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Synthesis and electrochemical behaviour of [60]fullerene possessing poly(arylacetylene) dendrimer addends

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61,61-Bis[4-{3,5-bis(3,5-di-*tert*-butylphenylethynyl)phenylethynyl}phenyl]-1,2-dihydro-1,2-methano[60]fullerene (**10**) and 61,61-bis[4-{3,5-bis[3,5-bis(3,5-di-*tert*-butylphenylethynyl)phenylethynyl]phenylethynyl}phenyl]-1,2-dihydro-1,2-methano[60]fullerene (**11**) with 1st and 2nd generation phenylacetylene dendrimer addends were synthesised according to the Wudl method. Both monoadducts are obtained as single isomers in 18% and 23% yields, respectively. The structures of the products were established by FTIR, ^{1}H NMR, ^{13}C NMR and UV/VIS spectroscopy, as well as by mass spectrometry. All spectroscopic data confirm the exclusive formation of methano[60]fullerenes with [6,6]-closed structures. The electrochemical and spectroelectrochemical properties of 2nd generation dendrimer **7** and of its fullerene derivative **11** have been investigated. The cyclic voltammetric study shows that no significant interaction occurs in the ground state between the fullerene and the dendrimer; the fullerene derivative retains the typical redox stability of 6,6-closed derivatives in both the cyclic voltammetry (CV) and bulk electrolysis timescales.

Due to the large size, spherical shape and properties of its π system, the use of [60]fullerene as a potential electron acceptor in new photochemical molecular devices has been the focus of many papers in recent years. Numerous fullerene derivatives with covalently-bound donor moieties, such as porphyrins,[1] tetrathiafulvalenes,[2] transition metal complexes,[3] and other photoactive groups[4] have been prepared and their electrochemical and photophysical properties investigated. Only limited attention has, to date, been paid to the use of dendrimers and fullerenes as components in such devices.

For example Fréchet type benzyl ether dendrimers with [60]fullerene as a core unit have been prepared by one of two different synthetic approaches. Either the dendrimers were transformed into derivatives suitable for direct coupling with [60]fullerene,[5] or the dendrimers were added to fullerene derivatives bearing functional groups.[6] In this paper we report on the synthesis and electrochemistry of poly(aryl)acetylene dendrimer-containing methano[60]fullerene derivatives. Extended phenylacetylene (PA) dendrimers have been shown to have light harvesting and energy focusing properties, thus they were described as molecular "antennas".[7,8] Dendrimers displaying these properties were therefore chosen as promising candidates in order to investigate the potential interactions between the dendrimer addends and the fullerene core.

Results and discussion

Synthetic strategy

The most promising method for coupling [60]fullerene with the PA dendrimers is the Wudl method,[9] *i.e.* the reaction of the dendrimer-substituted tosylhydrazones **8** and **9** with [60]fullerene in the presence of sodium hydride. The synthesis of the tosylhydrazones is described in Scheme 1. Compound **2** was generated by coupling two equivalents of (trimethylsilyl)acetylene with 4,4′-dibromobenzophenone under standard palladium(0) cross-coupling conditions. The subsequent deprotection of **2** with potassium carbonate in methanol gave **3** in nearly quantitative yield.

The first generation dendrimer **6** and the second generation dendrimer **7**, each bearing two monodendrons in the 4 and 4′ positions of the benzophenone, were synthesised by cross-coupling compound **3** with two equivalents of iodo-functionalised monodendrons **4** and **5** respectively.[8]

In the next step, carbonyl compounds **6** and **7** were converted into the corresponding tosylhydrazones **8** and **9** by reaction with tosylhydrazide in toluene at 110 °C. As shown in Scheme 2, the tosylhydrazones **8** and **9** were heated with [60]fullerene in toluene in the presence of sodium hydride for 12 h. The resulting products **10** and **11** were separated from unreacted [60]fullerene and traces of higher addition products by column chromatography on silica gel with cyclohexane–dichloromethane as eluent. The structures of the brown compounds were established by FT-IR, ^{1}H NMR, ^{13}C NMR and UV/VIS spectroscopy and mass spectrometry.

MALDI-TOF mass spectra of both **10** and **11** were recorded in the negative ion mode with norharmane as matrix.[10] The mass spectrum of **10** shows the molecular ion peak at 1936.2 amu, which is in very good accordance with the calculated mass of a monoadduct of [60]fullerene and the 1st generation dendrimer (calc. 1936.45). In the spectrum of **11**, the peak of the molecular ion appears at 3186.2 (calc. 3186.27), which is similarly consistent with a 1 : 1 adduct of [60]fullerene and the 2nd generation dendrimer unit. The peak of the parent ion in the spectrum of **11** is accompanied by a second peak 15 mass units higher. This could be due to a species being generated within the spectrometer, as we have not found any other evidence for the presence of a second compound. The ^{1}H NMR spectra of both **10** and **11** clearly show that in each case only one single isomer was formed during the reaction.

In both spectra the number and intensities of signals reveal that the products have C_{2v} symmetry. The signals due to the protons of the tri-connected rings of the dendrimer units remote from the fullerene cage appear at about the same

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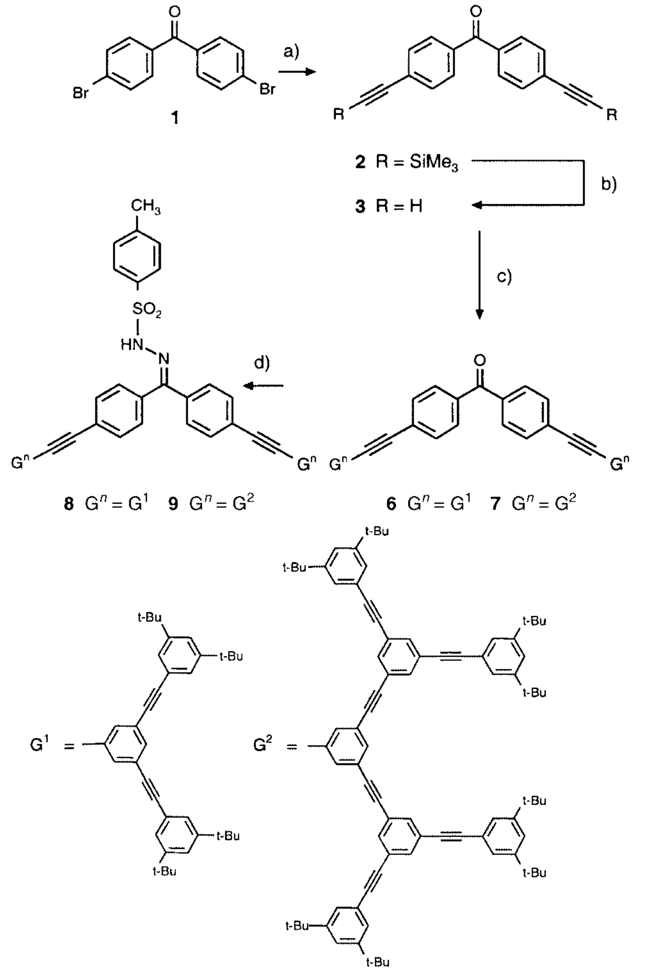
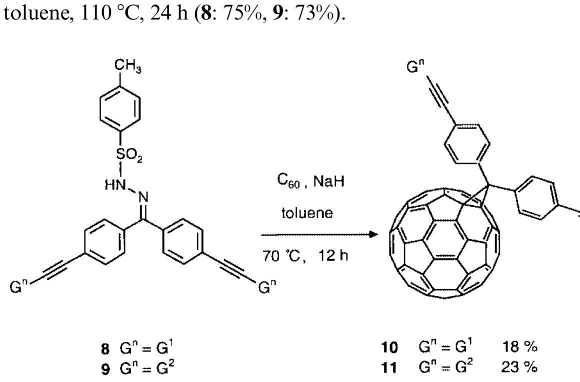


Scheme 1 Syntheses of the dendrimers **8** and **9**: a) TMS-acetylene, NEt_3, toluene, $Pd(dba)_2$, PPh_3, CuI, 55 °C, 24 h (72%); b) MeOH, CH_2Cl_2, K_2CO_3, RT (95%); c) G^1–I = **4**, G^2–I = **5**, NEt_3, toluene, $Pd(dba)_2$, PPh_3, CuI, 55 °C, 12 h (**6**: 82%, **7**: 80%); d) $TsNHNH_2$, toluene, 110 °C, 24 h (**8**: 75%, **9**: 73%).



Scheme 2 Syntheses of the methano[60]fullerene dendrimers **10** and **11**.

position as those in the spectra of the starting dendrons **6** and **7**.

By contrast, the doublets of the *ortho* hydrogens of the *para* aromatic rings adjacent to the fullerene cage are shifted downfield significantly. This deshielding effect is due to their position above five-membered rings of the fullerene cage and is commonly observed in the spectra of methanofullerenes.[11] Furthermore, the C_{2v} symmetry of **10** and **11** is in accord with the number of signals in their ^{13}C NMR spectra. In addition to the signals for the dendrimer units, both spectra contain 13 lines of four-fold and three lines of two-fold intensity in the fullerene sp^2 region and one signal of two-fold intensity at ~78 ppm representing the two equivalent sp^3 carbons of the fullerene cage. The electronic absorption spectra of the reddish brown solutions of **10** and **11** are dominated by the absorption bands of the dendrimer units, located in the UV. In the visible region, the characteristic bands for 6,6-bridged monoadducts of [60]fullerene are observed at $\lambda = 430$, 490 and 695 nm, indicating that there are no significant interactions between the fullerene cage and the dendrimer addend. All data are in accordance with a 6,6-closed methano[60]fullerene structure, thus the addition has taken place across a 6,6-bond.

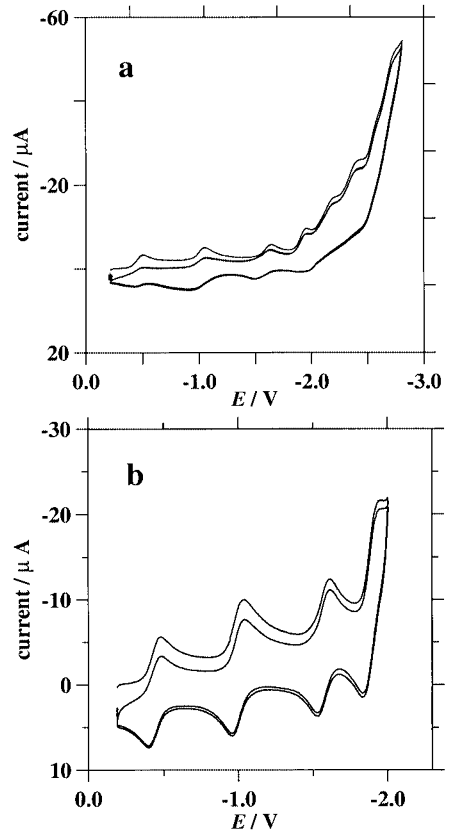


Fig. 1 (a) Cyclic voltammetric curves of a 0.5 mM **11**, 0.05 M TBAPF6 THF solution, scan rate = 0.5 V s^{-1}, $T = 25$ °C, working electrode: Pt; (b) same conditions as in (a), cathodic scan reversed at −2.0 V.

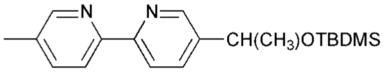
Electrochemistry

The cyclic voltammetric behaviour of compound **11** and of its model compound **7** were studied in THF, after employing high vacuum techniques and chemical pretreatment of the solvent for the careful exclusion of water from the electrochemical cell.[12,13] In Fig. 1a, the CV curve relative to a 0.5 mM solution of **11** in THF at $T = 25$ °C and $v = 0.5$ V s^{-1} is shown, where several reduction peaks are observed during the cathodic scan. The first four peaks correspond to reversible one-electron reductions as shown in the CV curve of Fig. 1b obtained under the same conditions as the above curve, but reversing the cathodic scan at −2.0 V. The next two peaks, observed at $E_p = -2.17$ and −2.42 V in Fig. 1a, correspond to the exchange of a larger charge and to a lower reversibility than the previous peaks. Finally, at more negative potentials, the cathodic current increases steadily to rather high values: two shoulders are observed in the rising part of the curve (at *ca.* −2.59 and −2.72 V) which indicate the occurrence of multielectron reduction processes. By comparison of both the height, and the charge comprised underneath the voltammetric peaks, the four processes observed beyond −2.0 V seem to each correspond to the exchange of two electrons at very close potentials. The $E_{1/2}$ values (E_p for irreversible peaks) for the various processes are reported in Table 1. For

Table 1 $E_{1/2}$ (V *vs.* SCE) measured in THF–TBAPF6 solutions at 25 °C; values are for the first members of pairs

11	−0.44	−1.01	−1.57	−1.94	−2.17[a]	−2.42[a]	−2.59[a]	−2.72[a]
7	−1.95	−2.41[a]	−2.55[a]	−2.68[a]				
C_{60}	−0.35	−0.94	−1.50	−1.97	−2.50			
$C_{61}R^1R^{2b}$	−0.43	−0.97	−1.58	−2.05				

[a] E_p (irreversible multi-electron peak). [b] $R^1 = CH_3$, R^2 =



TBDMS = *tert*-butyldimethylsilyl.[12]

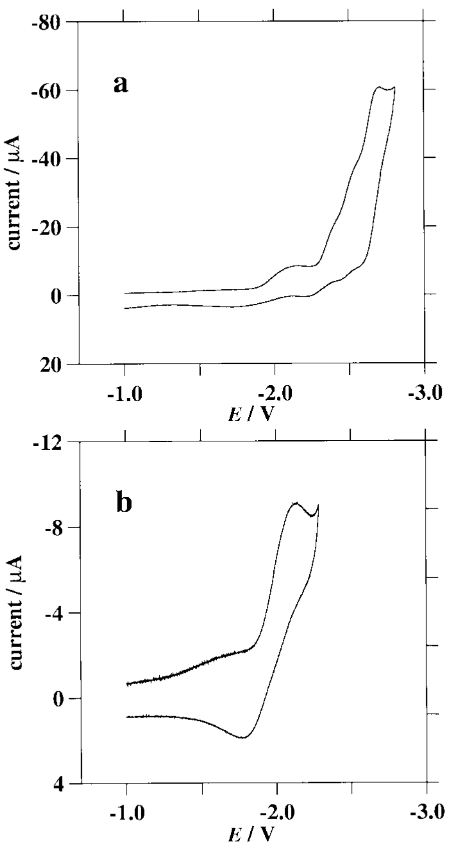


Fig. 2 (a) Cyclic voltammetric curves of a 0.5 mM **7**, 0.05 M TBAPF6 THF solution, scan rate = 0.5 V s^{-1}, T = 25 °C, working electrode: Pt; (b) same conditions as in (a), cathodic scan reversed at −2.6 V.

comparative purposes, the $E_{1/2}$ values for [60]fullerene under the same conditions are also reported. On the basis of this comparison, the first four reductions in **11** can be attributed to fullerene-centred processes. The observed shift to more negative potentials of such processes (with the exception of the fourth peak) with respect to [60]fullerene is expected on the basis that saturation of a double bond in C_{60} causes a partial loss of conjugation,[14] and agrees with that observed, under the same conditions, in other 6,6-closed methanofullerenes.[12,15]

The irreversible multi-electron reduction processes observed at more negative potentials were attributed to the dendrimeric moieties in **11** by comparison with the model carbonyl compound **7**, investigated under the conditions of Fig. 1. The CV curve for a 0.5 mM solution of **7** in THF, at 0.5 V s^{-1} and T = 25 °C is shown in Fig. 2a. A reversible peak at −1.95 V is observed (see also Fig. 2b) followed by a series of successive and nearly-coalescing multi-electron irreversible peaks between −2.4 and −2.8 V (Table 1). Dendrimer **7** differs from the dendrimeric addend in **11** by the presence of the central *p*-phenylacetylene-substituted benzophenone group. Benzophenone is known to reduce reversibly in aprotic media ($E_{1/2}$ = −1.68 V in dimethylformamide, DMF) leading to a stable radical anion, with the negative charge on the oxygen atom and the radical located on the carbonyl carbon atom.[16] The first reductions of a series of *p*-substituted benzophenones have been shown to also lead, with the exception of halo-derivatives, to stable radical anions, the $E_{1/2}$ values ranging between −1.4 and −1.9 V (in DMF), depending on the nature of the substituent.[16] The one-electron reversible peak observed in the CV of **7** with $E_{1/2}$ = −1.95 V may then be attributed to the reduction of the *p*-phenylacetylene benzophenone moiety, while the multielectron reduction processes observed at more negative potentials can be located onto the polyacetylene units.

Recently, the optical properties of dendrimers made up of a polyacetylene repeat unit connected by benzene rings substituted in the *meta* position, such as those used here, have been investigated.[17] Those studies have shown that, despite the availability of many delocalisable π-bonds in these systems, optical excitations are highly confined by the poor *meta*-conjugation, the dendrimers behaving as a collection of constituent *p*-phenylacetylene chromophores that interact only weakly with each other. Such a lack of electronic coherence across *meta*-substituted sites is expected to reflect also on the redox properties of the dendrimeric units in **7** and **11**. The observation in the CV curves of both species of successive sets of two-electron processes, only slightly separated from each other by a few tens of mV, is in fact in line, on the one hand with the presence of two equivalent dendrimeric branches, and on the other hand with the fact that the mutual interactions experienced by the various monomeric units are weak and may depend on the position of the latter within the dendrimeric framework. In summary, the above study indicates that the CV pattern is the superimposition of those of the 6,6-closed methanofullerene and of the polyacetylene dendrimeric units, with no significant interaction evident between the two moieties.

Finally, the stability of the reduced forms of **11**, already assessed on the CV timescale, was checked on a much longer timescale by performing a spectroelectrochemical experiment. A solution of **11** (0.2 mM) and TBAPF6 (0.05 M) in benzonitrile solution was electrolysed at −0.6 V, which corresponds to the first reduction of the species. As the electrolysis proceeded, the typical absorption features in the visible and NIR regions of fullerene-centred monoanion appeared and developed in the spectra: the NIR absorption maximum occurred at 1034 nm, slightly blue-shifted with respect to [60]fullerene under the same conditions (1075 nm), as usually observed for 6,6-closed derivatives. The electrolysed solution remained stable for several hours.

Experimental

All reactions were carried out under a positive pressure of argon using Schlenk techniques. Solvents were purified prior to use by standard procedures: toluene was distilled over sodium, dichloromethane over phosphorus pentoxide, triethylamine over calcium hydride. All other solvents and reagents were used as purchased without further purification. Products were purified by column chromatography (silica gel, 70–230 mesh, 60 Å, Aldrich). Compounds **4** and **5** were prepared according to a literature procedure.[8]

Bis{4-[(trimethylsilyl)ethynyl]phenyl}methanone (2)

Bis(4-bromophenyl)methanone (**1**) (1 g, 3.0 mmol), (trimethylsilyl)acetylene (1.7 ml, 12 mmol), Pd(dba)$_2$ (71 mg, 0.125 mmol), copper(I) iodide (24 mg, 0.125 mmol), triphenylphosphine (162 mg, 0.625 mmol) and triethylamine (15 ml) were placed in a heavy-walled glass tube fitted with a Teflon screw valve (Young's tap). Toluene was added to this stirred reaction mixture until **1** was completely dissolved (~5 ml). The mixture was degassed and back-filled with argon three times, sealed, and stirred at 55 °C for 24 h. When the reaction was complete, the mixture was filtered through 3 cm silica and the solvent was removed under reduced pressure. The crude product was purified by column chromatography, eluting first with *n*-hexane in order to remove high R_f impurities and then with 10:1 *n*-hexane–dichloromethane to obtain **2** as a white, amorphous solid (808 mg, 72%). R_f 0.26 (2:1 *n*-hexane–dichloromethane). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.72 (4 H, d, *J* 8.30 Hz), 7.57 (4 H, d, *J* 8.30 Hz), 0.28 (18 H, s). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 195.01 (1 C, C=O), 136.81 (2 C), 131.95 (4 C, CH), 129.94 (4 C, CH), 127.58 (2 C), 104.15 (2 C), 98.11 (2 C), 0.0 (6 C, CH$_3$). MS (EI); *m*/*z* (%): 374 (21) $[M]^+$, 359 (64) $[M - CH_3]^+$, 344 (77) $[M - 2\ CH_3]^+$, 262 (100) $[M - C_2Si(CH_3)_3]^+$.

Bis(4-ethynylphenyl)methanone (3)

Potassium carbonate (10 mg, 0.18 mmol) was added to a solution of **2** (400 mg, 1.07 mmol) in methanol (15 ml) and dichloromethane (15 ml). The solution was degassed, back-filled with argon and stirred at room temperature until the deprotection of the starting compound was complete (*ca.* 2 h, monitored by TLC). The mixture was then washed with water (three times), dried over magnesium sulfate and filtered through 3 cm silica gel. After evaporation of the solvent, **3** was isolated without further purification as a colourless solid (234 mg, 95%). R_f 0.18 (2:1 *n*-hexane–dichloromethane). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.76 (4 H, d, *J* 8.31 Hz), 7.61 (4 H, d, *J* 8.31 Hz), 3.27 (2 H, s). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C 194.96 (1 C, C=O), 136.97 (2 C), 132.04 (4 C, CH), 129.83 (4 C, CH), 126.45 (2 C), 82.68 (CH, 2 C), 80.36 (2 C). MS (EI); *m*/*z* (%): 230 (82) $[M]^+$, 129 (100) $[M - C_8H_5]^+$, 101 (52) $[M - C_8H_5, -CO]^+$.

Bis[4-{3,5-bis(3,5-di-*tert*-butylphenylethynyl)phenylethynyl}-phenyl]methanone (6)

A heavy-walled Schlenk tube was charged with **3** (46 mg, 0.2 mmol), 3,5-bis(3,5-di-*tert*-butylphenylethynyl)iodobenzene (**4**) (276 mg, 0.44 mmol), Pd(dba)$_2$ (9 mg, 0.016 mmol), copper(I) iodide (3 mg, 0.016 mmol), triphenylphosphine (21 mg, 0.08 mmol), triethylamine (3 ml) and toluene (*ca.* 1.5 ml). The Schlenk tube was then evacuated and back-filled with argon three times, sealed, and stirred at 55 °C for 12 h. When the reaction was complete, the mixture was filtered through 3 cm silica and the solvent was removed under reduced pressure. The crude product was purified by column chromatography, eluting first with *n*-hexane in order to remove high R_f impurities and then with 4:1 *n*-hexane–dichloromethane to obtain **6** as a white, amorphous solid (202 mg, 82%). R_f 0.50 (2:1 *n*-hexane–dichloromethane). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.83 (4 H, d, *J* 8.60 Hz), 7.75 (2 H, t, *J* 1.55 Hz), 7.71 (4 H, d, *J* 1.55 Hz), 7.66 (4 H, d, *J* 8.60 Hz), 7.44 (4 H, t, *J* 1.85 Hz), 7.41 (8 H, d, *J* 1.85 Hz), 1.36 (72 H, s). ^{13}C NMR (125 MHz, CDCl$_3$): δ_C 195.50 (1 C), 151.40 (8 C), 137.23 (2 C), 135.04 (2 C, CH), 134.39 (4 C, CH), 132.06 (4 C, CH), 130.51 (4 C, CH), 127.77 (2 C), 126.43 (8 C, CH), 124.86 (4 C), 123.77 (2 C), 123.63 (4 C, CH), 122.15 (4 C), 92.33 (4 C), 91.60 (2 C), 89.92 (2 C), 87.00 (4 C), 35.30 (8 C), 31.79 (24 C, CH$_3$).

Bis[4-{3,5-bis(3,5-di-*tert*-butylphenylethynyl)phenylethynyl}-phenyl]methanotosylhydrazone (8)

A heavy-walled Schlenk tube was loaded with **6** (200 mg, 0.16 mmol) and toluene-*p*-sulfonyl hydrazide (60 mg, 0.32 mmol). The reactants were dissolved in 10 ml toluene and heated under argon at 110 °C for 24 h. The solvent was removed under reduced pressure and crude **8** was purified by column chromatography on silica gel, eluting with 1:4 *n*-hexane–dichloromethane. After evaporation of the solvent, pure **8** was isolated as a colourless, amorphous solid (168 mg, 75%). R_f 0.15 (1:1 *n*-hexane–dichloromethane). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.90 (2 H, d, *J* 8.40 Hz), 7.75 (1 H, t, *J* 1.56 Hz), 7.72 (2 H, d, *J* 1.56 Hz), 7.71 (1 H, t, *J* 1.55 Hz), 7.70 (2 H, d, *J* 8.52 Hz), 7.67 (2 H, d, *J* 1.55 Hz), 7.61 (1 H, s), 7.46 (4 H, $[AB]_2$, $\Delta\nu$ 6, *J* 8.50 Hz), 7.44 (2 H, t, *J* 1.85 Hz), 7.43 (2 H, t, *J* 1.85 Hz), 7.41 (4 H, d, *J* 1.85 Hz), 7.40 (4 H, d, *J* 1.85 Hz), 7.38 (2 H, d, *J* 8.40 Hz), 7.18 (2 H, d, *J* 8.52 Hz), 2.47 (3 H, s), 1.36 (36 H, s), 1.35 (36 H, s). ^{13}C NMR (125 MHz, CDCl$_3$): δ_C 150.95 (4 C), 150.91 (4 C), 147.30 (1 C), 138.16 (1 C), 134.39 (1 C, CH), 134.07 (1 C, CH), 133.88 (2 + 1 C, CH), 133.81 (2 C, CH), 132.72 (2 C, CH), 132.42 (1 C), 131.56 (2 C, CH), 129.08 (2 C, CH), 126.29 (2 C, CH), 125.96 (4 C, CH), 125.95 (4 C, CH), 124.35 (2 C), 124.23 (2 C), 123.87 (1 C), 123.52 (1 C), 123.15 (2 C, CH), 123.07 (2 C, CH), 122.46 (1 C), 121.77 (2 C), 121.71 (2 C), 91.79 (2 C), 91.62 (2 C), 90.40 (1 C), 89.52 (1 C), 89.22 (1 C), 89.04 (1 C), 86.67 (2 C), 86.58 (2 C), 34.84 (4 C), 34.82 (4 C), 31.31 (24 C, CH$_3$).

61,61-Bis[4-{3,5-bis(3,5-di-*tert*-butylphenylethynyl)phenylethynyl}phenyl]-1,2-dihydro-1,2-methano[60]fullerene (10)

[60]Fullerene (120 mg, 0.16 mmol) was dissolved under argon in 250 ml anhydrous, degassed toluene. Sodium hydride (1 mmol) and **8** (130 mg, 0.093 mmol) were then added and the reaction mixture was heated for 24 h at 60 °C under argon. After cooling down to room temperature, the reaction mixture was washed with water (100 ml), dried over magnesium sulfate and filtered. The toluene was removed under reduced pressure and the residue was chromatographed on silica gel. After eluting excess [60]fullerene with pure cyclohexane, a red–brown fraction was collected with 50:1 cyclohexane–dichloromethane. After solvent evaporation, pure **11** was obtained as a brown, amorphous solid. Yield 32 mg, 18%. R_f 0.83 (8:1 cyclohexane–dichloromethane). UV/VIS (cyclohexane, λ_{max}/nm) 260.8, 291.2, 298.9, 309.2, 430.3, 491.2, 693.6. IR (KBr): ν/cm^{-1} 3068, 2961, 2902, 2865, 2207, 1590, 1506, 1464, 1447, 1428, 1393, 1362, 1247, 1201, 1187, 1139, 1019, 1001, 899, 876, 820, 745, 703, 680, 589, 575, 559, 527. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.14 (4 H, d, *J* 8.54 Hz), 7.72 (2 H, t, *J* 1.56 Hz), 7.68 (4 H, d, *J* 1.56 Hz), 7.67 (4 H, d, *J* 8.54 Hz), 7.44 (4 H, t, *J* 1.86 Hz), 7.41 (8 H, d, *J* 1.86 Hz), 1.35 (72 H, s). ^{13}C NMR (125 MHz, CDCl$_3$): δ_C 150.70 (8 C), 147.39 (4 C), 144.98 (4 C), 144.96 (4 C), 144.90 (4 C), 144.50 (4 C), 144.44 (2 C), 144.36 (2 C), 144.11 (4 C), 144.59 (4 C), 142.78 (2 C), 142.72 (8 C), 141.97 (4 C), 141.88 (4 C), 140.72 (4 C), 138.60 (2 C), 137.94 (4 C), 134.09 (2 C, CH), 133.63 (4 C, CH), 132.03 (4 C, CH), 130.80 (4 C, CH), 125.73 (8 C, CH), 124.07 (4 C), 123.43 (2 C), 122.88 (4 C), 122.86 (2 C), 121.50 (4 C), 91.52 (4 C), 89.55 (2 C), 88.91 (2 C), 86.40 (4 C), 78.24 (2C), 57.03 (1 C), 34.60 (8 C), 31.10 (24 C, CH$_3$). MS (MALDI-TOF); *m*/*z*: 1936.2 $[M]^+$, calc: $C_{153}H_{98}$ 1936.45.

Bis[4-{3,5-bis[3,5-bis(3,5-di-*tert*-butylphenylethynyl)phenylethynyl]phenylethynyl}phenyl]methanone (7)

A heavy-walled Schlenk tube was charged with **3** (46 mg, 0.2 mmol), 3,5-bis[3,5-bis(3,5-di-*tert*-butylphenylethynyl)phenylethynyl]iodobenzene (**5**) (550 mg, 0.44 mmol), Pd(dba)$_2$ (9 mg, 0.016 mmol), copper(I) iodide (3 mg, 0.016 mmol), triphenylphosphine (21 mg, 0.08 mmol), triethylamine (5 ml) and toluene (*ca.* 2 ml). The reaction vessel was then evacuated and back-filled with argon three times, sealed, and stirred at 55 °C for 12 h. When the reaction was complete, the mixture was filtered through 3 cm silica and the solvent was removed under reduced pressure. The crude product was purified by column chromatography, first eluting with *n*-hexane in order to remove high R_f

impurities and then with 4:1 *n*-hexane–dichloromethane to obtain **7** as a white, amorphous solid (396 mg, 80%). R_f 0.50 (2:1 *n*-hexane–dichloromethane). UV/VIS (cyclohexane, λ_{max}/nm): 292.3, 300.8, 310.3. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (4 H, d, *J* 8.57 Hz), 7.77 (4 H, t, *J* 1.55 Hz), 7.75 (4 H, d, *J* 1.54 Hz), 7.74 (4 H, t, *J* 1.54 Hz), 7.73 (8 H, d, *J* 1.55 Hz), 7.72 (4 H, d, *J* 8.57 Hz), 7.47 (8 H, t, *J* 1.85 Hz), 7.44 (16 H, d, *J* 1.85 Hz), 1.38 (144 H, s). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 195.00 (1 C), 150.93 (16 C), 136.87 (2 C), 134.50 (4 C, CH), 134.45 (4 C, CH), 133.90 (8 C, CH), 131.66 (4 C, CH), 130.05 (4 C, CH), 127.15 (2 C), 125.96 (16 C, CH), 125.82 (2 C, CH), 124.38 (8 C), 123.89 (4 C), 123.60 (2 C), 123.28 (4 C), 123.15 (8 C, CH), 121.69 (8 C), 91.83 (8 C), 90.75 (2 C), 89.84 (2 C), 89.43 (4 C), 88.44 (4 C), 86.54 (8 C), 34.83 (8 C), 31.32 (48 C, CH_3).

Bis[4-{3,5-bis[3,5-bis(3,5-di-*tert*-butylphenylethynyl)phenylethynyl]phenylethynyl}phenyl]methanotosylhydrazone (9)

A heavy-walled Schlenk tube was loaded with **7** (350 mg, 0.14 mmol) and toluene-*p*-sulfonyl hydrazide (53 mg, 0.28 mmol). The reactants were dissolved in 10 ml toluene and heated under argon at 110 °C for 24 h. The solvent was removed under reduced pressure and crude **9** was purified by column chromatography on silica gel, eluting with 1:4 *n*-hexane–dichloromethane. After evaporation of the solvent, pure **9** was isolated as a colourless, amorphous solid (270 mg, 73%). R_f 0.15 (1:1 *n*-hexane–dichloromethane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (2 H, d, *J* 8.25 Hz), 7.78 (2 H, t, *J* 1.55 Hz), 7.77 (2 H, t, *J* 1.55 Hz), 7.76 (2 H, d, *J* 1.55 Hz), 7.75 (1 H, t, *J* 1.55 Hz), 7.74 (4 H, d, *J* 1.55 Hz), 7.72 (4 H, d, *J* 1.55 Hz), 7.71 (3 H, AB_2, $\Delta\nu$ 5, *J* 1.60 Hz), 7.66 (1 H, s, br), 7.52 (4 H, $[AB]_2$), 7.48 (4 H, t, *J* 1.84 Hz), 7.47 (4 H, t, *J* 1.85 Hz), 7.45 (8 H, d, *J* 1.84 Hz), 7.44 (8 H, d, *J* 1.85 Hz), 7.41 (4 H, 2 d, *J* 8.60 Hz), 7.22 (2 H, d, 8.50 Hz), 2.49 (3 H, s), 1.39 (72 H, s), 1.38 (72 H, s). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 150.94, 150.93, 144.36, 136.15, 135.36, 134.51 (CH), 134.47 (CH), 133.90 (CH), 133.04 (CH), 131.64 (CH), 130.67, 129.76 (CH), 129.00, 128.58 (CH), 128.20, 127.95 (CH), 127.49 (CH), 125.96 (CH), 125.90 (CH), 125.82 (CH), 125.27, 124.40, 124.38, 123.92, 123.81, 123.32, 123.29, 123.14 (CH), 121.71, 91.86, 91.83, 90.29, 89.78, 89.65, 89.46, 89.35, 89.34, 88.52, 88.45, 86.55, 86.54, 34.83, 34.82, 31.32 (CH_3), 24.16 (CH_3).

61,61-Bis[4-{3,5-bis[3,5-bis(3,5-di-*tert*-butylphenylethynyl)-phenylethynyl]phenylethynyl}phenyl]-1,2-dihydro-1,2-methano-[60]fullerene (11)

[60]Fullerene (90 mg, 0.125 mmol) was dissolved under argon in 250 ml anhydrous, degassed toluene. Then **9** (170 mg, 64 mmol) and sodium hydride (1 mmol) were added and the reaction mixture was heated for 24 h at 70 °C under argon. After cooling down to room temperature, the reaction mixture was washed with water (100 ml), dried over magnesium sulfate and filtered. The toluene was removed under reduced pressure and the brown residue was chromatographed on silica gel. After washing down excess [60]fullerene with pure cyclohexane, a red–brown fraction was eluted with 50:1 cyclohexane–dichloromethane. After solvent evaporation, pure **11** was obtained as a brown, amorphous solid. Yield 47 mg, 23%. R_f 0.64 (8:1 cyclohexane–dichloromethane). UV/VIS (cyclohexane, λ_{max}/nm): 292.5, 300.7, 310.3, 430.5, 490.7, 694.4. IR (KBr): ν/cm^{-1} 3067, 2961, 2903, 2866, 2210, 1768, 1589, 1506, 1465, 1448, 1429, 1393, 1362, 1246, 1201, 1187, 1139, 1018, 1001, 899, 876, 819, 745, 703, 680, 589, 574, 559, 527. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (4 H, d, *J* 8.38 Hz), 7.75 (4 H, t, *J* 1.54 Hz), 7.70–7.72 (3 H, m), 7.71 (8 H, d, *J* 1.54 Hz), 7.70 (4 H, d, *J* 8.38 Hz), 7.45 (8 H, t, *J* 1.84 Hz), 7.42 (16 H, d, *J* 1.84 Hz), 1.37 (144 H, s). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 150.83 (16 C), 147.47 (4 C), 145.09 (8 C), 145.03 (4 C), 144.62 (4 C), 144.56 (2 C), 144.47 (2 C), 144.23 (2 C), 143.70 (4 C), 142.92 (2 C), 142.84 (8 C), 142.09 (4 C), 142.00 (4 C), 140.85 (4 C), 138.87 (2 C), 138.06 (4 C), 134.39 (4 C, CH), 134.31 (4 C, CH), 133.84 (8 C, CH), 132.23 (4 C, CH), 130.94 (4 C, CH), 125.89 (16 C, CH), 125.74 (2 C, CH), 124.29 (8 C), 123.90 (2 C), 123.71 (4 C), 123.27 (4 C), 123.05 (8 C, CH), 122.75 (2 C), 121.65 (8 C), 91.79 (8 C), 90.18 (2 C), 89.26 (4 C), 88.72 (2 C), 88.53 (4 C), 86.51 (8 C), 78.36 (2 C), 57.13 (1 C), 34.74 (16 C), 31.25 (48 C, CH_3). MS (MALDI-TOF) *m*/*z*: 3186.2 $[M]^+$, calc: $C_{249}H_{194}$ 3186.27.

Electrochemistry

Materials. Tetrabutylammonium hexafluorophosphate (TBAH, puriss. from Fluka) was used as supporting electrolyte as received. Benzonitrile (Fluka) was transferred, under argon, from the original air-tight container into a Schlenk flask containing activated 4 Å molecular sieves and kept under vacuum prior to use. Tetrahydrofuran (THF, LiChrosolv, Merck) was treated according to a procedure described elsewhere.[13] For the cyclic voltammetric experiments, the solvent, prior to use, was distilled into the electrochemical cell using a trap-to-trap procedure.

Electrochemical instrumentation and measurements. The one-compartment electrochemical cell was of airtight design with high-vacuum glass stopcocks fitted with either Teflon or Kalrez (DuPont) O-rings in order to prevent contamination by grease. The connections to the high-vacuum line and to the Schlenck containing the solvent were obtained by spherical joints also fitted with Kalrez O-rings. The pressure measured in the electrochemical cell prior to performing the trap-to-trap distillation of the solvent was typically 1.0–2.0 × 10^{-5} mbar. The working electrode consisted either of a 0.6 mm-diameter platinum wire (*ca.* 0.15 cm^2) sealed in glass or a Pt disc ultramicroelectrode ($r = 5$ µm) also sealed in glass. The counter electrode consisted of a platinum spiral and the quasi-reference electrode was a silver spiral. The quasi-reference electrode drift was negligible for the time required by a single experiment. Both the counter and the reference electrode were separated from the working electrode by ~0.5 cm. Potentials were measured with the ferrocene standard and always referred to saturated calomel electrode (SCE). $E_{1/2}$ values correspond to $(E_{pc} + E_{pa})/2$ from CV. For irreversible peaks, the peak potential, E_p, is given, measured at 0.5 V s^{-1}. Ferrocene was also used as an internal standard for checking the electrochemical reversibility of a redox couple.

Potential-controlled bulk electrolysis was carried out in a three-compartment electrochemical cell with both the SCE reference electrode and the platinum spiral counter electrode separated from the working electrode compartment by sintered glass frits. The working electrode was a large area platinum gauze. The electrolysed solution was monitored at intervals during the electrolysis by steady-state voltammetry and, at the same time, UV–Vis–NIR spectra were taken.

Voltammograms were recorded with an AMEL Model 552 potentiostat or a custom-made fast potentiostat controlled by either an AMEL Model 568 function generator or an ELCHEMA Model FG-206F. Data acquisition was performed by a Nicolet Model 3091 digital oscilloscope interfaced to a PC. The charge exchanged during bulk electrolysis was measured by an AMEL Model 731 digital integrator. Absorption spectra were taken using a VARIAN Cary 5E UV–Vis–NIR spectrophotometer. Temperature control was accomplished within 0.1 °C with a Lauda Klein-Kryomat thermostat.

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