New challenges in fullerene chemistry

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The aim of this focus article is to emphasize those aspects of fullerene chemistry which currently represent important challenges for the development and future applications of these new carbon allotropes, as well as to celebrate the tenth anniversary of the fullerenes Nobel Prize.

1 Fullerenes: ten years after the Nobel Prize

In 2006 we celebrate the tenth anniversary of the Nobel Prize received by Sir Harold W. Kroto, Robert F. Curl and the late Richard E. Smalley for the discovery of fullerenes. After a decade, it is timely to think about the achievements and future goals of researchers studying these carbon allotropes. The huge number of papers, reviews and books written over this last decade on fullerenes, as well as on the closely related carbon nanotubes, give an idea of the unabated interest in these fascinating three-dimensional molecules.[1]

Since the discovery of the fullerenes in 1985,[2] other important developments have appeared in the scenario of the fullerenes. The major breakthrough in fullerene science occurred in 1990,[3] when Wolfgang Krätschmer and Donald Huffman (two astrophysicists) prepared fullerene C_{60} for the first time in multigram amounts, thus opening the fullerene world to chemical functionalization and, therefore, to the unlimited imagination of chemists for synthesizing new and sophisticated fullerene architectures. It was in 1991 that Iijima achieved another major development in fullerene science with the discovery of the tube-like carbon nanotubes (NT),[4] thus paving the way for a new avenue in chemistry as well as giving birth to an important material for the emerging field of nanotechnology. The third important landmark occurred in 1996 when fullerenes' discoverers were awarded the Nobel Prize in chemistry.[5]

The aim of this focus article is to consider the expectations and major challenges for the near future of fullerene science, not to discuss the unfulfilled hopes for fullerenes following the initial excitement. A huge amount of literature published on fullerenes from the very beginning until the Nobel award accounts for the most important achievements concerning their nature, physical and electrochemical properties and chemical reactivity. The purpose of this article is to highlight some of the most remarkable aspects of fullerene science during the last decade, that is, from the Nobel award to date. Needless to say this is not a comprehensive review but a simple presentation of those aspects that this author considers to be among the most appealing and promising in fullerenes science. In this regard, the different concepts discussed will be classified according to the molecular, macromolecular and supramolecular achievements.

2 Molecular chemistry of fullerenes

2.1 New chemical reactivity of C_{60}

The unique 3D geometry of fullerenes with carbon spheres containing thirty or more highly reactive double bonds constitutes a rather rich scenario where a variety of different chemical reactions can be tested. The convex surface of fullerenes offers new possibilities for the study of new reactions and mechanisms under severe geometrical constraints on carbon atoms showing a rather unusual $sp^{2,3}$ hybridization.[6]

Although the chemistry of fullerenes is nowadays considered a well established

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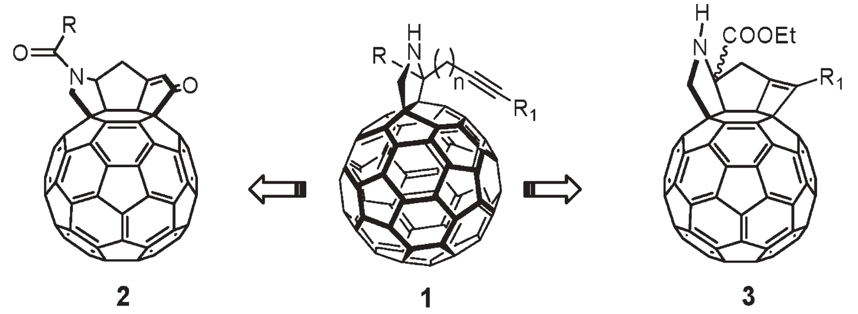


Fig. 1 New fuller-1,6-enynes (**1**) are highly versatile building blocks.

matter, with a high level of understanding of their chemical reactivity, a wide variety of important reactions involving alkenes and alkynes have never been carried out on the fullerene surface. Furthermore, many essential reactions in organic chemistry that involve the use of transition metal catalysts able to transform fullerenes into more sophisticated structures have not been reported so far.

Just to exemplify the above statement, one of the most successful reactions in organic synthesis, the [2 + 2 + 1] cycloaddition of alkyne, alkene, and carbon monoxide mediated or catalyzed by a transition metal (mostly cobalt), also known as the Pauson–Kahn (PK) reaction, has been widely used for the construction of biologically active five-membered carbocycles in a convergent approach. This reaction has also recently been carried out on fullerene C_{60} acting as the alkene component, and a highly efficient and regioselective intramolecular PK reaction afforded a new type of unprecedented fullerene derivatives (**2**) showing three (or five) fused pentagonal rings on the same hexagon of the fullerene surface.[7]

Another example where the singular geometry of fullerenes can result in a different chemical reactivity from that found in related molecules is reactions with 1,6-enynes. The transition metal catalyzed cyclization of enynes has been extensively studied because it provides a powerful method for the construction of carbo- and heterocyclic molecules in a simple way. It has recently been reported that the thermal treatment of fuller-1,6-enynes (**1**) leads very efficiently to the formation of stable cyclobutene adducts (**3**) without involving the presence of any catalyst, in a reaction that is the first example of a thermal [2 + 2] cyclization involving a fullerene double bond as the alkene moiety of the reactive 1,6-enyne[8] (Fig. 1).

Fulleropyrrolidines are among the most studied fullerene derivatives which have been used for many applications either in materials science or in the search for biological properties.[9] In contrast to other labile fullerene cycloadducts such as those prepared from Diels–Alder or Bingel reactions, fulleropyrrolidines, which are usually prepared by 1,3-dipolar cycloaddition reaction of azomethyne ylides to C_{60}, have been considered to be rather stable fullerene derivatives. However, the thermal quantitative retro-cycloaddition of fulleropyrrolidines to obtain the pristine fullerene with its typical magenta colour in solution has been very recently reported.[10] This new reaction confirms that the understanding of the reactivity of fullerene derivatives is still far from the level where it is possible to predict reliably the outcome of many reactions. Further more, this reaction constitutes a new protection–deprotection protocol which has recently been used for the separation of two isomers (I_h and D_{5h}) of endohedral $Sc_3N@C_{80}$ (Fig. 2). This reaction expands the applicability of the basic chemical reactivity of fullerenes and gives an insight into further studies on the reactivity of higher fullerenes and carbon nanotubes.

2.2 Endohedral fullerenes

Endohedral metallofullerenes are currently becoming one of the most studied classes of compounds within the field of fullerenes.[11] Although mass spectroscopic evidence of endohedral fullerenes was reported in 1985, there was a big controversy about the location of the metals inside or outside of the sphere, which was finally resolved by Smalley who showed unequivocally the existence of $La@C_{82}$ with a lanthanum atom encapsulated in a C_{82} fullerene.[12] However, despite the interest of these compounds, the limited quantities of isolated material have prevented the study of their reactivity during the last 15 years. Since they are currently prepared in multimilligram amounts, a flurry of activity has recently started to unravel their chemical reactivity.

Endohedral metallofullerenes show some common remarkable features: i) they are usually stable under ambient conditions, ii) they show electronic structures basically different from those of the parent empty cages and, iii) they are able to encapsulate metals with magnetic or radioactive properties. Therefore, they offer a wide variety of new possibilities in nanomaterials science and, particularly, in biomedical sciences where they are currently being considered as the next generation of magnetic resonance imaging (MRI) agents and radiotracers.[13]

The fact that the chemistry of fullerenes is not just routine can also be shown in the study of the chemical reactivity of these higher endohedral fullerenes whose chemical reactivity cannot be accurately predicted.

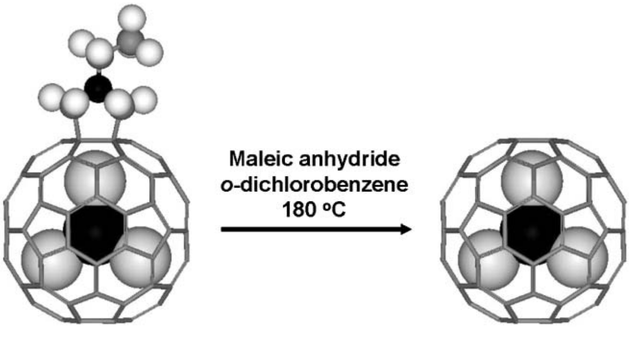


Fig. 2 Isolation of I_h-$Sc_3N@C_{80}$ isomer by retro-Prato reaction. Reproduced from ref. 10 with permission from Wiley-VCH.

Although different endohedral metallofullerenes are known, and a big effort has been devoted to the functionalization of $La@C_{82}$ endohedrals,[14] I would like to focus mainly on the trimetallic nitride templated (TNT) endohedrals which, so far, constitute one of the most abundantly formed and studied classes. The incorporation of a TNT (from groups III, IV and rare-earth metals) into the fullerene results in an electron transfer from the metallic cluster to the carbon cage forming a stable ion pair of ionic nature. Thus, for instance, in the well known $Sc_3N@C_{80}$ a total of six electrons are formally transferred from the three highest occupied TNT orbitals to three low-lying unoccupied cage orbitals. In fact, studies of photoemission and X-ray absorption spectroscopy determined an effective transfer of 6.3 electrons.[15] The resulting endohedral complex has a relatively large HOMO–LUMO gap, which gives it stability. Up to now, only four carbon cages have been capable of encapsulating TNT units: D_3-C_{68}, D_{3h}-C_{78}, D_{5h}-C_{80} and I_h-C_{80} (Fig. 3). All these cages, except C_{68}, satisfy the isolated-pentagon rule and, remarkably, the empty fullerene isomers isolated so far are different from the carbon cages found in isolable TNT endohedral metallofullerenes.[16]

The use of endohedral metallofullerenes for practical purposes, including biomedical applications, requires their chemical functionalization in order to control important aspects such as solubility or further chemical reactivity. This interest in the chemical modification of endohedrals has been very recently undertaken, and important reactions in fullerene chemistry such as Bingel–Hirsch,[17] Diels–Alder[18] or Prato[19] cyclizations, or radical reactions[20] have afforded new modified endohedrals. From a chemical viewpoint, it is important to understand how the exohedral functionalization is affected by the incarcerated metal-doping group. In this regard, experiments have shown a remarkable regioselectivity in addition and cycloaddition reactions due, mainly, to the six electron transfer from the TNT to the fullerene cage which significantly polarizes the cage with the charge densities not equally distributed over all carbon atoms, depending upon the proximity to the TNT unit. Theoretical DFT calculations successfully predict the most reactive exohedral sites, taking into account the double bond character and the pyramidalization angle of the C–C bonds.[21]

It has recently been shown that $Sc_3N@C_{80}$ has a lower thermal reactivity toward disilirane than $La_2@C_{80}$, despite both metallofullerenes having the same electronic structure ($C_{80}{}^{6-}$). This different reactivity has been accounted for by the significant difference in the energy level and spatial distribution of their respective LUMOs.[22]

The first experimental evidence for control of the motion of encapsulated atoms inside the fullerene cage has recently been reported for $Ce_2@C_{80}$ in which the free random motion of two Ce atoms is fixed at specific positions by exohedral chemical functionalization.[23]

The study of the reactivity of endohedral metallofullerenes is just in its very beginning and important questions are still open. How is the chemical reactivity influenced by the metals inside the sphere? Which are the more reactive sites in each type of endohedral (regioselectivity)? Is this exohedral reactivity dependent on the type of reaction (addition, cycloaddition, *etc.*)? How are the incarcerated metals influenced by the exohedral functionalization? These basic questions make endohedral metallofullerenes scientifically appealing enough to guarantee intensive research in this field during the next few years. As a result, these fullerenes can find important and realistic applications in a variety of fields ranging from molecular electronics and nanoscience and nanotechnology to biomedical applications where they are being used as contrast agents in magnetic resonance imaging[24] as well as in nuclear magnetic resonance analysis.[25]

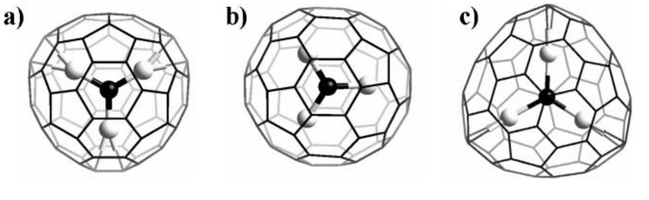


Fig. 3 Endohedral fullerenes: a) D_{3h}-$Sc_3N@C_{78}$, b) C_s-$Sc_3N@C_{80}$ (I_h-C_{80}) and c) D_3-$Sc_3N@C_{68}$. Reproduced from ref. 16 with permission from Wiley-VCH.

2.3 Fullerenes molecular surgery

One of the most outstanding and highly demanding synthetic efforts carried out in fullerene science has been devoted to the controlled opening of the fullerene cage in order to introduce atoms or small molecules inside and then close it, in a series of designed organic reactions. This task was considered to be a dream just ten years ago when the first opening of the C_{60} cage was originally reported by Wudl in his famous paper entitled “There is a hole in my bucky” describing an 11-membered ring opening.[26] Since then, other open-cage fullerene derivatives have been reported in the literature as forming a 13-membered ring bislactone;[27] also reported are other 13- and 14-membered ring openings from bisazide addition to C_{60}.[28]

A different approach, affording a 15-membered ring, was developed by Rubin from an overall sequential triple scission of a 6-membered ring involving a retro [2 + 2 + 2] ring opening step and a further Co(III) complexation.[29] The same group synthesized an open-cage C_{60} derivative with a 14-membered ring orifice and the insertion of molecular hydrogen in 5% yield was achieved, although the closure of the orifice was not attempted.[30]

Very recently, the encapsulation of molecular hydrogen in fullerene C_{60} by organic synthesis (molecular surgical method) has been achieved by Komatsu in a highly efficient method, thus opening the route to the preparation of endohedral fullerenes that encapsulate either small atoms or molecules not accessible by conventional physical methods.[31] The endohedral fullerene $H_2@C_{60}$ (Fig. 4) was found to be as stable as the parent C_{60}, keeping the hydrogen molecule even after heating at 500 °C for 10 minutes. The interest of this molecule is that it can be formally considered as a stable new hydrocarbon molecule that has neither C–H covalent bonds nor C···H interactions.

The importance of this work is similar to the importance of that reported by

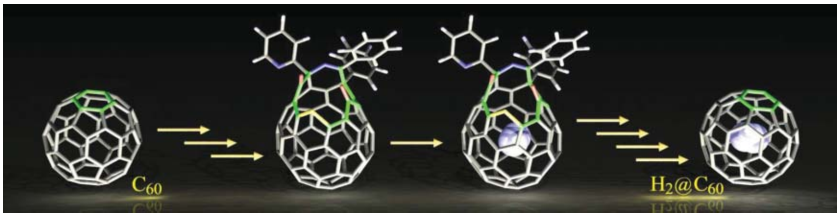


Fig. 4 Encapsulation of molecular hydrogen in C_{60} by molecular surgery. Reproduced from ref. 31(*b*) with permission from The Chemical Society of Japan.

Scott describing the total chemical synthesis of the pristine C_{60}[32] and by Wudl and Hirsch, who reported the azafullerene $C_{59}N$,[33] and shows that organic synthesis represents a powerful and alternative method for the production of unprecedented endohedral fullerenes.

2.4 C_{60}-Based electron transfer models

Photoinduced electron transfer is a fundamental process in Nature since it governs photosynthesis in plants and bacteria. This process occurs *via* a rapid charge separation at the reaction centres with quantitative quantum yield, thus enabling the transformation of sunlight into chemical energy.[34]

Fullerene C_{60} is a redox active chromophore which according to theoretical calculations exhibits a LUMO comparatively low in energy that is triply degenerate. Therefore, C_{60} behaves like an electron accepting molecule able to accept up to six electrons in solution. In comparison with other well known electron acceptors such as *p*-benzoquinone derivatives used by Nature in the photosynthetic process, the C_{60} molecule accelerates charge separation during photoinduced electron transfer processes to form a charge separated state and, however, slows down the charge recombination process in the absence of light. This behaviour has been rationalized by the smaller reorganization energy (λ) of C_{60} compared with other acceptors.[35] These unique electrochemical and photophysical properties of fullerenes have motivated the design of a wide variety of donor–acceptor systems, such as molecular dyads, triads, tetrads and pentads, in which the electroactive units are connected by covalent or supramolecular bonds.[36]

In the context of optimizing charge-separation processes in artificial photosynthetic model systems, photoinduced electron transfer (and energy transfer) from suitable electron donors—namely porphyrins, phthalocyanines, tetrathiafulvalenes, ferrocene and other metallocenes, amines, or π-conjugated oligomers and dendrimers[37]—to electron accepting fullerenes have been studied. The formation of these multicomponent "supermolecules" acting as artificial photosynthetic centres represents one of the most active research areas in fullerene science for the last ten years.[38]

The aim in the design of C_{60}-based photosynthetic mimics has been directed to the formation of long-lived charge separated states in a highly efficient way. For this purpose, the different factors which influence the competition between energy *versus* electron transfer have been analyzed, and factors such as the nature of the photo- and electro-active units, solvent, donor–acceptor distance, molecular topology in which donor and acceptor are connected and arranged in space, and the nature of the spacer connecting them, have been shown to have a strong impact on the photophysical outcome.

Unusually slow charge recombination dynamics has been reported in some molecular dyads which, despite the proximity between the donor and acceptor units, appear to be electronically isolated due to their singular geometry.[39] As a representative example, lifetimes of 230 μs in benzonitrile at 25 °C, an exceptionally long-lived intermediate for a simple molecular dyad, have recently been reported.[40]

We have recently shown the molecular wire behaviour of oligo-*p*-phenylenevinylene (oPPV) as π-conjugated oligomers in a series of "supermolecules" of the type C_{60}–oPPV–Donor (Donor = exTTF, TTF: tetrathiafulvalene; or zinc porphyrinate, ZnP) ranging from the monomer to the heptamer (Fig. 5). Photophysical studies carried out on these systems revealed an exceptionally low attenuation factor ($\beta \sim 0.01$ Å^{-1}) and a strong electronic coupling element ($V \sim 5.5\ \mathrm{cm}^{-1}$) even at distances as large as 5 nm.[41]

Temperature-dependent measurements showed that the charge recombination kinetics in these systems imply an efficient decoupling of the donor and acceptor moieties that leads to a significant slowdown in the rates of electron transfer, with lifetimes in the range of hundreds of nanoseconds.

Two triads (donor–spacer–acceptor), exTTF–BN–C_{60} and ZnP–BN–C_{60}, in which electron donors (*i.e.*, exTTF or ZnP) are covalently linked to C_{60} through a chiral binaphthyl bridge (BN), have been prepared in a multistep

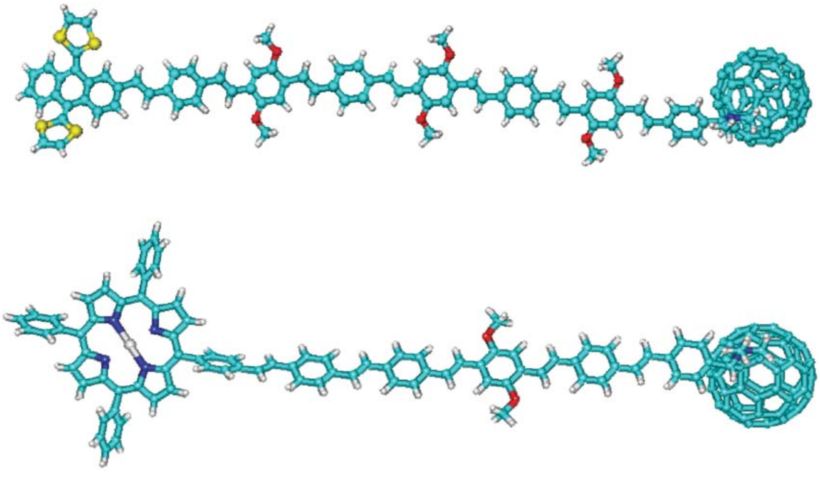


Fig. 5 Molecular modelling of photo- and electro-active exTTF–oPPV–C_{60} (above) and ZnP–oPPV–C_{60} (below) triads.

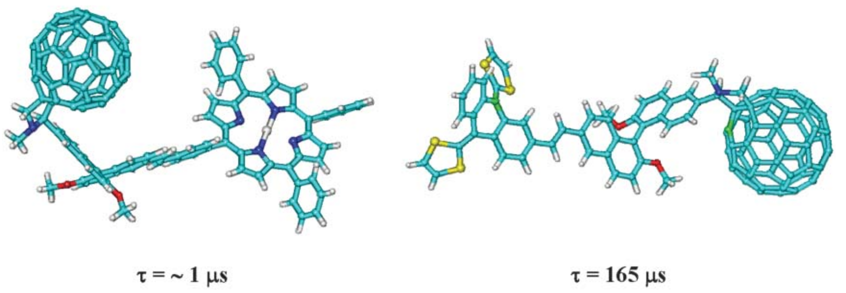


Fig. 6 Molecular modelling of photo- and electro-active exTTF–oPPV–C_{60} (right) and ZnP–oPPV–C_{60} (left) triads connected through a chiral binaphthyl bridge.

synthetic procedure starting from a highly soluble enantiomerically pure binaphthyl building block (Fig. 6). Unlike other oligomeric bridges, with binaphthyl bridges, the conjugation between the donor and the acceptor units is broken and geometric conformational changes are facilitated. Consequently, distances and electronic interactions between the donor and C_{60} are drastically changed. Appreciable differences were observed between the two systems, since geometry favours the electronic communication through donor–acceptor and π–π interactions in ZnP–BN–C_{60}, which is reflected in the measured redox potentials. Excited-state studies, carried out by fluorescence and transient absorption spectroscopy, also support through space rather than through-bond interactions. Although both triads form the corresponding radical-ion pair, that is, exTTFC^{+}–BN–C_{60}^{-} and ZnPC^{+}–BN–C_{60}^{-}, dramatic differences were found in their lifetimes: 165 μs and 730 ns, respectively.[42]

This study has provided an important strategy that allows the lifetime of charge-separated states to be controlled by means of topological effects, thus enabling new insights into photoinduced electron-transfer processes to be gained.

The above examples reveal the potential application of fullerenes for the study of artificial photosynthetic systems in which by means of different strategies it is possible to control the lifetime of the photo-generated charge separated states. These fundamental studies have involved a wide diversity of chemists with differing expertise who are interested in fullerene science and have made it possible to gain a better understanding of those basic principles required for the application of fullerenes in organic photovoltaic devices as will be discussed below.

3 Macromolecular chemistry of fullerenes

3.1 C_{60}-Based polymers

Combining the chemistry of fullerenes with macromolecular chemistry has allowed the preparation of new polymer materials which can be considered a new interdisciplinary field with an enormous scope of applications. To the unique geometrical and electronic properties of fullerenes, the resulting macromolecules provide advantages such as processability, applicability and low cost, affording materials that exhibit outstanding structural, electrochemical and photophysical properties which are currently under intensive research.

A variety of reviews have been devoted to this aspect of fullerene science on which a large number of articles have been published during the last decade.[43] Depending upon the position of the fullerene unit within the polymer chain, different classes of C_{60}-based macromolecules can be prepared. Among the many possibilities to link covalently the fullerene unit to the polymer chain, those molecules bearing the C_{60} sphere in the main polymer chain (pearl necklace or main-chain polymers) or as a pendant unit (charm bracelet or side-chain polymers) have been the most widely studied and were the first used to produce processable fullerene-containing materials. Crosslinked polymers constitute another interesting class of fullerene derivatives which contain multifunctionalized fullerenes but sometimes poorly characterized polymers. From a synthetic point of view, two different approaches have been followed involving: i) the introduction of the fullerene units into a suitably functionalized polymer or, ii) formation of a suitable monomer endowed with a fullerene moiety followed by further chemical polymerization or co-polymerization reactions.

An elegant and rational concept in polymer chemistry has been the design and synthesis of the so-called "double cable" in which a π-conjugated semiconducting polymer (p-type cable) is covalently connected to fullerene units able to interact electronically between them (n-type cable), thus forming a double cable with potential applications for the preparation of new photovoltaic devices.[44] These new polymer containing fullerenes exhibit *a priori* important advantages for the design of efficient photovoltaic materials such as: i) a larger contact between the donor polymer and the accepting fullerene, ii) better control of the electronic interaction between the donor and acceptor moieties by means of the nature of the π-conjugated polymer and the length of the spacer connecting them, and iii) the drawback of phase segregation found in polymer/C_{60} blends is prevented by the covalent linkage between them.

The approach for synthesizing plastic materials for photovoltaic applications presents some additional advantages such as lower production costs than the current silicon technology, lower environmental impact and the many possibilities that flexible devices offer for a wide variety of applications.

The first real example of a double-cable polymer was reported by Diederich, Gross, Seiler and coworkers in 1994[45] by electrochemical polymerization of bis(trimethylsilyl)methanofullerene, affording a polyacetylene derivative (**4**). Since then, many other remarkable examples obtained by electrochemical polymerization as well as chemical polymerization have been described in recent years.[46]

Some representative examples of electrochemically obtained polymers are shown in Fig. 7. The choice of bithiophene as a polymerizable unit leads to a higher degree of polymerization compared with the parent thiophene.[47] A very recent example of electropolymerized double-cable polymer with the C_{60} units connected to the terthiophene moiety through a thieno[3,4-*b*]pyrazine bridge as a bisfulleroid has been reported by Wudl, Rubin and co-workers.[48] The polymer band-gap determined by

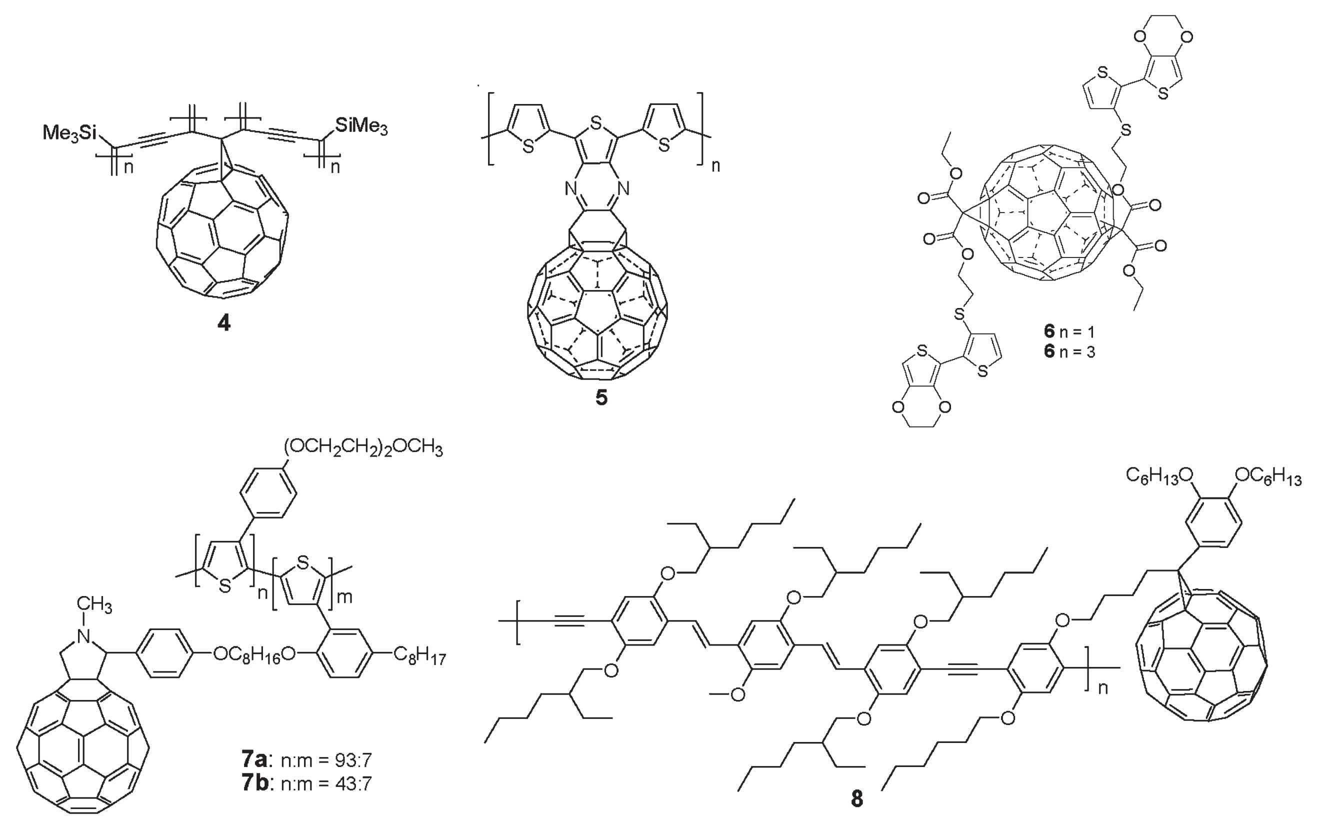


Fig. 7 Some representative examples of electrochemically- (**5–6**) and chemically- (**7–8**) polymerized fullerene derivatives.

different techniques afforded a remarkably low value on the order of 0.7 eV (**5**). In the search for improved stability and faster switching response, electropolymerization of precursors bearing two or more polymerizable groups has also been reported. A remarkable example has been described by Roncali, Blanchard *et al.* with polymers (**6**).[49] The peak potentials are shifted to less positive values, thus suggesting that electropolymerization of the two-site precursors gives rise to a more extensively conjugated polymer (Fig. 7).

An important drawback of polymers prepared by electropolymerization is that they often tend to be insoluble and difficult to characterize, thus limiting their potential applications. In order to prevent this problem, different chemical strategies have been followed which, in turn, result in synthetic time-consuming steps in a tedious process which affords materials in low total yields.

Some representative examples of polymer structures (**7–8**) obtained by chemical methods in which a part of the molecule, usually the donor unit, is responsible for the solubility of the final molecule, are shown in Fig. 7. However, the presence of long solubilizing alkyl chains in the molecule drastically reduces the fullerene content in the final polymer, thus decreasing the photovoltaic properties for which they were designed.

Polymers **7a,b**[50] and **8**[51] are the first examples of fullerene containing macromolecules used as the only electroactive layer in photovoltaic cells. Although remarkable open circuit voltages (V_{oc}) were measured in the PV cells, they showed low energy conversion efficiency values, probably as a consequence of the low fullerene content (**7a,b**: 7–14%; **8**: 38.5%) compared with the amount of fullerene in the more efficient cells reaching up to 80%.

Although the double-cable approach represents a different concept for the preparation of new materials for energy conversion with a high content of chemical design and imagination, their performance has not satisfied the expectations, and the efficiencies obtained with them have not so far reached the values found by simply blending the polymer with the fullerene derivative. A more detailed study is therefore necessary on these rational systems in order to determine those factors that control their energy conversion efficiencies.

3.2 Fullerenes for photovoltaic cells

The first evidence of the interest of fullerenes for photovoltaic (PV) applications stemmed from the discovery of a highly efficient photoinduced electron transfer process from a photoactive semiconducting π-conjugated polymer to C_{60} in 1992.[52] Since then, a lot of interdisciplinary effort has been devoted to these polymer/fullerene materials for the fabrication of organic photovoltaic devices.[53] In the former blends, the electronic interaction between the electron donor polymer (p-type component) and the fullerene as the acceptor n-type component in two layer (p/n) photovoltaic cells was limited to the interface between the two materials. The concept of "bulk heterojunction" solar cells improved drastically this interaction and, therefore, the efficiency of electron transfer, by mixing both components in the entire volume of material. A major drawback was, however, the lack of miscibility between the π-conjugated polymer and C_{60} resulting in phase segregation and clustering of the fullerene component, thus decreasing the donor–acceptor electronic interaction as well as the charge transport of the photogenerated electrons and holes.[54]

In order to overcome this problem and to form PV cells from polymer/fullerene blends in which both components are intimately mixed to create a larger interface, where exciton dissociation occurs preferentially, some soluble fullerene derivatives endowed with solubilising groups were synthesized. The most successful and studied fullerene derivative has been PCBM (**9**) {1-(3-methoxycarbonylpropyl)-1-phenyl[6,6]methanofullerene}, first obtained by Hummelen and Wudl in 1995 (Fig. 8).[55] This methanofullerene derivative is a quite robust compound, highly soluble in aromatic hydrocarbons (> 180 mg/ml in *o*-dichlorobenzene) and in CS_2.

The first PCBM-based bulk heterojunction solar cell, prepared by blending it with MEH-PPV (*p*-phenylenevinylene derivative), formed, in contrast to pristine C_{60}, homogeneous and stable blends with more than 80 weight percent of fullerene derivative which showed reasonable photovoltaic parameters. Power conversion efficiencies of 2.5% under AM1.5 illumination have been reported for bulk-heterojunction solar cells in which the active layer is a 1 : 4 weight percent mixture of poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and PCBM. More recently, PV cells prepared from MDMO-PPV and the related [70]PCBM (prepared from C_{70} as isomeric mixture, instead of C_{60}), which exhibits better absorption in the visible region of the electronic spectra in comparison with the related [60]PCBM, afforded 50% higher current densities with overall power conversion efficiency measured under standard conditions (AM1.5) of 3.0%.[56]

Although some other fullerene derivatives such as the DPM (diphenylmethanofullerene) derivative (**10**) have been synthesized and blended with other photoactive π-conjugated polymers (P3HT/DPM), and good photovoltaic parameters (V_{oc} = 0.92 V) have been found with energy conversion efficiencies as high as 2.3%,[57] most of the recently published studies showing better efficiencies have been carried out on poly-3-hexylthiophene as the conjugated polymer and PCBM as the acceptor component. In these studies reporting the highest efficiencies reached in organic bulk-heterojunction solar cells, the fundamental aspects are related with the device preparation rather than with the chemical modifications. Thus, Yang has reported efficiencies of 4.4% in P3HT/PCBM by controlling the active layer growth rate which results in turn in an increase of the mobility and balanced charge transport.[58] The last and highest result has been reported by Heeger using the same chemical components (P3HT/PCBM) but applying specific fabrication conditions and further annealing at 150 °C, to reach a power conversion efficiency approaching 5%.[59] The improved nanoscale morphology, increased crystallinity of the semiconducting polymer and the improved contact to the electron-collecting electrode remarkably facilitated charge generation, charge transport and charge collection to the electrodes, thus increasing the device efficiency.

These last results on readily available PV cells prepared by low cost and simple processing clearly bring this class of organic solar cells closer to commercialization.

4 Supramolecular chemistry of fullerenes

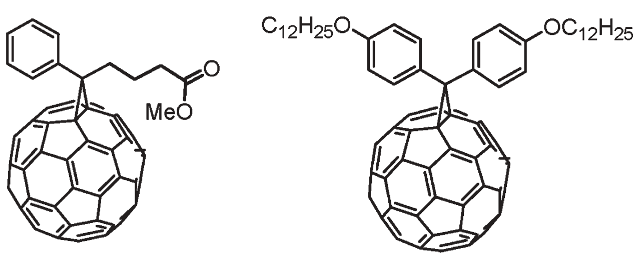
Since the coining of the term "supramolecular chemistry" defined by Lehn in 1978,[60] this branch of science has undergone a spectacular expansion. In this active research area, the application of supramolecular principles to fullerenes has received considerable attention.

The control of weak forces, on a molecular basis, to define the size and shape in relation to function of the resulting supramolecular ensembles is still a major task in chemistry. In this regard, the three-dimensional rigid structure of fullerenes as well as their remarkable electronic properties constitutes a unique scaffold for the development of unprecedented 3D architectures. For these purposes the different types of weak forces, namely hydrogen-bonding, π–π stacking, metal-mediated complexation and electrostatic interactions, have been used in fullerene chemistry to construct new non-covalently bonded architectures.[61] A fundamental aspect in the construction of new ensembles involving these biomimetic motifs is that, in contrast to covalently bonded structures, they are reversible and their binding energies can be tailored "at will" by means of the chemical environment and temperature.

Although a lot of work has been devoted to the synthesis of supramolecular ensembles involving fullerenes, we will focus only on the highly selective and directional hydrogen bond which has recently afforded a wide variety of new architectures in which electron transfer processes between different donor units and the electron acceptor fullerene occur as efficiently as in the related covalently connected dyads.[62] This supramolecular approach places the so obtained artificial photosynthetic systems of type donor···C_{60} one step closer to the electron transfer occurring in Nature, thus mimicking the photosynthetic process.

The first H-bonding supramolecular fullerene dimer (K_a = 970 M^{-1} in $CHCl_3$) was reported by Diederich, Echegoyen and Stoddart in 1999.[63] Other highly stable self-complementary dimers prepared from 2-ureido-4-pyrimidone moieties were also obtained soon after.[64] Since then, H-bonds have been used to construct more sophisticated ensembles involving photoinduced electron transfer processes which have recently received a lot of attention from the chemical community.

The first examples of electron transfer processes from an electron donor unit to C_{60} involving an H-bonding



9 **10**

Fig. 8 Some modified fullerenes (**9**: PCBM, **10**: DPM) for PV applications.

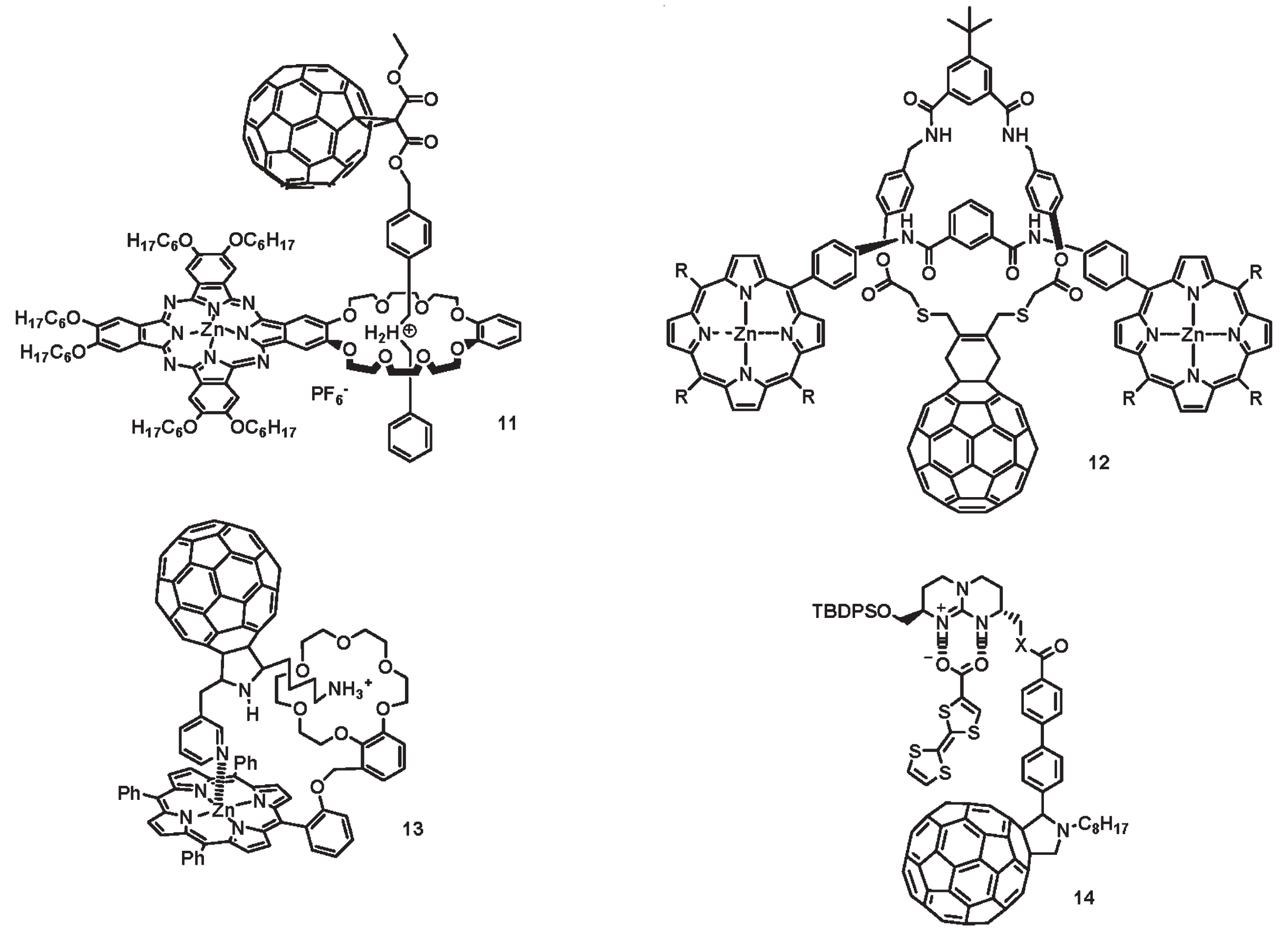


Fig. 9 Some representative supramolecular $C_{60}\cdots$Donor examples.

network have only recently been reported (Fig. 9). Guldi, Torres, Prato and co-workers described a $C_{60}\cdots$ZnPc (Pc: Phthalocyanine) (**11**) with a lifetime for the photo-generated charge separated state in the range of microseconds, which is significantly longer than those found for related covalently connected C_{60}–ZnPc dyads.[65]

Several H-bonded $C_{60}\cdots$ZnP (P: Porphyrin) model systems have been reported during the last three years. One such example was the rotaxane-type dyad **12** which showed a radical-ion pair with a lifetime of 180 ns.[66]

A remarkable type of highly stable supramolecular $C_{60}\cdots$ZnP complex (**13**), held together through a two-point binding strategy which allows control of the distance and orientation between the two photo- and redox-active chromophores, has recently been reported by D'Souza *et al.*[67] Another interesting example is the $C_{60}\cdots$ZnP dyad tethered by means of a guanosine–cytidine network which afforded photoinduced charge separated states of 2.02 µs.[68]

The first examples of $C_{60}\cdots$TTF (TTF: Tetrathiafulvalene[69]) dyads (**14**) with the electroactive units connected through complementary hydrogen bonds and strong electrostatic interactions through guanidinium and carboxylate ion pairs have afforded charge separated states with lifetimes in the range of hundreds of nanoseconds, reflecting through space electron transfer processes.[70]

It is interesting to note that in the above representative examples, H-bonding offers new possibilities for constructing biomimetic artificial photosynthetic systems as well as a general beneficial effect in terms of lifetimes for the photogenerated radical ion pairs. Therefore, this is a new and appealing approach to prepare [60]fullerene-based artificial photosynthetic systems which clearly resemble the natural photosynthetic processes.

An interesting cooperative effect has been found between ammonium hosts–crown ether guests and π–π interaction between fullerene C_{60} and the *o*-PPV (oligo-*p*-phenylenevinylene), which significantly increases the binding constants. Thus, complexes constituted by an *o*-PPV bearing a crown ether (**15**) and a fullerene derivative endowed with an ammonium salt (**16**) showed an association constant two orders of magnitude higher than those reported for related systems between crown ether receptors and alkyl- or arylammonium hosts (Fig. 10).[71]

This concept has also been extended to bis-ammoniumfullerene ligand complexed with a receptor bearing two crown ethers and a perfect complementarity has been observed with remarkable binding constant values. This methodology is a powerful tool for the design of new ensembles by following the easy "supramolecular click chemistry" recently defined by Dorsselaer, Albrecht-Gary

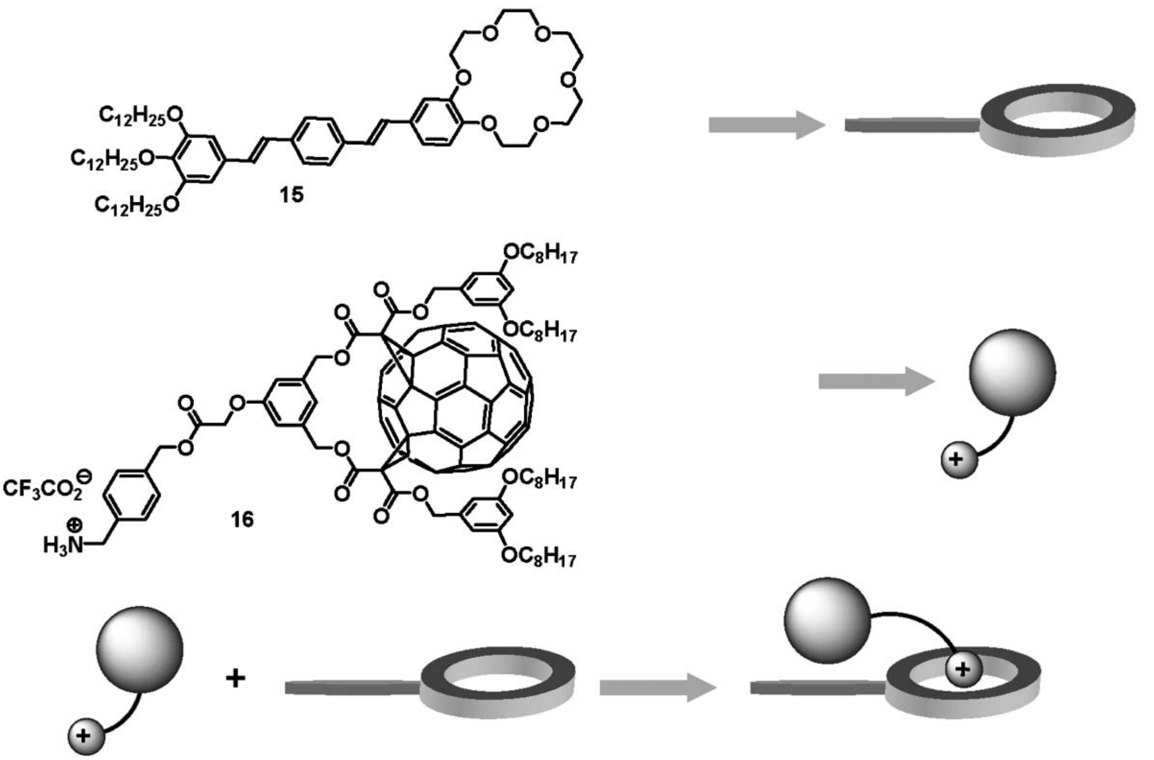


Fig. 10 Cooperative effects between hosts–crown ether guest and π–π interaction between C_{60} and the *o*-PPV moiety.

and Nierengarten,[72] in analogy to the interesting concept of "click chemistry" first defined by Sharpless.[73]

Another approach to supramolecular ensembles for PV applications has recently been reported by Bassani with the complex fullerene barbituric acid and pentathienylmelamine conjugate (**17**) (Fig. 11), in which the π-conjugated system allows better light harvesting in the visible region, thus improving the efficiency of the incident light and the PV response. In fact, the measured photocurrent in the PV cell prepared from this complex was three-fold that measured for the related device prepared by simply blending oligothiophene and C_{60}, suggesting the influence of the order in the solid state to improve the charge separation and charge transport phenomena in the PV devices.[74]

The application of the above supramolecular concepts to the construction of macromolecules has allowed the preparation of new supramolecular polymers in which the order induced by means of weak forces could result in better properties. This study is currently under intensive research and several examples have already been reported.

Hummelen and co-workers reported a supramolecular polymer **18** (Fig. 11) from a self-complementary monomer endowed with two ureidopyrimidinone units able to form a quadruple H-bonding network resulting in binding constants as high as $6{\cdot}10^7\ M^{-1}$.[75]

A most appealing supramolecular H-bonded polymer is that constituted by a π-conjugated polyphenylenevinylene-carbazole bearing uracil moieties which connect to complementary 2,6-diamino-pyridine–C_{60} units through a threefold H-bonding (**19**) (Fig. 11).[76] Although no PV devices have been reported so far, fluorescence measurements reveal remarkable interactions between the photo- and electro-active units.

The interest of these new C_{60}-based polymers lies in the order that supramolecular principles can induce in the solid state, thus improving the electronic interactions between the donor and acceptor units. This concept has not been properly developed so far but significant advantages in terms of synthetic availability of the components and better control of the solid state molecular organization can be clearly envisioned.

5 Summary and outlook

Important and emergent research areas have been presented in this short review on those aspects which represent new concepts in the advance and development of fullerene science, many of which will be properly exploited during the next few years.

Up to now, we can state that fullerenes have become a useful 3D building block in chemistry with application in many different fields. This aspect is important enough to consider fullerenes as a unique class of compounds in their own right. Although this is not enough to satisfy all the expectations that emerged from their initial discovery and preparation, important and in some cases really outstanding properties have been found in these carbon allotropes that probably will find real applications in the near future. Thus, fullerenes have not only contributed to the advance of chemical concepts at the basic research level, but they are also allowing the exploration of many new possibilities in applied fields.

The aim of this focus article is to show that although fullerenes are becoming a mature science, many aspects, from basic synthetic aspects and chemical reactivity to new unknown higher fullerenes and their application in the search for new material properties at a molecular level, are still waiting to be studied. The state of the art in fullerene synthesis has

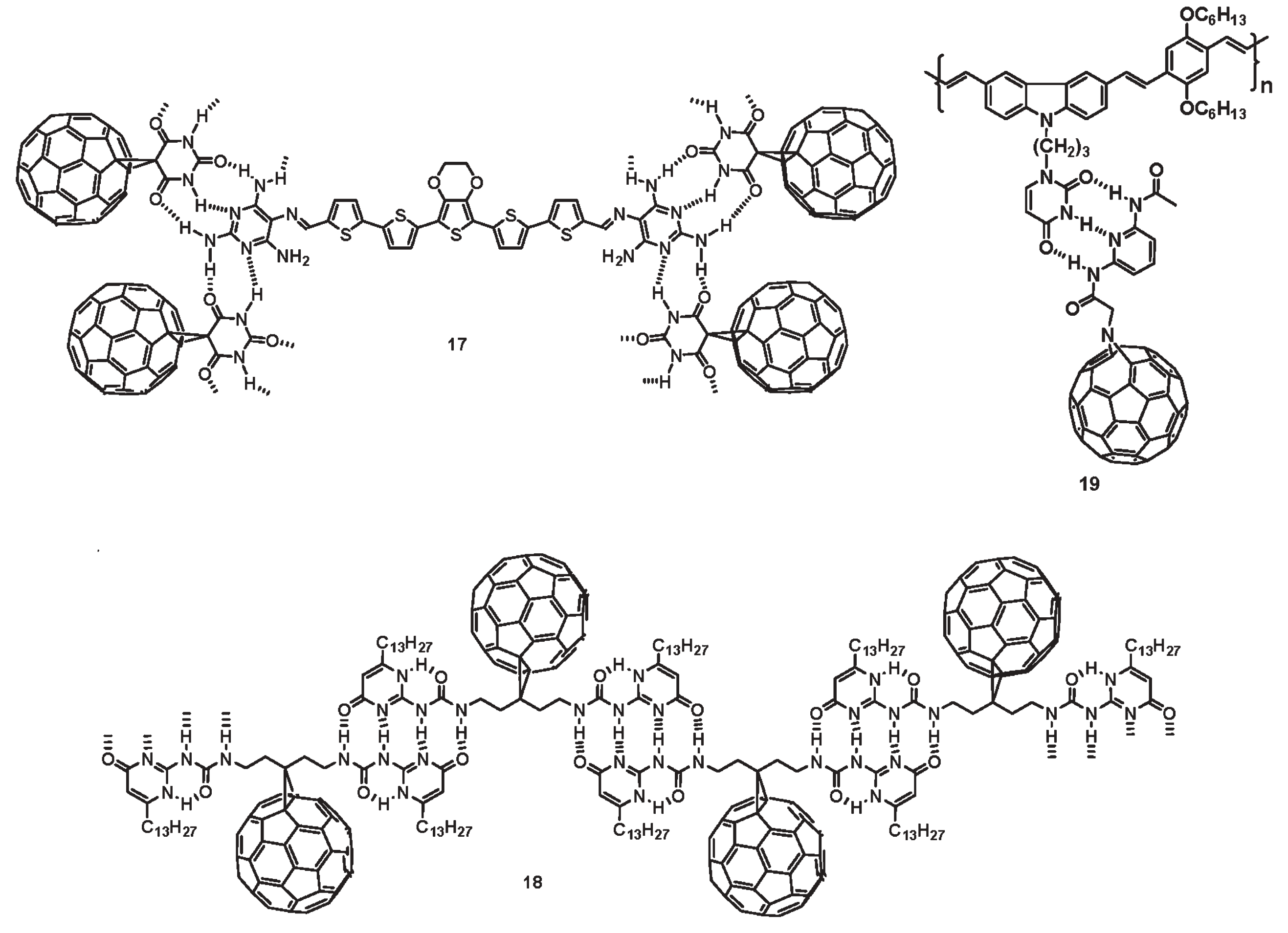


Fig. 11 Some representative examples of fullerene-containing supramolecular ensembles for photovoltaic applications.

allowed the preparation of amazing smart supermolecules able to perform a precise function. Macromolecular fullerenes represent another important research area in which, despite the efforts carried out on the synthesis of different classes of C_{60}-based polymers, relevant applications should result in the near future, provided that they can be easily produced and applied for different purposes. Among the potential uses of macromolecular fullerenes, as previously stated, photovoltaic cells constitute one of the most realistic applications. In this regard, recent results reporting solar energy conversion efficiencies close to 5% are promising for commercialization.

The less studied supramolecular aspects of fullerenes open new possibilities in fullerene science where new supramolecular architectures are currently being constructed. The different weak forces responsible for supramolecular order have allowed the study of new artificial photosynthetic systems, thus mimicking the fundamental photosynthetic processes. By following the same strategy, the first supramolecular fullerene containing polymers have recently been prepared and important results should stem from the combination of supramolecular and macromolecular fields.

No mention has been made in this focus article of the very promising carbon nanotubes which have already been solubilized and chemically functionalized with different functional groups, including photo- and electro-active units.[77] In addition, endohedral NT have also been obtained. Because of their outstanding electronic properties, they are currently under intensive research investigation in the emerging nanoscience and nanotechnology fields, where they are considered to be highly versatile building blocks. Closely related are the less known carbon nano-onions, some of which ($C_{60}@C_{240}@C_{540}$) have already been obtained in a controlled manner, which have also been recently functionalized,[78] thus starting the first steps towards the study of their chemical and photophysical properties.

Science has provided plenty of examples of molecules/materials that have resulted in significant advances in social development. Fullerenes have attracted the interest of scientists because of their unprecedented perfect round shape and high symmetry. It can be expected that they will also yield multiple applications but these will take some time. In the meantime we will continue to play and enjoy their interesting structures and properties.

Acknowledgements

I would like to apologize to all those colleagues whose work has significantly contributed to the development of fullerene science but, because of the length limitation and nature of this article, has not been mentioned or discussed

properly. This article is dedicated to all of them and, particularly, to Fred Wudl, for his outstanding contributions to fullerene science, on the occasion of his 65th birthday. Fred Wudl introduced to many young scientists (today not so young) the challenges of the third allotropic form of carbon.

I would also like to recognise the enthusiasm and efforts of the many young scientists who have been active in my research group during many years of intensive research in fullerene science. Thanks to all of them for their important contributions.

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