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Supramolecular polymers

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High Degree of Polymerization in a Fullerene-Containing Supramolecular Polymer**

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Abstract: *Supramolecular polymers based on dispersion forces typically show lower molecular weights (MW) than those based on hydrogen bonding or metal–ligand coordination. We present the synthesis and self-assembling properties of a monomer featuring two complementary units, a C_{60} derivative and an exTTF-based macrocycle, that interact mainly through π–π, charge-transfer, and van der Waals interactions. Thanks to the preorganization in the host part, a remarkable $\log K_a = 5.1 \pm 0.5$ in $CHCl_3$ at room temperature is determined for the host–guest couple. In accordance with the large binding constant, the monomer self-assembles in the gas phase, in solution, and in the solid state to form linear supramolecular polymers with a very high degree of polymerization. A MW above 150 kDa has been found experimentally in solution, while in the solid state the monomer forms extraordinarily long, straight, and uniform fibers with lengths reaching several microns.*

Supramolecular polymers consist of repeated units of monomers held together through noncovalent interactions.[1,2] The dynamic nature of these weak links endows supramolecular polymers with distinct properties, like self-healing or environment response abilities.[3,4] On the downside, it is difficult to obtain high molecular weight supramolecular polymers, since a very high association constant between the monomers is required. To this end, chemists have typically resorted to multiple hydrogen-bonding motifs, or metal–ligand coordination. For example, Meijer and co-workers implemented the 2-ureido-4-pyrimidone self-recognizing unit, which features a quadruple donor-donor-acceptor-acceptor hydrogen bonding motif, with a $\log K_{\mathrm{dim}} = 6.3$ in $CHCl_3$ at room temperature, to construct supramolecular polymers with a molecular weight (MW) of up to 500 kDa at 40 mM, approximately 700 repeating units of the monomer.[5] Exploiting coordination of Ni^{2+} or Zn^{2+} ions, a group led by Lehn described metallosupramolecular polymers with MW of up to 45 kDa, or 23 repeating units, at a concentration of 25 mM.[6] More recently, Gibson and co-workers have utilized the association of crown-ether cryptands and bisparaquat derivatives ($\log K_a = 3.8$ in acetone at room temperature) to yield polymers of 112 kDa (43 repeating units) at 290 mM.[7] The use of dispersion-type noncovalent forces to construct high molecular weight supramolecular polymers is perhaps more challenging, as they are typically weaker and intrinsically non-directional. Cyclodextrin-based supramolecular polymers, where association takes place mainly through solvophobic interactions, are perhaps the most noteworthy example. Within this family, Harada and co-workers described a supramolecular polymer of MW = 18 kDa (14 repeating units) at 10 mM in aqueous solutions.[8]

The rigid structure, round shape, and remarkable electronic properties of fullerenes make them appropriate scaffolds for the construction of unprecedented carbon-based nanoarchitectures.[9] Moreover, fullerenes are by far the most frequently used n-type materials in organic solar cells (OSCs).[10–12] This makes the self-assembly of fullerene-based molecular fragments a very attractive approach to control the nanometric organization of the active materials in OSCs, a factor that is seen as crucial towards improving the performance of the devices.[13] Hence, several supramolecular polymers featuring fullerenes have been described.[14–18] In this realm, precise control over the size and shape of the supramolecular polymer is particularly relevant.

Herein, we describe a high MW fullerene-containing supramolecular polymer with remarkably uniform linear shape. Our design is based on the association of a fullerene guest by a macrocyclic host featuring two π-extended tetrathiafulvalene recognizing units.

In the last few years, we have successfully employed 9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (exTTF) as a recognition moiety for fullerenes.[19,20] Our initial design consisted of two exTTF units connected through an aromatic diester spacer, forming a flexible pincer-like host which showed binding constants in the order of $\log K_a = 3$–4.[21–23] Utilizing this tweezers host, we synthesized linear[24] and hyperbranched[25] supramolecular polymers, with a relatively modest degree of polymerization. For instance, in the case of the linear polymer, up to 5 repeating units (MW = 9.2 kDa) could be detected by MALDI-TOF spectrometry. Later, we

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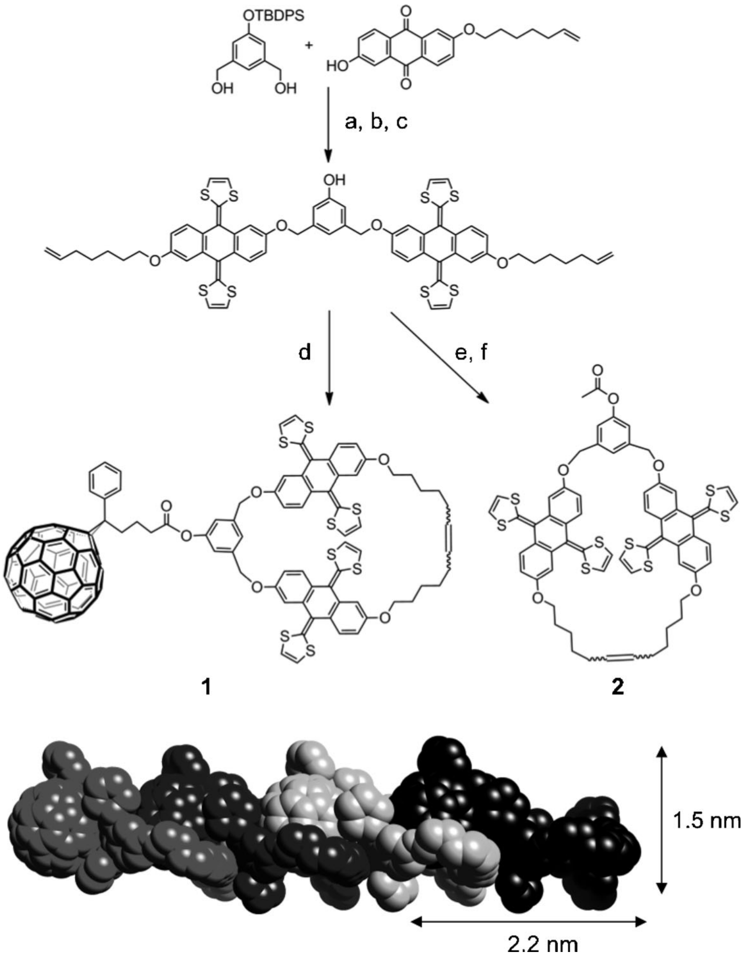
synthesized much more efficient receptors based on macrocyclic scaffolds,[26] which reach binding constants as high as $\log K_a = 7.5$ towards C_{60} in benzonitrile at room temperature.[27,28] Based on these results, we designed monomer **1**, in which a macrocyclic receptor with a C12 alkyl chain spacer was connected covalently to a $PC_{61}BA$ derivative, and synthesized it as shown in Scheme 1. We also synthesized the acetyl derivative of the macrocycle, **2**, to quantify its association with $PC_{61}BM$.

Typical results for a titration experiment of **2** versus $PC_{61}BM$ are shown in Figure 1. We observed the characteristic trends indicative of association of C_{60} by exTTF-based receptors, a decrease in the intensity of the absorption centered at 430 nm, accompanied by the rise of a broad charge-transfer band with a maximum at 480 nm, with a well-defined isosbestic point at 451 nm. Multivariable analysis of three separate titration experiments afforded a binding constant of $\log K_a = 5.1 \pm 0.5$ in $CHCl_3$ at room temperature.

In accordance with the large binding constant of the model system, MALDI-TOF analysis of a sample of **1** (Figure 2a and Supporting Information) showed aggregates up to the 46-mer, with a MW = 90 kDa in the gas phase, as well as the peak for the monomer (calcd. $m/z = 1985.2$, found = 1985.3). To our knowledge, this degree of polymerization has never before been observed in the mass spectra of fullerene-containing supramolecular polymers.



Scheme 1. Top: Synthesis of monomer **1** and reference compound **2**. Reaction conditions: a) PPh_3, DIAD, CH_2Cl_2, 0 °C to room temperature, 2 h; b) dimethyl 1,3-dithiol-2-ylphosphonate, BuLi, THF, −78 °C to room temperature, overnight; c) Bu_4NF, THF, 1 h; d) $PC_{61}BA$, EDC, DMAP, CH_2Cl_2, 0 °C to room temperature, overnight; e) DMAP, acetyl chloride, CH_2Cl_2, room temperature, 4 h; f) Grubbs' 1st generation catalyst, CH_2Cl_2, room temperature, overnight. DIAD = diisopropyl azodicarboxylate, EDC = 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, DMAP = 4-(dimethylamino)pyridine Bottom: molecular mechanics (MM+) space-filling model of a tetramer of **1**. Each monomer is depicted in different shade of gray. The size of **1** is also shown.

In solution, we did not find any significant changes in the ^1H NMR spectrum of **1** with increasing concentration (0.05 to 0.5 mM, 300 MHz, $CDCl_3$, 298 K). In all cases the spectra show broad, poorly defined signals, indicative of high molecular weight species (Figure S1 in the Supporting Information). Likewise, UV/Vis absorption spectra of **1** at concentrations ranging from 0.4 to 0.007 mM ($CHCl_3$, 298 K) showed only very small changes in the relative intensity of the absorption bands (Figure 2b). Remarkably, at all concentrations a charge-transfer band centered at approximately 480 nm is clearly visible. This band replicates the one found during the **2** versus $PC_{61}BM$ titration, and is the fingerprint of the exTTF-C_{60} interaction.[21,23,27,28] These findings indicate that, in agreement with the large binding constant calculated, the concentration of free **1** present in solution is low even at total concentrations in the order of 10^{-5} M. In contrast, in similar experiments with our previously reported monomer, in which the exTTF host part was not preorganized, we could clearly see that polymerization only took place at high concentrations, exceeding 20 mM.[24]

A comparison of the square-wave voltammetry (SWV) data of **1** with the reference compounds **2** and $PC_{61}BM$, obtained under identical experimental conditions, reveals that all electrochemical processes become more energetic in the case of **1**, that is, the first reduction potential of the C_{60} unit becomes more negative, while the oxidation potential of

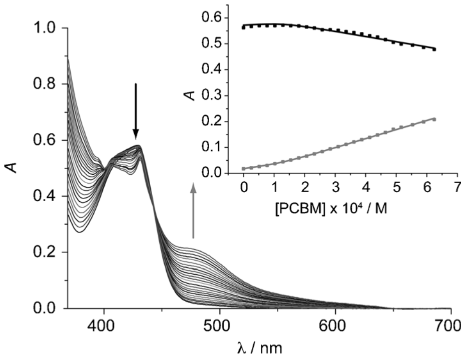


Figure 1. UV/Vis titration of **2** ($CHCl_3$, 0.13 mM) versus PCBM ($CHCl_3$, 1.3 mM, each addition corresponds to 0.2 equiv, up to a total of 4.8 equiv). Inset: the binding isotherms at 422 nm (black squares) and 480 nm (gray squares), solid lines represent the fits.

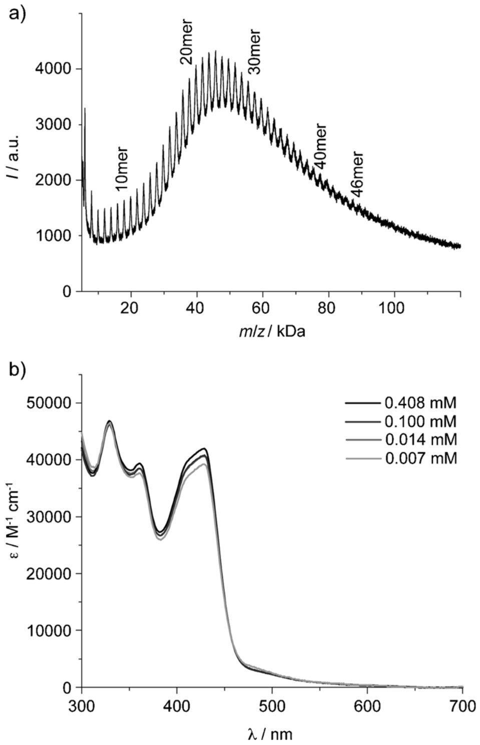


Figure 2. a) MALDI-TOF spectrum of **1** (DCTB matrix), showing aggregates of MW up to 90 kDa. b) UV/Vis spectra ($CHCl_3$, 298 K) of **1** at several concentrations.

exTTF becomes more positive (Table 1). We have previously demonstrated such observation to be a very good indication of binding, as the shift is caused by electron confinement in the bound species.[23]

Table 1: Redox potentials (in Volts) for **1**, **2**, and $PC_{61}BM$, as obtained by SWV.[a]

Compound	E_{ox}	E^1_{red}	E^2_{red}	E^3_{red}
1	0.25	−0.82	−1.37	−1.98
2	0.16			
$PC_{61}BM$		−0.80	−1.37	−1.97

[a] Measurements were performed at room temperature in dry THF, with 0.1 M $TBAPF_6$ as electrolyte, $Ag/AgNO_3$ as reference electrode and glassy carbon as working electrode.

The size of the supramolecular polymer in solution was determined experimentally through dynamic light scattering (DLS) measurements at 1, 0.1, and 0.01 mM in $CHCl_3$ at room temperature. The results of these DLS experiments are shown in Figure 3. The Z-average is considered the most reliable measurement of particle size that can be obtained by DLS (ISO 22412:2008). In our case, the mean Z-average of three separate measurements for each concentration afforded $R_H = 2455 \pm 56$ nm, 1495 ± 101 nm, and 962 ± 75 nm for 1, 0.1, and 0.01 mM, respectively. There is a clear decrease of the particle size with decreasing concentration, as would be expected. Remarkably, even at 10^{-5} M the mean particle size is in the μm range, highlighting the large degree of polymerization of **1** in solution.

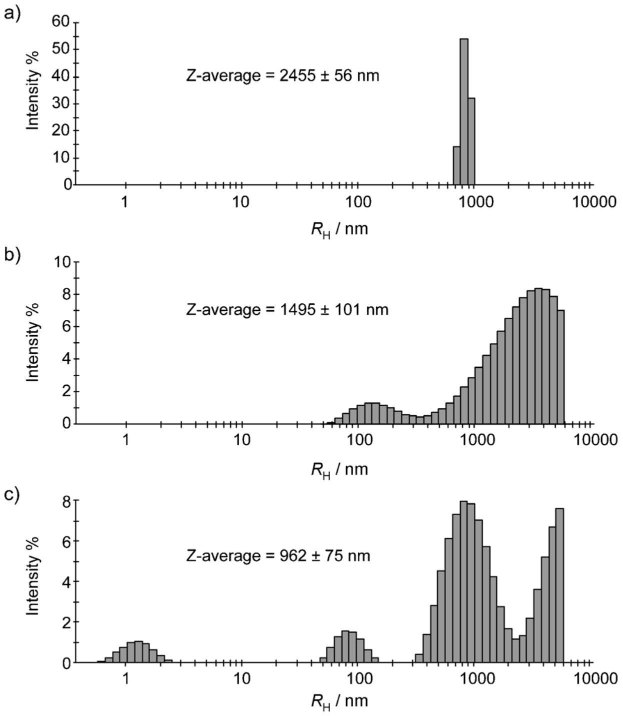


Figure 3. Distribution of hydrodynamic radii of aggregates of **1** as measured through DLS at a) 1 mM, b) 0.1 mM, and c) 0.01 mM.

In more detail, at 1 mM (Figure 3a), apparently only a very narrow distribution of sizes between 700 nm and 1 μm was found, but, besides this, the software in our DLS system warns of large polydispersity and/or the presence of excessively large particles (> 6 μm, its detection limit), in accordance with the large Z-average (see Figure S2 in the Supporting Information for original correlograms and quality reports). At 0.1 mM, the sample displays a very broad distribution ranging from approximately 40 nm to over 6 μm, with two broad maxima centered at hydrodynamic radii of 160 nm and 2800 nm. Remarkably, neither monomeric **1** nor small oligomers were observed at either 1 or 0.1 mM, in sound agreement with our ^1H NMR, UV/Vis, and cyclic voltammetry (CV) data. Finally, diluting to 0.01 mM allows for the observation of the monomer (ca. 2.2 nm in its longest dimension from molecular mechanics calculations, Scheme 1), even if in relatively small intensity. Besides the monomer, aggregates of 50–140 nm and a very broad distribution of sizes between 450 nm and over 6 μm were found. From these data, it is clear that the polymerization of **1** does not follow an isodesmic growth model, which assumes all binding events show the same binding constant. This model predicts that $n = (K_a C)^{0.5}$,[1] where n is the number of repeating units, and C the molar concentration of the monomer. If we introduce the binding constant of our **2**·$PC_{61}BM$ model system, an isodesmic growth would yield $n = 11.2$, 3.5, and 1.2 for a concentration of 1, 0.1, and 0.01 mM, respectively. Although it is difficult to extract the exact number of repeating units from the DLS data, it is clearly well above the predicted numbers for all three concentrations, taking into account that the longest dimension of **1** is 2.2 nm. Besides the numeric analysis, the fact that no intermediate species between the monomer and the large aggregates were observed at 0.01 mM is in support of a nucleation-elongation model with multiple nucleation steps, where at any total concentration of monomer above K^{-1} high polymer forms are dominant.[29,30]

Finally, the size and shape of the polymer were analyzed through AFM. Figure 4 shows two typical AFM images obtained by dropcasting a dilute solution of **1** (ca. 1×10^{-7} M, $CHCl_3$) onto HOPG. The micrographs show remarkably long and straight fibers, of lengths from several hundreds of nanometers to well above 2 μm, often stretching over several HOPG terraces.[31,32] The height of the vast majority of fibers is very uniform, at 1.4–1.6 nm, in very good agreement with the predicted size for **1**, which suggests that they are mainly formed by a single chain of $(\mathbf{1})_n$ polymer, although some fibers with heights between 3–5 nm were also found, which would correspond to unspecific aggregation of two or three chains of the linear polymer. The AFM data are, therefore, in very good agreement with the data in the gas phase and in solution, in which we observed a very high degree of polymerization. In contrast, when similar experiments were carried out with our previously reported supramolecular polymer, we observed only short (< 500 nm) and winding oligomers.[24]

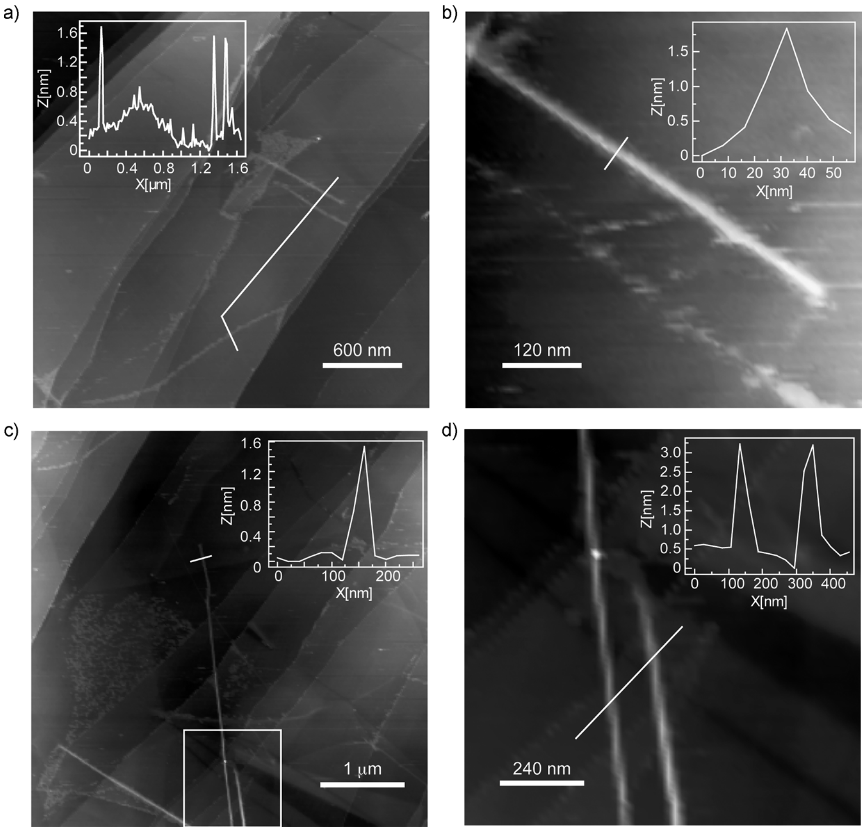


Figure 4. a–c) Different AFM images of a dropcast of a solution of **1** (ca. 1×10^{-7} M, $CHCl_3$) onto HOPG. d) Expansion of the area marked with a white square in (c). Insets show the profiles along the white lines.

If we revisit the DLS data taking into account the uniform size and shape of the polymer fibers found in AFM, we can approximate the geometry of our polymer in solution to a cylinder of radius 1.5 nm. Assuming that the hydrodynamic radius is similar to the radius of gyration of such cylinder, for $R_H = 2455$, 1495, and 962 nm one can calculate a MW of approximately 157, 123, and 97 kDa, respectively. These numbers correspond to polymers $(\mathbf{1})_n$ where $n = 78$, 61, and 48. Although these are but rough estimates, they are perfectly consistent with the MALDI-TOF quantitative experimental data, and give a very good idea of the high degree of polymerization of **1** in solution, which is comparable to that obtained in supramolecular polymers based on hydrogen-bonding or metal–ligand coordination, and unparalleled in those based on dispersion interactions.

In conclusion, we have described a donor–acceptor supramolecular polymer based on the association of a C_{60} derivative by an exTTF macrocyclic receptor. By introducing preorganization in the exTTF host part of the monomer, we have obtained a very remarkable degree of polymerization, reaching estimated MW > 150 kDa in solution, with up to 90 kDa measured experimentally in the gas phase. To our knowledge this degree of polymerization is well above any other fullerene-based supramolecular polymer reported to date. These materials might find use in the construction of self-organized optoelectronic devices, where polymers of high molecular weight are typically found to yield more efficient devices.[33,34]

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