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The first water-soluble main-chain polyfullerene†

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The synthesis of the first water-soluble polyfullerene is accomplished by nucleophilic reaction of a diamine supramolecularly shielded in a cyclodextrin cavity with fullerene, leading to a versatile new field for main-chain fullerene polymers.

Although a versatile derivatization chemistry of fullerenes has been developed,[1] solubilizing fullerenes in water while preserving the intrinsic properties of the carbon allotropes has met with limited success and consequently only a few reports are available in this field.[2] Previous attempts to synthesize fullerene main-chain polymers have been based on multi-step synthetic concepts and resulted in water-insoluble products.[3] In view of the potential biological and biomedical applications of water-soluble fullerene compounds,[4] we synthesized polyfullerenes following a general strategy, which we call the supramolecular masking concept, in which fullerene molecules are connected in the polymer main chain with bifunctional guest compounds that are supramolecularly shielded by a macrocyclic host. In a typical experiment, the cyclodextrin–amine complex (**2**), dissolved in dimethylformamide, was treated with a solution of [60]fullerene in dichloromethane, at room temperature, facilitating a nucleophilic polyaddition reaction between the accessible amino groups of the diamine moiety in the cyclodextrin cavity and C_{60}, leading to the water-soluble polyfullerene (**3**) (Scheme 1).

Initially, we thought of using *p*-phenylenediamine (PPD) as the simplest aromatic diamine for complexation with β-cyclodextrin (CD), the cyclic glucose hepta-oligomer, and subsequent use of the complex (CD–PPD) as the monomeric precursor for the synthesis of the fullerene main-chain polymer. The result was a species with a molecular mass of ~2.8 kg mol^{-1} (GPC data). Spectral data provided evidence of reaction between the inclusion complex and C_{60}. Formation of a short segment instead of a polymer was ascribed to the low probability of reaction of C_{60} with the PPD nitrogens (N–N distance 576 pm) embedded in the depth of the CD cavity (780 pm).

A similar reaction between the inclusion complex CD–bis(*p*-aminophenyl) ether (CD–BPE, N–N distance 968 pm) and C_{60} resulted in polymer **3**, (poly[(β-cyclodextrin–bis(*p*-aminophenyl) ether)-*co*-[60]fullerene], M_n = 18.9, M_w = 20.0 kg mol^{-1}; polydispersity 1.06) that exhibited a high solubility in water (> 10 mg ml^{-1}). The inclusion complex registered absorption peaks in the UV-Vis spectrum at 243 and 295 nm, whereas **3** registered peaks at 243, 286, and 343 nm (Fig. 1). Additionally there was substantial peak broadening beyond 350 nm (inset). Dynamic light scattering studies of water-soluble fullerenes have established that this peak broadening is due to scattering

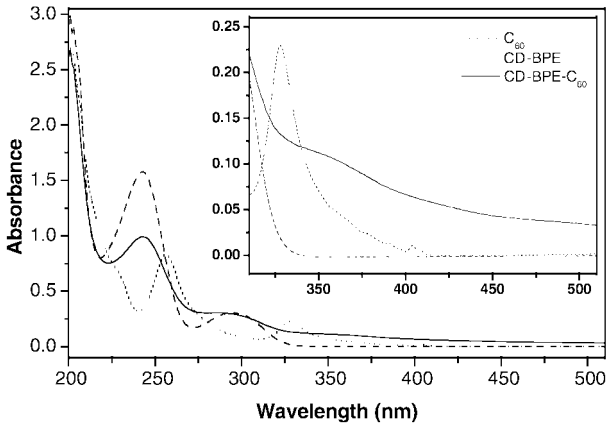
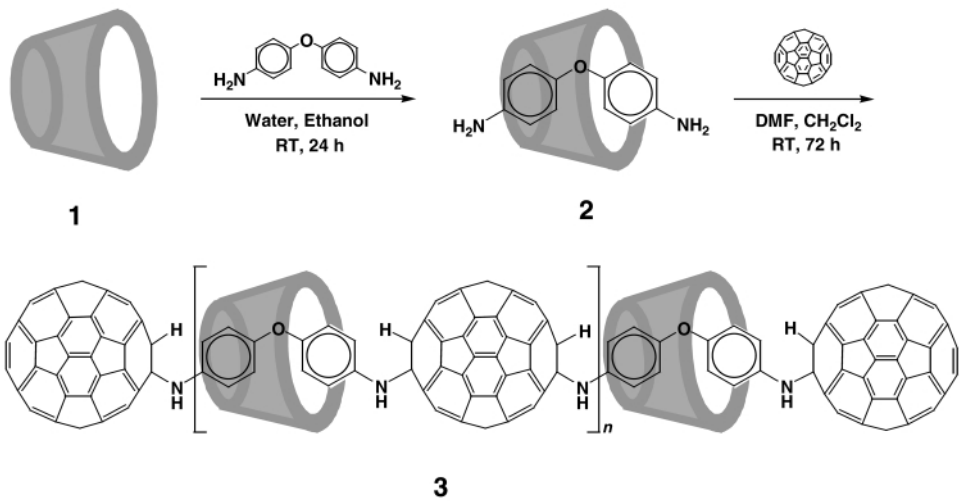


Fig. 1 UV-Vis spectra of C_{60} inclusion complex CD–BPE, and the polyfullerene CD–BPE–C_{60} (**3**).

† A colour version of the space-filling model of the supramolecularly shielded polyfullerene (Fig. 2) is available as electronic supplementary information (ESI). See http://www.rsc.org/suppdata/cc/b0/b003881o/



Scheme 1 Reaction scheme for the synthesis of polyfullerene (**3**).

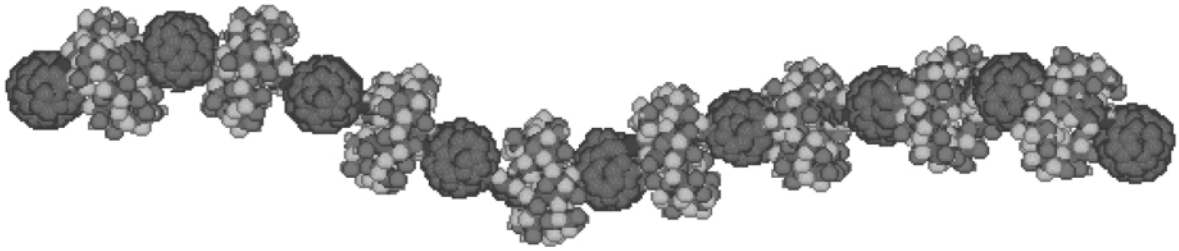


Fig. 2 Space-filling model of the supramolecularly shielded polyfullerene. For colour version, see http://www.rsc.org/suppdata/cc/b0/b003881o/

by fullerene aggregates.[5] The FT-IR spectra of the polyfullerene had distinct differences from the inclusion complex. In the case of the species from the reaction of CD–PPD and C_{60}, the fullerene peak was seen at 527 cm^{-1}, whereas for **3**, this peak was prominent at 513 cm^{-1}.

The ^1H NMR spectrum of the complex CD–BPE was well-defined, with the aromatic protons at 6.48, 6.51, 6.59, 6.62 ppm, contrary to the weak aromatic proton peaks of the CD–PPD complex, possibly due to the guest being deeply embedded in the CD cavity. The aromatic ring carbon atoms were registered at 114.7, 118.8, 144.0 and 148.3 ppm. All the characteristic peaks of the CD and BPE components were present in the polyfullerene **3**. Additionally, in the ^{13}C NMR spectra, there were peaks between 139–144 ppm assigned to the fullerene component.

In a comparative study without CD, C_{60} and BPE reacted to furnish a water-insoluble product. The material was characterized and found to be a polysubstituted fullerene, as could be expected of fullerene–amine reactions. Interestingly, such polysubstitution could be effectively prevented by the simple routine of placing the amine moiety within a cyclodextrin ring. The spatial dimensions of the macrocycle effectively prevented multifunctionalization of the fullerene units. At the moment we have not ascertained if C_{60} is connected at the *trans*-1 positions with the diamine and if there is any branching. Branching would mean strong stereochemical constraints, since each fullerene ball in the copolymer chain is already flanked by two CD units (see Fig. 2 for a space-filling model). Studies in this direction are being pursued, examining the spatial dimensions of the macrocycle and the fullerene in the molecular models.

In exploring the application potential of this novel polymer, preliminary experiments have shown that the material could be useful in biological and biomedical fields. The polyfullerene was found to strongly scavenge a living free radical, 1,1-diphenyl-2-picrylhydrazyl, even more strongly than [60]fullerene itself. Furthermore, the polymer was also found to cleave DNA oligonucleotide in the presence of light, which was ascertained from the GPC studies in conjunction with membrane filtration of the nucleotide before and after cleaving experiments. These preliminary results indicate that the polymer has retained the properties of the pristine [60]fullerene.

Although the above model reaction involves β-cyclodextrin and [60]fullerene, it is rather unlikely that the results described here are confined to these specific molecules. It might also allow the direct use of other fullerenes of the fullerene family such as higher homologues and exo- and endohedrally modified species, and the macrocyclic part may also be modified using a great variety of building units. The materials are expected to have a strong application potential in the biomedical area due to their hydrophilicity, but also many other applications of these interesting molecules can be envisaged such as their use as building blocks for molecular machines and robotics.[6] Further studies to elucidate the full potential of the approach are in progress.

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