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Fullerenes

Synthesis and Electrochemical Properties of Fullerene-Rich Nanoclusters Synthesized by Cobalt-Catalyzed Cyclotrimerization of Bis(aryl)alkyne Fullerodendrimers[**]

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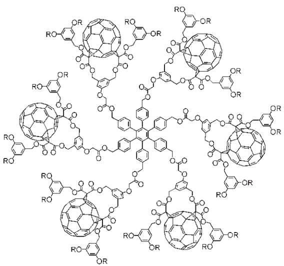
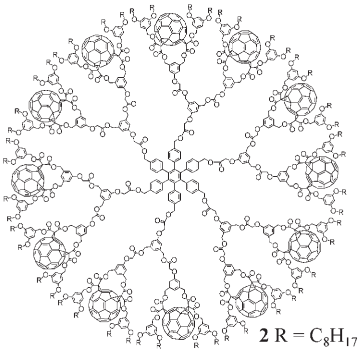
In memory of André Rassat

Dendrimers are high-molecular-weight compounds with well-defined structures and multiple controllable functionalities. The possibility of tuning their properties by changing the number, chemical nature, and relative position of functional units within the branched structure is certainly one of the most appealing features of these compounds.[1] However, even though the synthesis of dendritic macromolecules is iterative and often involves simple repetitive synthetic steps, it is still tedious to generate large dendrimers. Self-assembly offers an attractive option by which dendritic building blocks, many of which can be relatively small and synthetically accessible, can be assembled simply into more complex architectures.[2] This strategy has been investigated intensively in the past years and has led to numerous noncovalent dendritic architectures with intriguing properties.[2] In contrast, only a few specific tools of classical organic chemistry can be used to generate large dendritic molecules efficiently in a single synthetic step starting from small dendritic precursors. Among them, the covalent grafting of six dendritic malonate functions to a fullerene core reported by Hirsch and co-workers[3] and the metal-catalyzed cyclotrimerization of dendritic bis(aryl)alkynes described by Hecht and Fréchet[4] are the most spectacular examples. Herein, we show that the cyclotrimerization route is well suited to the synthesis of fullerene-rich dendrimers. Indeed, the synthesis of dendritic scaffolds substituted with multiple C_{60} moieties is quite challenging. Even though a few examples of fullerene-rich dendrimers have been reported,[5] the development of efficient synthetic strategies for their preparation is still needed to allow in-depth investigations of their properties and to evaluate their potential for applications.

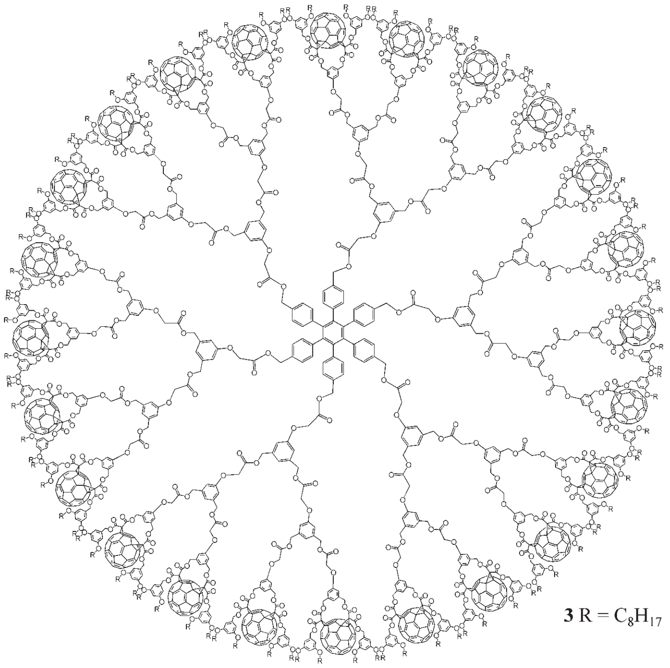
Fullerodendrimers **1**–**3** with hexaphenylbenzene cores and peripheral C_{60} units were prepared by metal-catalyzed cyclotrimerization of the corresponding dendritic bis(aryl)alkyne (Scheme 1). The alkyne precursors **5**–**7** were



1 R = C_8H_{17}



2 R = C_8H_{17}



3 R = C_8H_{17}

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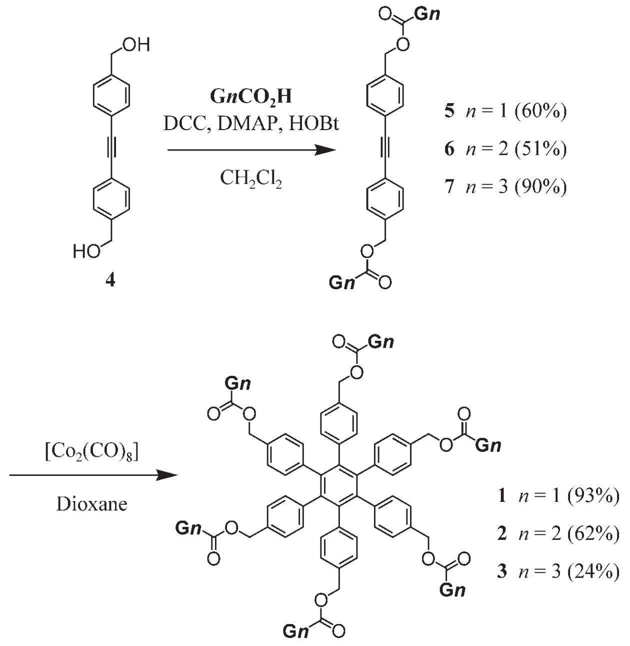

Scheme 1. Preparation of compounds **1**–**3**.

obtained by reaction of diol **4** with fullerodendron **G1CO$_2$H**, **G2CO$_2$H**, and **G3CO$_2$H**,[6] respectively, under esterification conditions using *N*,*N*′-dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt), and 4-dimethylaminopyridine (DMAP).

The reaction conditions for the cyclotrimerization were first optimized for the first-generation compound. The choice of the appropriate catalyst was the key to this synthesis. Indeed, [Co$_2$(CO)$_8$] appeared as a good candidate. It is a known catalyst for the cyclotrimerization of alkynes[7] and Martín et al. have shown that C$_{60}$ is only reactive in the presence of [Co$_2$(CO)$_8$] under Pauson–Khand conditions when a very specific stereochemical orientation is possible.[8] We found that [Co$_2$(CO)$_8$] is an efficient catalyst for the preparation of compound **1** from alkyne **5**. Under optimized conditions, treatment of **5** with a catalytic amount of [Co$_2$(CO)$_8$] in dioxane at room temperature for 24 h afforded **1** in 93% yield. The same conditions were used for the preparation of the highest-generation compounds. The reaction of the second-generation derivative **6** was finished after one day and compound **2** was isolated in 62% yield. In contrast, the reaction of the highest-generation precursor was very slow, most probably as a result of steric effects. After five days, the starting material was not completely consumed but the reaction was stopped because significant degradation was observed. The product was purified by column chromatography on SiO$_2$ and subsequent gel permeation chromatography, and compound **3** was isolated in 24% yield.

The ^{1}H NMR spectrum of **1** is quite simple and shows that all six peripheral C_s-symmetrical 1,3-phenylenebis(methylene)-tethered fullerene *cis*-2 bis-adduct subunits are equivalent (see the Supporting Information). Slight, but significant, downfield shifts relative to the corresponding alkyne precursor are observed for the aromatic protons of the *p*-substituted phenyl units. Similar changes in the chemical shifts of the signals of these protons are observed for **2** and **3** relative to **6** and **7**, respectively. The latter observations are consistent with the formation of the hexaphenylbenzene-core derivatives **1**–**3**.[9] Further conclusive evidence came from a comparison of the ^{13}C NMR spectra of **1**–**3** and **5**–**7**. In particular, the characteristic signal corresponding to the sp-hybridized C atom detected around $\delta = 89.5$ ppm for compound **5**–**7** is not present for **1**–**3**, whereas an additional resonance is detected around $\delta = 139$ ppm in the spectra of **1**–**3**. The latter signal is attributed to the six equivalent sp^2-hybridized C atoms of the central phenyl core of **1**–**3**.

The electrochemical behavior of these dendrimers is depicted in Figures 1 and 2. Three reduction waves are observed between 0 and -1.3 V. The first is always reversible. The second is irreversible at low scan rates, which is in accordance with observations for other C$_{60}$ derivatives. This irreversibility suggests bond breaking in the cyclopropane ring, known as the retro-Bingel reaction.[10] The reduction wave becomes partially reversible upon increasing the scan rate *v*, and we could estimate a lifetime of approximately 0.1–0.5 ms for the intermediate. The third wave gradually disappears when the second wave becomes reversible, which suggests reduction of the product formed after the second reduction of the starting compound.

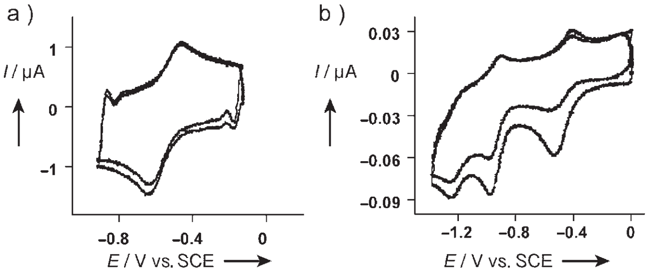

Figure 1. Cyclic voltammograms of **1** (a) at 8000 V s^{-1} and **2** (b) at 140 V s^{-1} in THF + 0.3 M tetrabutylammonium hexafluorophosphate.

Below, we detail the processes that occur with the first reduction.[11] In Figure 2a, the reduction wave of **3** is symmetrically bell-shaped and the peak current is proportional to v for $v < 400$ V s^{-1}. These observations reveal that **3** is adsorbed onto the surface.[12] The area under the peak is proportional to the amount of reduced adsorbed dendrimer. From the voltammogram in Figure 2a and a molecular area of 2240 Å^2 for **3**,[13] one may estimate that approximately a bilayer is deposited onto the electrode. Adsorption is a very common characteristic of dendrimer systems because van der Waals forces with the surface increase with increasing generation, while the solubility diminishes.[14] Indeed, we observed that **1** is not adsorbed; for **2**, the signal is dominated by diffusion at low scan rates, and adsorption at high scan rates.[15]

Figure 2c represents the peak current divided by $v^{1/2}$ versus $v^{1/2}$ for **3**. This graph shows that for $v > 10\,000$ V s^{-1}, the current does not scale with v but rather with $v^{1/2}$, even though this compound is adsorbed. The decrease in peak height is too large to be due solely to a limitation by the

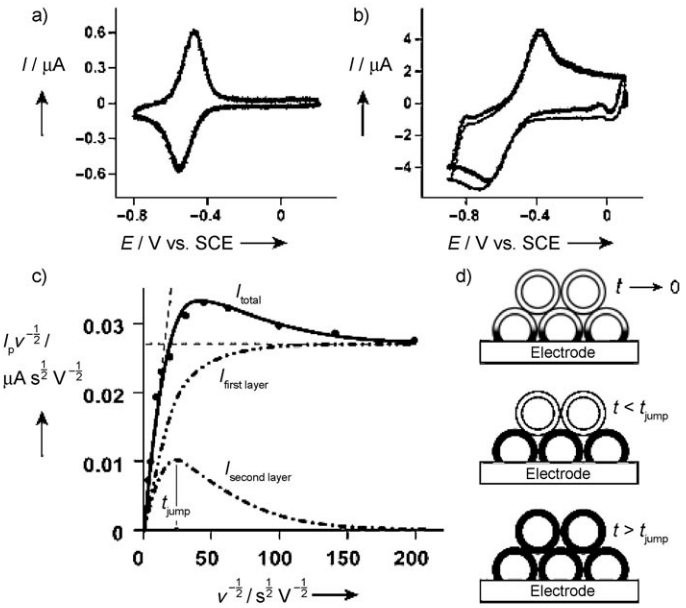

Figure 2. Cyclic voltammograms of **3** at 400 V s^{-1} (a) and 20000 V s^{-1} (b) in THF + 0.3 M tetrabutylammonium hexafluorophosphate. c) Peak current versus scan rate. d) Propagation of the electrochemical perturbation over various distances at increasing timescales (i.e., decreasing scan rates). The dark area corresponds to the parts of the dendrimer in which the C$_{60}$ entities are mostly in their reduced form.

heterogeneous electron transfer (responsible for the large peak splitting at high scan rates).[16] Therefore, only a fraction of the C$_{60}$ units are reduced during the forward scan. We have no structural data about the adsorbed layer, but it is likely that **2** and **3** are globular systems, thus only a fraction of the C$_{60}$ entities are close enough to the surface to allow direct electron transfer. Further C$_{60}$ units can then be reduced by successive electron hopping between C$_{60}$ units according to Equation (1).[14]

$$C^{\bullet-}_{60,\,\text{site A}} + C_{60,\,\text{site B}} \rightleftharpoons C_{60,\,\text{site A}} + C^{\bullet-}_{60,\,\text{site B}} \qquad (1)$$

If all adjacent C$_{60}$ pairs within a single dendrimer molecule are assumed to communicate identically with each other, Equation (1) defines an equivalent diffusion coefficient $D_{\text{hop}} \propto k_4$,[16] in which k_4 is the 2D bimolecular rate constant for electron transfer between adjacent C$_{60}$ centers within a dendrimer molecule. Thus, whenever the timescale is small enough for the electrochemical perturbation to remain confined within the dendrimers that form the first monolayer, namely, that adjacent to the electrode, the phenomenon is diffusion-limited and the current function $i_p v^{-1/2}$ is constant. This situation corresponds to the limit in Figure 2c (dashed horizontal line) that is reached at the highest scan rates and to the schematic view $t \rightarrow 0$ in Figure 2d.

The same situation should formally apply to the propagation within dendrimer molecules in the successive monolayer. However, the communication at the boundary between the monolayers involves an electron exchange between C$_{60}$ moieties of two different molecules. The corresponding rate constant is necessarily smaller than that for electron transfer between adjacent C$_{60}$ centers within a single molecule, which limits the propagation within the next layer. The kinetic situation is equivalent to that of a three-step kinetic sequence in which the slowest step is interposed between a first and third reaction with identical rates. As such, the scan rate may be sufficiently low for the first monolayer to be almost fully reduced, but nevertheless too high to allow significant communication with the second monolayer. The current intensity is then mostly attributable to the first monolayer and expected to behave as if a single monolayer were present (i.e., it involves a smooth transition from a constant value of $i_p v^{-1/2}$ at high scan rates to a linear dependence of $i_p v^{-1/2}$ on $v^{1/2}$ at the lowest scan rates).[16] This case is represented schematically by the curve labeled $I_{\text{first layer}}$ in Figure 2c and corresponds to a transition from the situation labeled $t \rightarrow 0$ to that labeled $t < t_{\text{jump}}$ in Figure 2d.

Propagation into the second monolayer requires a scan rate that is sufficiently small for the voltammetric timescale to become comparable to or larger than the half-life t_{jump} of electron transfer between the two monolayers. Only then may the reduction front penetrate into the second monolayer. Formally, as explained above, at small enough scan rates, this front is expected to propagate diffusionally within the second layer until it reaches the edge of this layer. In other words, the voltammetric contribution from the second monolayer increases from zero when $RT/Fv \ll t_{\text{jump}}$ to a current that varies linearly with v when $RT/Fv \gg t_{\text{jump}}$, as sketched in Figure 2c (curve labeled $I_{\text{second layer}}$). The value of $I_{\text{second layer}} v^{-1/2}$ at small scan rates is then linearly proportional to $v^{1/2}$ with a slope identical to that of $I_{\text{first layer}}$. Figure 2c shows that the current function $I_p v^{-1/2}$ relative to the overall experimental current (labeled I_{total}) proceeds through a maximum located in between the limit at high scan rates, for which the current function is constant and diffusion is restricted to within the first layer only (sketch $t \rightarrow 0$ in Figure 2d), and the linear variation of the current function with $v^{1/2}$ at low scan rates, at which both layers are fully reduced. The qualitative analysis shown in Figure 2c shows that this maximum corresponds roughly to $v_{\max} \approx RT/Ft_{\text{jump}}$.

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[11] The electrochemical measurements on **1**–**3** were performed with a high concentration (0.3 M) of supporting electrolyte that can screen the electrostatic repulsion between the reduced C_{60} units within the same dendrimer or between adjacent ones so that each C_{60} moiety retains the same standard reduction potential irrespective of the reduced status of the nearby C_{60} units. As a consequence, a single reduction wave is obtained for all generations of the compound.

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