Fullerodendrimers with a tris-isothiocyanate core allowing their anchoring onto gold electrodes†

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Dendrimers with peripheral fullerene subunits and a tris-isothiocyanate core have been prepared and self-assembled onto a gold surface; detailed electrochemical studies revealed that electron transfer from the electrode to the fullerene subunits occurs through space at a short distance from the electrode.

In recent years, fullerene-rich dendrimers have generated significant research activities.[1] In particular, the peculiar electronic properties of fullerene derivatives[2] make such dendrimers attractive candidates for a variety of interesting features in materials science.[3] As part of this research, we have recently shown that dendrimers bearing multiple C_{60} units are interesting candidates for solar energy conversion.[4] This prompted us to study in detail their electrochemical properties as the accepting ability of the fullerene subunits as well as the charge mobility in thin films are key parameters in photovoltaic devices.[5] In this respect, ultrafast cyclic voltammetry has proven to be a powerful tool to understand intra- and intermolecular interactions between C_{60} units within thin films of fullerene-rich dendritic materials deposited onto the electrodes during their electrochemical analysis.[6] To gain further insight in the electrochemical behavior of such molecules, we have decided to develop dendrimers with peripheral fullerene subunits and a head-group allowing the preparation of self-assembled monolayers onto gold surfaces. With this idea in mind, we have designed compounds **G1–3** with a tris-isothiocyanate core. Indeed, Tour revealed that isothiocyanate derivatives may chemically adsorb onto gold substrates[7] in an analogous manner with what is very commonly observed with thiols.[8]

The synthesis of **G1–3** is depicted in Scheme 1. Reaction of compound **1**[9] with tosyl chloride (TsCl) in the presence of pyridine gave **2** in 80% yield. Subsequent treatment with KSCN afforded the corresponding tris-isothiocyanate derivative, however cleavage of the benzyl unit failed to give targeted alcohol **4**. Thus, the protecting group in **2** was exchanged for a *tert*-butyldimethylsilyl (TBDMS) ether. Cleavage of the benzyl group was achieved by treatment of **2** with Pd/C in THF under H_2 atmosphere (1 bar). Reaction of the resulting alcohol with TBDMSCl in the presence of imidazole gave **3** in 99% yield. Treatment of **3** with an excess of KSCN in DMF at 140 °C afforded directly compound **4**, the TBDMS being cleaved during the work-up procedure. Dendrimers **G1–3** were then obtained by reaction of **4** with the corresponding fullerene-containing dendrons bearing a carboxylic acid group at the focal point (**G1–3CO$_2$H**)[10] under esterification conditions using *N*,*N*′-dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt) and 4-dimethylaminopyridine (DMAP).

We let gold ball ultramicroelectrodes,[11] obtained by melting a 25 μm gold wire in a blue flame, bathe during 72 h in THF solutions of compounds **G1–3**. After a quick rinse with neat THF, these electrodes were transferred into the electrochemical cell where no electroactive compound was present. All compounds give several reduction waves, but only the first one is chemically reversible, as was previously observed for similar products.[6] We focus below on the first reduction wave of the C_{60} entities. Cyclic voltammograms are presented in Fig. 1. We observed that the current scales proportionally with the scan rate v (with a maximum error of 10%), *i.e.* is typical for species anchored onto electrodes.[12] It is difficult to measure precisely the dendrimer coverage since the area of the gold ball electrode can only be roughly measured. However, considering that the gold ball is a hemisphere with a 25 μm radius, and that the molecular area of **G2** is 310 Å^2,[13] the charge integration of the faradaic peak reveals that there is less than a monolayer adsorbed onto the electrode. However, the data acquisition needs to be performed within a short time (15 min) to avoid desorption of the compound. Indeed, since these compounds are soluble in THF, their desorption is slow but thermodynamically favored. Moreover, a fast decrease of the signal is also observed if slow scan rates (less than 30 V s^{-1}) are used, attesting that the negatively charged radicals desorb faster than their neutral parent. In that case, cyclic voltammetry is a powerful technique since it allows one to position the starting potential at a potential where the monolayer is kinetically stable, thus minimizing the dynamic instability. This is an advantage compared to other techniques where the potential has to remain in the faradaic region during a longer time.[14]

In order to minimize the impact of the slight variation in charge during the experiment, we decided to extract the

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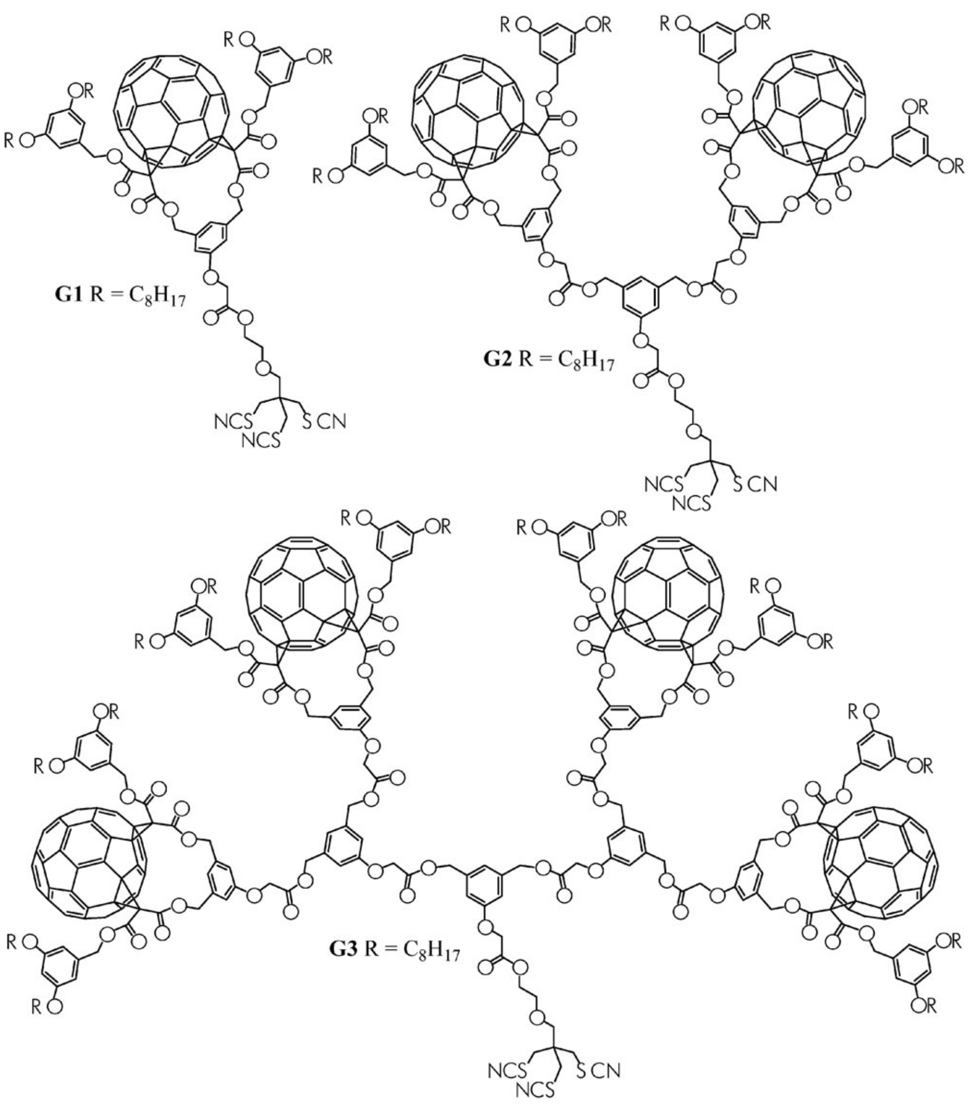
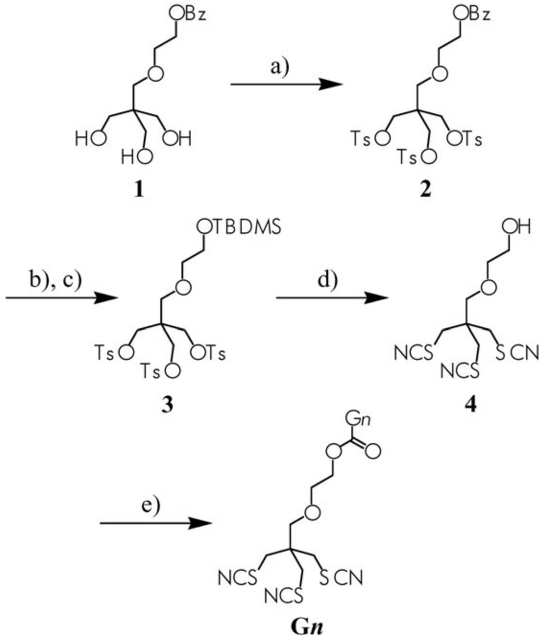


G1 R = C_8H_{17}

G2 R = C_8H_{17}

G3 R = C_8H_{17}

electron transfer rate constant from the peak potential evolution with the scan rate since this quantity is independent of the precise number of molecules adsorbed (as long as the electroactive entities from different adsorbed molecules do not interact as is the case in this study).[12] Moreover, the peak potential is only very slightly sensitive to the rather flat capacitive background underlying below the faradaic current. At slow scan rates, there is a very slight (about 10 mV) peak to peak potential difference which we ascribe to a structural reorganisation of the monolayer after electron transfer (this phenomenon is commonly observed). When the scan rate increases, there is only a very slight evolution of the anodic and cathodic peak potentials between 40 and 3200 V s^{-1}. From comparison with theory, we could extract a rate constant $k^0_{\text{ads}} = 1 \times 10^5\ s^{-1}$ for **G2** and **G3**, and $k^0_{\text{ads}} = 2 \times 10^5\ s^{-1}$ for **G1**. It is well known that the electron transfer rate through molecular bridges decreases exponentially with the distance to the electrode. For single C–C bonds, the attenuation factor β is estimated at about 1.2 per methylene unit. It has also been observed that an ester linkage behaves essentially as two methylene units.[15] We have no experimental data about electron transfer through the chains constituting the dendritic branches of our compounds. However, we can notice that there are 16 non-conjugated (C–C or C–O) bonds for **G1**, 22 for **G2** and 28 for **G3**. Therefore, the electron transfer efficiency should decrease by several orders of magnitude within our series if it occurred along the dendritic branches. Moreover, a comparison with the literature indicates that for **G1** a rate constant in the range of 1–100 s^{-1} should be obtained for electron transfer through the chain linkers.[15] Our experimental values are several orders of magnitude above this estimate, which evidences that when the charge transfer occurs the C_{60} entities are close enough to the electrode surface to give rise to direct efficient electron transfer through the solvent. Therefore, the dendritic branches necessarily have the possibility of folding to reach the electrode. A similar situation was previously examined experimentally and theoretically by Moiroux and co-workers[16] in the case of ferrocene moieties attached by polyethyleneglycol linkers. Two limiting situations are possible. If the flexibility of the chains is large, or if the electroactive entities lie very close to the electrode, adsorption behaviour is observed. Conversely, if the chains are stiff and the electroactive centers are far enough from the electrode, their diffusive movement should limit the current and a voltammogram

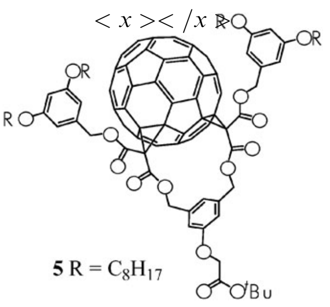


Scheme 1 *Reagents and conditions*: (a) TsCl, pyridine, 0 °C to room temp., 24 h (80%); (b) H_2, Pd/C, THF, room temp., 12 h (78%); (c) TBDMSCl, imidazole, CH_2Cl_2, 0 °C to room temp., 24 h (80%); (d) KSCN, DMF, 140 °C, 6 h (54%); (e) **G*n*CO₂H**, DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to room temp. (**G1**: 64%; **G2**: 58%; **G3**: 85%).

having the characteristics of diffusion is observed. We presently do not have structural data about the formed monolayers, such as the effective thickness and the position of the C_{60} entities. Since the current peak is proportional to v within 10% in the whole scan range of this study, we deduce that the eventual diffusional movement of the C_{60} moieties is transparent in the registered data.

Following this assumption, we compared our experimental value ($k^0_{\mathrm{ads}} = 1 \times 10^5\ \mathrm{s}^{-1}$) to the one obtained for fullerene derivative **5**. In this case, **5** is well soluble in THF and there is no anchoring group so that the signal is purely diffusive. From the peak current intensity of the voltammogram (Fig. 2a), we could extract an approximate diffusion coefficient of $1.6 \times 10^{-6}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$.

The peak potential evolution gives a heterogeneous rate constant of $k^0_{\mathrm{diff}} = 0.14\ \mathrm{cm\ s}^{-1}$, in qualitative agreement with previous measurements performed by Bard and co-workers[17] onto pristine C_{60} under different conditions. Electron transfer



5 R = C_8H_{17}

for **5** may occur at varying distances from the electrode, so that in order to compare both quantities we should compare k^0_{ads} with:[18]

$$k^0_{\mathrm{diff}}/\int_0^\infty \exp(-\beta_S x)\mathrm{d}x = \beta_S k^0_{\mathrm{diff}} \qquad (1)$$

where β_S is the attenuation factor for the solvent. We are not aware of a calculated or experimental value for β_S. However, taking $1 < \beta_S < 2\ \text{Å}^{-1}$ seems reasonable. This leads to $1.4 \times 10^7\ \mathrm{s}^{-1} < \beta_S k^0_{\mathrm{diff}} < 2.8 \times 10^7\ \mathrm{s}^{-1}$. k^0_{ads} is then two orders of magnitude smaller than what could be expected if electron transfer occurred at the same distance from the electrode. Taking into account that x_{diff}, the closest distance for **5**, and x_{ads}, the distance for **G1**, **G2** or **G3**, may be different, eqn (1) should be corrected to yield:[17]

$$k^0_{\mathrm{diff}} = k^0_{\mathrm{ads}} \times \exp(\beta_S(x_{\mathrm{ads}} - x_{\mathrm{diff}}))/\beta_S \qquad (2)$$

We thus obtain $2.8 < x_{\mathrm{ads}} - x_{\mathrm{diff}} < 5$ Å. This analysis then suggests that the local organisation of the film allows the redox centers to approach the electrode, but not to touch it. Nevertheless, we want to stress that this analysis remains subordinate to other factors such as double layer effects or a different local dielectric constant which may induce slight variation in the reorganisation energy of C_{60} or in the electronic coupling with the electrode. Indeed, eqn (2) is valid only provided all parameters are the same for both homogeneous and linked systems except for the electronic coupling.

In conclusion, we have developed fullerene-substituted dendrimers with a tris-isothiocyanate core moiety enabling us to self-assemble them onto gold electrodes. Detailed cyclic voltammetry studies revealed an efficient through space electron transfer from the electrode to the fullerene moieties revealing that these entities are or can get very close to the electrode.

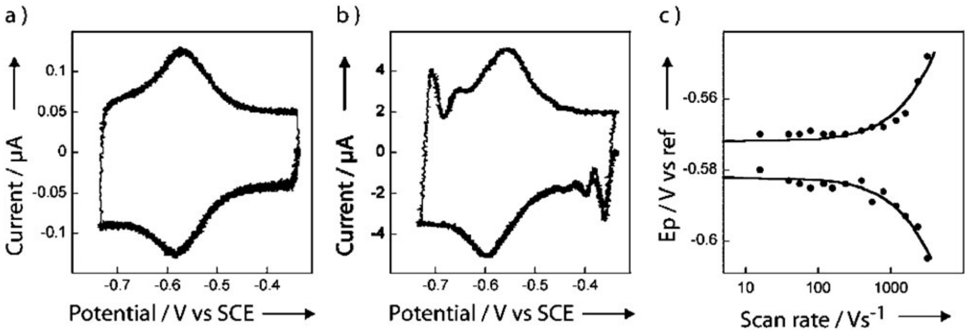


Fig. 1 Cyclic voltammograms of **G2** adsorbed onto a gold ball ultramicroelectrode at 60 V s^{-1} (a) or 2400 V s^{-1} (b). (c) Peak potential evolution with the scan rate. Filled circles: experimental values. Solid line: theoretical evolution for $k^0_{\mathrm{ads}} = 1 \times 10^5\ \mathrm{s}^{-1}$.

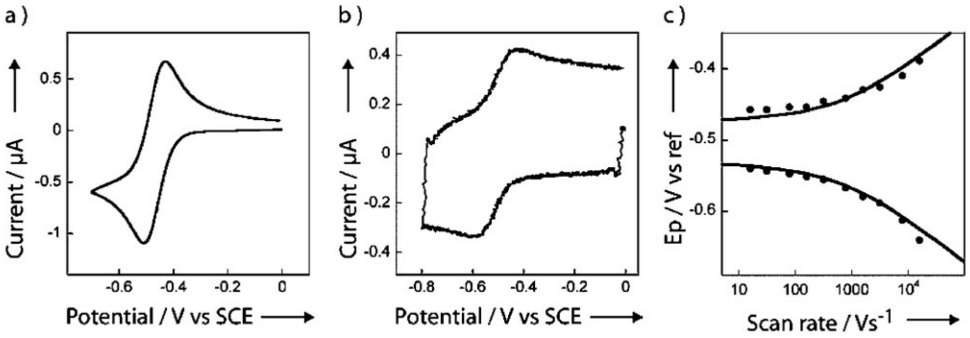


Fig. 2 Cyclic voltammograms of a 4.8 mM solution of **5** at 0.1 V s^{-1} onto a 0.5 mm diameter electrode (a) or at 3200 V s^{-1} onto a 25 µm diameter electrode (b). (c) Peak potential evolution with the scan rate. Filled circles: experimental values. Solid line: theoretical evolution for k^0_{diff} = 0.14 cm s^{-1}.

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Experimental

General procedure for the preparation of G1–3

DCC (1 equiv.) was added to a stirred solution of **4** (1.1 equiv.), the appropriate fullerene derivative (**G*n*CO$_2$H**, 1 equiv.), and DMAP (0.4 equiv.) in CH_2Cl_2 at 0 °C. After 1 h, a catalytic amount of HOBt was added, the mixture allowed to slowly warm to room temperature and stirred at this temperature for several days (**G1**: 1 d, **G2**: 2 d, and **G3**: 4 d). The resulting solid was filtered off, the solvent evaporated and the crude product purified as outlined in the following text.

Compound G1. Prepared from **G1CO$_2$H** and purified by column chromatography on silica gel (SiO_2, CH_2Cl_2 to CH_2Cl_2 + 0.2% MeOH) followed by gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) to yield **G1** (290 mg, 64%) as a dark orange glassy product. IR: ν/cm^{-1} = 1746 (C=O); UV/Vis (CH_2Cl_2): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) = 260 (174 100), 315 (54 250), 378 (19 920), 438 (4790); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7 Hz, 12 H), 1.20–1.43 (m, 40 H), 1.71 (m, 8 H), 3.20 (s, 6 H), 3.58 (s, 2 H), 3.76 (m, 2 H), 3.84 (t, J = 7 Hz, 8 H), 4.41 (m, 2 H), 4.73 (s, 2 H), 5.05 (d, J = 13 Hz, 2 H), 5.29 (s, 4 H), 5.81 (d, J = 13 Hz, 2 H), 6.35 (t, J = 2 Hz, 2 H), 6.46 (d, J = 2 Hz, 4 H), 6.78 (s, 2 H), 7.16 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2, 22.8, 26.2, 29.4, 29.5, 31.9, 36.8, 46.1, 49.1, 64.0, 65.7, 67.0, 67.2, 68.2, 68.8, 69.2, 70.0, 70.7, 101.7, 107.2, 111.6, 112.8, 116.3, 134.5, 135.9, 136.1, 136.6, 138.0, 138.6, 140.1, 141.2, 141.3, 142.3, 142.8, 143.3, 143.7, 143.9, 144.1, 144.26, 144.30, 144.36, 144.7, 145.0, 145.1, 145.3, 145.5, 145.7, 145.81, 145.84, 145.88, 146.2, 147.4, 147.6, 148.7, 158.1, 160.5, 162.6, 162.7, 168.8; MALDI-TOF-MS: m/z = 2080.13 $[M + H]^+$; Anal. calc. for $C_{132}H_{99}O_{16}N_3S_3$ (2079.43): C 76.24, H 4.80, N 2.02; found: C 76.45, H 4.82, N 1.88%.

Compound G2. Prepared from **G2CO$_2$H** and purified by column chromatography on silica gel (SiO_2, CH_2Cl_2 to CH_2Cl_2 + 0.2% MeOH) followed by gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) to yield **G2** (184 mg, 58%) as a dark orange glassy product. IR: ν/cm^{-1} = 1747 (C=O); UV/Vis (CH_2Cl_2): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) = 260 (305 990), 315 (93 400), 378 (32 475), 438 (10 100); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 7 Hz, 24 H), 1.23–1.45 (m, 80 H), 1.71 (m, 16 H), 3.18 (s, 6 H), 3.56 (s, 2H), 3.69 (m, 2H), 3.82 (t, J = 7 Hz, 16 H), 4.38 (m, 2 H), 4.68 (s, 2 H), 4.70 (s, 4 H), 5.03 (d, J = 13 Hz, 4 H), 5.22–5.30 (m, 12 H), 5.71 (d, J = 13 Hz, 4 H), 6.32 (s, 4 H), 6.45 (s, 8 H), 6.78 (s, 4 H), 6.89 (m, 2 H), 6.98 (s, 1 H), 7.12 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3, 22.8, 26.2, 29.4, 29.6, 32.0, 36.9, 46.1, 49.2, 64.0, 65.4, 65.6, 66.5, 67.0, 67.2, 68.2, 68.9, 69.3, 70.1, 70.7, 101.7, 107.2, 111.7, 112.7, 114.7, 116.2, 121.4, 134.5, 135.9, 136.2, 136.6, 137.5, 137.9, 138.6, 140.1, 141.2, 141.3, 142.3, 142.8, 143.3, 143.7, 143.9, 144.1, 144.3, 144.4, 144.7, 145.0, 145.1, 145.3, 145.4, 145.7, 145.8, 146.2, 147.4, 147.6, 148.7, 157.9, 158.4, 160.5, 162.6, 162.7, 168.5, 168.6; MALDI-TOF-MS: m/z = 4050.86 $[M + H]^+$; Anal. calc. for $C_{264}H_{195}O_{34}N_3S_3$ (4049.63): C 78.30, H 4.85, N 1.04; found: C 78.51, H 4.86, N 0.86%.

Compound G3. Prepared from **G1CO$_2$H** and purified by column chromatography on silica gel (SiO_2, CH_2Cl_2 to CH_2Cl_2 + 0.2% MeOH) followed by gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) to yield **G3** (185 mg, 85%) as a dark orange glassy product. IR: ν/cm^{-1} = 1748 (C=O); UV/Vis (CH_2Cl_2): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) = 260 (551 830), 315 (177 290), 378 (63 580), 438 (18 000); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7 Hz, 48 H), 1.20–1.43 (m, 160 H), 1.71 (m, 32 H), 3.20 (s, 6 H), 3.57 (s, 2 H), 3.72 (m, 2 H), 3.83 (t, J = 7 Hz, 32 H), 4.34 (m, 2 H), 4.64 (s, 2 H), 4.71 (m, 12 H), 5.05 (d, J = 13 Hz, 8 H), 5.15–5.28 (m, 28 H), 5.71 (d, J = 13 Hz, 8 H), 6.32 (s, 8 H), 6.45 (s, 16 H), 6.78 (s, 8 H), 6.89 (m, 7 H), 6.98 (s, 2 H), 7.12 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2, 22.8, 26.2, 29.4, 29.5, 31.9, 37.0, 45.9, 49.1, 63.9, 65.4, 65.5, 66.4, 66.9, 67.2, 68.2, 68.8, 69.3, 70.2, 70.7, 101.7, 107.2, 111.8, 112.6, 114.5, 114.6, 116.1, 121.3, 121.4, 134.5, 135.8, 136.1, 136.6, 137.4, 137.5, 137.9, 138.6, 140.0, 141.1, 141.2, 142.3, 142.8, 143.2, 143.6, 143.8, 144.0, 144.2, 144.3, 144.6, 145.0, 145.1, 145.2, 145.4, 145.6, 145.8, 146.1, 147.4, 147.5, 148.7, 157.9, 158.2, 158.3, 160.5, 162.6, 162.7, 168.3, 168.4, 168.5; MALDI-TOF-MS: m/z = 7992.47 $[M + H]^+$; Anal. calc. for $C_{528}H_{387}O_{70}N_3S_3$ (7990.04): C 79.37, H 4.88, N 0.53; found: C 79.37, H 4.89, N 0.48%.

Electrochemistry

All electrochemical experiments were conducted in freshly distilled THF + 0.3 M tetrabutylammonium hexafluorophosphate (Aldrich) as supporting electrolyte. We used a conventional three electrode cell with a platinum counter electrode and a saturated calomel electrode as a reference. The working electrodes were gold balls obtained by melting a 25 μm gold wire in a blue flame.[19] The home-made potentiostat allows full ohmic drop compensation at scan rates up to 50 000 V s^{-1}.[20]

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