Supramolecular Polymers

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Self-Organization of Electroactive Materials: A Head-to-Tail Donor–Acceptor Supramolecular Polymer**

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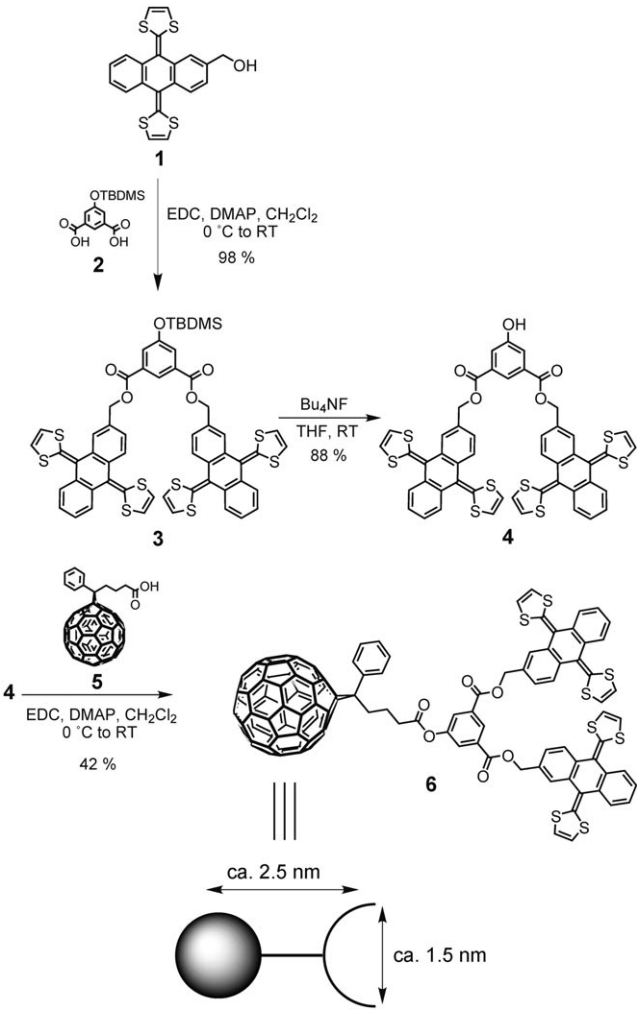
Supramolecular polymers[1] consist of repeated units of molecular monomers designed to self-assemble in solution or in the bulk. One of the main approaches to build this kind of architectures is based on the introduction of self-recognizing hydrogen-bonding motifs.[1b] The pioneering work led by Lehn, in which three hydrogen-bonding groups are used[2] and which was later expanded to four hydrogen bonds by Meijer and co-workers[3], has proven to be particularly fruitful. Another common strategy employed to construct supramolecular polymers makes use of metal coordination.[4] Finally, a variety of supramolecular polymers based on solvophobic interactions—primarily containing cyclodextrins as hosts[1c,5]—has also been reported. To date, little effort has been devoted to the study of supramolecular polymers based on π–π aromatic interactions. Recently, Fukazawa and co-workers described the realization of supramolecular polymeric nanonetworks based on this kind of noncovalent interactions.[6]

We recently described the first receptor for [60]fullerene, which is based on a π-extended analogue of tetrathiafulvalene (TTF), 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9*H*)-ylidene]-1,3-dithiole (exTTF).[7] Our receptor is composed of two units of exTTF connected through an isophthalic diester spacer. The large and concave aromatic surface of the exTTF units serves as a recognizing motif for the convex surface of C_{60}, and binding constants of greater than $10^{-3}\,M^{-1}$ were measured. This finding prompted us to exploit this host–guest system for building novel organized donor–acceptor arrays.

Several covalent[8a] and supramolecular[6,8] polymers containing C_{60} have been described to date. However, to the best of our knowledge, none of them are redox-amphoteric. Herein, we report a fullerene–exTTF supramolecular polymer, based on π–π aromatic interactions, in which the recognizing units are complementary both in a supramolecular and an electronic sense.

We designed monomer **6** to self-assemble in a head-to-tail fashion by covalently connecting a C_{60} derivative with our pincerlike fullerene receptor. To increase the solubility, we chose PCBA (compound **5** in Scheme 1) as the fullerene-containing fragment. The synthesis of monomer **6** is depicted in Scheme 1.

Figure 1 shows the ^{1}H NMR spectra of monomer **6** ($CDCl_3$, 300 MHz, 298 K) at concentrations between 0.6 and 30 mM. As the concentration increases, a slight shielding of most of the resonances can be observed. This phenomenon is accompanied by a broadening of all signals, which indicates



Scheme 1. Synthesis of monomer **6**. TBDMS = *tert*-butyldimethylsilyl, EDC = *N*-ethyl-*N*′-(3-dimethyldiaminopropyl)carbodiimide hydrochloride, DMAP = 4-dimethylaminopyridin.

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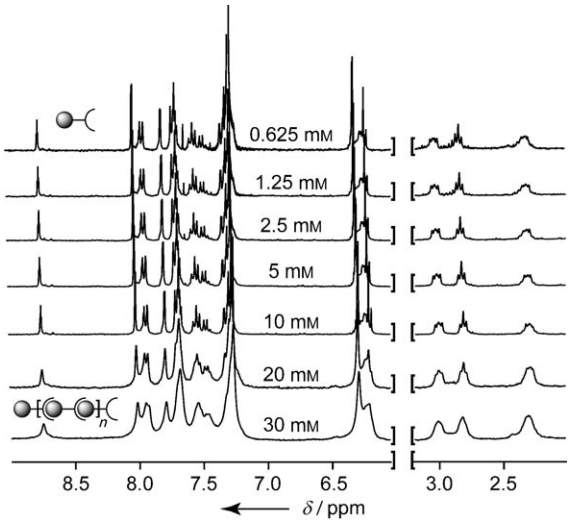

Figure 1. Partial ^{1}H NMR spectra of **6** at different concentrations ($CDCl_3$, 300 MHz, 298 K).

the formation of high-molecular-weight aggregates at high monomer concentrations.[9]

The competition between linear chain extension and oligomeric cyclization[10] of monomer **6** was studied by means of variable-temperature ^{1}H NMR spectroscopy experiments ($CDCl_3$, 300 MHz) performed at a concentration of 6 mM. At room temperature and above, the ^{1}H NMR spectra show well-defined sharp signals (see Figure 2), which indicates a low concentration of high-molecular-weight species. As the temperature decreases, most of the aromatic signals are shifted upfield ($\Delta\delta \approx -0.05$ ppm) whereas the dithiole resonances are shifted downfield ($\Delta\delta \approx +0.05$ ppm). This pattern mirrors that previously reported for a similar family of TTF-derived fullerene receptors upon complexation[11] and is indicative of a preferential association of fullerene on the aromatic side of exTTF. These shifts are accompanied by a progressive broadening of the resonances, although to a lesser extent than in the concentration experiment. As expected, the concentration of aggregates increases upon lowering the temperature. However, the most remarkable feature is the significant shielding of the alpha-methylene group with respect to the PCBA ester unit ($\Delta\delta \approx -0.13$ ppm), a characteristic that is not observed in the concentration experiments and points to the formation of more rigid, cyclic oligomers (a type of association in which the methylene groups of PCBA play a more prominent role than in the linear chain extension).

Despite the high molecular weight of **6**, we observed aggregates up to the pentamer under MALDI-TOF mass-spectrometry conditions. Experiments with **6** were carried out using dithranol as matrix. Besides the molecular peak corresponding to the monomer mass (m/z 1845), we observed signals at m/z 3689 (dimer), 5535 (trimer), 7380 (tetramer), and 9225 (pentamer; see the Supporting Information).

The self-diffusion coefficients of **6** were estimated by pulse-field-gradient NMR (PFG-NMR) studies of two different monomer solutions (1 and 15 mM, $CHCl_3$, 298 K). As expected, the diffusion coefficients decreased with an

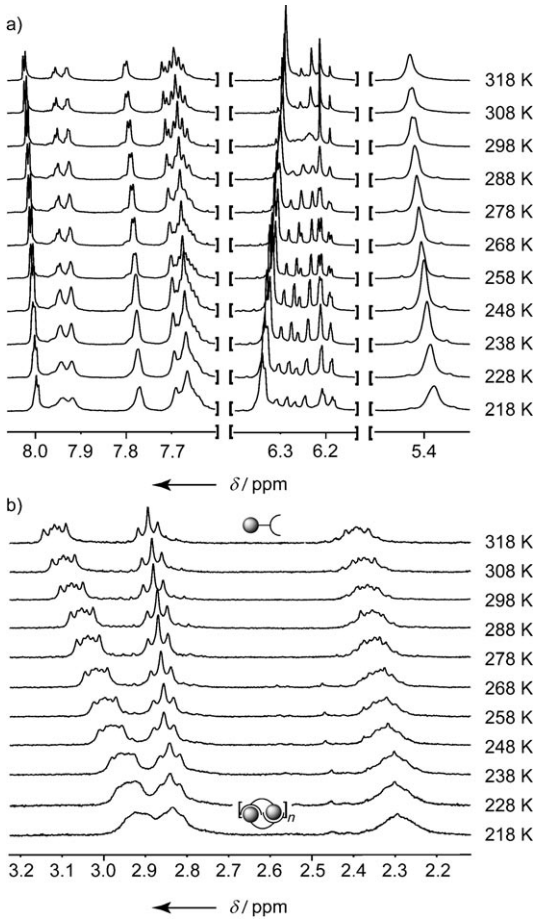

Figure 2. Partial VT-^{1}H NMR spectra of **6** ($CDCl_3$, 300 MHz, 6 mM) showing a) the aromatic region, the dithiol groups, and the exTTF methylene groups, and b) the methylene signals of the PCBA unit.

increase in the concentration as a result of the larger size of the oligomers of **6**. Dynamic light-scattering measurements (DLS) were carried out on solutions of **6** in chloroform (0.5 mM) to obtain an estimation of the molecular weight of the polymers. A broad particle-size distribution was found—ranging from 2 nm (for the monomer) to several micrometers (greater than 400 mer), with a maximum at 378 nm (160 mer; see the Supporting Information). Considering the association constant between the parent receptor and [60]fullerene,[7] the species found in the DLS experiment are somewhat larger than expected, which might be attributed to the formation of nonspecific oligomer aggregates.

The influence of the self-assembly process on the electronic properties of **6** was analyzed through cyclic voltammetry performed at different concentrations (in tetrahydrofuran, THF, using $Ag/AgNO_3$ as the reference electrode, glassy carbon as the working electrode, and Bu_4NClO_4 as the supporting electrolyte; scan rate: 100 mV s^{-1}; temperature: 298 K). Figure 3a shows the cyclic voltammograms (CVs) of **6** at 0.2, 0.4, 0.6, and 1.0 mM. The CV of PCBM, that is, the methyl ester of PCBA (measured at 1.0 mM) is also shown as reference. Upon concentration of **6**, the reduction processes become more energetic and irreversible. Analogously, the exTTF oxidation wave is shifted anodically as concentration

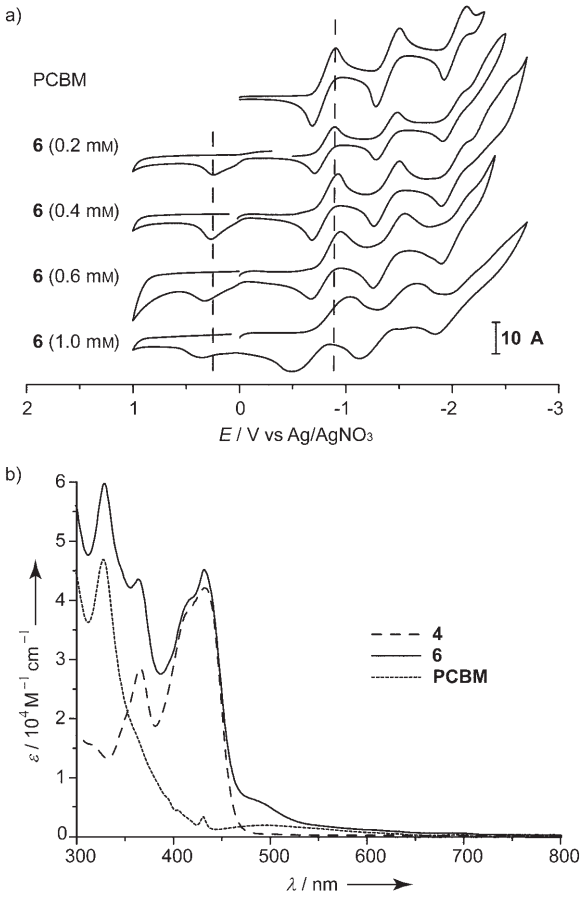

Figure 3. a) Cyclic voltammograms of PCBM (1 mM) and **6** (0.2, 0.4, 0.6, and 1.0 mM) in THF using $Ag/AgNO_3$ as the reference electrode, glassy carbon as the working electrode, and Bu_4NClO_4 as the supporting electrolyte (scan rate: 100 mVs^{-1}; temperature: 298 K). b) Electronic absorption spectra ($CHCl_3$, 298 K) of **4** (-----), **6** (——), and PCBM (•••••).

increases. The reduction of the positively charged species generated upon oxidation of the exTTF units becomes highly irreversible and occurs nearly at the same potential as the first reduction process of the C_{60} cage (at about −0.8 V). All these data indicate that electronic communication between the electroactive units takes place in the ground state and is enhanced by complexation, a fact that is also reflected in the UV/Vis spectrum of **6** by the presence of a charge-transfer band at $\lambda_{max} = 487$ nm (see Figure 3b). Qualitatively identical changes occur in the previously reported receptor upon complexation with fullerene.[7]

Final evidence to support the formation of oligomeric linear species was obtained by means of atomic force microscopy (AFM). A solution of **6** (1.0 μM) in dichloromethane was drop-casted onto mica. Tapping-mode AFM images were then recorded under air at room temperature. The images show long (15–300 nm), winding, necklacelike fragments of 1.7–2.5 nm in height. These dimensions are in accordance with those expected for associated fragments of **6** (see Figure 4 and cartoon in Scheme 1). An insight into a 77-nm-long tubular formation (which corresponds to the 35 mer) is shown in Figure 4b–d. In sharp contrast, the AFM images

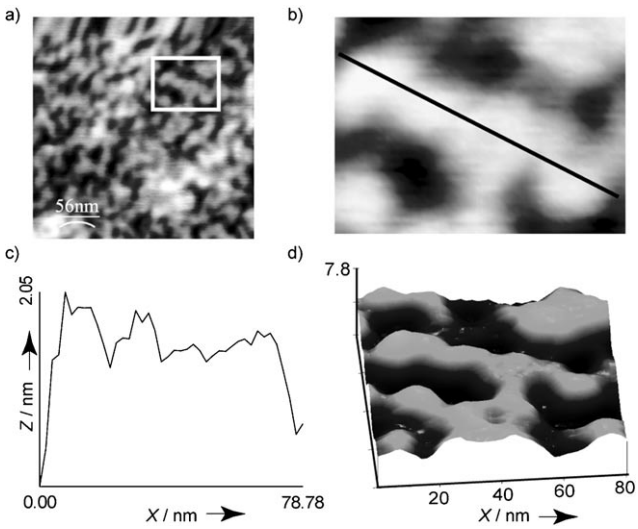

Figure 4. AFM images (tapping mode, air, 298 K) of a drop-cast of a dichloromethane solution of **6** on mica. a) 277×277 nm; b) 80×65 nm; c) profile of the structure shown in (b) (black line); d) 3D image of (b).

of PCBM samples, obtained under experimentally equivalent conditions, show randomly distributed and approximately circular aggregates of variable height and diameter (less than 50 nm, see the Supporting Information).

In conclusion, we have described a head-to-tail linear supramolecular polymer based on a new host–guest fullerene–exTTF system. As demonstrated by ^{1}H NMR and PFG-NMR spectroscopy, MALDI-TOF mass spectrometry, DLS, CV, UV/Vis spectroscopy, and AFM, monomer **6** readily self-assembles through noncovalent interactions to form multimeric species both in solution and on a solid surface. Besides being one of the first examples of supramolecular polymers in which π–π aromatic interactions are the chief driving force for the self-association of the monomer,[6] this system represents a fundamentally new approach to the organization of electroactive donor–acceptor fragments.[12] Its validity for the construction of more-efficient optoelectronic devices will be investigated in the near future.

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