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Fullerene materials

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Materials containing a spherical π-electron moiety have the added advantage of enhanced intermolecular interactions. Buckminsterfullerene is a special spherical π-electron carbon cluster which, unfortunately, is only sparingly soluble in most common solvents. It is therefore imperative that the cluster be derivatized (functionalized) to be incorporated into most familiar solids for materials science applications.Addition and cycloaddition reactions are the only synthetic methods available to functionalize C_{60}. Of these, the so called Bingel, Bingel–Hirsch, Prato and azoalkane cycloaddition reactions are the most useful and have been used over the past decade to produce a myriad of C_{60}-based molecules as well as many materials.So far, there are only two areas where functionalized fullerenes have had an impact: plastic solar cells and optical limiting glasses, with lesser applications in polymeric materials and fullerene-modified traditional materials. The emphasis of this article is therefore on photodiodes and optical limiting glasses.

Introduction

Of the large family of room temperature, atmosphere-stable all-carbon hollow clusters, buckminsterfullerene (C_{60}) and its slightly larger homologue (C_{70}) are the protagonists. In fact, buckminsterfullerene is by far the most investigated member of the family. Two main factors are responsible for this: 1. it is the most abundant product of any fullerene method of preparation and 2. it is, so far, the cluster which has exhibited the most attractive chemical and physical properties. In addition, due to symmetry considerations, monofunctionalized C_{60} is the simplest fullerene-based molecular construction. It should therefore not be surprising if this review will be restricted, with some minor exceptions, only to the condensed matter/materials science aspects of monofunctionalized C_{60}.

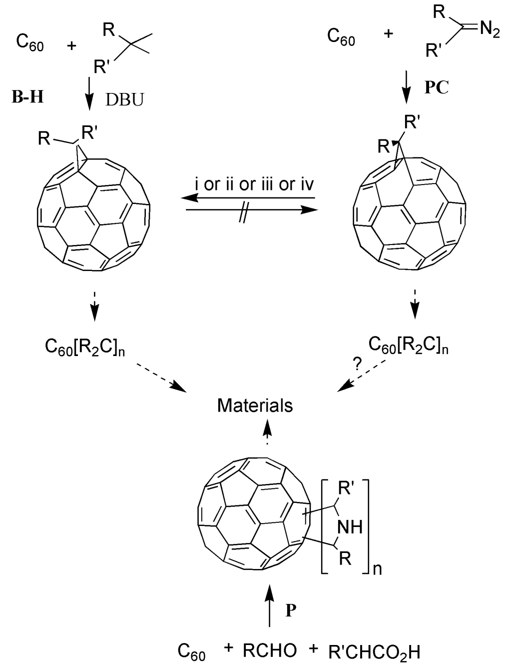
Buckminsterfullerene's spherical π-electron surface has provided scientists and engineers with an unprecedented fundamental building block whose condensed matter properties demanded to be explored. This applied especially to the electronic, magnetic and optical properties of ensembles of C_{60} and its reduction products (doped materials) as well as its covalently modified derivatives (functionalized C_{60}). As the articles in this special issue reveal, the condensed matter/materials aspects of buckminsterfullerene, particularly functionalized C_{60}, have been approximately a decade's endeavor of a large number of researchers throughout the world. The field of materials based on modified fullerenes has most recently been reviewed by Prato.[1]

Though the semiconducting[2] magnetic[3–8] and superconducting properties[9–11] of unmodified buckminsterfullerene have been thoroughly investigated, these properties remain to be explored in the case of the functionalized cluster. On the other hand, the nonlinear optical and photophysical properties of functionalized buckminsterfullerene compounds have been, and are currently, avidly investigated.

Synthesis

Functionalized fullerenes can be prepared by a potentially large family of synthetic reactions. Due to the nature of the covalent bonds of buckminsterfullerene, essentially all synthetic modifications are ultimately reduced to addition reactions. Also, the strain in the carbon–carbon bonds of C_{60} provides the driving force for their reactivity,[12] not only as 2-π electron partners in cycloaddition reactions but also as electrophiles susceptible to nucleophilic and free radical addition.[13,14] Of this relatively large number of reactions, the most popular approaches to the modification of fullerene C_{60} are depicted below. Note that two (P and PC) of the three depicted reactions (B–H, PC and P) are dipolar cycloadditions to double bonds of C_{60}.

In Scheme 1, B–H stands for the Bingel–Hirsch reaction, PC stands for polar cycloaddition and P stands for the Prato reaction. The conditions i–iv in the Scheme (thermolysis, photolysis, acid catalysis and electron addition, respectively) indicate that in the fulleroid–methanofullerene rearrangement,



Scheme 1 Most frequently used syntheses of fullerene derivatives for materials applications.

the thermodynamic "sink" is the methanofullerene. The chemistry of buckminsterfullerene has been reviewed over the years in the form of books or book chapters[15–17] where the fullerene modification reactions are described in some detail. The most expeditious method of functionalization of C_{60} is the addition of a haloester anion, followed by substitution of the halide (reaction B–H, Scheme 1) developed by Bingel as well as Hirsch and the next most useful method is the azomethine ylide addition developed by Prato (reaction P, Scheme 1). The reactions have led to a large number of modified fullerenes for applications in optical limiting glasses and photodiodes. In the most general terms, a large variety of malonates (or 2-halomalonates) are easily accessible. For the B–H reaction, the most convenient approach is the *in situ* formation of bromomalonate from a malonate, carbon tetrabromide and DBU (1,8-dazabicyclo[5.4.0]undec-7-ene).[18] These procedures and, to a lesser extent, reaction PC have led to the preparation of gram-quantities of functionalized fullerenes. Because the functionalization reactions are quite forgiving, very large molecular residues can be attached to the fullerene cage. For example, large dendrimer and other units have been attached to C_{60} using the B–H approach.[19–21] These reactions also lend themselves to the preparation of fullerene-containing polymers. These have been dubbed pearl necklace, or charm bracelet types, depending on whether the cluster is part of the backbone or is attached to the backbone through a sidechain, respectively. In addition, living polymers can be terminated with a fullerene, leading to fullerene end-capped materials. A more detailed discussion will be in the appropriate section.

Photodiodes

The high electronegativity of C_{60} was expected to produce charge transfer complexes with conjugated polymers which are weak electron donors. In fact, no charge transfer in the ground state was observed when composites with conjugated polymers were prepared. On the other hand, both components are better acceptors and donors, respectively, in the excited state and this is the basis of fullerene-based photodiodes ("plastic solar cells"). The photodiode effect is the exact reverse of the light emitting diode (Fig. 1). To understand better the mode of action, one needs to backtrack and examine the conjugated polymers first.

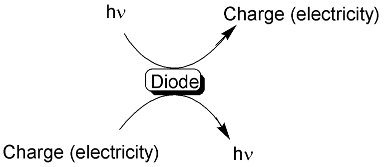
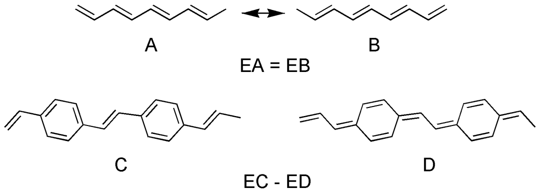
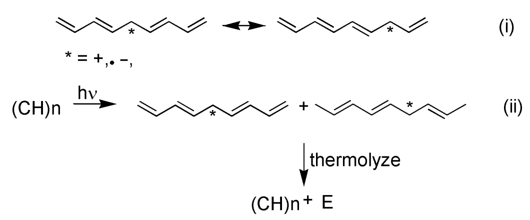


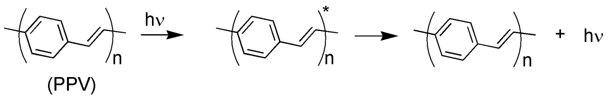
Fig. 1 The reversible action of a diode.



Scheme 2 Schematic representation of degenerate and non-degenerate ground state conjugated polymers.

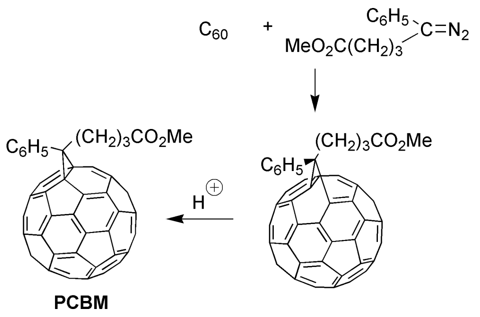


Scheme 3 Delocalization of an excitation in a polyene (i) and photoexcitation–de-excitation (recombination) in polyacetylene (ii).



Scheme 4 Photoexcitation–de-excitation (recombination) in PPV.

Conjugated polymers can be divided into two classes, those with a degenerate ground state and a non-degenerate ground state. Conjugated polymers which have a non-degenerate ground state are photoluminescent, whereas degenerate ground state polymers are not. These unsaturated systems are shown schematically in Scheme 2. Here a polyene A can be described equally well by polyene B; *i.e.*, A and B are degenerate in energy. On the other hand, it is obvious that C and D are not isoenergetic. Excitations in A (B) lead to a species with the properties of a solitary wave, meaning that the excitation can propagate (delocalize) in either direction without dissipation of energy (see (i) in Scheme 3).[22] As a result, photoexcitation leads very rapidly (picoseconds) to two solitons (soliton–antisoliton pair) which, upon recombination, do not produce a photon. Hence, polyacetylene is not a luminescent polymer. On the other hand, non-degenerate ground state conjugated polymers form delocalized excitons[23] (electron-hole pairs, see Scheme 4). The electron-hole recombination occurs at some trap site in the polymer.[23] The overwhelming majority of conjugated polymers are non-degenerate ground state macromolecules. In fact, polyacetylene is the only *fully characterized* degenerate ground state macromolecule. When a very thin film of a fluorescent polymer is sandwiched between an anode and cathode, the source of the exciton is a hole and electron injection at the respective electrode. The result is electroluminescence.[23] Clearly, if the electron or hole can be diverted before they reach a recombination site, the fluorescence (electroluminescence) will be thwarted (quenched). It should therefore not be surprising that if a very efficient electron acceptor or electron donor is "dissolved" in the polymer, the fluorescence (electroluminescence) will be quenched. This is precisely what was observed when C_{60} was added to a polythiophene derivative[24] and a poly(phenylenevinylene) (PPV) derivative.[25] Photophysical and electron spin resonance studies reported by Sariciftci *et al.*[25] revealed that, indeed, electron transfer occurred from the excited state of the conjugated polymer to C_{60} and, more important, the forward electron transfer was in the high femtosecond regime but the back electron transfer was only in the millisecond range. This was a strong indication that the charge separated state {MEH-PPV$^{+\bullet}$ $C_{60}^{-\bullet}$, MEH-PPV = poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylenevinylene)]} lived long enough for charges to migrate to the anode and cathode. Indeed a photodiode was constructed and characterized.[26] Though the mechanism was understood, the efficiency of electrons per photon was very low. This was attributed, correctly as was found later, to the planar design of the cell and to the very low compatibility of C_{60} with MEH-PPV. The problem was solved by a functionalized C_{60},[27,28] prepared by method PC of Scheme 1 and shown below in Scheme 5. Of a number of different addends similar to **PCBM** (Scheme 5), the methyl ester proved to be the most effective for composite formation with MEH-PPV.[28] Later it was discovered that photodiodes fabricated from these composites produced the highest efficiency in photoconversion (electrons/photons).[29] This was due to the fact that **PCBM** tends to phase-segregate into microfilaments so that a continuous network exists for negative charge transport to the anode. By various chemical engineering stratagems, the efficiency has



Scheme 5 Preparation of functionalized fullerene **PCBM**.

recently been improved to 2.5%, sufficient to power a hand-held calculator with room fluorescent lights.[30]

These investigations have inspired a number of synthetic chemists to develop dyad and triad molecules for intramolecular photoinduced charge separation. One of the most impressive results in this respect is that of Gust *et al.*[31] where light-driven production of ATP was demonstrated by an artificial photosynthetic membrane containing a porphyrin C_{60} dyad coupled to a retinene.

Much more recently it was discovered that under certain circumstances there is essentially no electron transfer but only ultrafast energy transfer from the donor of the dyad to C_{60}.[32–34] Potentially this is a feature which may place an upper limit on the efficiency of devices consisting of C_{60}-based dyads for intramolecular photoassisted charge separation. On the other hand, the first polymer solar cell made of a conjugated polymer with a pendant methanofullerene has recently been reported, where the polymer backbone can be considered a macromolecular donor component of a dyad. The fullerene content was relatively dilute with one fullerene per 4 monomer units. The functionalized fullerene monomer was prepared by a PC reaction (Scheme 1) approach.[35]

Optical limiting

Early in the days of fullerene research it was discovered that C_{60} had the unusual property that its triplet photoexcited state absorbed light more efficiently than its ground state. The result is that as the intensity of the incoming radiation on a buckminsterfullerene sample increased, the intensity of the transmitted radiation did not increase nearly as rapidly. Or, the relation between incident radiation and transmitted radiation was non-linear. This phenomenon is known as optical limiting (OL) by reverse saturation absorption. The original experiments were performed with toluene solutions of C_{60}[36] but shortly thereafter, the same scientists showed that solid polymer films containing C_{60} also exhibited OL properties which were essentially of the same magnitude as those observed in solution.[37] Soon it was established that due to the fullerene's low solubility, only very small amounts could be composited with commercial polymers. Further, it was important to develop silicon dioxide-based, *transparent glasses* for use, for example, in optical lenses. This challenge was, once again, met by functionalized fullerenes. Enhanced OL behavior was reported for a PCBM in solution[38] but not in sol–gel glasses.[39] Fullerenes specifically designed to be incorporated into silicate glass, which showed enhanced OL, were reported by an Italian group (see **1** and **2**, Fig. 2).[40,41] as well as others.[42]

Indeed, attractive, magnificently transparent brown glasses have been fabricated from these "hybrid" organic–inorganic composites, where the C_{60} derivative is covalently incorporated into the glass matrix. A very interesting fallout from this research is an application to separation technology materials, where another triethylsilyl-containing fullerene derivative (**3**) was grafted onto the surface of chromatography grade silica (Scheme 6). HPLC stationary phases containing this graft showed excellent separation properties both in water and organic solvents.[43]

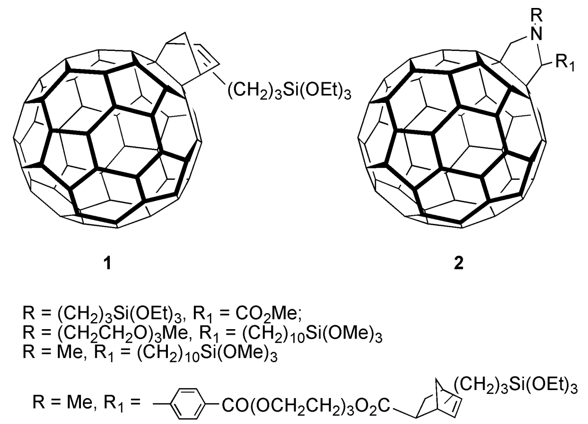
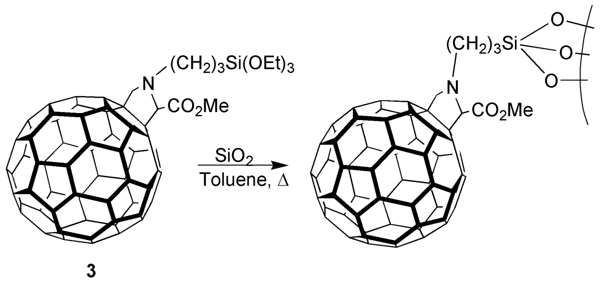


Fig. 2 Fullerene derivatives for sol–gel glasses.[40]

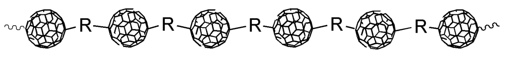


Scheme 6 Fullerene modified silica gel for HPLC applications.[43]

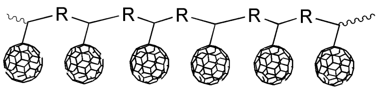
This modified silica gel is excellent for separations of bulky and aromatic molecules and has been recently reviewed and extended to gas chromatography.[44–48]

Polymers

The very low solubility and high crystallinity of C_{60} make it essentially useless as a material for engineering applications. It is therefore not surprising that almost immediately after its discovery, scientists and engineers have examined methods of incorporating fullerenes into polymers with the ultimate goal of producing a processable fullerene-containing material with the usual properties of organic polymeric materials. The first incorporation into a traditional polymer, polystyrene,[49] and the electronic packaging polymer "parylene"[50] were reported in 1992. The former was dubbed "flagellene" and exhibited rather unusual self-assembly characteristics. Electron microscopy revealed small spherical (*ca.* 20 nm diameter) features. Thermal annealing (50 °C) of thick films showed behavior more akin to typical diblock copolymer self-segregation into rod-like morphology. These materials should actually be considered to be related to starburst polymers rather than either dendrimers or block copolymers. In the same year, the "pearl necklace" and "charm bracelet", names which were coined the previous year[51] for the polymers depicted schematically below, were synthesized. Actually only a two "pearl" segment was prepared[52] but a true charm bracelet was published the same year[53] and in the intervening years a substantial number of publications claiming the preparation of C_{60} charm bracelet polymers have appeared.[54–56] Unfortunately these, for the most part, are complex mixtures of relatively poorly characterized materials.



Pearl Necklace



Charm Bracelet

One is required to be sceptical of polymer-derived modifications that are based on synthetic reactions which are known to afford relatively low yields of complex mixtures, separable only by chromatography. Such is the case, particularly in ref. 55 and to some extent in ref. 54. On the other hand, the very recent work on polymers for plastic solar cell development mentioned above[35] describes a fully characterized charm bracelet polymer with pendant **PCBM**-derived (see Scheme 5) units.

Other polymeric materials which take advantage of the polyvalence of C_{60} are highly crosslinked polyurethanes[57] with polyhydroxylated C_{60}. Polysulfonated C_{60} was also used to prepare conductive elastomers.[58] Though from an engineering/materials science perspective these are quite interesting materials, unfortunately they are based on C_{60} derivatives which are not nearly as well characterized as those employed in other materials mentioned above. In a much better characterized polymeric system, a C_{60} with two polystyrene "flagella" was reported, which was prepared by living free radical addition to C_{60}. Typical fullerene electronic properties were retained in this material, yet it was also reported to have retained typical polystyrene properties.[59] Another study[60] of the behaviour of controlled living anionic polymers with C_{60} showed that only the hexaanion of fullerene polymerizes MMA without incorporation of the fullerene into the PMMA, strongly indicating that electron transfer is responsible for anionic initiation by the C_{60}. When polystyryllithium was added to C_{60} "living" star molecules with a C_{60} core bearing a well-controlled number of arms was produced. Six carbanionic sites need to be on the fullerene in order to initiate anionic polymerization of styrene by addition onto the monomer. The more reactive acrylate requires only a pentacarbanion. Stars with seven PS branches and heterostars with six PS and two PMMA were also prepared.

Using much more energetic free radicals, it was shown that styrene and methyl methacrylate give surprisingly different C_{60} incorporation densities.[61] Whereas PS incorporates between 10 and 100 fullerene units per branched polymer, the PMMA macromolecules contain, on average only one fullerene per macromolecule. These macromolecules exhibit lower viscosities than the parent systems, indicating that they are very likely star-like macromolecules. Also, the results of initial kinetic studies revealed that C_{60} reacts with free radicals at essentially diffusion controlled rate.

Summary

In summary, the most promising future in fullerene research is that of applications of functionalized fullerenes because the unmodified molecules are too intractable for technological applications. Of the three areas reviewed, the photodiodes (plastic solar cells) is the one with the *brightest* future. As more and better conjugated polymers are developed for the technologically highly valued organic light emitting diodes (OLEDs), more materials will be available for the development of plastic solar cells.

One of the main bottlenecks in the development of fullerene science in engineering and pharmaceuticals is the availability and cost of fullerenes. This impediment may be removed in 2002. A new corporation (Frontier Carbon Corporation, or FCC) that was recently created in Japan, has as its mandate to produce ton-quantities of fullerenes with the promise to reduce the price by one order of magnitude within one year and two orders of magnitude in the near future. With such low cost C_{60} (*ca.* \$0.25 per gram) starting material, functionalized fullerenes will be of greater interest to industrial scientists throughout the world and will have their future assured in the burgeoning endeavor of organic materials science.

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