Polymer Receptors

DOI: 10.1002/ange.201303032

Rationally Designed Polymer Hosts of Fullerene**

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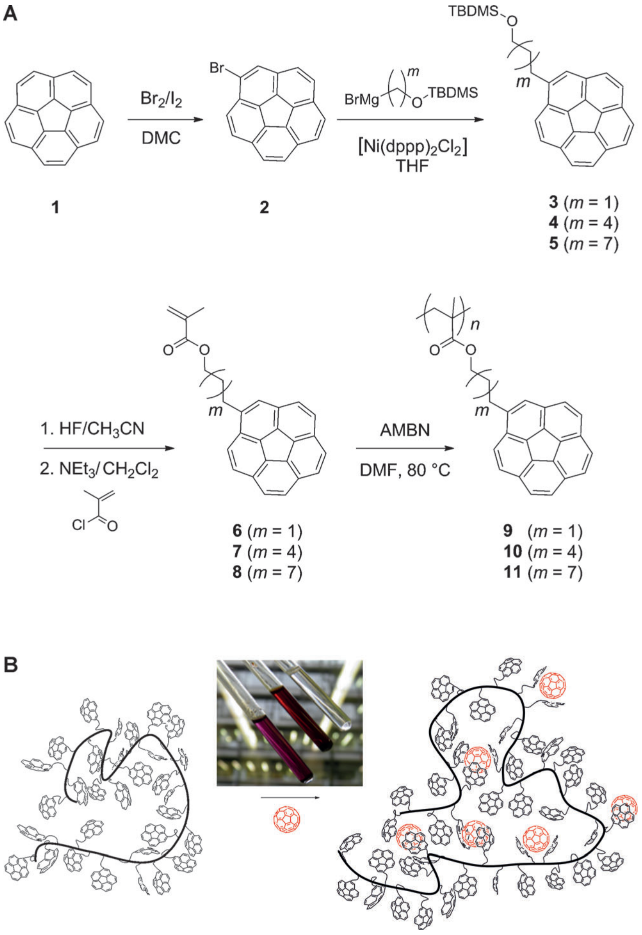
The development of hosts for fullerenes is an active area of research with technological implications.[1–8] In this context, macrocycles,[9,10] dendrimers,[4,11] π-conjugated linear and cyclic oligomers,[12–14] molecular clips,[4,15–20] and self-assembled small molecules[21] have been developed for their fullerene-encapsulation properties. A shift in this paradigm is possible by the design of polymer-based receptors. Progress in this direction, however, is restricted to the use of commercial materials, such as poly(vinyl pyrrolidone)s, that do not possess any molecular-recognition capacity towards fullerenes and therefore have limited potential as hosts.[22,23] Herein, we describe a general class of pristine C_{60} hosts based upon a novel family of corannulene-encoded[24–27] polymers (Scheme 1) synthesized by a free-radical-polymerization technique. Each repeat unit of these polymers contains the necessary information to interact with fullerene C_{60} through a "ball-and-socket"-type π–π stacking interactions (Scheme 1).[17,20,28–30] Since the free-radical synthesis enables the preparation of different polymer architectures (linear and branched) of varying compositions (homopolymers, random copolymers, block copolymers),[31–33] the described new family of hosts can be readily transformed into materials of a desired chemical composition and architecture appropriate for use in a specific application. For example, block copolymers with an electron-donating block can give rise to materials for photovoltaic applications,[34,35] whereas the introduction of a water-soluble comonomer into the polymer structure can yield C_{60}-rich water-soluble materials. Specifically, such water-soluble materials are constructed by preparing an amphiphilic block copolymer in which one block is water-soluble and the other block is composed of the host repeat units. This block copolymer is capable of dispersing hydrophobic C_{60} molecules in water by forming a core–shell type of micellar structure in which the corannulene core hosts the water-insoluble C_{60} molecules. Furthermore, the described system allows for tuning of the host–guest interaction in three different ways: a) by changing the linker length between the polymerizable site and the recognition unit, b) by altering the chemical nature of the solvent, and c) by varying the temperature. Moreover, powders as well as freestanding and transparent polymer films could be prepared from the C_{60}/polymer composites. The modularity of the designed system, the ease of synthesis, the ability to fine-tune the host–guest interactions, and the processability due to the polymeric nature of the system distinguish the described new class of hosts from previous host classes and indicate broad applicability of the described approach to polymer-based fullerene-host materials. Such materials will be of significant value in the arena of photovoltaics and plastic electronics.



Scheme 1. A) Synthesis of polymer receptors **9**–**11**. B) Schematic representation of fullerene encapsulation by the polymer receptor. A digital photograph of NMR tubes containing C_{60} (bottom), C_{60} + **10** (middle), and **10** (top) in chlorobenzene is also shown. dppp = 1,3-bis(diphenylphosphanyl)propane, DCM = dichloromethane, DMF = *N*,*N*-dimethylformamide, TBDMS = *tert*-butyldimethylsilyl.

Initially, we decided to prepare a homologous series of corannulene-containing homopolymers with linkers of different lengths between the polymer backbone and the receptor unit. In this way, we could compare the linker-length-dependent properties of the newly designed receptor materials with respect to their fullerene-encapsulation ability. For

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[**] I thank my mentor Prof. Jay S. Siegel (University of Zürich) for his constant support. Financial support from the Swiss National Science Foundation (SNSF), Ambizione (PZ00P2-126615), is gratefully acknowledged. Thanks are also due to Jingyi Rao (ETH-Z) for help with the micellization and microscopy studies.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201303032.

this purpose, methacrylate monomers **6**, **7**, and **8** containing C_3, C_6, and C_9 spacers were targeted (Scheme 1). Starting from corannulene (**1**), now available on a kilogram scale,[36] a bromination step gave bromocorannulene (**2**). A nickel-catalyzed Kumada coupling was then employed to install the alkyl spacer.

Compounds **3**–**5** were then subjected to a deprotection reaction followed by esterification with methacryloyl chloride to furnish monomers **6**, **7**, and **8** in 55–60 % overall yield. These monomers were then subjected to a conventional free-radical-polymerization process with 2,2′-azobis(2-methylbutyronitrile) (AMBN) as the initiator. This procedure afforded the target polymers **9**, **10**, and **11** with number-average molecular weights ranging from 125 to 520 kDa (see Table 1 in the Supporting Information). As expected, the glass-transition temperature of these polymers decreased as the linker length increased (see Table 1 in the Supporting Information). The ^{1}H NMR spectra of polymers **9**–**11** exhibited typical signals for the methacrylate backbone from 0.5 to 1.5 ppm (see Figure S7 in the Supporting Information). The signal for the methylene group located adjacent to the ester unit was observed at 3.9 ppm for polymers **10**–**11** and at 4.2 ppm for polymer **9**, whereas the methylene group adjacent to the corannulene showed a signal at 3 ppm. The aromatic resonances of the corannulene units in **9**, **10**, and **11** were in the range of 7–7.5, 7.2–7.7, and 7.4–7.9 ppm, respectively. The difference in the chemical shifts of the aromatic groups is most likely a reflection of their packing behavior along the polymer backbone. For example, polymers with a short linker length are expected to show tight packing and high contact of the aromatic side chains.

The interaction between the homopolymers and fullerene C_{60} was investigated by ^{13}C NMR spectroscopy, as demonstrated previously by Fukazawa and co-workers,[37–40] Sanders and co-workers,[21] and others.[41–43] To aid the measurements and analysis, ^{13}C-rich C_{60} was used.[42] Figure 1 shows ^{13}C NMR spectra of C_{60} and mixtures of C_{60} with each of the polymers **11**, **10**, and **9** in chlorobenzene. Signal shifts of 0.61, 1.00, and 1.05 ppm were observed in the ^{13}C-resonance signal of C_{60} upon complexation with the host polymers **11**, **10**, and **9**, respectively. To confirm that this shift was due to the interaction between the corannulene moieties and the C_{60} molecules, an external-standard tube (of smaller diameter than that of the original NMR tube) containing a pure solution of C_{60} in chlorobenzene was inserted into the NMR tube containing the solution of the polymer and the C_{60}. These samples showed both the signals from the uncomplexed fullerene (present as an external standard, as marked with an arrow in Figure 1) and the signal from the complexed C_{60} molecules. The observed increase in the signal shift as the linker length decreased indicated a stronger interaction in the case of structurally rigid systems. In the case of **9**, broadening of the C_{60} signal was observed, possibly as a result of the restricted rotational freedom of complexed C_{60} molecules or a reduced exchange rate between free and complexed C_{60} molecules in the solution. This result again suggests a stronger interaction between the structurally rigid host and the guest molecules.

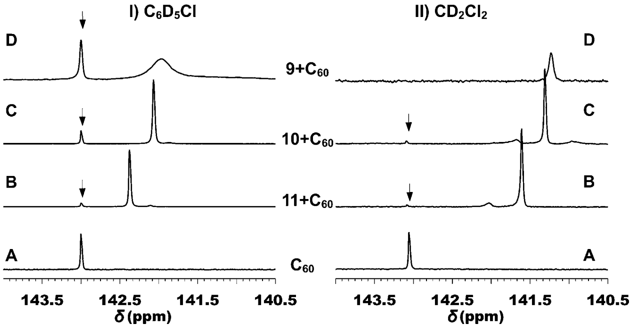


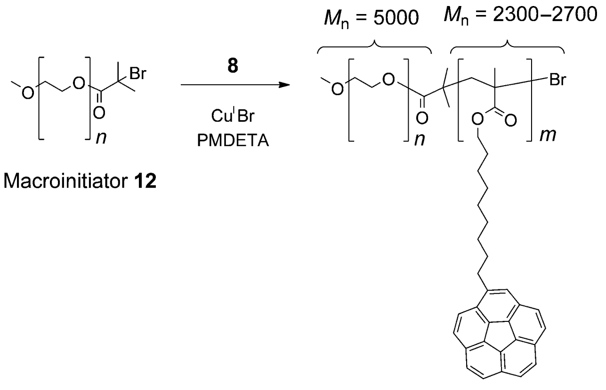
Figure 1. ^{13}C NMR spectra in I) chlorobenzene (0.3 mL) and II) dichloromethane (0.3 mL) of ^{13}C-rich C_{60} (3 mg) in the absence (A) and in the presence of polymers **9** (B), **10** (C), and **11** (D; 10 mg of the polymer in each case). In each case, the signal from C_{60} used as an external standard is marked with an arrow. The f1 chemical shift is shown.

Besides the use of an external standard, two different control experiments were carried out to further confirm that the signal shifts in the ^{13}C NMR spectra were due to a well-defined complexation event between the corannulene units of the host polymers and the C_{60} molecules. These ^{13}C NMR spectroscopic experiments were identical to those described above, with the exception that in one case poly(methyl methacrylate) (PMMA) and in the other polystyrene (PS) was used instead of the host polymers. PMMA was chosen because it constitutes the backbone of the designed host polymers. PS was chosen because of its pendent phenyl group, which is aromatic yet cannot form a well-defined "ball-and-socket" type of complex with C_{60}. The molecular weights of the control polymers were in a similar range to those of the described host polymer family. In both cases, no shift in the ^{13}C signal of C_{60} was observed (see Figure S20). These control experiments further suggested that the interaction between the designed host polymers and the guest C_{60} was due to the specific interaction between the corannulene unit of the host repeat unit and the guest molecule, and not due to nonspecific interaction with the polymer backbone or the side chain.

Next, the effect of the solvent on the complexation capability of the newly designed host polymers was investigated. Chlorobenzene is a good solvent for both C_{60} and the polymers. When ^{13}C NMR spectra were recorded of mixtures of C_{60} and the polymers in dichloromethane, in which fullerene is sparingly soluble, the C_{60}-signal shifts were now observed to be 1.46 (**11**), 1.77 (**10**), and 1.85 ppm (**9**; Figure 1). This set of experiments indicates that the interaction of the fullerene with the receptor polymers could be enhanced by choosing an appropriate solvent. Dichloromethane is a good solvent for the polymer but a poor solvent for the C_{60} molecules. The polymer backbone enables the host to maintain good solubility in the medium, and the corannulene parts of the polymer offer refuge to the C_{60} molecules. In this way, contact between the guest molecules and the host polymer could be enhanced.

Owing to the supramolecular nature of the complexation, another way of modulating the interaction between the guest and the host in the present system can be envisaged in the form of temperature variation. This possibility was investigated with polymers **10** and **11**. An increase in the temperature led to a decrease in the shift of the C_{60} resonance, whereas a decrease in the temperature led to an increase in the shift (see Figures S14 and S15). These results indicated that the association between the host and the guest could be further increased upon cooling, whereas an increase in the temperature weakened the association.

To demonstrate the generality of the present receptor system, a diblock copolymer containing the host as one block was targeted. For this purpose, a 5 kDa poly(ethylene glycol) (PEG) polymer was converted into an initiator, **12**, for atom-transfer radical polymerization (ATRP)[32] ($M_{n(NMR)} = 5000$, $PDI_{(GPC)} = 1.12$; Scheme 2; PDI = polydispersity index, GPC = gel permeation chromatography). Monomer **8** was then polymerized under ATRP conditions with macroinitiator **12**. The diblock copolymerization was confirmed by NMR spectroscopic and GPC techniques (see Figures S16–S18). By end-group analysis on the basis of ^{1}H NMR spectroscopy, the degree of polymerization of the receptor block was determined to be 5–6.



Diblock Copolymer **13**

Scheme 2. Synthesis of the amphiphilic host copolymer **13**. PMDETA = *N*,*N*,*N*′,*N*′,*N*′′-pentamethyldiethylenetriamine.

Block copolymer **13** ($M_{n(NMR)} = 7300\text{-}7760$, $PDI_{(GPC)} = 1.11$) is an amphiphilic copolymer, as the PEG block constitutes a hydrophilic segment and the corannulene acrylate block constitutes a hydrophobic segment. Since the hydrophilic block is the major block, the amphiphilic copolymer **13** is expected to form a micellar structure in water.[44] In this micellar structure, the host—being hydrophobic—will organize in the core to minimize its interaction with water. Secondary-structure formation by copolymer **13** was investigated by ^{1}H NMR spectroscopy. Figure 2 shows the ^{1}H NMR spectra of copolymer **13** in deuterated dichloromethane and water. In deuterated water, only signals from the PEG segments were observed. As established by various other researchers,[45] this result indicated that copolymer **13** assembles into a micellar structure in water. The hydrophilic block, PEG, forms a micellar shell that can be observed by ^{1}H NMR spectroscopy, whereas the hydrophobic block, poly(corannulene acrylate), forms the core and remains invisible in the ^{1}H NMR spectrum. Dynamic light scattering (DLS) confirmed micelle formation by copolymer **13** in water (see Figure S25). When C_{60} was added to the aqueous solution of copolymer **13** and the mixture was sonicated for a few minutes, a brown solution resulted. It was visually apparent that C_{60} remained insoluble in water unless the polymer was present in the system (Figure 3). Sonication probably disrupts the micellar structure and enables C_{60} to enter the corannulene-rich core. The association between C_{60} and the block copolymers was also analyzed in dichloromethane by ^{13}C NMR spectroscopy and was found to be in line with the results discussed for the homopolymers. The DLS study further confirmed that the mixture of copolymer **13** and C_{60} exists in a micellar form in water. The micelle diameter was larger than that of the micelle formed from the diblock copolymer alone. It is reasonable to assume that this increase in size is a result of micelle impregnation with C_{60} molecules (see Figure S25).

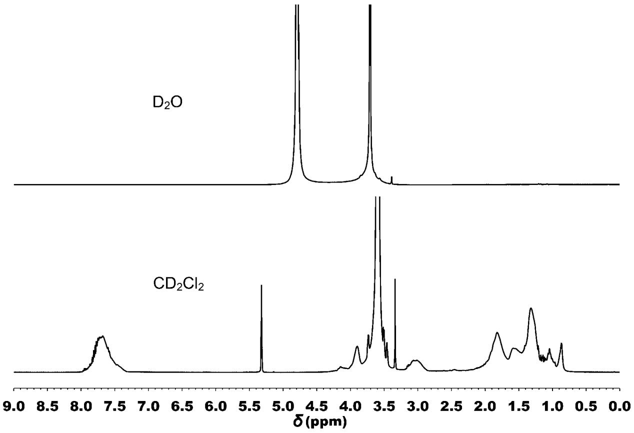


Figure 2. ^{1}H NMR spectra of the block copolymer **13** in dichloromethane (bottom) and in water (top). The f1 chemical shift is shown.

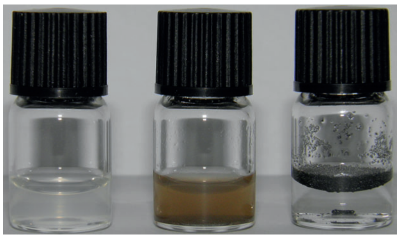


Figure 3. Visual appearance of polymer **13** (left), **13** + C_{60} (center), and C_{60} (right) in water.

The self-assembled architecture was further investigated by atomic force microscopy. For these studies, a micellar solution of copolymer **13** in water was spin coated onto mica and HOPG (highly oriented pyrolitic graphite) substrates. No structure was observed on HOPG, whereas spherical structures with a narrow size distribution were observed on mica (see Figure S21). The absence of structure on the graphite substrate can be explained by the affinity between the corannulene units and the graphene surface; this affinity leads to breaking of the micelles and molecular deposition of the polymer chains on the surface. However, since mica is hydrophilic, it interacts with the PEG segments and protects the secondary structure; thus, the spherical micelles remain intact. Next, a micellar solution of copolymer **13** and C_{60} was spin coated in a similar fashion. Now, the spherical structures found for the copolymer alone were observed on mica, whereas on HOPG, dendritic structures were observed (Figure 4). The dendritic structures perhaps result from the "gluing" effect of the C_{60} molecules on the micellar core (a form of physical cross-linking of the structure). This effect prevents micellar disruption; however, the hydrophilic PEG segments still do not show affinity for the hydrophobic substrate, and hence aggregation leads to the formation of a continuous dendritic structure. TEM investigations on carbon-coated copper grids were also carried out (Figure 4). In the absence of C_{60}, no structures were observed for the diblock copolymer **13**, whereas C_{60} alone in water gave rise to macroscopic structures (see Figure S26). However, when both the diblock copolymer **13** and C_{60} were present, spherical nanometer-sized structures were observed. The TEM images were produced without staining of the sample; hence, dark spots are due to the C_{60}-rich corannulene core of the micelles, and the PEG shell remains invisible. The results were in accordance with the AFM study.

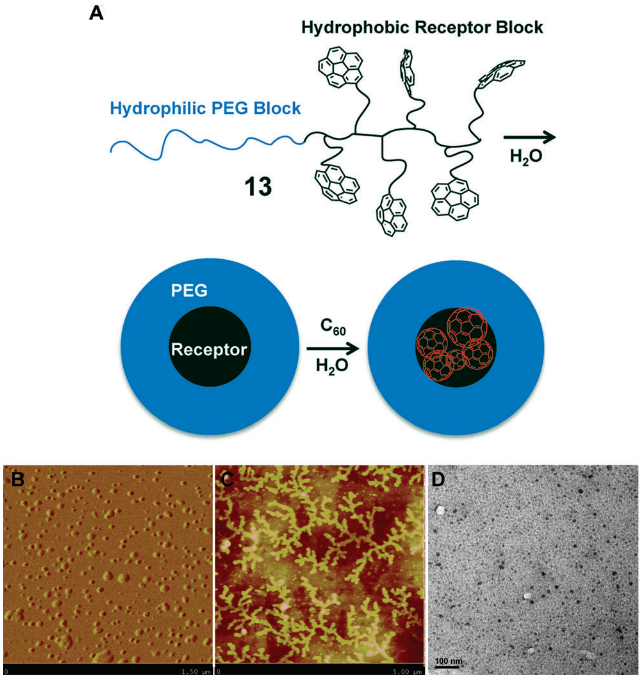


Figure 4. A) Schematic representation of micelle formation and C_{60} encapsulation by copolymer **13** in water. B,C) AFM images of the nanostructures formed by **13** + C_{60} in water on mica (B) and on HOPG (C). D) TEM image of **13** + C_{60} in water on a carbon-coated copper grid (scale bar: 100 nm).

Removal of the solvent from the homopolymer composite systems gave rise to brown-colored powders. Thin films could be cast by redissolution of the powders in an appropriate solvent. Remarkably, the films were completely transparent (Figure 5), which indicates a homogeneous dispersion of C_{60} in the polymer matrix.

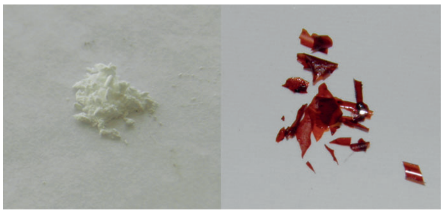


Figure 5. Visual appearance of polymer **10** (left) and its film composite with C_{60} (right).

In conclusion, a new class of fullerene C_{60} hosts based on polymers has been developed by careful design of the molecular structure of the repeat unit and the mode of interaction between the polymer unit and the C_{60} molecule. These hosts were synthesized by free-radical polymerization. Therefore, hosts with various chemical compositions and architectures can be constructed readily by appropriate design of the monomer receptor. Initially, homopolymers were synthesized by the conventional protocol for free-radical polymerization, and their C_{60}-encapsulation properties were investigated. From these studies, it became clear that three different methods could be adopted for the modulation of the host–guest interaction in the present receptor system: a) variation of the linker length, b) variation of the nature of the solvent, and c) variation of the temperature. To further demonstrate the generality of the approach, block copolymers were prepared by a controlled radical-polymerization procedure in which the radical polymerization of the designed host monomers was controlled and initiated by a polymer block of a different chemical nature. This procedure enables the synthesis of heterogeneous block-type structures. In the present case, a 5 kDa PEG polymer was used as a macroinitiator, and it was established that the obtained amphiphilic block copolymer could transport hydrophobic C_{60} molecules into water through the formation of micellar-type structures. In light of these developments, initiation by an electron-donor polymer block, such as polythiophene, can be envisaged. The use of polythiophene as the initiator would give rise to polythiophene-*b*-polycorannulene acrylate copolymers. The polycorannulene block could host C_{60} to produce a donor/acceptor system. Since the composition and the rigidity of the host block can be changed, it should be possible to fine-tune the structure and polarity of the acceptor block to obtain a microphase-separated morphology, typical of block copolymers, in thin films. Such materials with defined donor (polythiophene) and acceptor (C_{60} + receptor polymer) domains at the nanometer scale in thin films will be of use in photovoltaic applications.[35] This supramolecular route to donor–acceptor materials is superior to the covalent immobilization of C_{60} on a polymer segment,[46] as covalent C_{60} derivatization is synthetically tedious and affects the electronic properties of the fullerene by disrupting π-electron conjugation.

Received: April 11, 2013

Keywords: corannulenes · fullerenes · host–guest systems · polymer receptors · radical polymerization

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