FEATURE ARTICLE

[60]Fullerene chemistry for materials science applications

Maurizio Prato

Dipartimento di Scienze Farmaceutiche, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy

Since their first detection and bulk production, the fullerenes have gained a primary role on the scientific scene, reaching their climax when the 1996 Nobel Prize for Chemistry was awarded to Kroto, Curl and Smalley for their seminal discovery. The unique physical and chemical properties of these new forms of carbon led many scientists to predict several technological applications. This created a heavy disappointment when it was clear that fullerene-based materials would not soon be ready for the market. However, the fullerenes have so far delighted several dozens of researchers who found that C_{60} and its relatives undergo a variety of chemical reactions. In most cases, the new derivatives retain the main properties of the original fullerene, and it is now not unlikely that some functionalized fullerenes may find useful applications in the field of materials science and technology. In this Article we summarize the basic principles of the organic chemistry of fullerenes, together with a description of the physicochemical properties that have made these carbon cages popular in materials science, and review the most recent achievements in the functionalization of fullerenes aimed at the production of new molecular materials.

[60]Fullerene, the most abundant representative of the fullerene family,[1] was produced for the first time on a preparative scale in 1990, by resistive heating of graphite.[2] The availability of milligram quantities of C_{60} generated an extraordinary outburst of academic and industrial research that led to the discovery of several interesting physical properties, along with a careful definition of the chemical reactivity of the fullerenes.[3–10] Among the most spectacular findings, C_{60} was found to become a superconductor in M_3C_{60} species (M = alkali metal),[11–14] an organic soft ferromagnet in $TDAE^{+}VC_{60}^{-}V$ (TDAE = tetrakisdiethylaminoethylene),[15] a relatively stable hexaanion in cyclic voltammetry,[16,17] and an interesting material with non-linear optical properties.[18,19]

It was immediately clear that a new molecular material had been discovered with enormous potential in several different disciplines. Especially in materials science, the rich electronic and electrochemical behaviour generated great expectations. However, the difficult processibility of the fullerenes has represented a major problem in the hectic search for practical applications. C_{60}, in fact, is insoluble or only sparingly soluble in most solvents and aggregates very easily, becoming even less soluble.[20] This serious obstacle could be, at least in part, surmounted with the help of the 'functionalization chemistry of the fullerenes'.[21–29] The organic derivatization of C_{60} has put forth an increasingly high number of compounds which, while retaining most of the original properties of the fullerene, become much easier to handle.

In this review we will focus on the use of fullerene chemistry to produce compounds useful in materials science and technology. An exhaustive review of all the literature produced so far on this argument is beyond the scope of the present work. An attempt will be made to give an idea of the potential of the fullerene materials in practical applications.

First, we will briefly review the basic principles of the chemical reactivity of C_{60}, as the chemistry of fullerenes has already been reviewed in detail by several authors.[21–29] We shall then illustrate the main physicochemical properties that have made fullerenes popular materials. We will finally address the main subject of this review, considering only materials derived from functionalized C_{60}. For unmodified C_{60}-based thin films and materials, the reader is referred to a recent, excellent review.[30]

Basic Principles of C_{60} Chemistry

The C_{60} surface contains 20 hexagons and 12 pentagons. All the rings are fused, all the double bonds are conjugated. Initially hypothesized as a 'super aromatic' molecule, C_{60} was rather found to possess a polyenic structure, with all the double bonds inside the six-membered rings.[31] X-Ray crystal structure determinations on C_{60} and on some of its derivatives have proved the existence of two different types of bonds: 'short bonds' or 6,6 junctions, shared by two adjacent hexagons (*ca.* 1.38 Å long) and 'long bonds', or 5,6 junctions, fusing a pentagon and a hexagon (*ca.* 1.45 Å long). The geometric demand of the spherical cage is such that all the double bonds in C_{60} deviate from planarity.[13] This pyramidalization of the sp^2-hybridized carbon atoms confers an excess of strain to C_{60} which is responsible for the enhanced reactivity of the fullerene. A release of strain is in fact associated with the change of hybridization from sp^2 to sp^3 that accompanies most chemical reactions.[32]

The chemical reactivity of C_{60} is typical of an electron-deficient olefin. C_{60}, in fact, reacts readily with nucleophiles and is a reactive 2p component in cycloadditions.[33] The vast majority of reactants will attack the 6,6 ring junctions of C_{60}, which possess more electron density. Insertions into 5,6 bonds have been reported only as rearrangements following a 6,6 junction attack (see below).

The main objective of fullerene chemistry is the production of well-defined, stable and characterizable adducts. In this respect, several different approaches have given excellent results. The reaction types can be of widely different nature, but the single-addition products can be classified into a few broad categories, based on the structure which is obtained. In particular, with relation to the geometrical shape built on a 6,6 ring junction of C_{60}, there can be: an open structure; a three-membered ring, which also includes carbon or nitrogen insertion into a 5,6 ring junction; a four-membered ring; a five-membered ring; a six-membered ring (Fig. 1).

In general, the word dihydrofullerenes has been coined to specifically indicate a monofunctionalized fullerenes, or else the word organofullerene more widely indicates a fullerene derivative containing an organic appendage.

Open structures

Adducts can be obtained by careful hydrogenation (Nu = E = H),[34–38] or by addition of a nucleophile followed by quenching with acid or an electrophile (Scheme 1).

Usually a 1,2-addition is observed, but 1,4-additions have been reported in a few cases where hindrance between sterically demanding addends becomes relevant. Nucleophiles success-

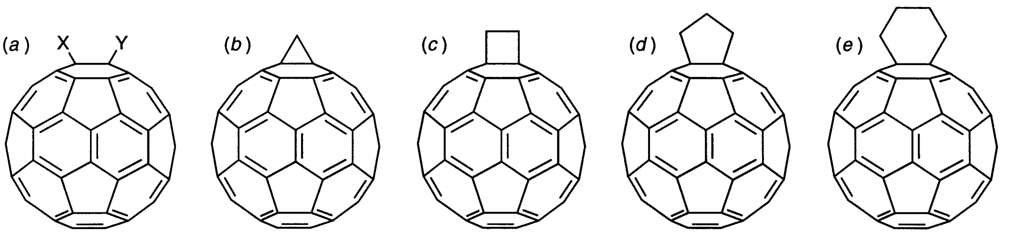
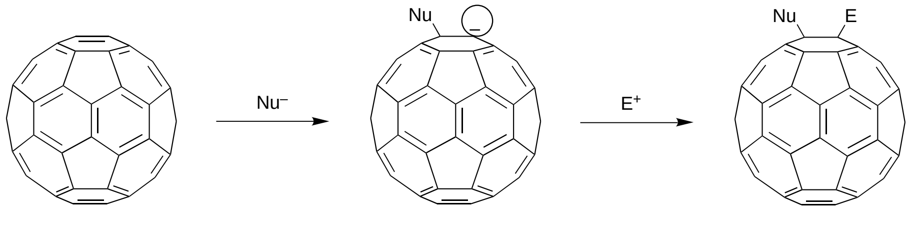


Fig. 1 Geometrical shapes built onto a 6,6 ring junction of C_{60}: (*a*) open, (*b*) three-membered ring, (*c*) four-membered ring, (*d*) five-membered ring and (*e*) six-membered ring



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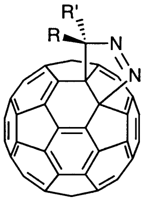
Scheme 1

fully employed include Grignard reagents,[33,39,40] organolithium derivatives,[39–41] cyanide ion,[42] *etc.*[43–55] A case which illustrates the utility of this approach to produce interesting materials is reported in Scheme 1. Cyanide addition to C_{60}, followed by quenching with toluene-*p*-sulfonyl cyanide, led to the synthesis of a dinitrile derivative **1** (Nu = E = CN).[42] As detected by cyclic voltammetry, **1** and also other monocyano-dihydrofullerenes display interesting properties, allowing a fine-tuning of the electron-accepting capacity of cyanodihydrofullerenes.

Three-membered rings

This category represents one of the most fascinating and thoroughly investigated classes of functionalized fullerenes. The addition of diazomethane derivatives to C_{60}, pioneered by the Wudl group,[21,25,56] can lead to two different structures, commonly called fulleroids **3** and methanofullerenes **4**.



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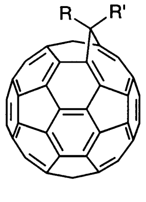

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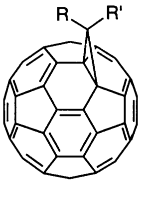

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The first step of the reaction is a 1,3-dipolar cycloaddition of diazomethane to C_{60}, yielding a pyrazoline derivative **2**, isolated only in the case of diazomethane,[57] but not in other cases. Extrusion of nitrogen leads typically to a mixture of fulleroids and methanofullerenes.[58,59] Conversion of fulleroids to methanofullerenes can be achieved (in most cases, but not for R = R′ = H[60]) thermally,[25,58] electrochemically[61] or photochemically.[62] It can also be acid-catalysed.[63] A wide variety of diaryl, aryl-alkyl and dialkyl fulleroids and methanofullerenes[21,25] have been prepared so far, providing materials for potential applications in many fields (see below).

Three-membered rings fused on 6,6 junctions of C_{60} can be produced cleanly (without formation of fulleroids) electrochemically[64] or by addition of nucleophiles,[65–67] diazirines,[68] carbenes,[69–72] sulfonium ylides.[73]

Azide additions to C_{60} follow closely the reaction course of diazo compounds. In this case, triazoline derivatives can be isolated and characterized,[74] which, after extrusion of nitrogen, lead to azafulleroids.[75–77] If nitrenes are generated instead, azamethanofullerenes are formed.[77–83]

It is interesting to note that, among the many families of organofullerenes, fulleroids and azafulleroids are the only derivatives which maintain the 60p electron configuration typical of C_{60}.

Four-membered rings

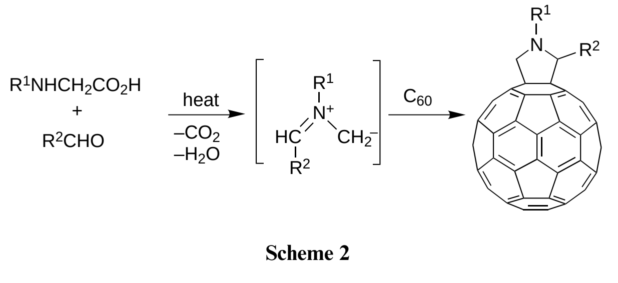
Cyclobutanofullerene derivatives are typically obtained by [2+2] cycloadditions. Benzyne addition was reported first,[84,85] followed by addition of electron-poor alkenes,[86–88] electron-rich alkenes and alkynes.[89–92] [2+2+2] Cycloaddition of quadricyclane to C_{60} gave rise to a norbornene derivative[93] which was used for polymer preparation.[94]

Five-membered rings

These are usually prepared by [3+2] cycloadditions. A variety of carbocyclic or heterocyclic systems have been reported, which include cyclopentane derivatives,[95,96] pyrrolidines,[81,97–101] isoxazolines,[102–104] pyrazolines,[105] furans,[106] *etc.*[107,108] The addition of azomethine ylide to C_{60}, leading to fulleropyrrolidines, is becoming increasingly popular (see below). The reason for such success is probably due to the simple approach, as starting materials are usually commercially available or easily prepared, and a single product of monoaddition across a 6,6 junction of the fullerene is obtained (Scheme 2).

Six-membered rings

The classical [4+2] cycloaddition to C_{60} produces six-membered rings fused to 6,6 junctions.[95,109–122] This is also a very

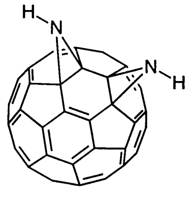


Scheme 2

popular reaction, utilized by many groups, which has offered entries to a wide variety of functionalized fullerenes (see below).

Holes

Ever since the fullerenes were discovered, the idea of trapping atoms, molecules or ions inside the carbon cage has fascinated the scientific community.[1,123] It is in fact believed that novel materials with peculiar properties may be produced. Whereas some fullerenes containing transition metals inside have been isolated,[124] the preparation of bulk quantities of inclusion assemblies would require a chemical modification of C_{60} such that a hole is opened on the fullerene surface by breaking one or more double bonds. Then the atom, molecule or ion must be forced inside the cage and trapped by restoring the carbon–carbon bonds. Conceptually very simple, the opening of a hole on the fullerene cage proved very difficult. The first orifice generated was obtained by oxidative light incision.[125] The sample, however, was prepared on an analytical scale, and was only characterized by IR spectroscopy. An eleven-membered ring hole was produced on the fullerene surface by means of regioselective diaddition of azides.[76] Other holey spheres have been obtained on preparative scales, and the resulting compounds fully characterized.[126–128] A very interesting result has been disclosed recently by Hirsch and collaborators, who reported the first example of chemical modification of fullerenes that allows the synthesis of open and closed valence isomers with the same addition pattern. They found that diadducts **5** and **6** formed by addition of azides to C_{60} possess different structures, depending on the substituent on the nitrogen atom. Unsubstituted diadduct **5** is locked in the ring-closed form, whereas a carbamate functionality gives rise to the open form, which has a relatively large hole.



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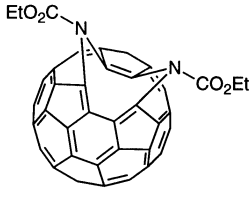

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Saunders and collaborators have demonstrated that at very high temperatures (650 °C) and pressures (3000 atm) the noble gases helium, neon, argon, krypton and xenon can be introduced inside the cage in one in every 1000 molecules of C_{60}.[129] A temporary bond breaking of the cage has been proposed to explain the process. For obvious reasons this methodology cannot be extended easily to other guests but noble gases. In addition, Saunders warned that conventional chemical synthesis at ambient pressures, though elegant, may not succeed, due to the small free volume inside the fullerene sphere.

Heterofullerenes

Another objective of fullerene chemistry relates to the possibility of substituting one or more carbon atoms of the cage with heteroatoms.[130–132] This substitution leads to heterofullerenes, which may possess properties different from the parent fullerenes. The most popular heteroatom so far incorporated in fullerenes is nitrogen,[133,134] and the C_{60} homologue has been isolated in bulk quantities as its dimer is $(C_{59}N)_2$.[135,136] The chemical and physical properties of these new compounds are the object of intense current investigations.[137,138]

Multiple additions

Without taking into account 5,6 bonds (which can undergo insertions, see above), C_{60} possesses 30 equivalent double bonds, all sharing the same reactivity. Typically, the addition of a nucleophile to a 6,6 bond of C_{60} in a stoichiometric amount leads to a complex mixture containing one product of monoaddition together with several multiple addition products. Usually, the monoadduct is separated by chromatography and the multiple adducts discarded. This is because a mixture of diadducts (from a symmetrical reagent) can contain up to eight different positional isomers, with the number of possible isomers increasing with the number of additions. Isomers inside each family of adducts (monoadducts, diadducts, triadducts, *etc.*) tend to possess the same chromatographic properties, and this makes the separations a very complex operation. Therefore, addition conditions are usually optimized for the maximum yield of the monoaddition product, with little attention to more highly functionalized fullerenes.

Recently, the chemistry of multiple additions to the fullerene core has become a fundamental issue in the design of useful C_{60} derivatives, and several research groups have taken the challenge of isolating and characterizing diadducts as well as higher adducts. Investigations of polyadditions have been carried out using osmylation,[139] g^2-metal complexation,[140–142] hydrogenation,[143,144] cyclopropanation,[145–150] azide addition,[76,77,151,152] [4+2] cycloaddition,[113,148,149,153,154] [3+2] cycloaddition,[155] azomethine ylide cycloaddition,[156] silylation,[157] epoxidation[158,159] and amine addition.[50,160]

In particular, the Hirsch group and the Diederich group have engaged in a systematic study aimed at determining the factors that govern the regiochemistry of these additions and at gaining control over multiple additions. The German team, after isolating and characterizing all diadducts formed in the base-catalysed addition of bromomalonates,[145] reached the conclusion that the addition of a second nucleophile does not occur randomly, but is controlled by the frontier molecular orbitals of the monofunctionalized fullerene.[146] Furthermore, in a decisive step toward the synthesis of hexakis adducts, the same group employed the reversible addition of 9,10-dimethyl anthracene to produce the T_h-symmetrical hexakis adduct of cyclopropanation of C_{60} with an octahedral addition pattern in an astonishing 48% yield.[161] On the other hand, the strategy used by the ETH group has been the tether-directed functionalization of C_{60}, which produces exclusively adducts derived by equatorial addition.[29,148] This approach has allowed the Swiss group to achieve outstanding results, like two solubilized representatives of a new class of carbon allotropes, C_{195} and C_{260}.[162] A unique case of topochemically controlled fullerene difunctionalization has been recently reported.[153] In the solid state, when heated at 180 °C for 10 min, the crystalline monoadduct of C_{60} and anthracene evolved to the antipodal diadduct in a quantitative way.

Polyhydroxylated C_{60} derivatives, fullerenols $C_{60}(OH)_{10-12}$, can be obtained by different methods.[163–166] The hydroxy groups are randomly distributed on the fullerene surface, generating mixtures of isomeric structures, but providing a high density of reactive sites useful for practical applications (see below).

Although complete control over the addition chemistry of the fullerenes has yet to be reached, the encouraging results reported so far give way to the hope that, in the future, the fullerenes, and in particular C_{60}, may be used as building blocks in the construction of very complex molecular assemblies.

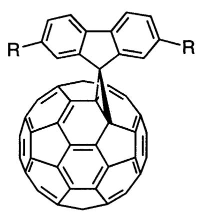
Physicochemical properties of fullerene derivatives

Electrochemical properties

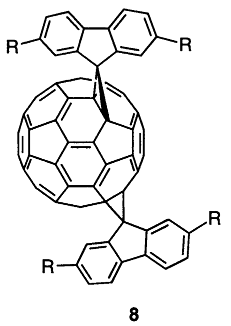
From the early days of the functionalization chemistry, the electrochemistry of fullerene derivatives has been systematically studied by the Wudl group at the University of California at Santa Barbara. In fact, a striking feature of C_{60}, as shown by cyclic voltammetry, is that, in solution, this fullerene can accept reversibly up to six electrons. The UCSB group found that both fulleroids and methanofullerenes essentially retain the electronic properties of C_{60}.[21,56,61,75,95,167–171] The same behaviour has been observed for most C_{60} derivatives, whose cyclic voltammograms are typically characterized by a small shift to more negative values of the reduction potentials. This is expected on considering that saturation of a double bond in C_{60} causes a partial loss of conjugation. Due to this effect, at most five reduction peaks for the C_{60} moiety in fullerene derivatives have been detected so far in the accessible potential range.[172–176]

An extensive investigation of the redox properties of several variously functionalized organofullerenes has been reported by Suzuki *et al.*, who studied the influence of the groups attached directly to C_{60} on CV potentials.[177] A small inductive effect was found, revealed by changes in the reduction and oxidation (where possible) potentials and mainly related to the electronegativity of the atoms attached.

A more incisive control of the electronic properties of the fullerenes might still be a relevant issue. The conjugated p-system of C_{60} seems ideally suited for non-linear optical (NLO) applications.[18] Molecules with large NLO properties are often characterized by an electron-donating group and an electron-withdrawing group at opposite ends of a conjugated p system. In principle, attachment of donors and acceptors in conjugation with the fullerene p system should result in an interesting push–pull assembly. However, most reactions of the fullerenes lead to derivatives in which the addends are attached to C_{60} *via* sp^3 carbons, an event that breaks the conjugation. This problem was ingeniously faced by Wudl and co-workers, who used fluorenyl systems spiro-linked to a methanofullerene moiety. An interaction through a 'periconjugation' mechanism between the fluorene group and the fullerene spheroid was detected by cyclic voltammetry.[168,171] It was found that the electrochemical behaviour of compounds **7** is relatively sensitive to the presence of substituents on the fluorene moiety. With electron-donating groups (**7b**) the reduction potentials are shifted to more negative values. On the other hand, the first reduction potential becomes less negative if strong electron-attracting groups are placed in the 9-fluorenyl moiety (**7c**). The electronic properties of spiromethanofullerenes **7** can be attributed to their peculiar geometry, as the fluorenyl planar skeleton is held rigidly perpendicular to the surface of the spheroid. This unique arrangement may be responsible for 'through-space' interactions between the fluorenyl moiety and the spheroid, which thus becomes sensitive to electronic changes in the fluorenyl counterpart. The promising NLO molecules **8** were also synthesized as a mixture of diadducts (R = electron-withdrawing and electron-donating groups). A linear free energy relationship of the reduction potentials on the Hammett s_m of the substituent inside a family of methanofullerenes was also reported by Wudl and collaborators.[178]



7a R = H
b R = NBn_2
c R = NO_2



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Optical properties

The ground state absorption properties of C_{60}, characterized by strong bands in the UV region and weaker absorptions in the visible region up to 650 nm, are retained in most derivatives. In addition, dihydrofullerenes extend their absorptions throughout the entire visible region, with a weak maximum at *ca.* 700 nm. This additional feature makes excitation possible by means of irradiation at very low energy.

Analogously to C_{60}, dihydrofullerenes are excited to a short-lived singlet which converts rapidly into a long-lived triplet, with quantum yields slightly lower than C_{60}.[179,180] Whereas C_{60} exhibits a triplet–triplet absorption at 750 nm, the same peak is shifted to *ca.* 700 nm in C_{60} derivatives.[180–185] This triplet–triplet transition is characterized by a higher absorption coefficient than the ground state, and may be responsible for its non-linear behaviour. Accordingly, solutions of C_{60} and C_{70} exhibit optical limiting (OL) properties, which compare very well with those of materials currently in use.[18] This feature holds great promise for practical applications, such as incorporation of fullerene derivatives in proper transparent matrices for protection against high-energy laser pulses. As compared to C_{60}, fullerene derivatives show a lower singlet–triplet quantum yield,[179,180] so that they are expected to exhibit a lower OL efficiency. However, it has been demonstrated that the optical limiting properties of C_{60} and its derivatives depend on the excitation wavelength.[186,187] When the latter is closer to the triplet–triplet absorption maximum of the fullerene derivative (700 nm) than to the equivalent transition of C_{60} (750 nm), the OL performance of the organofullerene becomes more efficient. Differences in the ground-state absorption can also play a role.

Multiple adducts

The physicochemical properties of the multiple adducts are largely dependent on the number of addends.[56,146,188] In a systematic electrochemical investigation, it was found that the reduction and oxidation characteristics depend very heavily on the number and pattern of the addends in fullerene derivatives. As a general trend, the fullerene derivatives become harder to reduce going from mono to hexakis adducts. This has been attributed to the reduced conjugation occurring in multiply functionalized fullerene compounds, which leads to a corresponding increase of the energy of the LUMO.[188] The same trend is observed in the study of UV–VIS absorption features, where changes due to loss of conjugation are observed.[146,188]

Spin-labelled derivatives

A series of C_{60} derivatives incorporating a nitroxide unit has been synthesized (Fig. 2).[189–192] These compounds possess a paramagnetic probe useful for investigating the electronic properties of the fullerenes. Indeed, they were successfully employed for the study of the anions[192] and the excited triplet states[189] of the C_{60} moiety.

Applications

Polymers

As we have already seen, the fullerenes possess several outstanding properties. The incorporation of fullerenes in polymers would potentially endow the polymer of most of the fullerene properties.[193] Thus, electroactive polymers can be obtained, or polymers with optical limiting properties.[194] On the other hand, fullerenes embedded in polymers become more easily processible. The resulting materials can be used for surface coating, photoconducting devices, and also to create new molecular networks.

There may be several ways to combine polymers with fullerenes. The simplest way is the plain mixing of the two components, either as a solid mixture, or as a solution in a

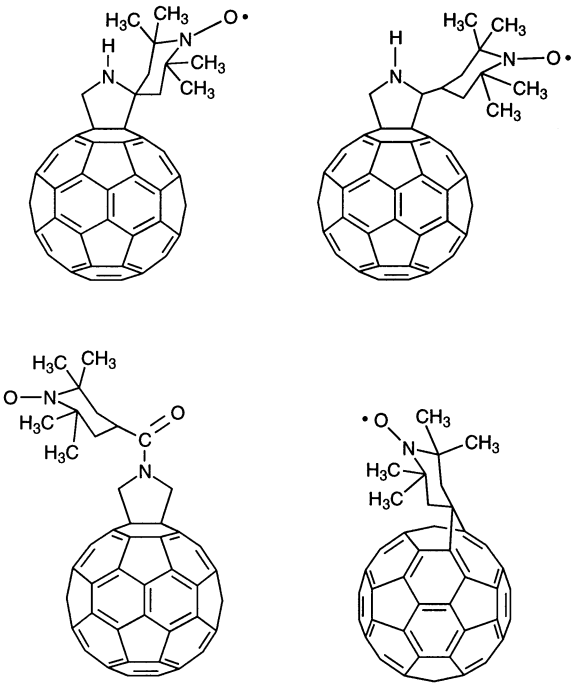


Fig. 2 A series of C_{60} derivatives incorporating a nitroxide unit

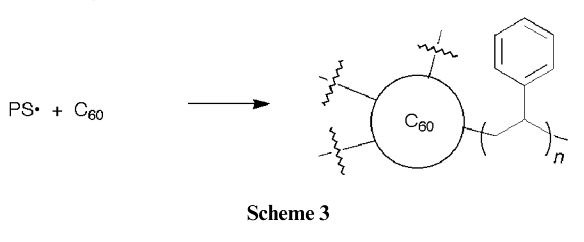
common solvent which is then evaporated. The latter mixing produces more homogeneous samples. This practice usually leads to non-covalent interactions between the two components.

The chemical linking of polymers and fullerenes can be obtained by four main ways.

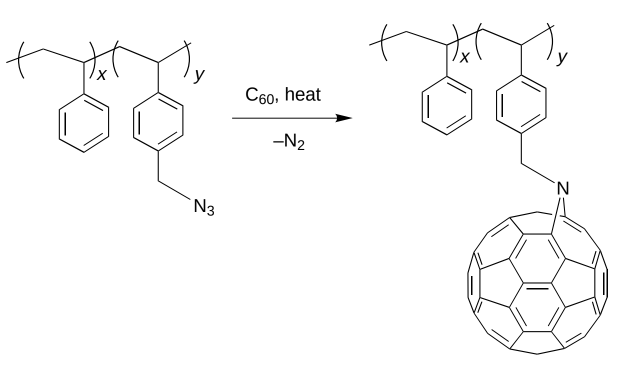
(*a*) Fullerenes that are present during the polymerization of a monomer can react and be attached to the polymer chain.[194–201] Typically, this happens in anionic and free radical polymerizations, where species are generated that react randomly with the double bonds of the fullerene. In this case there is no chemical control: multiple additions to the fullerene double bonds occur, so that the fullerene structure is not well-defined. Cross linked materials are usually obtained (Scheme 3).

(*b*) A preformed polymer is treated under conditions that favour the chemical linking to the fullerenes.[202–209] This is generally obtained by generating nucleophilic polymeric species. Also in this case the chemical attack to the fullerene double bonds is indiscriminate, and mixtures of isomeric fullerene species can be obtained (Scheme 4).

(*c*) A monomer containing a fullerene unit is polymerized or co-polymerized.[94,210] In this case, if the fullerene monomer is a well-defined monoaddition product and if the conditions employed are chemically inert to the fullerene double bonds, the final polymer contains a fullerene species with an almost intact electronic configuration, in which only one double bond (or none, in the case of fulleroids or azafulleroids) of the pristine fullerene has been saturated (Scheme 5). The electronic and electrochemical properties of C_{60} were shown to be retained in the polymers.[94,210]



Scheme 3

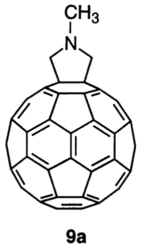


Scheme 4

(*d*) A dendrimer can be built on a fullerene nucleus (Fig. 3).[211,212]

In addition, three-dimensional, starburst polyurethane networks have been prepared using fullerenols as molecular cores and condensing them with isocyanate prepolymers. High-performance elastomers with enhanced thermal stability are thus obtained.[213,214]

A comparison between different ways of producing C_{60} polymers has been reported recently.[215] Free radical polymerization of methyl methacrylate (MMA) was carried out in the absence (PMMA) and in the presence (PMMA-**9**) of derivatives **9**, and compared to simple embedding compounds **9** in preformed PMMA (emb-**9**). It was found that samples from different preparations differ significantly. PMMA-**9** clearly shows cross linking of the polymer chains, which leads to an increase in T_g of *ca.* 8 °C with respect to plain PMMA. In addition, the cross linked material did not dissolve in chloroform, a solvent in which PMMA and emb-**9** were readily soluble. Cross linking was not observed when C_{60} was used in place of **9** during the polymerization process. This was attributed to the lower solubility of C_{60} in MMA as compared to **9**.



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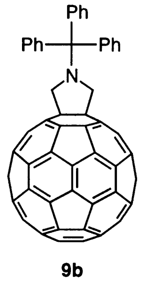
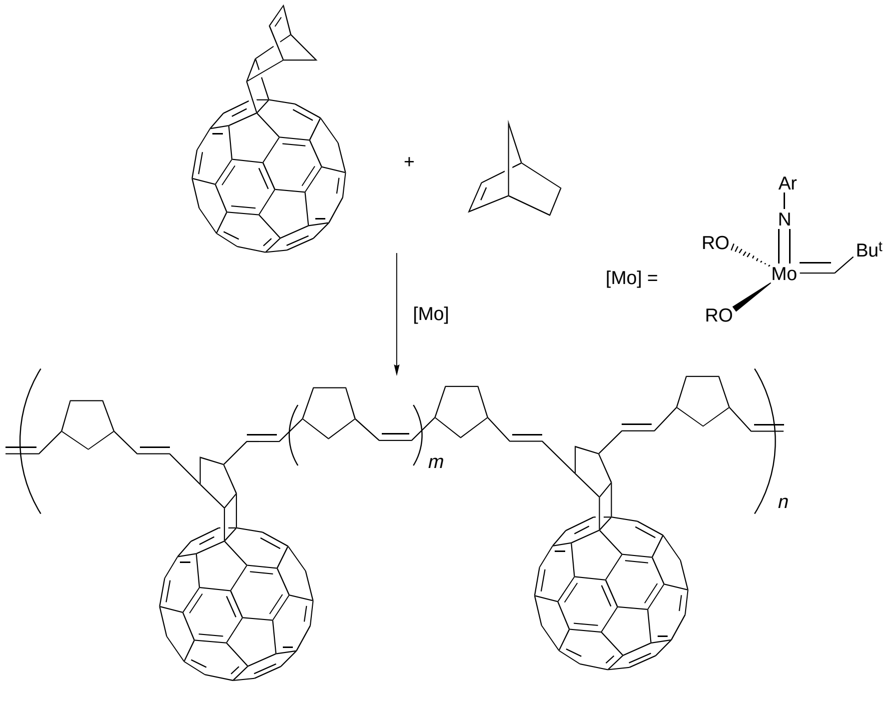


9b

Information on the structure of the cross linked species was obtained from the analysis of the EPR spectra recorded for the lowest excited triplet of PMMA-**9**. An unusually large electron dipolar splitting *D* parameter of positive sign was observed. The spectrum was simulated using a simple model calculation which considers C_{60} and derivatives as a collection of fully localized double bonds. A positive sign of *D* is expected for PMMA-**9** in which cross linking has occurred in the equatorial belt of the molecule.[215]

A peculiar type of fullerene polymers (all-carbon polymers) has been obtained by irradiation of oxygen-free films or solutions of C_{60}[216,217] as well as by heating AC_{60} crystals (A = K, Rb, Cs).[14] A quasi-linear structure, derived from [2+2] cycloadditions of C_{60} double bonds leading to four-membered rings, has been proposed for these polymers.[218,219]

Fullerenes, and C_{60} in particular, show very limited solubility in any medium, especially polar solvents. For any molecule that contains more than one C_{60} sphere, this experimental problem is amplified. Therefore, when preparing fullerene-based polymers, one of the main issues that needs to be



Scheme 5

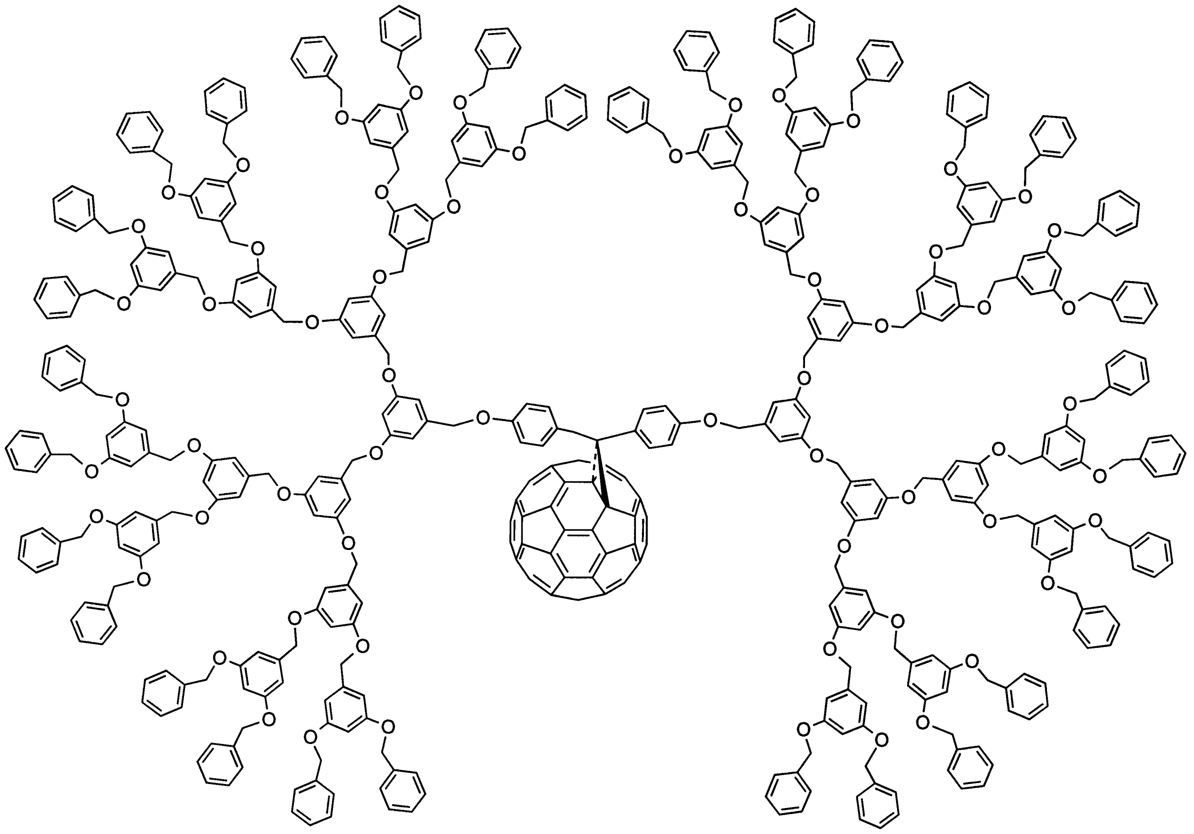
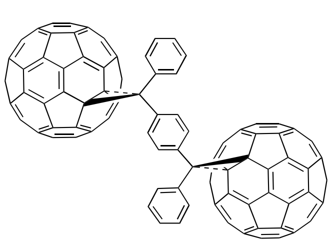


Fig. 3 A dendrimer built on a fullerene nucleus

addressed is the solubility of the material. The typical result is that only oligomers are obtained with relatively low molecular weights. Wudl and co-workers reported the synthesis of derivatives containing two C_{60} units (**10**),[167] which were shown to retain the original electronic fullerene properties. But, owing to the diminished solubility of **10** in most solvents, Wudl warned that polymers containing C_{60} should be expected to be insoluble and intractable, unless a solubilizing group is attached. The same conclusions were reached by other groups, during the synthesis of compounds **11** and **12**.[110,220]



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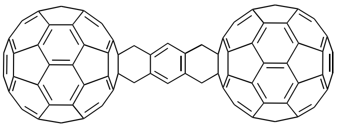

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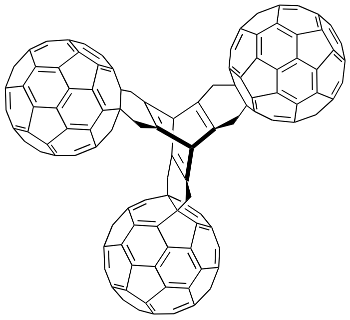

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However, even when solubilizing hexyloxy chains were introduced in the polymer, the number of fullerene moieties involved was still low, and precipitation of oligomers ($n = 0$–5) occurred due to cross linking.[221] The facile cross linking of C_{60}-containing polymers represents, in fact, another, strictly connected problem. The number of reactive double bonds in C_{60} is such that up to eight or ten chains can radiate from a fullerene nucleus. This leads to a very tight, cross linked structure, whose solubility and processibility become problematic. A higher T_g is usually observed upon addition of C_{60} or organofullerenes to a polymer,[94,207,215] which suggests that fullerenes may be used as additives for increasing the thermal stability of a material. Eventually, when cross linking was avoided, a soluble polymer with M_w of *ca.* 80 000 was prepared. The improvement was obtained using a mixture of two different *o*-quinodimethanes, one of which helped avoid cross linking while increasing the solubility.[221]

An interesting example of a C_{60} end-capped polystyrene star has been recently reported (Fig. 4). The attachment to C_{60} was obtained *via* azide addition, and the resulting polymer was shown to retain the basic C_{60} electrochemical properties.[222]

Rotello and co-workers took advantage of the reversibility of the addition of cyclopentadiene to C_{60} for the temporary attachment of the fullerene to a modified Merrifield resin.[223] Addition of the cyclopentadiene-modified resin to C_{60} was achieved at room temperature, whereas the fullerene was released at 180 °C upon addition of maleic anhydride as a cyclopentadiene trap. The authors proposed the methodology for a non-chromatographic purification of the fullerenes.[224]

A few examples of electrochemical polymerization of C_{60} derivatives have been reported. Starting from a dialkynylated methanofullerene, Diederich *et al.* observed formation of an electrically conducting film on the surface of the platinum cathode.[225] A redox-active fullerene polymer with interesting mechanical and electrical properties was also obtained by electrochemically polymerizing the fullerene oxide $C_{60}O$.[226,227] A monomer unit, having a cyclopentadithiophene moiety attached to C_{60} was electrochemically polymerized, leading to a conjugated polymer that contains C_{60} covalently attached.[228] Although some solubility problems arose, leading to a low polymerization degree, the authors reported that both components, namely the conjugated polymer and C_{60}, retain their original electrochemical properties, and that some new properties may be expected from their interactions.

Thin films

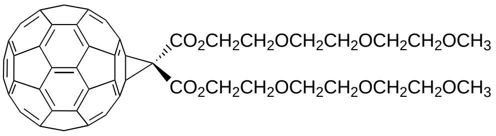
Thin films containing fullerenes are of current high interest, owing to the possibility of transferring the interesting fullerene properties to bulk materials by simple surface coating. In this respect, self-assembled monolayers (SAM)[30,229,230] and Langmuir films are being increasingly used, as controlled organized structures can be obtained.

In a very stimulating experiment, Echegoyen and Kaifer used molecular recognition to induce the formation of molecular monolayers of the 18-crown-6 functionalized fullerene **13**.[231] A gold surface was modified using a thiol-terminated ammonium salt (Scheme 6). When the modified gold layer was immersed into a CH_2Cl_2 solution of **13**, surface coverage was obtained which corresponds to a compact monolayer of C_{60}, as found by OSWV measurements. The attachment of **13** to the ammonium salt, and thus to the gold surface, was demonstrated to be reversible in a CH_2Cl_2 solution.

A major problem encountered during the preparation of Langmuir films of fullerenes is related to the high hydrophobicity of the carbon cage compounds. Efforts have been aimed at the preparation of fullerene derivatives which present a hydrophilic end.[111,232–244] In these cases, monomolecular layers with an area per molecule of approximately 10 $Å^2$ have been often obtained. Langmuir–Blodgett transfers to solid substrates, however, proved very difficult, and only a few successful cases have been reported. Only two recent representative examples of successful transfers will be discussed here (for a more detailed discussion on Langmuir films of fullerenes, see ref. 30).

An extensive investigation on the Langmuir behaviour of several C_{60} derivatives was reported recently.[235] The amphiphilic fullerene monoadducts studied include carboxylic acid and amine derivatives, a bis-phenol, a crown ether and a cryptate, together with some protected and deprotected sugars. Monomolecular layers were obtained for the cryptate derivative, but were not very stable as assessed by compression–expansion cycles. Langmuir–Blodgett transfer of films derived from some sugar derivatives was only possible using highly hydrophobic, phenyl-functionalized glass or quartz substrates.

Spreading behaviour independent of concentration in the range 0.1–2.0 mM and area/molecule of 96 $Å^2$, with thickness of 7 ± 3 Å, in excellent agreement with theory, was obtained for methanofullerene **14**.[233] The monolayers were transferred to solid substrates (quartz or mica) with transfer ratios close to unity.



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Thin films useful for laser protection can be obtained by incorporation or covalent attachment of fullerenes to transparent solid matrices. The optical limiting properties of C_{60}, originally detected in toluene solutions (see above),[18] can be transferred to solid substrates without significant activity loss.[245]

Whereas polymeric substrates are damaged by high power laser pulses,[245] glasses show very high damage thresholds, which makes them ideal for OL purposes. Sol–gel processing provides an excellent means for the preparation of glassy matrices at reasonable temperatures, compatible with the stability of most organic compounds.[246–250] However, C_{60} has

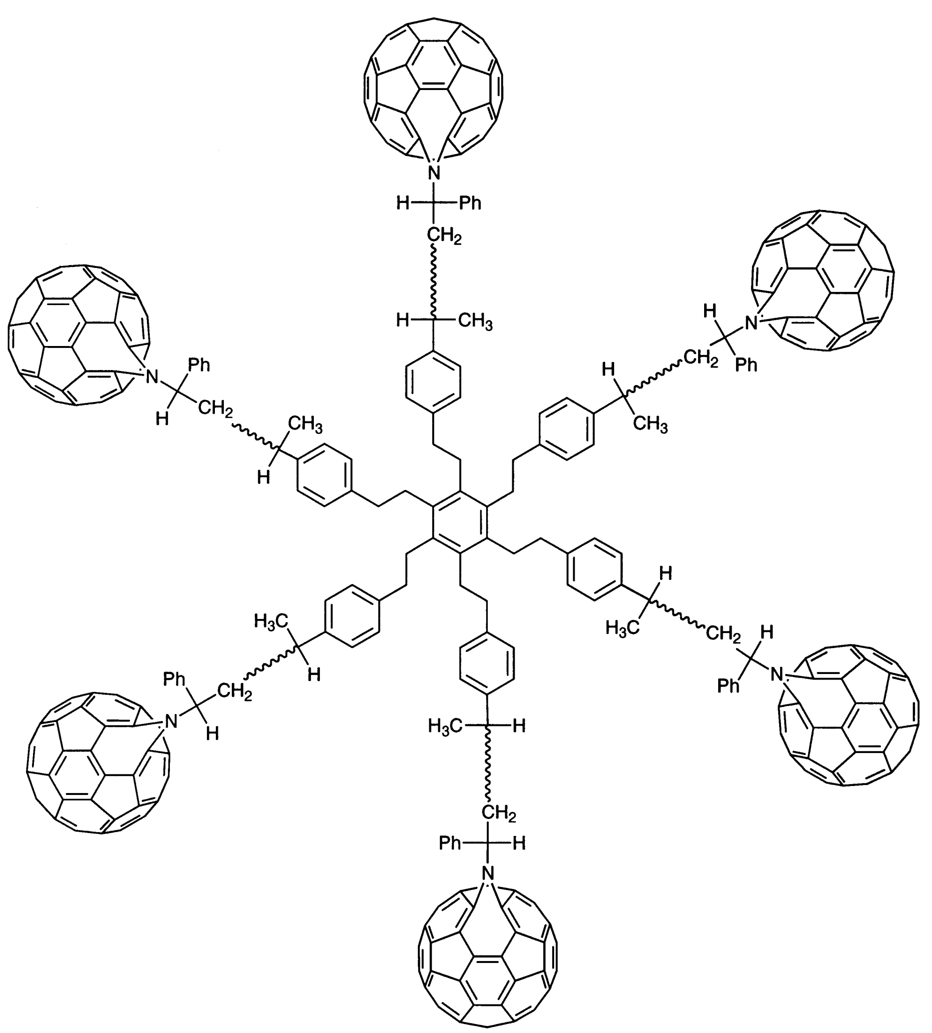
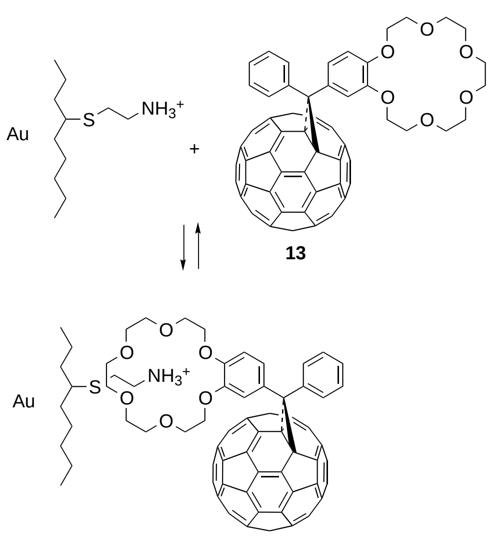


Fig. 4 A C_{60} end-capped polystyrene star



Scheme 6

no or very low solubility in the polar solvents typically used during the sol–gel process. In addition, C_{60} has a high tendency to form clusters, thus making it very difficult to prepare optical-quality films. When solubilized in the form of organofullerene, the optical properties of C_{60} can be transferred to sol–gel materials.[251] The best way to pursue the preparation of homogeneous thin films of optical quality, with tunable amounts of dihydrofullerene for applications in the OL field is to covalently attach the monofunctionalized fullerene to the silicon matrix. This can be achieved by introducing a silicon alkoxide functionality in the diene or the 1,3-dipole that will add to C_{60}. To this aim, the derivatives shown in Fig. 5 were synthesized, whose OL properties in solution have been reported.[186] Their chemical attachment to silicon matrices has been obtained and the OL properties of the resulting materials are under investigation.[252]

Electrooptical devices

The combination of the rich electronic and electrochemical properties of C_{60} with those of other electroactive species is currently a field under intense investigation. It is in fact believed that chemically modified fullerenes may play a relevant role in the design of novel molecular electronic devices, and in particular for applications in artificial photosynthesis. To this end, a number of electron-rich groups have been covalently attached to C_{60}, which acts as an electron acceptor, for the creation of a large variety of dyads. Donor units used to this end include aromatics,[119,182,183,253–255] porphyrins[181,256–259] and phthalocyanines,[260] a rotaxane,[261] tetrathiafulvalene,[176,262] a carotene unit,[263] Ru–bipy[264] and Ru–terpy[265] complexes, as well as ferrocene.[172,176] Some of these dyads have been studied with respect to photoinduced charge separation.[181,182,263,266–268]

Both energy and electron transfer processes between the donor and the acceptor (C_{60} moiety) have been reported. For instance, intramolecular quenching of C_{60} singlet excited state was detected, from electron transfer by the ferrocene moiety

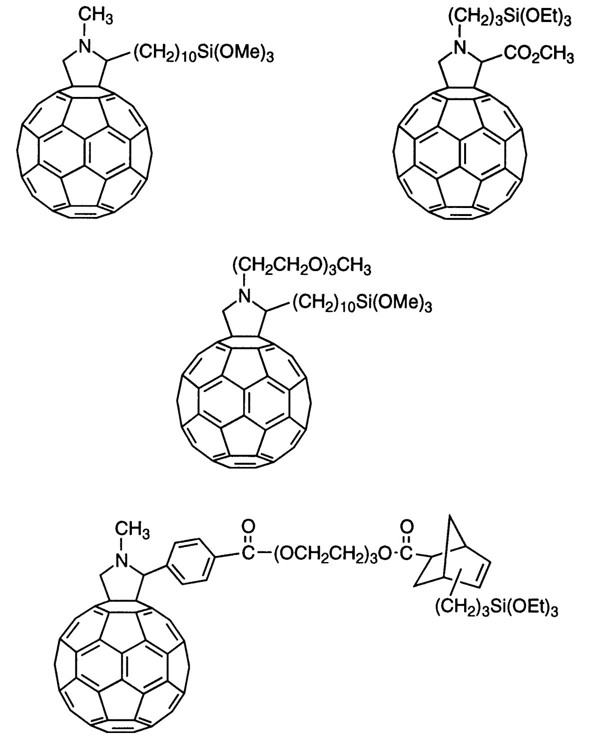
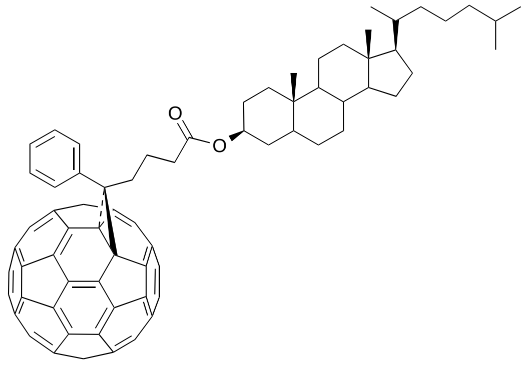


Fig. 5 Silicon-functionalised fullerene derivatives

in dyads **15–19**.[269] The nature of the spacer was found to play a role: through bond electron transfer was shown for dyads **15–17**, whereas formation of a transient intramolecular exciplex was observed for compounds **18** and **19**. While in **15–17** fast charge recombination probably prevents sufficient stabilization, the saturated hydrocarbon bridge in dyads **18** and **19** is able to avoid charge recombination and long-lived charge separated states are detected in polar solvents ($t_{1/2} = 1.8$ and 2.5 ms in benzonitrile).

In a real step toward the manufacturing of efficient photovoltaic devices, photoinduced electron transfer from p-conjugated polymers to C_{60} has been reported by several groups.[270–272] The electron transfer is very fast and the photoluminescence of the polymer is heavily quenched, which implies a competition between radiative emission and electron transfer from the excited polymer to C_{60}. Composite films made by simple mixing of p-conjugated polymers and C_{60} in different molar ratios have been employed during these investigations. However, a major drawback in the use of C_{60} in these polymer blends is the high tendency of the fullerene to form clusters and to crystallize. This results in poor homogeneity and low optical quality of the films. These problems have been partially overcome with the use of soluble fullerene derivatives, such as the methanofullerenes **20** and **21**. Efficient charge transfer in composite films of poly(bis-2,5-*epi*-cholestanoxy-1,4-phenylene vinylene) and **20** or **21** showed that the increased miscibility of the functionalized fullerene with the conjugated polymer can represent an important prerequisite for the construction of electrooptical devices.[273–276]



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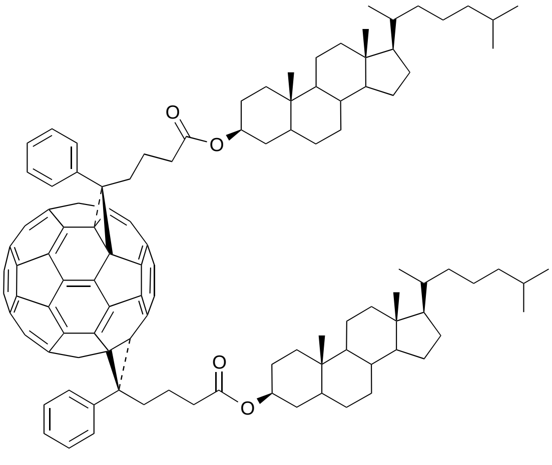

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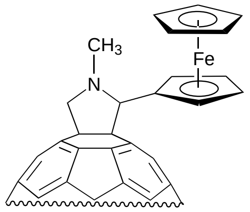
Liquid crystals

The first thermotropic liquid crystal containing two cholesterol units attached to a methanofullerene has been synthesized and



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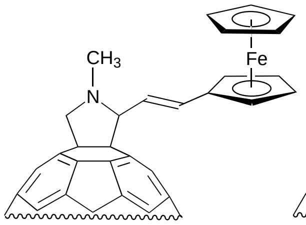

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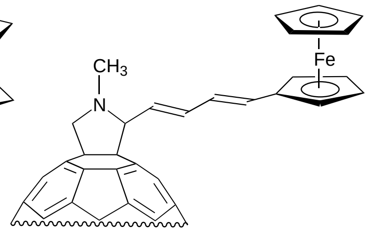

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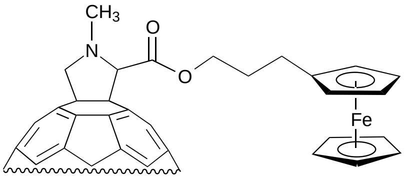

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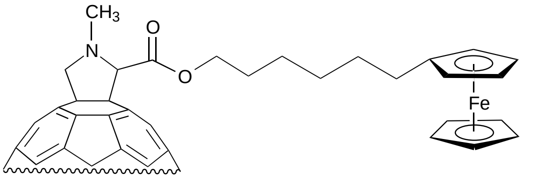

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its mesomorphic behaviour was investigated.[277] A high melting point was obtained, which was attributed to the fullerene moiety. Other mesogenic groups were covalently linked to C_{60}.[278] Phase transitions were detected at relatively low temperatures, but the detailed thermotropic properties were not reported.

Conclusions

The prospects for useful applications based on fullerene materials have had fluctuating fortune. The great excitement generated by the discovery of a new form of carbon and the high potential of the fullerenes in different fields has soon given way to the pessimistic feeling that fullerenes would not find any practical application,[279] or at least that fullerenes would not be a sort of wonderful all-purpose material useful for a myriad of technological uses.[280,281] Today, the development of efficient methodologies for the functionalization of fullerenes has widened the perspectives, and it is now not unlikely that fullerene-based devices may find their way to the market.

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Paper 7/00080D; *Received* 8th *January*, 1997