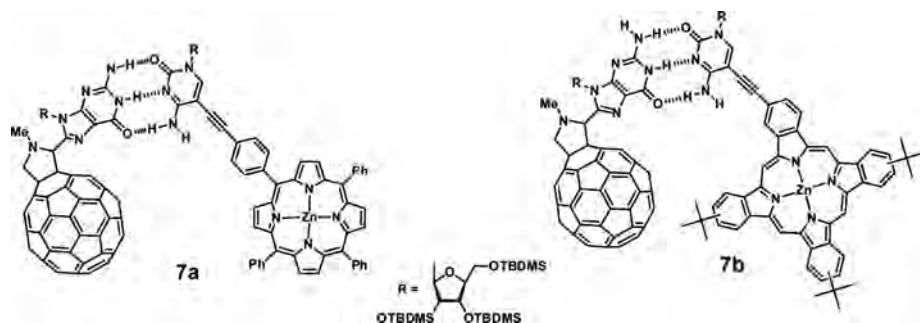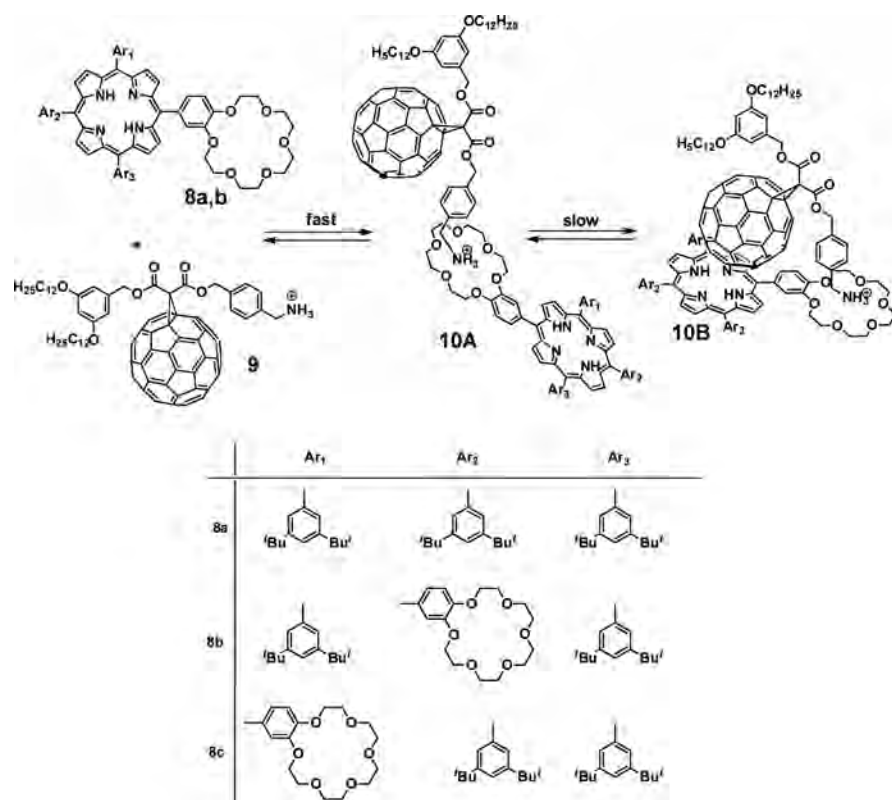
Figure 6.8 Watson–Crick H-bonded D•A diads.

Scheme 6.1 Complexation process between porphyrin receptor **8** and fullerene ammonium host **9**. Schematic representation of the formation of both conformers of conjugate **10**.

studies carried out for compositions **10** showed that after the initial fast ammonium-crown ether complexation, which gives rise to conformer **10A**, a slow exchange takes place to give rise to conformer **10B** (Scheme 6.1).

6.2.2   H-bonding Tethered π-Conjugated Oligomer•C$_{60}$ Diads

Fullerenes and π-conjugated oligomers/polymers are being widely used as building blocks for optoelectronic devices – light-emitting diodes (LEDs),[29] and plastic photovoltaic devices.[30] It is well known how the morphology of the active layer in photovoltaic cells conditions the final efficiency of the devices. A potential way to attain better morphologies comprises the supramolecular assembly of their constituents. The orientation of the electroactive components could give rise to an enhanced charge separation and charge-carrier movement.[31]

In this context and in order to control the organisation in active layers of PV cells, conjugate **11**[32] and its covalent analogue **12**[33] were synthesised. In both cases, a strong quenching of the OPV fluorescence was observed, being a singlet-energy transfer from the excited OPV to the fullerene responsible for the quenching. Surprisingly, whereas in the covalently bonded **12** an ultrafast electron transfer is followed by an intramolecular energy transfer, this sequence does not occur in the H-bonded **11**. This is primarily a consequence of the low electronic coupling in **11** between the electroactive units (Figure 6.9).[34]
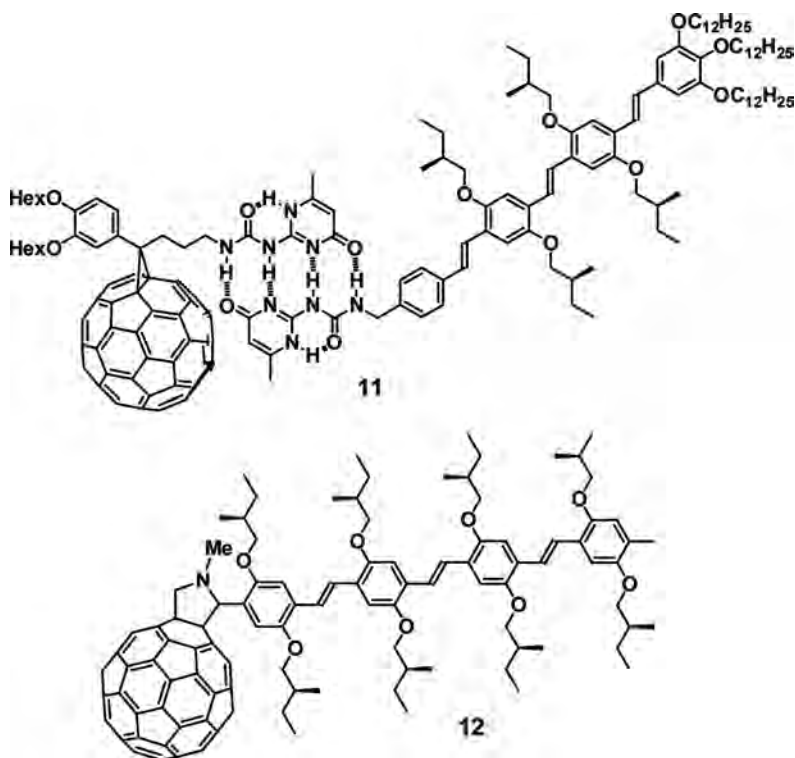

Figure 6.9   H-bonding interfaced (**11**) and covalent (**12**) C$_{60}$–OPV diads.

The combination of an UP oligomer (*vide infra*) with OPVs endowed with UPs allowed the formation of heterodimers linked through quadruple H bonds (**13**).

This strategy resulted in a supramolecular donor–acceptor–donor triad (Figure 6.10).[35] Remarkably, in contrast to previous examples in which the self-complementary nature of such H-bonding motifs leads to a statistical mixture of homo- and heterodimers, triad **13** represents the first experimental observation of preferential formation of functional supramolecular heterodimers linked by UPs moieties.
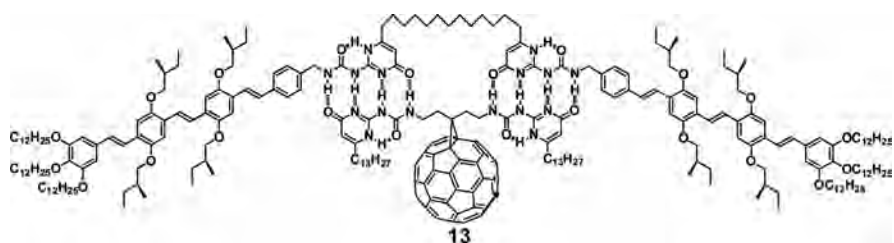

Figure 6.10 Supramolecular OPV•C_{60}•OPV triad, **13**.

It has already been mentioned in the previous section how the cooperative effect between ammonium hosts – crown ethers guests and π-stacking increases the K_a value in comparison with some other related complexes (see Figure 6.6). This beneficial effect over the association process has also been observed in analogous examples in which the π-conjugated oligophenylene vinylene (OPV) **14** is mixed with C_{60} host **15**. Again, the binding studies carried out in the complex **14•15** demonstrates a beneficial effect on the association constant stemming from the π–π interaction between the fullerene and the OPV moieties (Figure 6.11).[36] As occurs in C_{60}•ZnP complexes **4**, a strong stabilisation of about two orders of magnitude is observed for K_a in comparison with many other examples of complexes formed between crown ether receptors and ammonium, alkylammonium or arylammonium hosts.[37]

Surprisingly, and despite the expected steric hindrance between the two fullerene-based hosts, when a ditopic OPV-type crown ether guest (**16**) is used to form the corresponding supramolecular complex, similar values of K_a to that measured for complex **14•15** are observed.[36] These findings have been accounted for by the sum of secondary weak interactions, like π–π stacking, between host **15** and receptor **16**. In addition, the flexible character of the spacer seems to be the reason why the expected steric repulsion between the two hosts **15** is avoided and, therefore, the complexation of two C_{60}-ammonium hosts with just one receptor **16** is observed. The complex thus obtained can adopt either a *syn* or *anti* conformation (Figure 6.12). The authors claim that the thermodynamic data point out to a preferential *syn* aggregation as a consequence of the strong π–π interaction between the two C_{60} cages.

When bis(ammonium) fullerene ligand **17** is complexed with the previously mentioned ditopic OPV receptor **16**, a perfect complementarity between them is observed.[38] This methodology represents a powerful tool to control the formation of new supramolecular macrocyclic arrays. Analogously to the concept
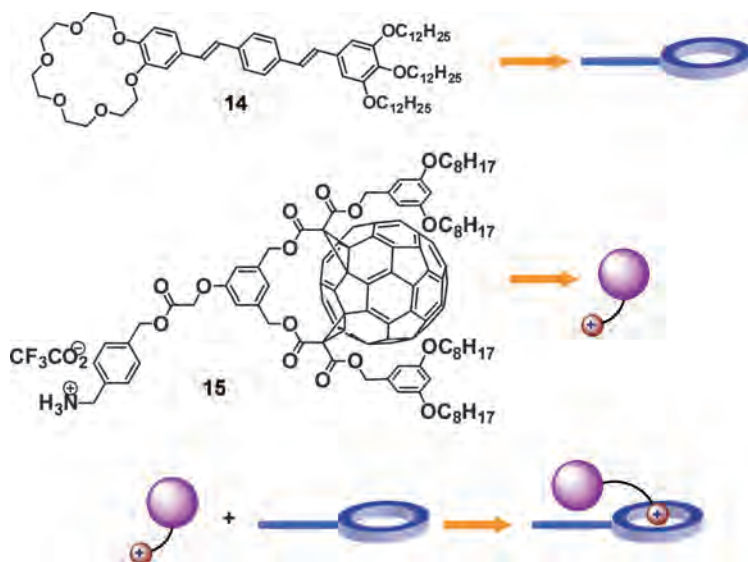
Figure 6.11   Complexation of OPV guest **14** and fullerene ammonium host **15**.
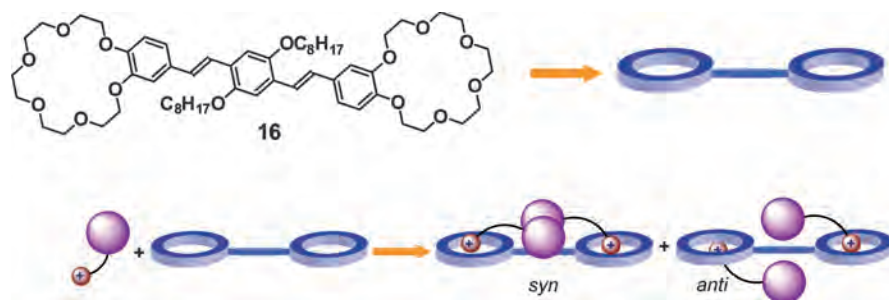

Figure 6.12   *Syn/anti* complexation of ditopic OPV guest **16** and fullerene ammonium host **15**.

of click chemistry coined by Sharpless *et al.*,[39] Dorsselaer, Albrecht-Gary and Nierengarten have named this perfect fit "supramolecular click chemistry". In fact, bis-cationic host **17** "clicks" onto the OPV receptor **16** giving rise to the noncovalently bonded macrocyclic complex **16•17** (Figure 6.13) with a binding constant of log $K_1 = 6.3 \pm 0.4$ M^{-1}. This K_a value is three orders of magnitude higher than those previously reported for other analogous complexes formed by crown ethers and ammonium derivatives.[28]

In the search for H-bonded assemblies capable of undergoing an inter-molecular ground-state electron-transfer process, Bassani, de Cola and cow-orkers have used the C_{60}-based barbituric acid host (**18**) to form a C_{60}–oligothienylenevinylene conjugate (**18•19**) showing a K_a value of 5500 M^{-1}
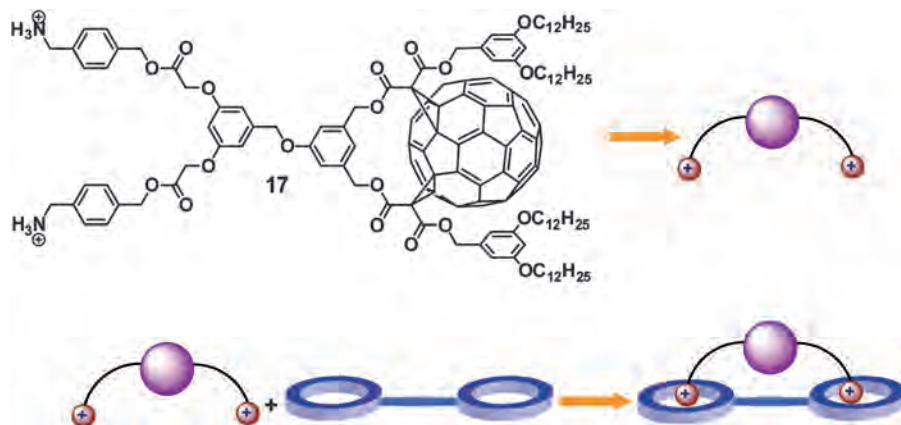
Figure 6.13 "Click" complexation of ditopic OPV guest **16** and fullerene bis-ammonium host **17**.

(in oDCB).[40] Steady-state fluorescence emission studies showed a strong quenching for the supramolecular conjugate **18•19** when compared with the free species **18** and **19**. A diagnostic absorption band at 560 nm is observed in the transient absorption spectra of the **18•19** pair that could be assigned to the formation of the radical-cation for guest **19**. These findings clearly support an efficient electron-transfer process between the two redox centres in composition **18•19** (Figure 6.14).

18•19 (R= Hex)

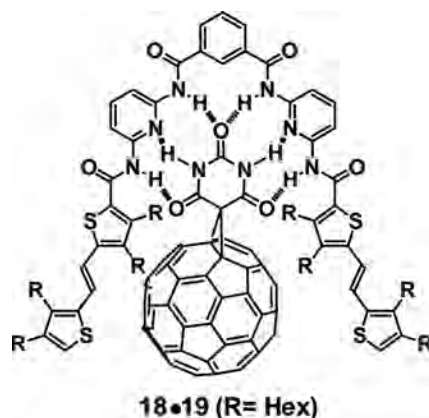**Figure 6.14** Structure of the H-bonded barbituric acid–oligothienylenevinylene pair **18•19**.

Within this supramolecular oligomer•C_{60} approach, another remarkable example is the fullerene barbituric acid (**18**)-pentathienylmelamine (**20**) conjugate reported by Bassani and coworkers.[41] The directionality of the H-bonding framework in complex **18•20** is a useful tool to control the exact

geometries of the electron donor and acceptor beyond the molecular level. It is well known that one of the main drawbacks of organic solar cells is the incomplete utilisation of the incident light due to the poor match between the absorption spectrum of the materials and the incident solar irradiation.[30] Interestingly, the conjugation of the melamine **20** allows its absorption in the visible region of the spectrum, which supposes that it is not necessary to synthesise longer oligomers in order to increase this property. In order to evaluate the suitability of these H-bonded materials for their application in the construction of solar cells, simple photovoltaic devices were fabricated. For comparison purposes, devices from oligothiophene–melamine (20) and from mixtures **18•20** and **20•C$_{60}$** were prepared. The photovoltaic response of these three devices is depicted in Figure 6.15. The incorporation of C$_{60}$ (device B in Figure 6.15b) onto the device induces a two-fold gain in the performance of the device in comparison with device A (fabricated from pure oligothiophene **20**). In device C, in which the active layer is the conjugate **18•20**, the enhancement of the photocurrent is five-fold, thus suggesting a higher
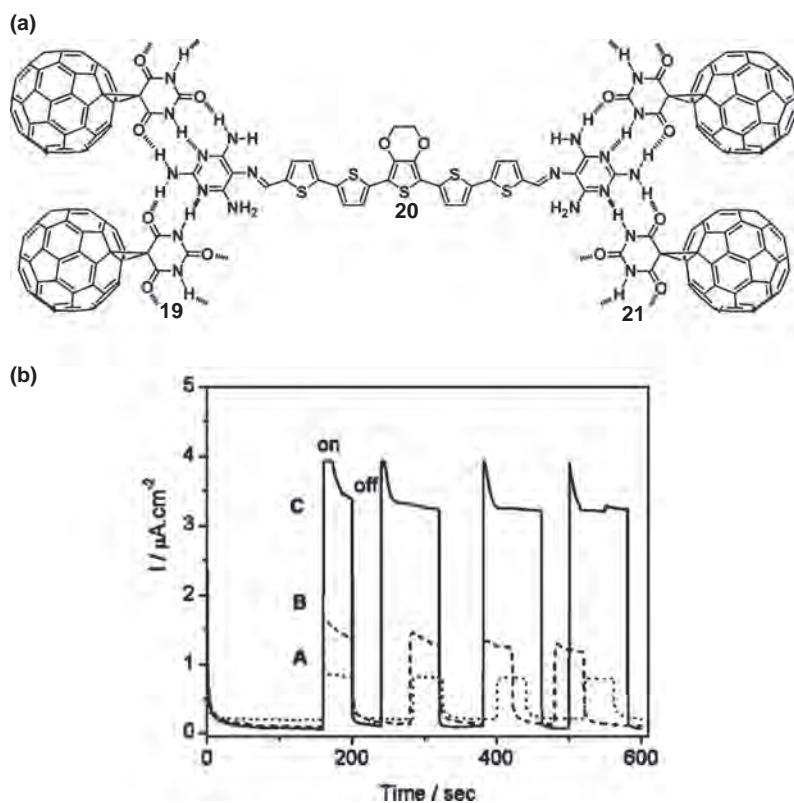

Figure 6.15   (a) Tape-like structure of melamine-barbituric acid pair **18•20**; (b) Photovoltaic response of devices A (solid line), B (dashed line) and C (dotted line). The applied potential was –100 mV. Reprinted with permission from ref. 41. Copyright (2005) American Chemical Society.

organisation (Figure 6.15a) degree in the blend, which leads to an improved charge-separation process.

6.2.3 Other Electron-Donor Moieties H-Bonding Interfaced with [60]Fullerene

Tetrathiafulvalene, TTF, has demonstrated to be a useful building block in macrocyclic and supramolecular chemistry.[42] Due to its nonaromatic 14 π-electron character, TTF and its π-extended derivatives (exTTFs) undergo a reversible oxidation process leading to aromatic and planar cation and/or dication species, respectively.[43] These effects have been successfully used to improve significantly the radical-ion pair lifetimes of the species formed upon visible-light irradiation.[43] The groups of Martín and Mendoza have synthesised a series of H-bonded C_{60}•TTF ensembles **21**,[44] in which the tetrathiafulvalenes (TTFs) act as electron donors. The photo- and redox-active units are held together not only through complementary H bonds, but also by strong electrostatic interactions through guanidinium and carboxylate ion pairs (Figure 6.16). Two chemical spacers of different lengths (*i.e.* phenyl *versus* biphenyl) as well as two functional groups (*i.e.* ester *versus* amide) have been used in order to modulate the molecular architectures.
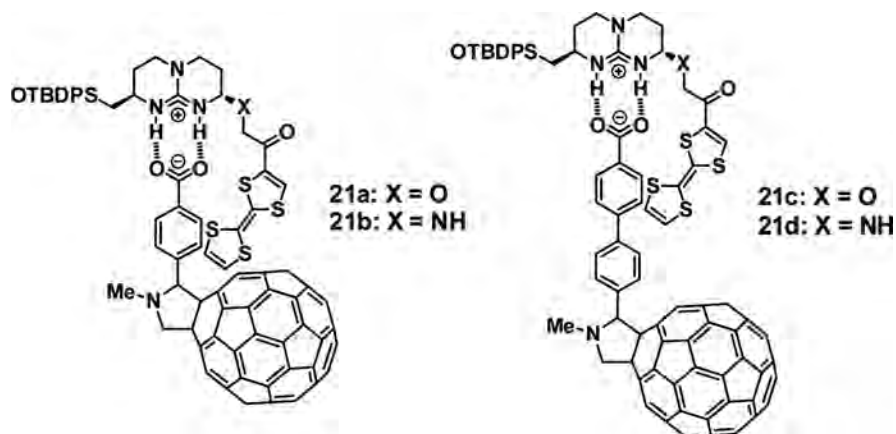
Figure 6.16 H-bonded C_{60}•TTF diads (**21a–d**).

In these supramolecular diads, the flexible nature of the spacer results in through-space electron-transfer processes. The lifetime measured for the radical-ion pair states, *i.e.* $C_{60}{}^{•-}$•TTF$^+$, are in the range of hundreds of nanoseconds, thus being several orders of magnitude higher than those reported for related covalently linked C_{60}–TTF diads.[43]

In a more recent work, different exTTF based secondary ammonium salts have been assembled to fullerene-crown ether derivatives with K_a values up to

1.4×10^4 M^{-1} (in CH$_3$CN:CH$_2$Cl$_2$ 1:1) for triad **22**.[45] Since the length and flexibility of the spacers between the complementary ammonium-crown ether bonding motifs is critical to allow the intramolecular interaction between the fullerene sphere and the π concave surface of exTTF, a new exTTF-crown ether derivative has been prepared, and its supramolecular interaction with the highly soluble fullerene ammonium salt **9** studied (**23**, Figure 6.17).[46] UV-Vis and fluorescence titrations evidenced the formation of the supramolecular complex that has a binding constant of $1.58 \pm 0.82 \times 10^6$ M^{-1} in chlorobenzene. Upon complexation, an anodic shift of $\sim$ 100 mV was observed for the oxidation potential of the exTTF by cyclic voltammetry, thus accounting for the high K_a value obtained. Time-resolved transient absorption spectroscopy experiments revealed the photoinduced generation of a charge-separated state with a short lifetime (9.3 ps in chlorobenzene).
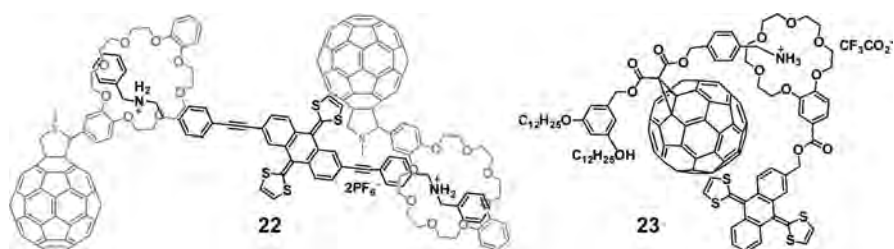
Figure 6.17   Chemical structure of the supramolecular complexes **22** and **23**.

Similar cooperative forces were explored in the preparation of the bioinspired cyclopeptidic heterodimers **24** built on β-sheet-like hydrogen-bonding networks (Figure 6.18).[47] A remarkable association constant of 10^6 M^{-1} was determined for the equilibrium mixture of three species with different relative

Figure 6.18   Structure of the cyclopeptidic heterodimer **24**.

positions of the exTTF and C_{60} fragments. In addition, steady-state and time-resolved spectroscopies evidenced an electron-transfer process from the exTTF to the photoexcited C_{60} that results in the generation of a radical-ion pair 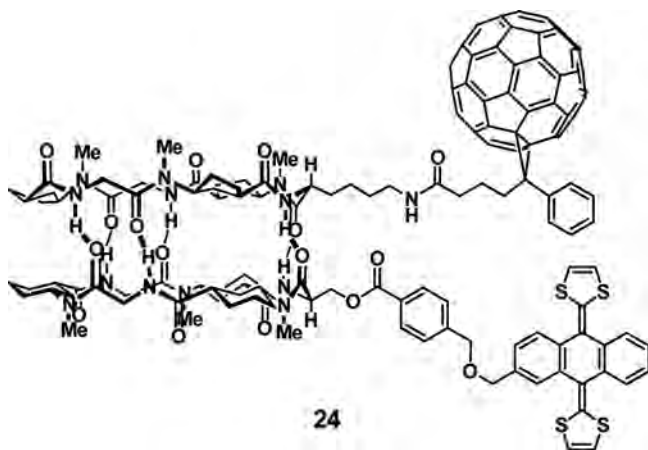state stabilised for up to 1 μs before recombining to the ground state. The structure of **24** could be extended to form a nanotubular self-organised material for electronic and photonic applications.

Several donor systems, such as triphenylamine (TPA)[48] or ferrocene,[49] have also been used to obtain H-bonding diads by combining them with C_{60} in a rotaxane fashion. In these rotaxanes, a through-space intrarotaxane photo-induced electron transfer gives rise to long-lived CS states. The control of the kinetics of the electron transfer has been investigated in rotaxanes that incorporate ferrocene macrocycles (Figure 6.19).[50] The addition of hexafluoro-2-propanol weakens the hydrogen bonds between the macrocycle and the peptide in **25** and, it results in a shortening of the lifetime of the corresponding charge-separated state as a consequence of the closer proximity between the ferrocene and the C_{60} moieties and a higher shuttling rate. In the structurally similar triad **26**, a unidirectional cascade of two consecutive through-space charge-transfer reactions between the three eletroactive units has been observed.[51] Time-resolved absorption measurements demonstrate that, after excitation of the central Ru(CO)TPP unit, an electron transfer from the porphyrin to C_{60} is produced. Subsequently, a charge shift promotes the formation of the $C_{60}\bullet^{-}$-$Fc\bullet^{+}$ radical-ion pair, and elongates the lifetime of $C_{60}\bullet^{-}$.
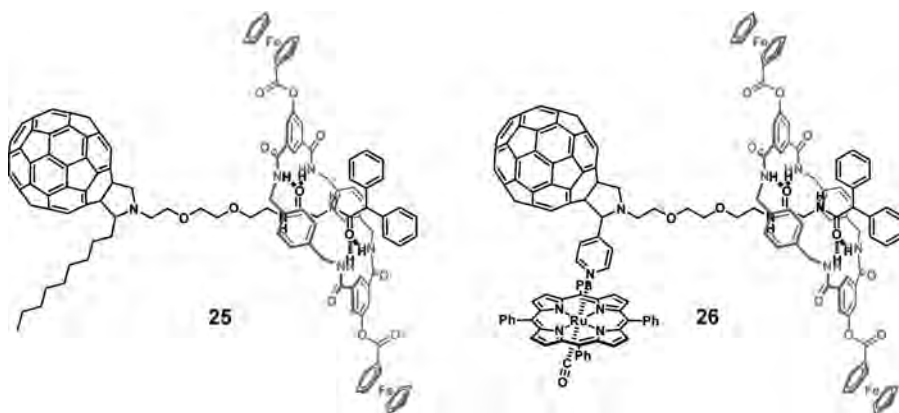
Figure 6.19   Fullerene–ferrocene rotaxanes **25** and **26**.

6.3   H-Bonded Supramolecular C_{60}-Based Polymers

In the previous section we have presented a wide variety of H-bonding donor–acceptor assemblies endowed with C_{60}. However, fullerene-containing supramolecular polymers have been scarcely studied and, despite their huge potential applicability, only a few examples of this class of supramolecular structures are known so far.[52] In this section we will concentrate on the scope of C_{60}-based

polymer chemistry to develop unprecedented architectures at the supramolecular level, with special emphasis on the more relevant examples including H-bonding architectures and the complementary interactions between pristine C_{60} and ditopic concave guests.

Based on DDAA principles, Hummelen and coworkers prepared the supramolecular polymer **27** from a self-complementary monomer able to form quadruple hydrogen bonds (Figure 6.20).[63] In polymer **27**, the presence of the UP units – as the molecular-recognition motif – confers high K_as. The dynamic behaviour of **27** was investigated by ^{1}H-NMR spectroscopy. When the spectra were analysed at low concentrations (10 mM), different sets of multiple signals appeared. A likely rationale infers polymeric and low molecular weight cyclic aggregates, as has been proposed in related systems.[54,55]
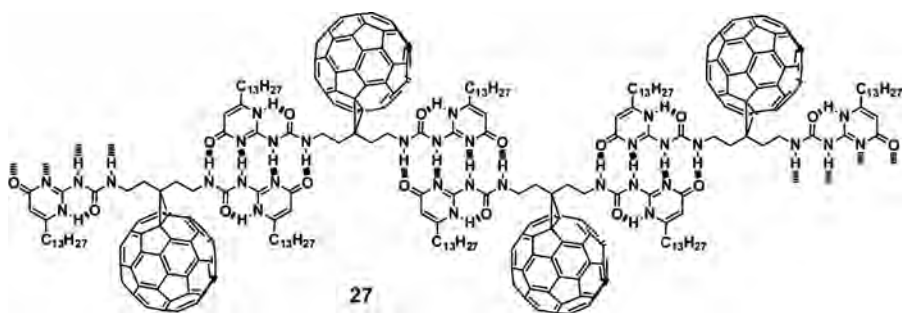

Figure 6.20   Supramolecular C_{60}-based polymer **27**.

An interesting class of supramolecular binding between C_{60} derivatives and polymers involves multisubstituted fullerenes, which can interact with a properly functionalised polymer. For this purpose, Dai, in 1998, described the behaviour of polyaniline emeraldine base (PANI-EB) **28** doped with a C_{60} structure (**29**) endowed with an average number of hydrogenosulfated and hydroxylic groups of six (Figure 6.21).[56]

After doping a PANI-EB film with **28**, the conductivity increased up to 11 orders of magnitude, reaching values of ca. 106 S/cm at 250 K. This value was 10^6 times higher than the typical value for fullerene-doped conducting polymers.[57] Furthermore, dedoping could be achieved after exposure to NH_3 vapours, recovering both optical and electronic properties and these processes could be repeatedly reproduced. This huge enhancement of the conductivity has been attributed to the doping-induced ''uncoiling'' of the PANI-EB chains when **28**•**29** is formed. The unravelling of polymeric chains leads to enhanced intrachain carrier mobility but, at the same time, results in an improvement of the interchain ordering augmenting the final conductance. An analogue attempt to complex **28** with the accepting H-bonding poly-(4-vinylpyridine) (P4VPy), demonstrates the ionic nature of the interactions in the complexes.[58]

A number of polymers carrying C_{60} as a side substituent have been prepared and their interpolymer complexes, when mixed together with P4VPy
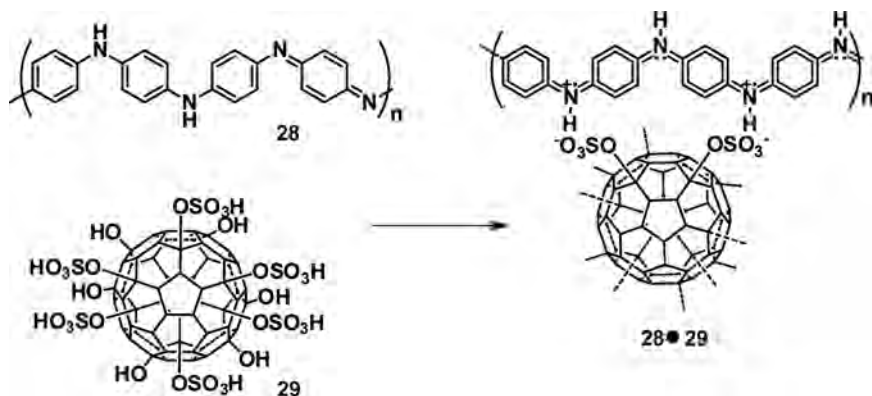
Figure 6.21 Doped polyaniline emeraldine base chains (**28**) with the hydrogen-sulfonated fullerenol derivatives containing multiple $-OSO_3H$ groups (**29**).

and poly(1-vinylimidazole) as proton acceptors, investigated.[59] C_{60}-end-capped polyethylene glycols such as **30** (Figure 6.22) also form interpolymer complexes with different H-donating polymers such as poly(*p*-vinylphenol),[60] poly(vinylchloride),[61] poly(methacrylic acid),[62a] or poly(acrylic acid).[63b] Furthermore, by melt blending of poly(methyl methacrylate) (PMMA) and **30**, pseudo-semi-interpenetrating polymer networks have been prepared showing a storage modulus as high as 42 kPa, 16 times larger than that of PMMA.[63]
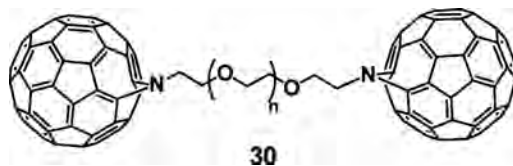

Figure 6.22 Poly(ethyleneglycol)-based polymer **30**.

Li and coworkers have prepared an original H-bonding assembly between C_{60} and a π-conjugated polymer (**31•32**) that at the same time avoids high C_{60} contents in the polymer, which prevents the structure becoming insoluble or not processable.[64] The synthetic procedure involves the preparation of a poly-*p*-phenylenevinylenecarbazole endowed with an uracil moiety (**31**) able to connect a complementary 2,6-diacylaminopyridine-C_{60} derivative (**32**) through a three-fold hydrogen bonding (Scheme 6.2). Fluorescence experiments are symptomatic of strong interactions between uracil-PPV (**31**) and diaminopyridine-C_{60} (**32**).

By using random-coil diblock polystyrene-poly(4-vinylpyridine) polymers (**PS-*b*-P4VP, 33**) as hosts and N-methylfulleropyrrolidine carboxylic acid (**34**) as guest, Shinkai *et al.* have reported the formation of spherical C_{60}-based nanoclusters bearing controlled size and morphology (Figure 6.23).[65] The
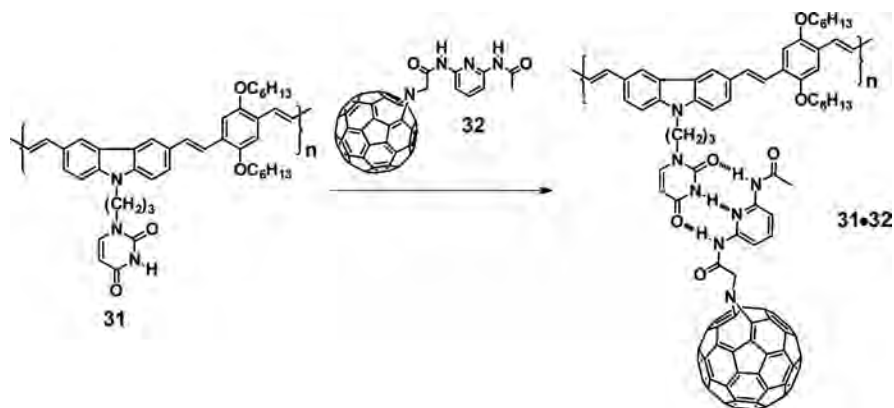
Scheme 6.2 Synthesis of the three-point H-bonded C$_{60}$•PPV assembly **31•32**.
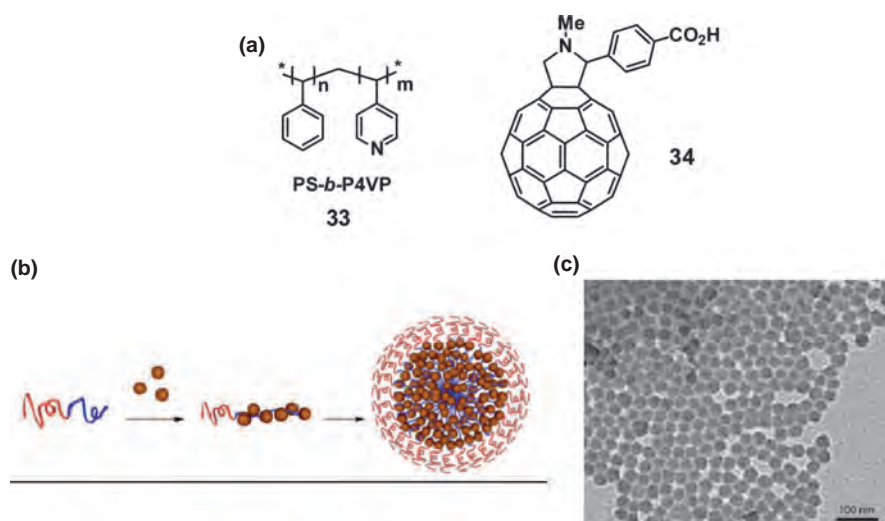
Figure 6.23 (a) Structure of the Ps-b-P4PV host **33** and the C$_{60}$-based carboxylic acid guest **34**, (b) schematic representation of the formation of supramolecular rod–coil polymers leading to the generation of micelles (c) TEM image of polymer **33•34** composite. Reprinted from ref. 65 with permission from Wiley-VCH.

authors claimed the formation of micelle-like superstructures in which the P4VPy blocks of the random-coil structure of **33** adopts a rod-like rigid conformation by interacting with **34**. This P4VPy-**33** complex possesses a poor solubility that forces the highly soluble PS blocks to orientate in the outside of the micelle, thus forming a shell, as is shown in Figures 6.23b and c. This practical methodology, carried out just by mixing the respective components,

represents a novel approach to nanomaterials chemistry and could be a milestone for the controlled construction of organic nanoparticles.

In 2005, Reynolds and Schanze described several photovoltaic devices based on an active layer formed by electrostatic layer-by-layer (LBL) deposition of bilayers of PPE-SO$_3^-$ (**35**), PPE-EDOT-SO$_3^-$ (**36**), and a fullerene modified with two ammonium groups (**37** – Figure 6.24).[66] When the bilayers were deposited onto an ITO electrode (50 layers), uniform films were obtained, as indicated by morphology studies.
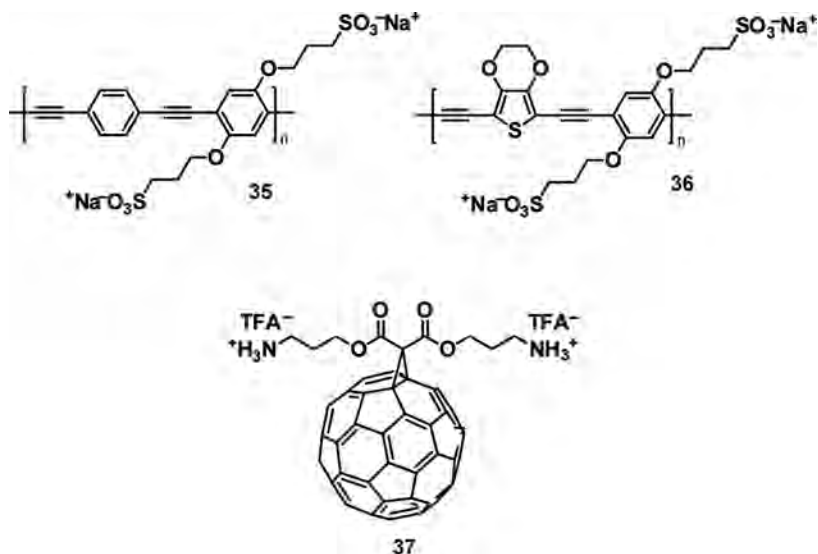
Figure 6.24 π-conjugated polymers **35** and **36** and fullerene-modified structure **37** used in the construction of photovoltaic devices by the LBL approach.

In the LBL assemblies some interpenetration of the polymer chains within the layers was observed, leading to some kind of bulk heterojunction. After deposition, the active layer showed an absorbance of 0.5–0.7 units at the λ_{max}, allowing the capture of 50% of visible light. When the device was completed with the vacuum deposition of LiF and aluminium layers and, irradiated under AM1.5 conditions, it displayed a good photovoltaic response, although the overall efficiency was rather low (**35/37**: $\eta = 0.04\%$; **36/37**: $\eta = 0.01\%$). However, to date these values represent the best results obtained within the LBL approach.

The combination of pristine C$_{60}$ with macrocyclic hosts, such as crown ethers, cyclodextrines (CD), calixarenes or porphyrins results in the formation of spectacular inclusion polymers, where van der Waals dispersion interactions greatly add to H-bonding and donor–acceptor interactions in providing stability to the assemblies formed.[67] In the following paragraphs we will review the D–A supramolecular C$_{60}$-based polymers prepared considering this approach.
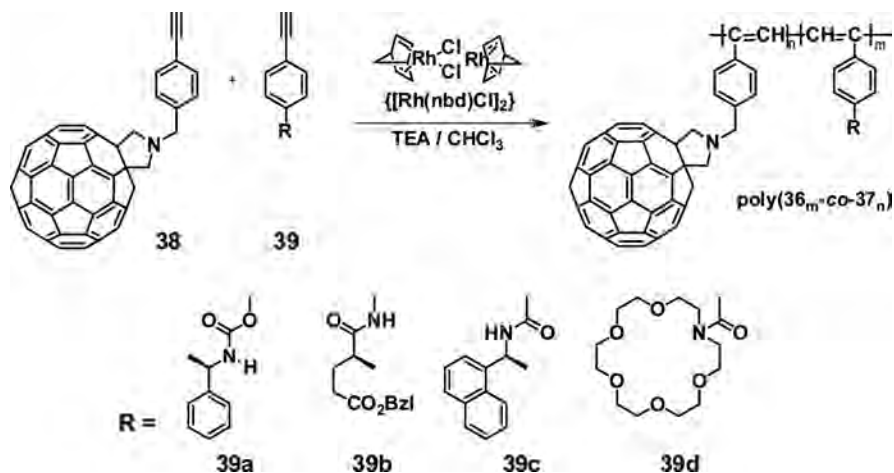
Scheme 6.3   Synthesis of copolymers poly(38_m-co-39_n).
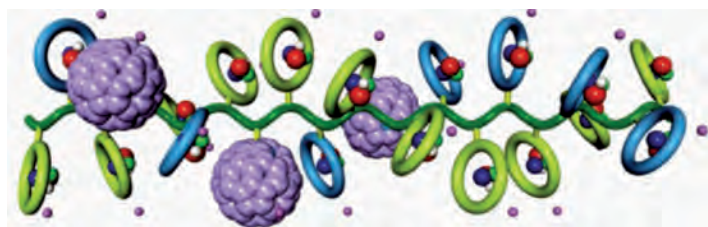
Figure 6.25   Cartoon representing poly($38_{0.15}$-co-$39d_{0.85}$). The achiral lateral fullerene and crown ether moieties arrange in a helical array along the one-handed helical polymer backbone induced by noncovalent chiral interactions with L-alanine.[69] Reproduced by permission of the Royal Society of Chemistry.

Yashima *el al.* prepared a series of copolymers of fulleropyrrolidine **38** and phenyleneacetylenes (**39a–d**) and demonstrated that they form predominantly one-handed helical structures (Scheme 6.3). In the aggregates, the pendant achiral fullerene groups are arranged in helical arrays with a predominant screw sense along the polymer backbone.[68]

More interestingly, when monomer **39d**, bearing a crown ether substituent, is incorporated in the final polymer, the desired predominantly one-handed helical conformation is reached by mixing together with L-or D-alanine perchlorate in acetonitrile. Upon complexation of the optically active amino acid by means of the pendant crown ether units, the achiral C_{60} moieties arrange in a helical array with the desired helix sense along the polymer backbone *via* chiral, noncovalent bonding interactions (Figure 6.25).[69]

Very recently, Granja *et al.* have reported on the synthesis of a α,γ-octapeptide bearing fullerene side chains (**40**) and hydrophilic residues that, besides increasing the solubility in polar solvents, facilitate the self-assembly of the
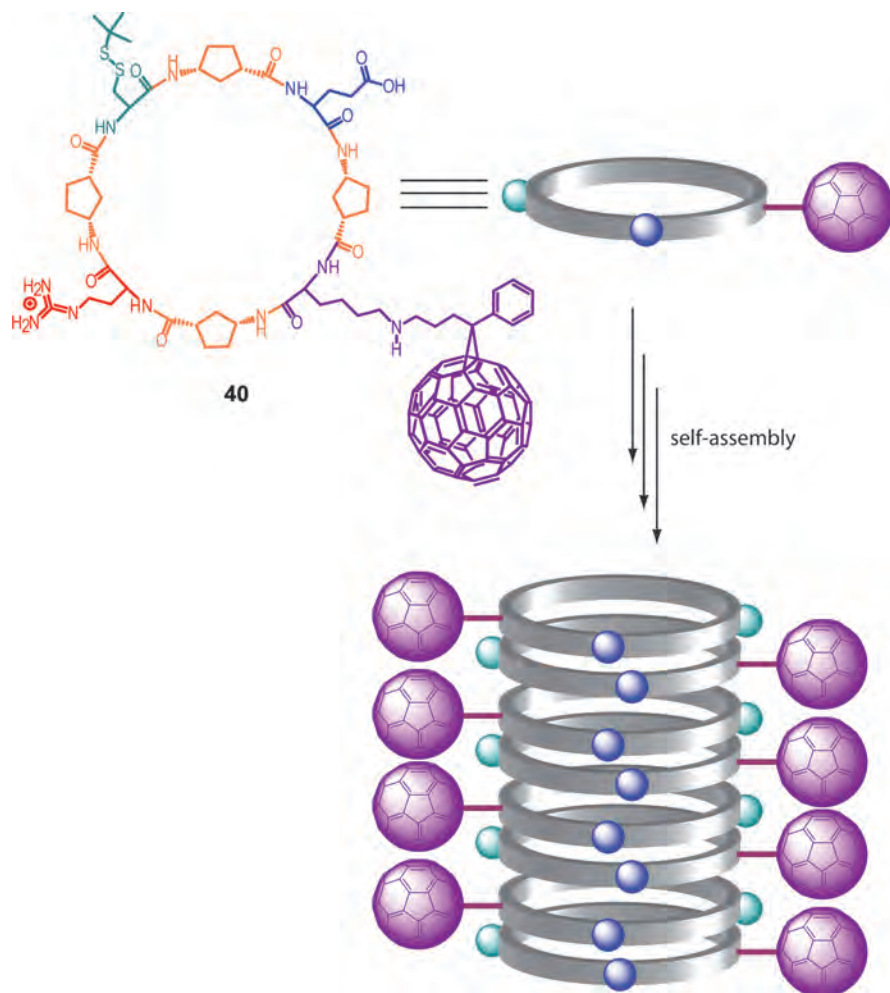
Figure 6.26 Chemical structure of the α,γ-octapeptide **40** and schematic illustration of its self-assembly forming nanotubes.

circular octapeptide **40** by hydrogen bonding (Figure 6.26).[70] The 1D arrangement obtained may be directed by salt-bridge interactions, or induced by the surface where the morphology of the molecules is investigated. In this case, the anionic mica may direct all the arginine residues toward the same side, orienting the fullerenes into two parallel wires.

Different CD-based polyrotaxane doubly end-capped with β-CD units have been employed to form aggregates in the presence of [60]fullerene.[71] In a remarkable example, Liu and coworkers prepared a water-soluble assembly by the intermolecular inclusion complexation of metallobridged bis(β-CD) and C_{60}.[72]
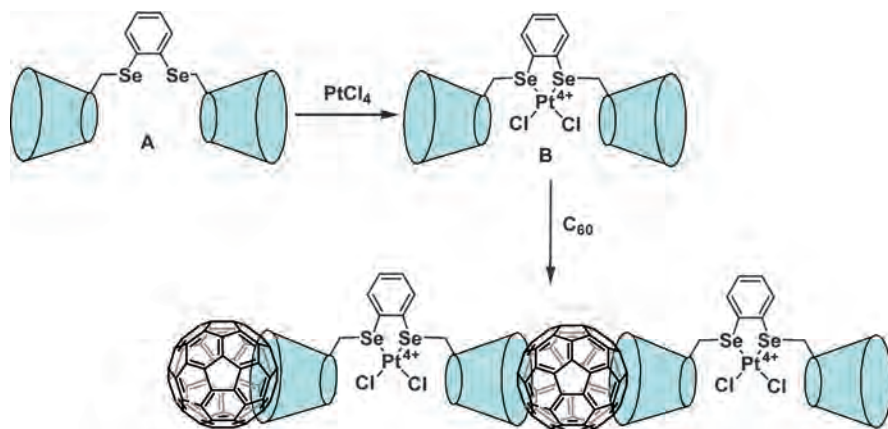
Scheme 6.4   Intermolecular inclusion complexation of metallobridged bis(β-CD) and C_{60}.

The supramolecular fullerene polymer was prepared according to the procedures shown in Scheme 6.4. TEM micrographs display the presence of linear structures with length in the range of 150–250 nm, constituted by 60–80 units of the complex **B**:C_{60}. Moreover, this complex showed an effective DNA-cleavage ability under light irradiation, which has potential application in biological and medicinal chemistry.

Recently, the same group has obtained linear supramolecular architectures in water by complexing a fullerene-bridged bis(permethyl-β-cyclodextrin) together with tetrakis(4-sulfonatophenyl) porphyrin, both in the free base or as the zinc complex form. In these supramolecular architectures it is noteworthy that the photoinduced electron transfer (PET) process takes place in both complexes as noted in fluorescence decay and nanosecond transient absorption experiments.[73]

The complementary molecular affinity between C_{60} and calix[5]arenes has been extensively exploited as the driving force for the preparation of self-assembly networks. In particular, the mixing of the dumbbell [60]fullerene **41** with the ditopic calix[5]arene host **42**, resulted in its self-assembly directed by molecular recognition to afford the formal supramolecular copolymer **41•42** (Figure 6.27).[74]

At a low concentration, diffusion coefficients obtained by pulsed field gradient NMR studies (2×10^{-4} M), demonstrated that the supramolecular complexes mainly adopt a trimeric structure.

The capability that cyclic bisporphyrin systems have to create multicapsular structures was elegantly considered by Shinkai and coworkers in the preparation of H-bonding supramolecular polymers.[75] For this purpose, the amide-appended porphyrin **43** (Figure 6.28) was designed as a system in which π–π stacking interactions among the porphyrins and hydrogen-bonding interactions among the amide moieties could operate cooperatively.[76] Upon addition of C_{60}
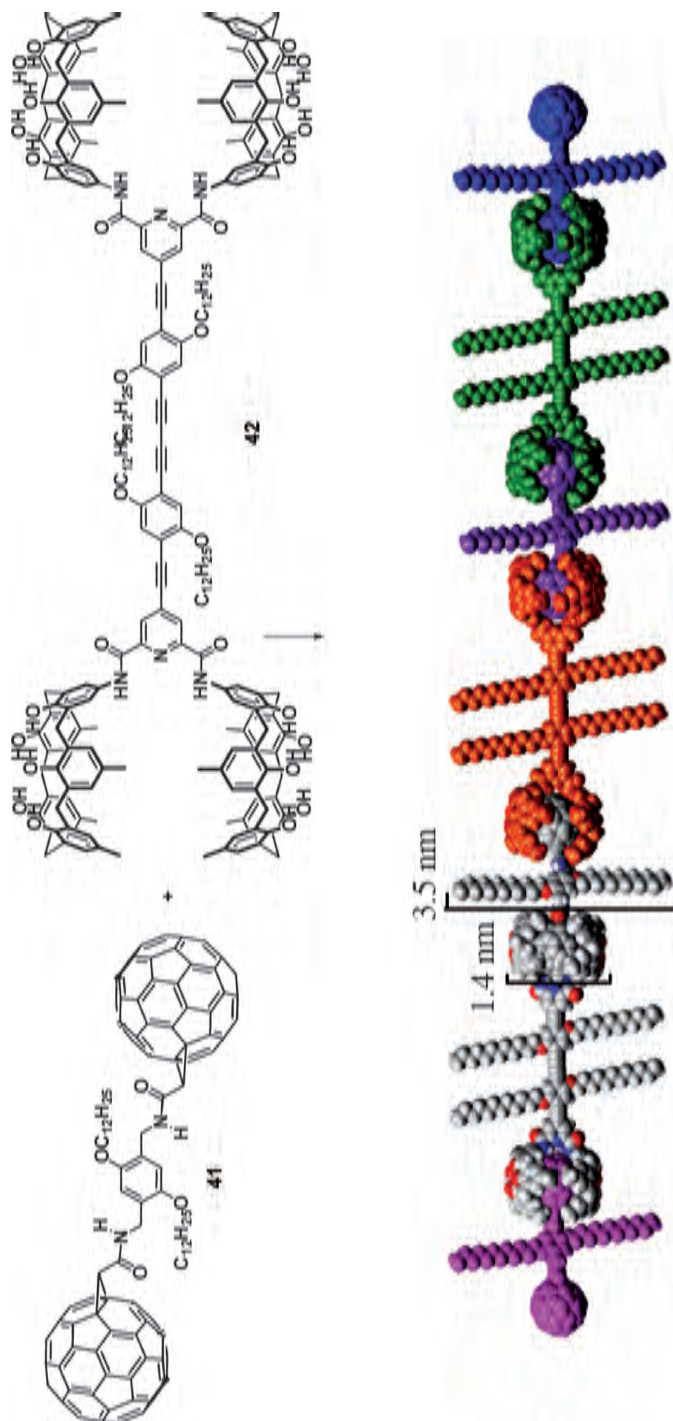
Figure 6.27 Representation of the self-assembling polymer formation by the host–guest complexation between fullerene **41** and calyx[5]arene **42**. Reprinted with permission from ref. 74. Copyright (2005) American Chemical Society.
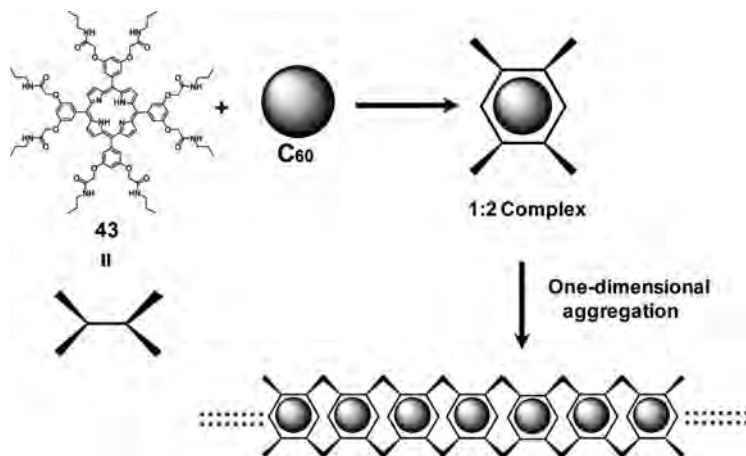
Figure 6.28   Synthesis of supramolecular polymers with programmed hydrogen bonding for the encapsulation of C_{60}.

to **43**, on a gel phase, the formation of a 1:2 complex is observed and confirmed by SEM and TEM techniques (**43** forms a two-dimensional sheet-like structure that in the presence of C_{60} changes to a fibril one-dimensional multicapsular structure).

An interesting potential application of these assemblies could be in photo-induced electron-transfer events, the preliminary experiments carried out by the authors evidenced a strong fluorescence quenching of porphyrin **43** in the one-dimensional $(43)_2 \bullet C_{60}$ aggregate.

6.4   H-Bond Interactions in Supramolecular Carbon Nanotubes (CNTs) Aggregates

An entire area of research dedicated to the chemistry of carbon nanotubes (CNTs) has developed during the past decade.[77] In general, CNTs posses unique structural, electronic, mechanical and optical properties that make them ideal components for a variety of different fields, such as field-effect transistors (FETs), light-emitting diodes (LEDs), organic solar cells (OSCs), biochemical sensors, memory elements or additives in composite materials.[78]

Unfortunately, major setbacks in the chemical processability of CNTs are the strong, mutual π–π stacking interactions that held together CNTs, yielding agglomerates of intimately associated long tubes. In this context, chemical functionalisation is an especially powerful tool as it might lead to the improvement of solubility and processability of CNTs. In addition, chemical functionalisation allows blending of the unique properties of CNTs with those of other functionalities. For these reasons, the development of chemical strategies aimed at solubilising SWNTs has been an important motivation in driving the surface chemistry of SWNTs.[77]

Among the different chemical modification possibilities for CNTs, the non-covalent one is particularly attractive, because it offers the possibility of associating functional groups to the CNT surface without modifying the π system of the graphene sheets and, therefore, their electronic properties.[79] In addition, if nanotubes are ever to be utilised as components of practical, macroscopic devices on a large scale, there is a complementary need for CNTs to be controllably assembled into more sophisticated and hierarchical architectures.

As examples of noncovalent functionalisation, CNTs can be solubilised in water by "wrapping" them with surfactants, ionic liquids, or different polymers, through electrostatic interactions or using a combination of van der Waals and complementary electrostatic interactions.[79] However, in the design of a self-organisation methodology, hydrogen-bond systems produce reliable and predictable noncovalent interactions, specific and directional, between donor and acceptor units.[80]

In this section, we will briefly review those recent examples that illustrate the role of hydrogen bonding in the supramolecular aggregation of CNTs.

In the early stages, most studies on CNT chemistry focused on separating and dispersing CNTs by chemical oxidation in acidic media, where the acid, however, not only dissolves any remaining metal catalyst but it also removes the CNT caps, leaving carboxylic acid (-COOH) residues behind. These oxidised CNTs are easily dispersible in various amide-type organic solvents under the influence of an ultrasonic force field.[81]

A noncovalent alternative to the commonly used oxidative acid treatment functionalisation of CNTs has recently been considered. Stable dispersions of SWNTs in water were obtained when pyrenecarboxylic acid (PCA) is non-covalently attached to the surface of SWCNTs. Composites of SWCNTs and polycarbonate were prepared and tested to determine the effect of PCA on the adhesion of the SWCNTs to the polymer matrix. These tests confirmed that PCA improved the SWNT–polycarbonate adhesion and enhanced the dispersion of the SWCNTs throughout the matrix.[82]

Microwave chemistry has been introduced to CNTs also in recent years.[83] Mitra *et al.* managed to introduce carboxylic and sulfonated groups on the sidewalls of single-walled carbon nanotubes (SWCNTs) after the microwave treatment with a mixture of nitric and sulfuric acid for a short period of time.[84] The modified tubes showed a great dispersibility in deionised water and ethanol.

However, the specific use of H bonding to control the architecture in supramolecularly bonded CNT networks has only been exploited in several examples. In 2002 a simple method to fabricate self-organised long carbon nanotube ribbons was described.[85] In this study, multiwalled CNTs synthesised by the catalytic decomposition of propylene were treated with concentrated nitric acid, sulfuric acid and hydrofluoric acid and, the resulting solutions were annealed at 373 K in a vacuum oven for 12 h. Long ribbons of aligned CNTs self-assembled on the wall of the container. The –C=O and –OH functional groups found in the aggregates by infrared spectroscopy play a bonding role between the CNTs to form the ribbons. Since it was confirmed that as-prepared

CNTs, free of these oxygenated groups, could not form the ribbons. Self-organised ribbons have also been found when droplets of CNT solutions were dried at room temperature on a wettable surface.[86]

More recently, the formation of an assembled bundle structure of thin multiwalled carbon nanotubes (t-MWCNTs) modified with hydroxyl groups was demonstrated to be held by the intertube hydrogen-bonding interaction.[87] FTIR spectra of the t-MWCNT-OH films obtained in this study provide the evidence of the intertube hydrogen-bonding interaction. In addition, the enhanced graphitic layer interaction of the assembled CNT films was demonstrated by the upshift and sharpening of the G-band in the Raman spectra.

Nevertheless, the strength of this type of H bond is relatively low when compared to cooperative systems. Only recently, Prato and coworkers have described thymine-functionalised CNTs able to self-assemble, by forming H bonds through the –C=O acceptor group and the –N–H donor group, into different DA–AD superstructures (Figure 6.29).[88] The CNT functionalisation has been achieved using two different reactions, the 1,3dipolar cycloaddition of azomethine ylides (**44**) and the diazonium salt-based arylation reaction (**45**).
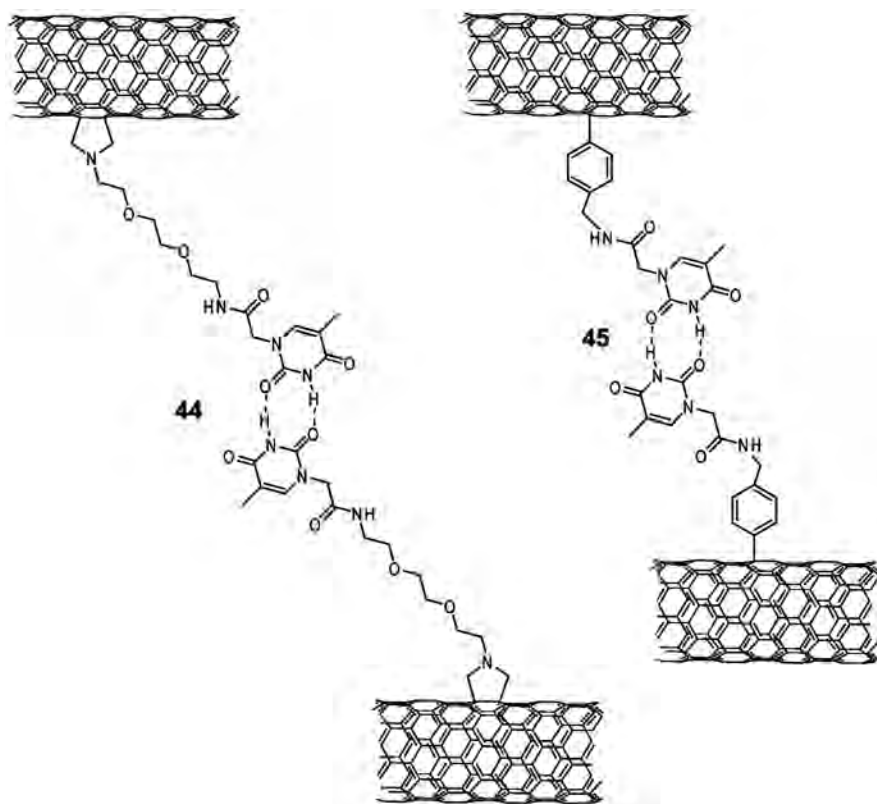

Figure 6.29   Thymine-functionalised CNTs able to self-assemble into DA–AD superstructures.

All compounds were dispersed in DCM, a noncompetitive solvent unable to generate H-bonding interactions, and also in DMF, which is a dipolar aprotic solvent, able to interfere with H bonds. In general, all the compounds were dispersible in DMF, while aggregates were always observed in DCM. The nature and the length of the chain between the CNTs and the thymine groups, as well as the degree of the functionalisation allowed the control of the morphology and size of the aggregates formed.

6.4.1 H Bonding in CNT–Polymer Composites

Besides possibly improving the mechanical and electrical properties of polymers, the formation of polymer–CNT composites is considered a useful approach for incorporating CNTs into polymer-based devices.[89] In particular, conjugated polymers have been shown to serve as excellent wrapping materials for the noncovalent functionalisation of SWCNTs as a result of π–π stacking and van der Waals interactions between the conjugated polymers and the surface of SWCNTs.[90] Stoddart and coworkers synthesised a family of poly[*m*-phenylenevinylene)-co-(*p*-phenylenevinylene)]s, functionalised in the synthetically accessible C-5 position of the *meta*-disubstituted phenylene rings.[91] They are essentially poly{(5-alkoxy-*m*-phenylenevinylene)-*co*-[(2,5-dioctyloxy-*p*-phenylene)-vinylene]} (PA*m*PV) derivatives bearing tethers or rings that form pseudorotaxanes with matching rings or threads.

The self-assembly of these pseudorotaxane-containing PA*m*PV polymers is based on two different recognition motifs, one involving hydrogen-bonding interactions between secondary dialkylammonium centres (*i.e.* dibenzylammonium ions) and suitable crown ethers (*i.e.* benzo[24]crown-8) and, the other involving π–π stacking, [C-H•••O], and [C-H•••π] interactions between π-electron-deficient hosts [such as cyclobis(paraquat-*p*-phenylene)] and π-electron-rich guests [such as 1,5-bis(hydroxyethoxyethoxy)naphthalene]. Wrapping of these functional PA*m*PV polymers around SWCNTs results in the grafting of pseudorotaxanes along the walls of the nanotubes in a periodic fashion (Figure 6.30). The results hold out the prospect of developing future arrays of molecular actuators and switches.[77c]

On the combination of CNT and conducting polymers, polyaniline (PANI) bears particularly great potential in synthesising polymer–CNT composites due to its environmental stability, good processability and reversible control of conductivity both by protonation and charge-transfer doping. Several reports have focused on the design and the fabrication of PANI/CNT composites.[92] For example, Wu *et al.*,[93] described the synthesis of doped polyaniline in its emeraldine salt form (PANI-ES) with MWCNTs fabricated by *in situ* polymerisation. The as-prepared MWCNTs were treated using a 3:1 mixture of concentrated H_2SO_4:HNO_3, which produced carboxylic acid groups at the defect sites (see Scheme 6.5).

On the basis of the π–π* electron interaction between aniline monomers and MWNTs together with hydrogen-bonding interactions between the amino

(a)

(b)
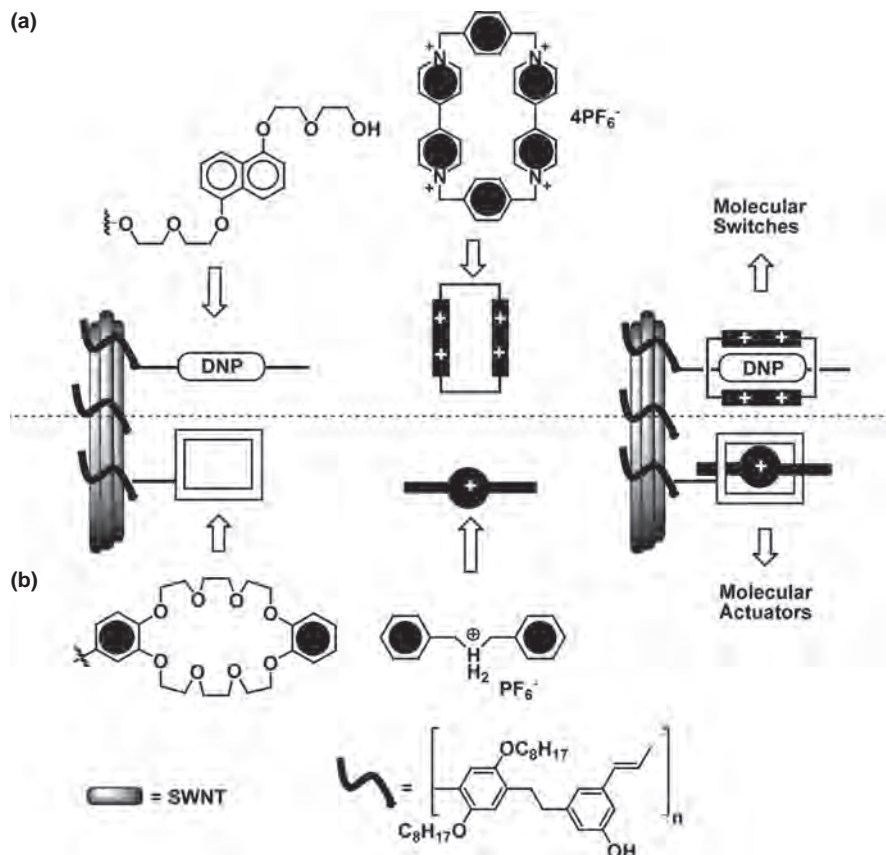
Figure 6.30 Schematic representation for the formation of polypseudorotaxanes grafted along the walls of SWCNTs. (a) From a naphthalene-containing PAmPV polymer or (b) from a dibenzo[24]crown-8-containing PAmPV polymer.

group of aniline monomers and the carboxylic acid groups of the modified MWCNTs, aniline molecules were adsorbed and polymerised on the surface of MWCNTs. The structural analysis of the composites formed by spectroscopic techniques showed the formation of tubular structures with diameters of several tens to hundreds of nanometres, depending on the PANI content. The electric conductivities at room temperature of PANI-ES/MWCNTs composites are 50–70% higher than those of PANI without MWCNTs.[92]

6.4.2 H Bonding in the Interaction of CNTs with Biomolecules

The solubilisation of SWCNTs associated noncovalently with biomolecules in both aqueous and organic solutions has been investigated recently at considerable length. The biomolecules employed in the supramolecular
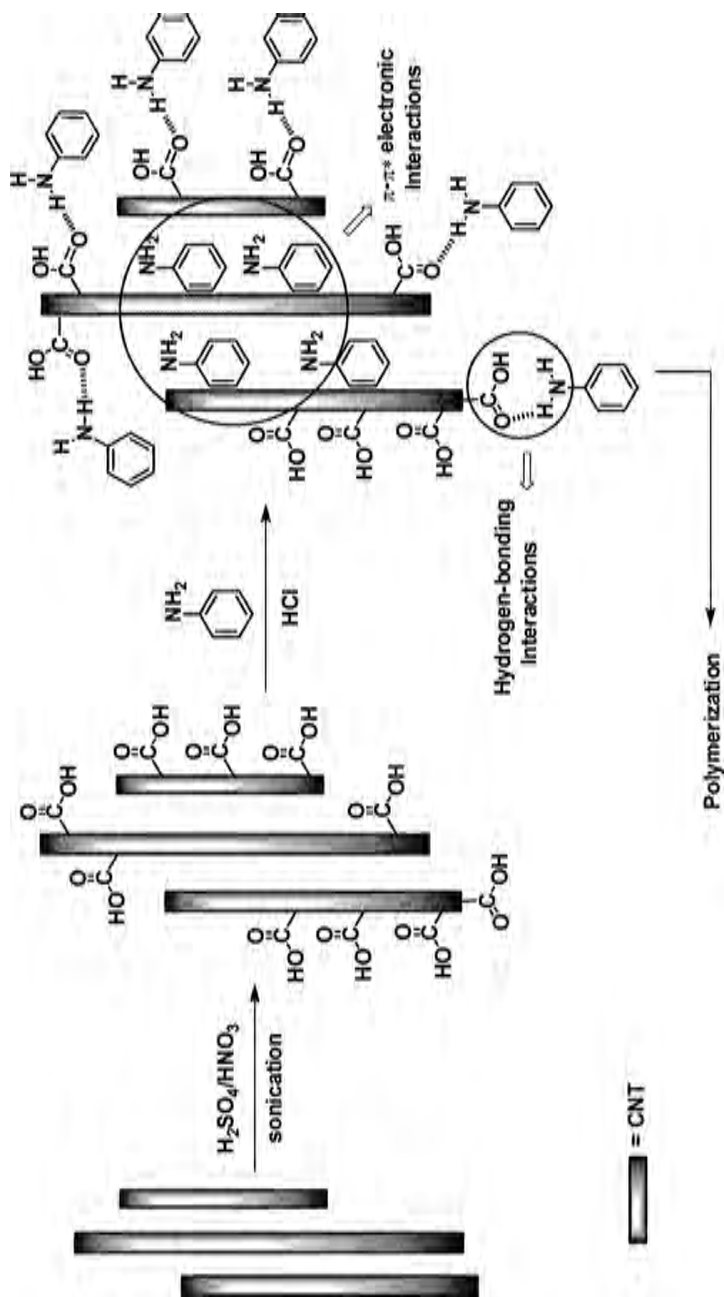
Scheme 6.5 Schematic representation of the mechanism governing the formation of PANI-ES/MWCNTs composites.

functionalisation of SWCNTs include simple saccharides and polysaccharides, peptides, proteins, enzymes or DNA and RNA.[77f]

Within all these molecules of biological interest, nucleobases are the fundamental constituents of nucleic acids and provide hydrogen-bonding molecular recognition for the formation of duplexes, triplexes or higher-order architectures. The noncovalent interactions and the ability of nucleobases to disperse SWCNTs have recently been evaluated theoretically and experimentally. It has been reported that poly(T) single-stranded DNA could more efficiently dispersed SWCNTs in water than poly(A) and poly(C),[94] as confirmed by theoretical calculation that predict binding energies of nucleobases with SWCNTs with the following decreasing order in solution: $G > T > A > C$.[95] It has also been reported that carboxyl- or hydroxyl-modified SWCNTs can facilitate the self-structuring of single-stranded RNA poly(rA) to form an $A \bullet A^+$ duplex-like structure.[96] In addition, nucleobases have recently bonded covalently to CNTs, and the nanoconjugates obtained were able to form horizontally aligned structures on a HOPG surface.[97] Such ordered organisation is likely induced by the presence of the nucleobases and TEG chains (also contained in the structure), which eventually interdigitate, allowing the exfoliation and the parallel arrangement.

The coenzyme flavin adenine dinucleotide (FAD) has also been attached to the CNT surface through π–π stacking interactions.[98] In fact, due to cooperative hydrogen bonding between adjacent flavin moieties absorbed onto the SWCNTs, a helical ribbon organises around the nanotube backbone (Scheme 6.6).

More interestingly, in these aggregates a strong chirality dependency was evidenced that led to the enrichment of the aggregates on (8,6) SWCNTs.[99] When an appropriate amount of the surfactant sodium dodecylbenzene
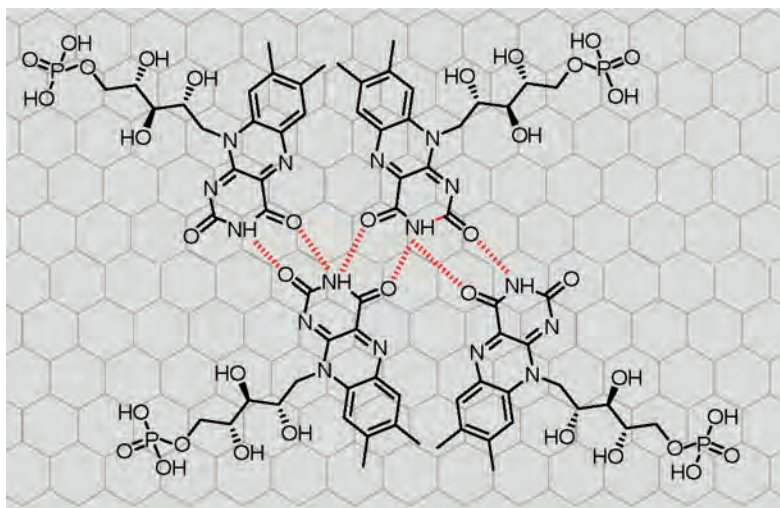

Scheme 6.6 Cartoon representing H-bonded flavin moieties absorbed onto SWCNTs.

sulfonate (SDBS) was added to SWCNTs dispersed in a solution of flavin mononucleotide it is observed the controlled replacement of the flavin moieties of all chiralities with the only exception of the (8,6) CNTs. All the nanotubes enclosed in SDBS micelles could be precipitated by the addition of NaCl, whereas the CNTs remaining in solution are highly enriched in a single chirality.[100]

6.4.3   H bonding for the Assembly of CNTs in the Search for New Properties

The preparation of CNT/nanoparticle hybrid materials is an important research area as the new generation of hybrid materials possess unique properties and are potentially useful for nanotechnological applications.[101] To avoid potentially complicated and tedious surface modifications of CNTs, many methods of preparation have taken advantage of the hydrophobic interactions established between appropriately functionalised nanoparticles and pristine CNTs to develop simple and effective strategies to assemble both nanomaterials. For example, Zhong *et al.* have prepared nanoparticle-coated carbon nanotube composite materials, considering the molecular assembly of alkanethiolate-capped gold nanoparticles of 2–5 core sizes on MWCNTs *via* a combination of the hydrophobic interaction between the alkyl chains of the gold nanoparticles at the hydrophobic backbones of the nanotubes and, the hydrogen-bonding interactions between carboxylic groups of the alkanethiolate-capped gold nanoparticles and the functional groups on the surface of the nanotube (Scheme 6.7).[102] The morphology and packing density for the nanoparticle assembly on CNTs depend on the particle size and the relative concentrations of nanoparticles, linking molecules and nanotubes, even though the distribution of nanoparticles on the CNT is quite uniform.
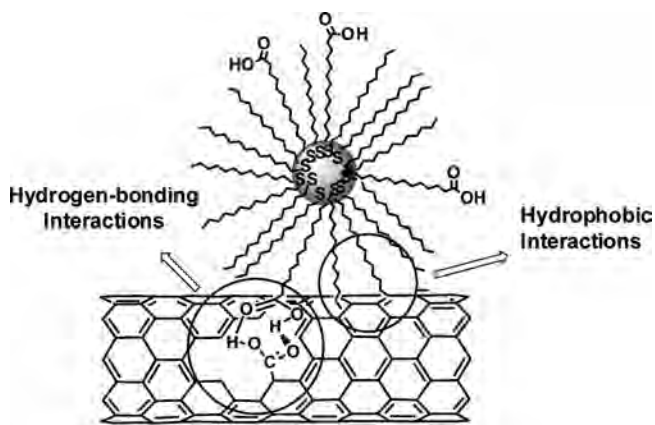
Scheme 6.7   Cartoon illustrating the molecularly mediated assembly of monolayer-capped nanoparticles on CNTs.

Another topic of recent interest in CNT chemistry is the preparation of gels. Typically, the CNTs are added to preformed gels or are present in a reaction mixture where a gelator is added to form the gel. In this way, CNTs have been used to support gels of different polymers[103] or organogelators.[104] However, there are very few examples where CNTs are directly responsible for the gel formation. Poly(ethyleneimine)-functionalised SWCNTs have been used to crosslink collagen in the presence of a carbodiimide coupling agent,[105] and cyclodextrin-modified SWCNTs have been used to take advantage of the host–guest interactions to form a hydrogel with dodecylated poly(acrylic acid).[106] In recent work, it has been demonstrated that pyridine-functionalised SWCNTs (**46**) – obtained *via* reaction with a pyridine diazonium salt generated *in situ* (Scheme 6.8) – act as gelators for the pH-responsive polyelectrolyte poly(acrylic acid).[107] In particular, the hydrogen bonding between the pyridine groups on the SWCNTs and the carboxylic groups on the polymer were responsible for holding the network together and stabilising the formation of an SWCNT-poly(acrylic acid) hydrogel.
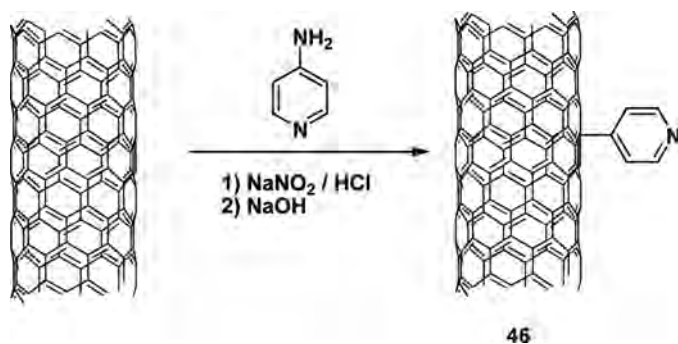
Scheme 6.8   Synthesis of the pyridine-modified SWCNTs **46**.

6.5   Conclusions and Outlook

Electronic donor–acceptor interactions constitute one of the basic processes used by Nature to transform and store energy. Following biomimetic principles it is possible to carefully design new energy-harvesting materials in which energy- and electron-transfer events are primary processes for which a better understanding is required in order to achieve a control on these phenomena for specific device applications.

Since the discovery of fullerenes it was realised that these new carbon allotropes offered new possibilities for the development of materials for the coming technologies. Although a lot of studies have been carried out on covalently bonded C_{60}-based donor–acceptor systems, this is not the case for H-bonding donor–acceptor diads, which have only been studied during recent years. Thus, a wide variety of supramolecular architectures involving the highly directional and selective H-bond between [60]fullerene and a variety of electron-donor

units have been described. Interestingly, the electron transfer through a H-bonding network results to be as efficient as that found in the covalent related systems. This finding prompted the fast development of this new interdisciplinary field of supramolecular fullerenes that present a closer resemblance to the natural photosynthetic process than previous covalently bonded supermolecules.

The imagination of chemists has produced a wide variety of H-bonding C_{60}-based donor–acceptor ensembles in which the induced supramolecular order results, for example, in improved photovoltaic properties.

H-bonded supramolecular C_{60}-based polymers is an emerging field with an enormous potential applicability. Because of the ease of the synthetic methodology, as well as the intrinsic reversibility of the engaged weak forces, a wide variety of fullerene-containing supramolecular polymers can be considered. In this regard, although a few outstanding examples have recently been reported, more work is needed in order to fully exploit the potentiality of this novel approach for the fabrication of structurally organised optoelectronic devices.

The same basic principles of supramolecular organisation can also be applied to carbon nanotubes. Although considerably less studied, H-bonding CNT-based donor–acceptor ensembles reveal that these new carbon allotropes are as efficient as the parent fullerenes in electron-transfer events. In this regard, a remarkable advantage of the supramolecular functionalisation, in contrast to the covalent functionalisation, of CNTs is that they preserve the π-system structure and, therefore, the electronic properties of pristine CNTs.

In summary, H-bonding fullerene and carbon-nanotube-based supramolecular architectures emerge as a readily available and highly efficient approach to advance our understanding of the molecular principles that Nature deploys for energy harvesting, which offer new possibilities for their use in molecular electronics as well as in the emerging nanotechnologies.

Acknowledgements

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