Fullerodendrons: synthesis, electrochemistry and reduction in the electrospray source for mass spectrometry analysis

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The synthesis of fullerene-functionalized dendritic branches (fullerodendrons) containing C_{60} spheres at each branching unit has been carried out by a convergent approach using successive esterification and deprotection steps. The *tert*-butyl protected fullerodendrons containing one, three or seven methanofullerene subunits can be characterized by ESMS owing to their reduction in the electrospray source. The MS analysis of the reduced species also confirmed that all the methanofullerene subunits in the fullerodendrons of highest generation behave as independent redox centers, as shown by their electrochemical behavior.

The recent developments in the functionalization of fullerenes allow the preparation of covalent fullerene derivatives with increasing complexity.[1] Since X-ray suitable crystals of sufficient quality are often difficult to obtain with fullerene derivatives, mass spectrometry (MS) and NMR spectroscopy appear to be the most important tools for their structural analysis. As far as MS is concerned, several ionization techniques such as electron impact (EI),[2] matrix-assisted laser desorption/ionization (MALDI),[3] or fast-atom bombardment (FAB)[4] have been used to characterize functionalized fullerenes. Unfortunately, these techniques are not always well adapted for C_{60} derivatives of high molecular weights. In effect, with these methods, the MS analysis leads to fragmentations and the molecular ions are not observed. This is due to the fact that too much energy is deposited in the evaporation/ionization process and/or that the matrices used are not well adapted. Despite the problems and difficulties that may arise with the increasing size of such molecules, encouraging perspectives are offered by the use of electrospray mass spectrometry (ESMS)[5] for their characterization. Indeed, under carefully controlled experimental conditions, ESMS has the ability to desolvate, without fragmentation, ions pre-existing in solution. A wide variety of large biomolecules[6] and coordination complexes,[7] where the charge is respectively conferred by protonation (deprotonation) and successive loss of counterions, have been successfully characterized by ESMS. Unfortunately, fullerene derivatives are generally uncharged in solutions and therefore not suitable for ESMS analysis. However, several strategies of ionization have been developed to analyze uncharged compounds by ESMS, using ESMS-active tags[8] or reducing agents in solution.[9] In the same way, but without prior chemical or electrochemical treatment, we have already described the characterization of C_{60} and other neutral species by ESMS, using their redox properties to induce ionization for MS analysis.[10] As a matter of fact, radical cations (positive mode) or radical anions (negative mode) can be generated during the ES process owing to the ability of the ES source to behave like an electrolysis cell.[11]

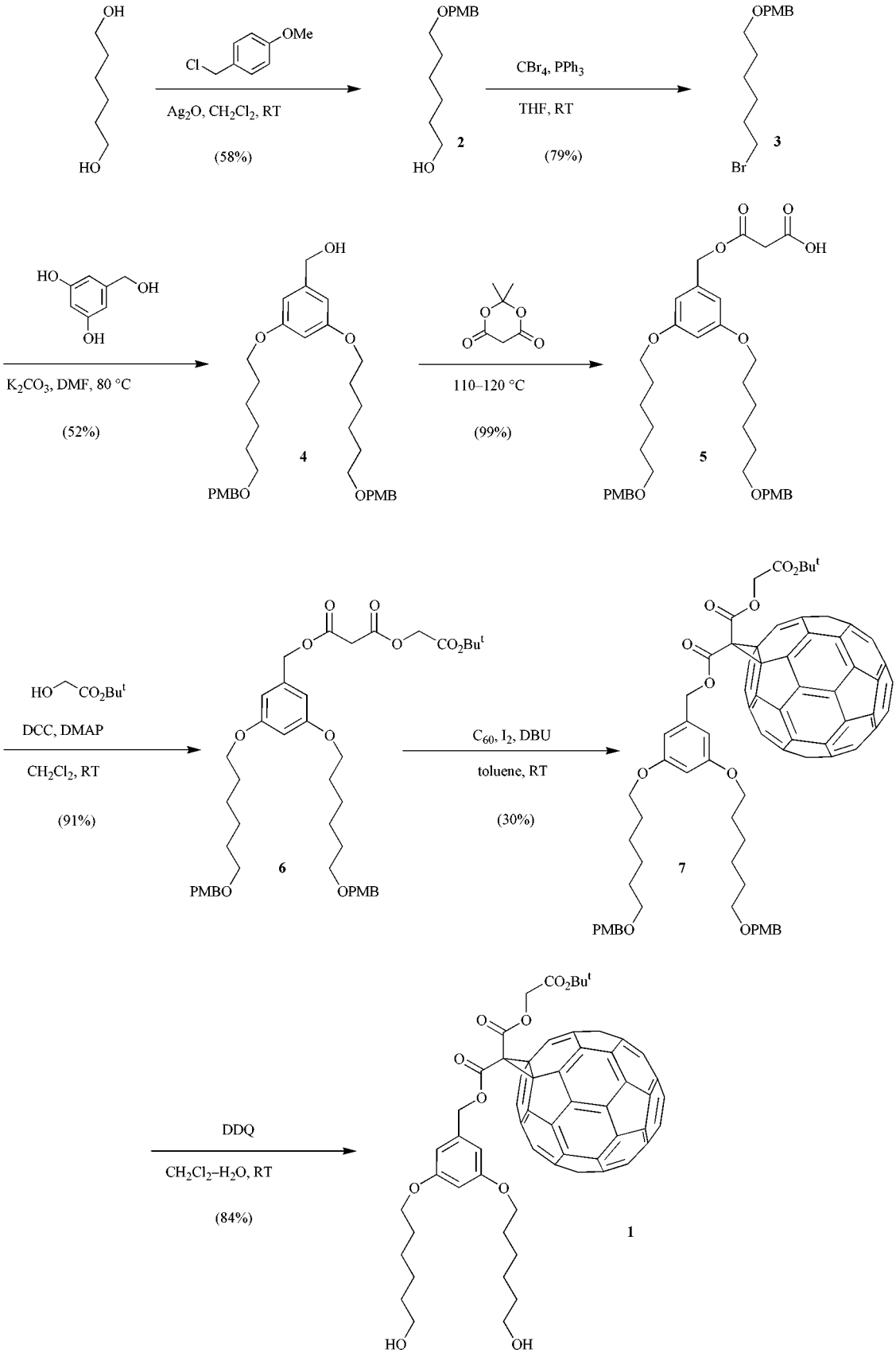
In this paper, we report in detail the synthesis of fullerene-functionalized dendritic branches (fullerodendrons) containing a C_{60} sphere at each branching unit[12] and show that these compounds can be characterized by ESMS on account of their reduction in the electrospray source.

Results and discussion

Synthesis

The preparation of the fullerodendrons with a C_{60} group at each branching unit was carried out by a convergent approach,[13] using successive esterification and deprotection steps. The preparation of the key building block **1** is depicted in Scheme 1. This diol containing one *tert*-butyl ester function is the branching unit for the construction of the fullerodendrons.

The mono-protection of 1,6-hexanediol was carried out by treatment with Ag_2O and *p*-methoxybenzyl chloride (PMBCl) according to the conditions reported by Bouzide and Sauvé.[14] Treatment of the resulting mono-protected derivative **2** with CBr_4 and PPh_3 in dry THF at room temperature afforded bromide **3** in 79% yield. Reaction of **3** with 3,5-dihydroxybenzyl alcohol in DMF at 80 °C in the presence of K_2CO_3 yielded **4** in 52% yield. Subsequent reaction with 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid)[15] at 120 °C gave the mono-ester **5** of malonic acid in 99% yield. *N*,*N*′-Dicyclohexylcarbodiimide (DCC) mediated esterification of **5** with *tert*-butyl 2-hydroxyacetate[16] in CH_2Cl_2 yielded malonate **6** in 91% yield. The functionalization of C_{60} is based on the Bingel reaction.[17] Nucleophilic addition of a stabilized α-



Scheme 1 Preparation of methanofullerene **1** (5% overall yield from 1,6-hexanediol).

halocarbanion to the C_{60} core, followed by intramolecular nucleophilic substitution, leads to clean cyclopropanation of C_{60}. The α-halomalonate derivative was prepared *in situ* from the reaction of the malonate with iodine.[18] Treatment of C_{60} with **6**, iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded methanofullerene **7** in 30% yield. The choice of the appropriate protecting group for the two alcohol functions in **7** was the key to this synthesis. The deprotection conditions must not be acidic to preserve the *tert*-butyl ester function and may not be basic to preserve the other ester functions. Furthermore, the decomposition of fullerene derivatives under reaction conditions using fluoride[19] prevents the use of silyl protecting groups. The PMB protecting groups in **7** could be removed under neutral

conditions by treatment with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in CH_2Cl_2 containing a small amount of water[20] at room temperature. All the ester functions remained unchanged and key building block **1** was thus obtained in good yield (84%).

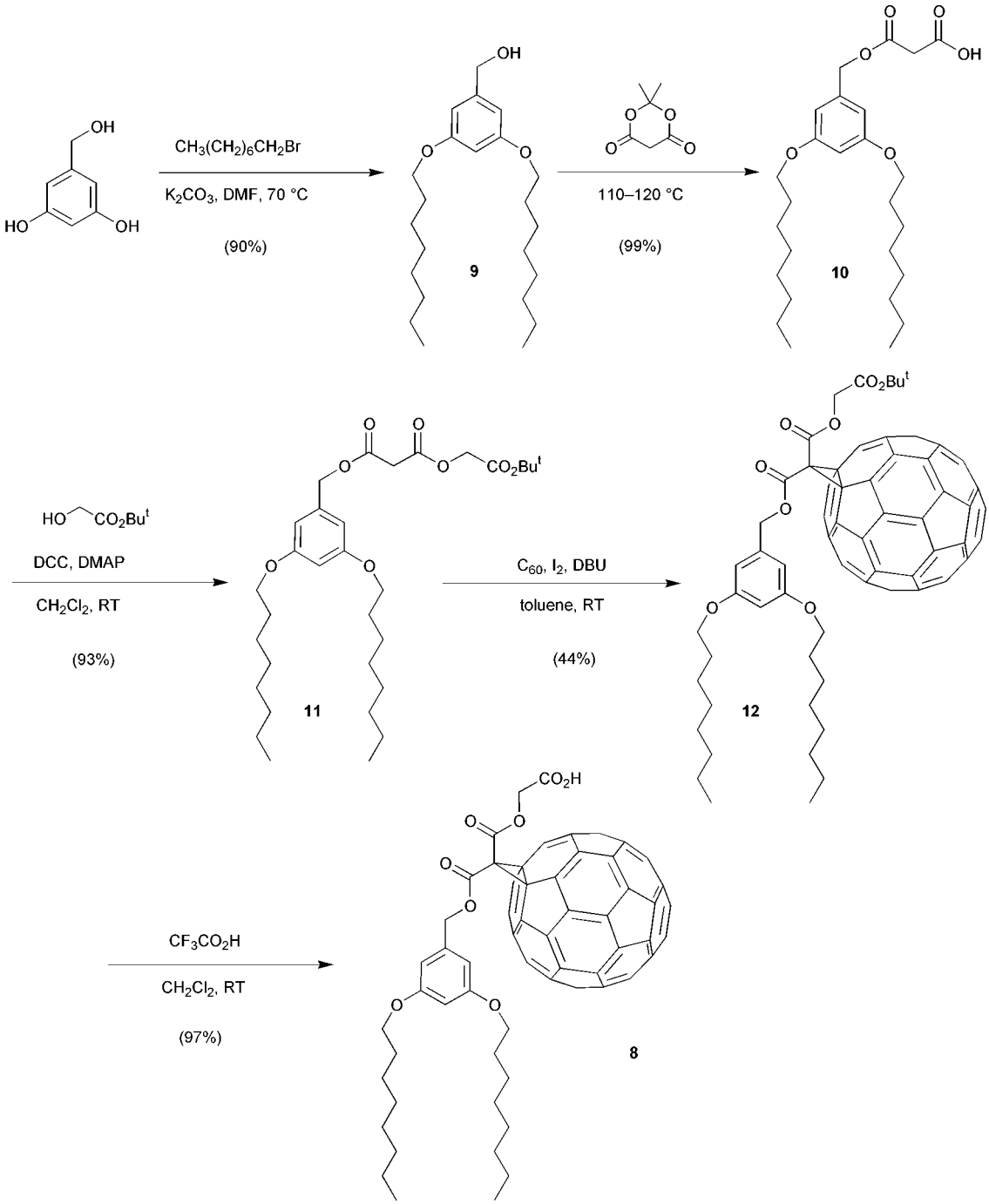
Fullerene derivative **8** substituted with two long alkyl chains (solubilizing groups) and a carboxylic function was used as a peripheral subunit for the constructions of the dendrons. Its preparation is depicted in Scheme 2.

Alcohol **9** was obtained in 90% yield by alkylation of 3,5-dihydroxybenzyl alcohol with 1-bromooctane in DMF at 70 °C with K_2CO_3 as base. Subsequent treatment with Meldrum's acid at 120 °C afforded the corresponding malonic mono-ester **10** in 99% yield. Reaction of acid **10** with *tert*-butyl 2-hydroxyacetate under esterification conditions using DCC and 4-dimethylaminopyridine (DMAP) led to malonic ester **11** in 93% yield. Treatment of C_{60} with **11** in the presence of iodine and DBU under Bingel conditions afforded methanofullerene **12** in 44% yield. Subsequent hydrolysis of the *tert*-butyl ester group with CF_3CO_2H[21] gave carboxylic acid **8** in 97% yield.

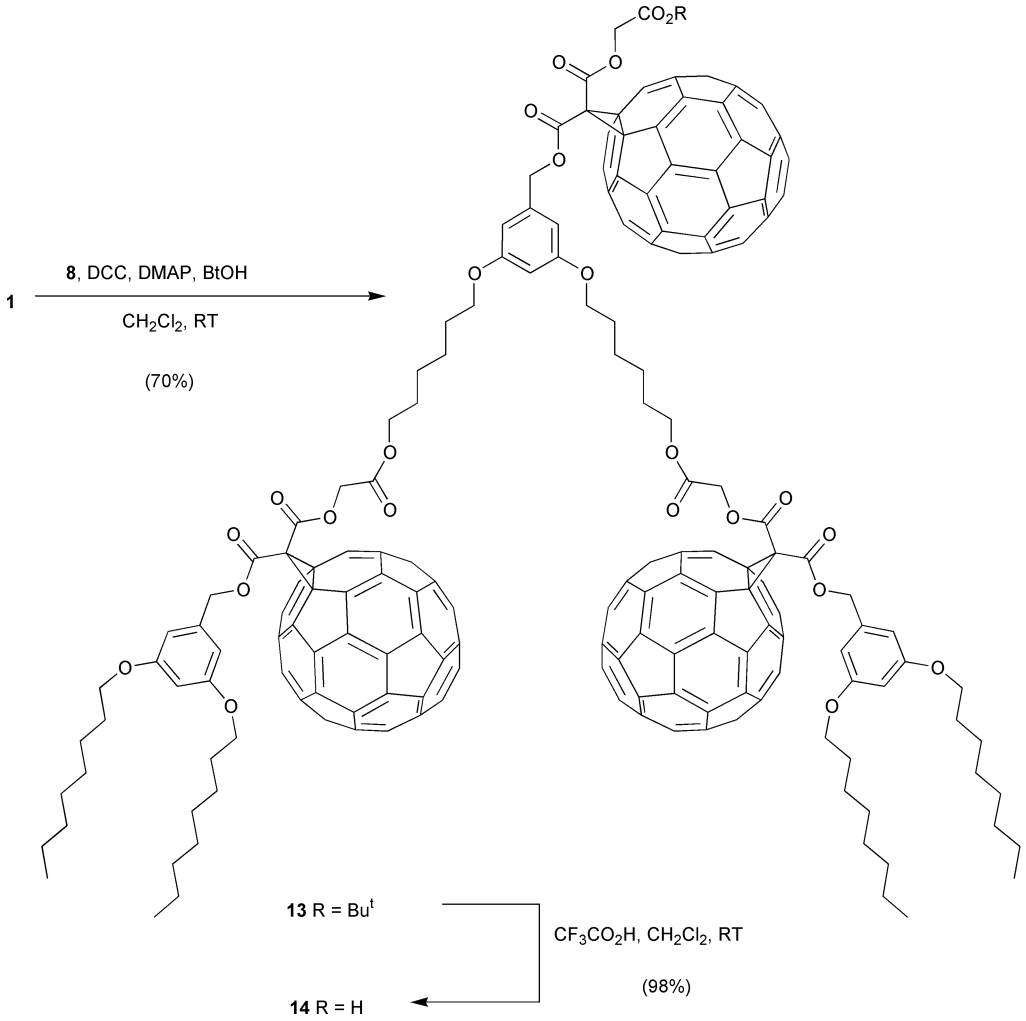
Esterification of acid **8** with diol **1** under conditions using DCC, 1-hydroxybenzotriazole (BtOH) and DMAP afforded the *tert*-butyl-protected fullerodendron **13** in 70% yield (Scheme 3). Selective hydrolysis of the *tert*-butyl ester under acidic conditions afforded acid **14** in 98% yield. Subsequent reaction of **14** with the branching unit **1** in the presence of DCC, BtOH and DMAP afforded fullerodendron **15** (Scheme 4), which after treatment with CF_3CO_2H gave **16**. The ^1H and ^{13}C NMR, MS, IR, UV/Vis and elemental analysis data were consistent with the proposed molecular structures assigned to the fullerodendrons of each generation.

Electrochemistry

The electrochemical properties of fullerodendrons **12**, **13** and **15** have been investigated by cyclic voltammetry (CV) and by



Scheme 2 Preparation of methanofullerene **8** (35% overall yield from 3,5-dihydroxybenzyl alcohol).



Scheme 3 Preparation of fullerodendron **14**.

steady state voltammetry (SSV) on a rotating disk electrode. All experiments have been performed at room temperature in CH_2Cl_2 + 0.1 M Bu_4NPF_6. The cyclic voltammograms of **12**, **13**, and **15** are shown in Fig. 1 and Table 1 summarizes the redox potentials of the three compounds along those of C_{60}.

Compound **12** shows the characteristic behavior previously reported for methanofullerenes.[22,23] By CV, up to three one-electron reduction steps are seen [Fig. 1(*a*)] and no oxidation could be observed at potentials below +1 V *vs.* Fc/Fc^+. Whereas the first reduction is perfectly reversible, the second reduction step shows the characteristics of an E.C. mechanism at sweep rates lower than 1 V s^{-1} and is followed by a chemical reaction[24] giving rise to the small amplitude signals seen in Fig. 1(*a*). By SSV, a fourth well-resolved reduction step could be seen. The first three reduction potentials determined by SSV are similar to those obtained by CV. The additional wave at −2.08 V *vs.* Fc/Fc^+ actually corresponds to the reduction of an electrogenerated species.[24]

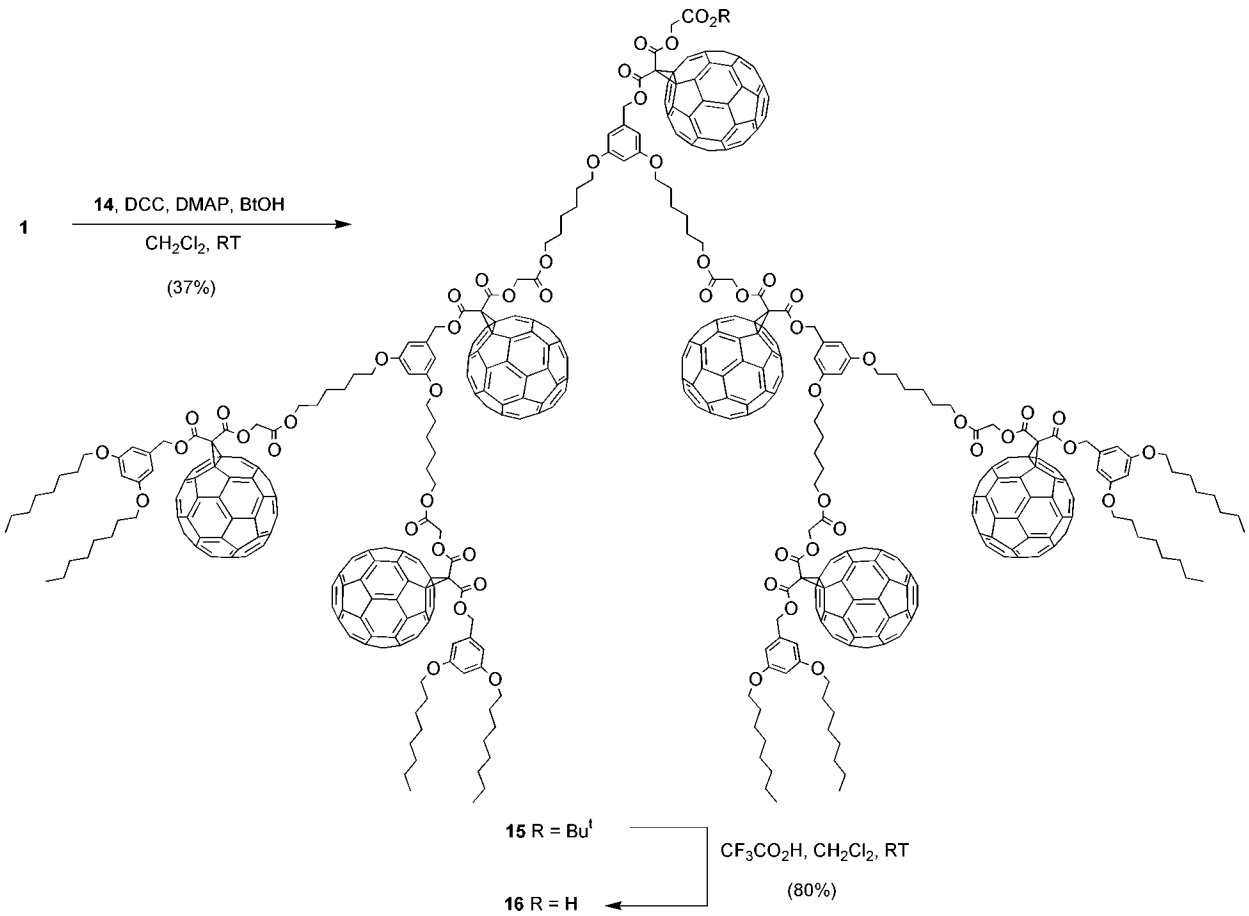
Methanofullerene **12** essentially retains the cathodic electrochemical pattern of the parent fullerene but the reduction potentials are shifted to more negative values when compared to those of C_{60} (Table 1). This is the classical behavior of most fullerene derivatives, whose cyclic voltammograms are typically characterized by small shifts to more negative values as the saturation of a double bond on the C_{60} surfaces causes a partial loss of "conjugation".[22,23]

The electrochemical behavior of fullerodendron **13** in both CV (Fig. 1) and SSV (Fig. 2) appears to be similar to that of compound **12**. The reduction potentials are also quite similar (Table 1). This seems to indicate that the three methanofullerene units in **13** behave as independent redox centers. It should be noted that the wave amplitudes are only 2.4 times

Table 1 Electrochemical data on the reduction of C_{60} and fullerodendrons **12**, **13** and **15** determined by CV and SSV on a glassy carbon working electrode in CH_2Cl_2 + 0.1 M Bu_4NPF_6 at room temperature

	CV[a]			SSV[b]			
	E_1	E_2	E_3	E_1	E_2	E_3	E_4
C_{60}[c]	−0.98(59)	−1.37(61)	−1.83(60)				
12	−1.03(85)	−1.41(80)	−1.84(110)	−1.04(60)	−1.42(70)	−1.90(70)	−2.08[d]
13	−1.05(90)	−1.41(80)	−1.85(120)	−1.06(70)	−1.42(60)	−1.90(80)	−2.08[d]
15	−1.06(80)	−1.41(80)	−1.85(100)	−1.07(65)	%[e]	%[e]	%[e]

[a] Values for $(E_{pa} + E_{pc})/2$ in V *vs.* Fc/Fc^+ and ΔE_{pc} in mV (in parentheses) at a scan rate of 0.1 V s^{-1}. [b] Values in V *vs.* Fc/Fc^+ and slope in mV per log unit (in parentheses). [c] From ref. 22(*a*). [d] Small amplitude wave corresponding to an electrogenerated species obtained after the third reduction step. [e] Badly resolved, spread out wave.



Scheme 4 Preparation of fullerodendron **16**.

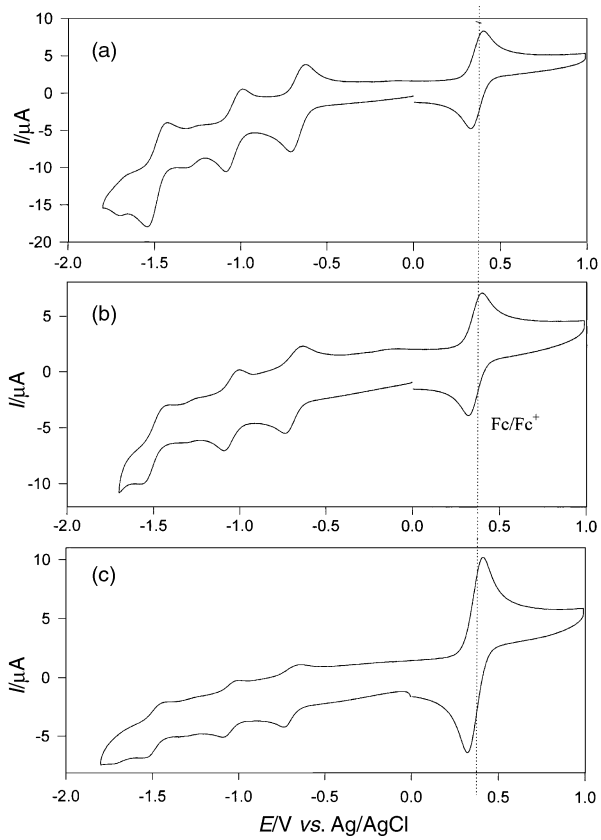


Fig. 1 Cyclic voltammetry of fullerodendrons (*a*) **12**, (*b*) **13** and (*c*) **15** on a glassy carbon electrode at $v = 0.1$ V s^{-1} in $CH_2Cl_2 + 0.1$ M Bu_4NPF_6 in the presence of ferrocene used as internal reference.

larger for **13** than for **12** at the same analytical concentration despite **13** containing three reducible methanofullerene units. This is mainly due to the large difference in diffusion coefficients. The limiting current at a rotating disk electrodes is given by the Levich equation:[24] $I_d = 0.62 \cdot nFACD^{2/3}\ v^{-1/6}\ \omega^{1/2}$ where n is the number of electrons exchanged, F the Faraday constant, A the electrode area in cm^2, C the analytical concentration in mol L^{-1}, D the diffusion coefficient in cm^2 s^{-1}, v the cinematic viscosity in cm^2 s^{-1}, and ω the rotation speed in rad s^{-1}. The limiting current ratio I_{d2}/I_{d1} (where I_{d2} stands for **13** and I_{d1} for **12**) reduces to: $I_{d2}/I_{d1} = (n_2/n_1) \cdot (D_2/D_1)^{2/3}$.

In this equation, the diffusion coefficient is given by the Stokes–Einstein equation and can be reduced to $D = \text{csts.}(d/M)^{1/3}$ where d is the density of the electroactive species and M its molecular weight.[25] Under these conditions, assuming similar d values, the expected current ratio becomes: $I_{d2}/I_{d1} = (n_2/n_1) \cdot (M_1/M_2)^{1/3}$ and is equal to 2.25. Within

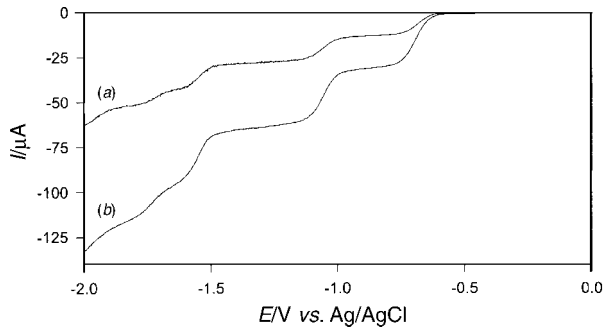


Fig. 2 SSV of (*a*) **12** and (*b*) **13** recorded at the same concentration (0.39 mmol L^{-1}) in $CH_2Cl_2 + 0.1$ M Bu_4NPF_6 on a glassy carbon rotating electrode ($\omega = 209$ rad s^{-1}).

experimental errors (due to uncertainty in the concentration), this theoretical value is in good agreement with the observed current ratio of 2.4 ± 0.2, which means that each step in **13** involves three electrons.

In addition, wave analysis by plotting E *vs.* log $I/(I_d - I)$ where I is the current, I_d the limiting current and E the applied potential, gave straight lines for both **12** and **13**. Taking into account the fact that the slopes of the waves are similar, the present results prove that the three methanofullerene units in **13** behave effectively as independent redox centers.[26]

By CV, fullerodendron **15** behaves like the above depicted species [Fig. 1(*c*)]. By SSV, only one clearly defined reduction step could be observed, the further reductions being less well defined and the wave spreading out along the potential axis. However, the slope of the first reduction wave as well as the observed amplitude are characteristic of a simultaneous reduction of the seven independent methanofullerene redox centers in **15**. Since a hepta-anionic species is generated after the first reduction step, the poor resolution of the further waves could be due to the poor solubility of this highly charged species in CH_2Cl_2.

Mass spectrometry

Whereas the FAB-MS spectrum of methanofullerene **12** showed the expected molecular ion peak, no characteristic peaks could be observed for the fullerodendrons of higher generations **13** and **15**. In fact, due to condensation reactions resulting probably from fullerene-fullerene interactions under the high energy of the FAB gun or due to fullerene aggregation in the matrix, the FAB-MS analysis yields only fragmentations. Furthermore, the molecular mass of compound **15** (8466.85 Da) is quite high for FAB analysis. Finally, no protonation or deprotonation sites are available in **12**, **13** and **15**, which usually prevents FAB analysis. We have already described the characterization of C_{60} by ESMS, using a new approach based on its redox properties.[10] Radical anions (negative mode) can be generated during the ES process, owing to the ability of the ES source to behave like an electrolysis cell.[11] In the present case, from the electrochemical data compounds **12**, **13** and **15** appear to be good candidates for this ESMS characterization method. The compound under study (**12**, **13** or **15**) was dissolved in anhydrous CH_2Cl_2 and stirred at room temperature for 5 min. Direct analysis of this solution yielded no observable ions. Therefore, the solution was then carefully degassed under nitrogen in order to remove oxygen from the sample. Indeed, in the case of reduction reactions, oxygen may be reduced before the analyte, thus preventing the reduction, and therefore the detection with ESMS, of the studied fullerene derivative. The degassed solution was directly analyzed by ESMS in the negative mode (reduction mode) and spectra with intense ion peaks were observed.

The ES mass spectrum obtained with **12** is depicted in Fig. 3 and shows one singly charged peak at $m/z = 1283.2$ (calculated $m/z = 1283.41$), corresponding to the expected radical anion or in other words to the mono-reduced compound. The isotopic pattern of this ion corresponds to the theoretical one and confirms the charge state of the peak.

The ES mass spectrum obtained in the negative mode with fullerodendron **13** shows three peaks (Fig. 4): the expected peak at $m/z = 1226.3$, corresponding to the radical tri-anion (calculated $m/z = 1225.95$), and two other peaks at $m/z = 1839.7$ and 3680.2. Since the three fullerenes behave as independent redox centers, only the radical tri-anion was expected. However, partial protonation of the generated tri-anion occured, giving rise to the two other peaks corresponding to the mono-protonated ($m/z = 1839.7$) and to the di-protonated ($m/z = 3680.2$) species of the radical tri-anion. These protonations are confirmed by the m/z values and are

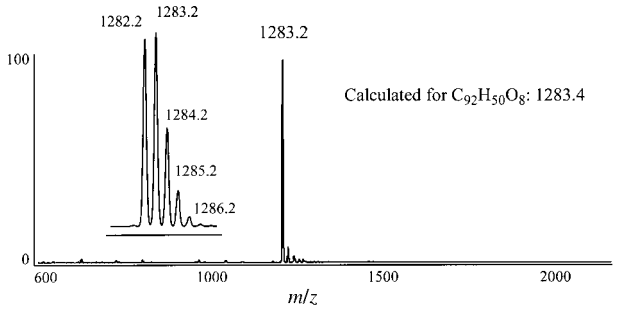


Fig. 3 ES mass spectrum of **12** recorded in the negative mode; the inset shows the isotopic pattern of the anion at $m/z = 1283.2$.

certainly due to the presence of residual quantities of water in the solvent. Indeed, when a more concentrated solution of **13** is analyzed by ESMS under the same conditions, a more intense peak at $m/z = 1226.3$ is observed, showing the correlation between the quantity of residual water in the solvent and the presence of protonated species.

The ES mass spectrum obtained with **15** also showed three peaks (Fig. 4): the expected radical hepta-anion at $m/z = 1209.6$ (calculated $m/z = 1209.55$), the mono-protonated compound at $m/z = 1411.1$ and the di-protonated compound at $m/z = 1693.1$.

Other experiments using pre-ionized compounds have also been carried out by ESMS. Indeed, the reduced species are relatively stable and can be generated by a classical electrochemical reaction. The studied anions were generated by intensiostatic reduction using tetra(*n*-butyl)ammonium hexafluorophosphate (TBA-PF_6) at 10^{-2} M as supporting electrolyte and analyzed by ESMS. Unfortunately, it was not possible to obtain a very informative spectrum; the presence of salts disturbs spray formation and a dramatic loss of intensity is observed.

Conclusion

The synthesis of fullerene-functionalized dendritic branches containing C_{60} spheres at each branching unit has been carried out by a convergent approach using successive ester-

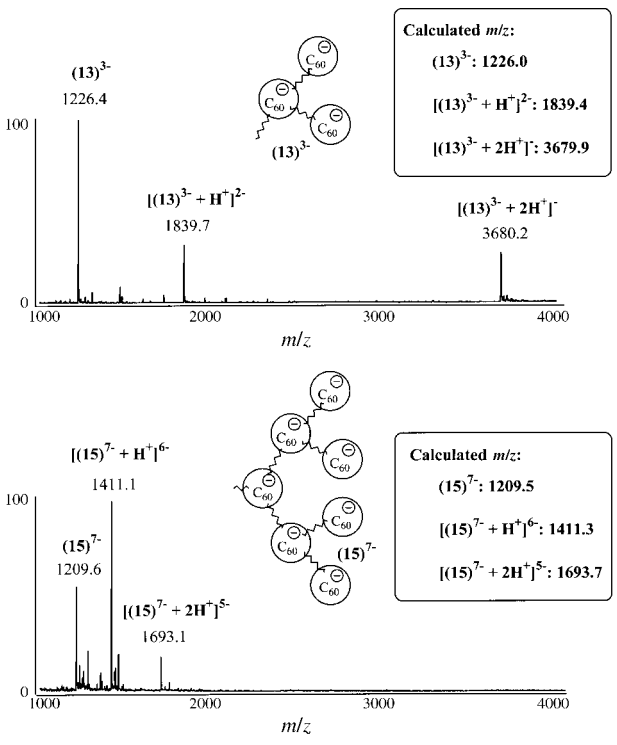


Fig. 4 ES mass spectra of **13** (top) and **15** (bottom).

ification and deprotection steps. The *tert*-butyl-protected fullerodendrons containing one, three or seven methanofullerene subunits have been characterized by ESMS, exploiting their reduction in the electrospray source. The MS analysis of the reduced species also confirmed that all the methanofullerene subunits in the fullerodendrons of highest generation behave as independent redox centers, as suggested by their electrochemical behavior. This new ionization strategy of uncharged fullerene derivatives appears to be very efficient and offers new perspectives in the characterization of complex molecular architectures larger than 10 kDa.

Experimental

Materials and methods

Reagents and solvents were purchased as reagent grade and used without further purification. *tert*-Butyl 2-hydroxyacetate was prepared according to the literature.[16] All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration was carried out at water aspirator pressure and drying *in vacuo* at 10^{-2} torr. Column chromatography: silica gel 60 (230–400 mesh, 0.040–0.063 mm) was purchased from E. Merck. Thin layer chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from E. Merck, visualization by UV light. UV/Vis spectra were measured on a Hitachi U-3000 spectrophotometer. IR spectra were measured on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AC 200 (200 MHz) or a Bruker AM 400 (400 MHz) with solvent peaks as reference. Elemental analyses were performed by the analytical service at the Institut Charles Sadron, Strasbourg.

Electrochemistry. The electrochemical studies were carried out in CH_2Cl_2 (Fluka, spectroscopic grade used without further purification) containing 0.1 M Bu_4NPF_6 (Merck, electrochemical grade) as supporting electrolyte. A classical three-electrode cell was connected to an Autolab (Eco Chemie B.V. Utrecht, Holland) computerized electrochemical device. The working electrode was a glassy carbon disk (3 mm in diameter), the auxiliary electrode a platinum wire and the reference electrode an aqueous Ag/AgCl reference electrode. All potentials are given *vs.* Fc/Fc^+ used as internal standard.

Electrospray mass spectrometry. Samples for ESMS were prepared by dissolving the compound under study in anhydrous CH_2Cl_2 at a concentration of 10^{-4} M. After stirring at room temperature for 5 min, the solution was intensively degassed under nitrogen to remove oxygen from the sample. The degassed solution was then directly analyzed by ESMS. Negative ES mass spectra were obtained on a Quattro II (Micromass, Altrincham, UK) ES triple quadrupole mass spectrometer. The ES source was heated to 45 °C. The sampling cone voltage (V_c) was at 100 V; at this voltage no fragmentation processes were detected and reproducible spectra were obtained. Sample solutions were introduced into the mass spectrometer source with a syringe pump (Harvard type 55 1111: Harvard Apparatus Inc., South Nattick, MA, USA) with a flow rate of 4 μl min^{-1}. Calibration was performed using protonated horse myoglobin. Scanning was performed in the MCA (multi channel analyzer) mode and several scans were summed to obtain the final spectrum.

Syntheses

Compound 2. Freshly prepared Ag_2O (29.4 g, 126.92 mmol) was added to a stirred solution of 1,6-hexanediol (10 g, 84.61 mmol) and PMBCl (14.57 g, 156.61 mmol) in CH_2Cl_2 (250 mL) at room temperature. After 4 h, the reaction mixture was filtered and evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2–2% MeOH) yielded **2** (11.82 g, 58%). Colorless oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.36–1.60 (m, 8H), 3.43 (t, J = 6 Hz, 2H), 3.61 (t, J = 6 Hz, 2H), 3.80 (s, 3H), 4.42 (s, 2H), 6.88 (d, J = 8 Hz, 2H), 7.27 (d, J = 8 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 50 MHz): δ = 25.32, 25.68, 29.34, 32.27, 54.94, 62.09, 69.75, 72.18, 113.42, 129.02, 130.23, 158.77. $C_{14}H_{22}O_3$ (238.3): calcd C 70.56, H 9.30; found C 70.15, H 9.11.

Compound 3. PPh_3 (1.91 g, 5.77 mmol) was added to a stirred solution of **2** (1.1 g, 4.61 mmol) and CBr_4 (1.91 g, 5.77 mmol) in dry THF (20 mL) at room temperature. After 30 min, the reaction mixture was poured into water. The aqueous layer was extracted with CH_2Cl_2 (3 ×). The combined organic layers were dried ($MgSO_4$), filtered and evaporated to yield **3** (1.1 g, 79%), which was used without further purification. Colorless oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.38 (m, 4H), 1.62 (m, 2H), 1.86 (m, 2H), 3.41 (t, J = 7 Hz, 2H), 3.45 (t, J = 6.5 Hz, 2H), 3.81 (s, 3H), 4.43 (s, 2H), 6.89 (d, J = 8 Hz, 2H), 7.24 (d, J = 8 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 50 MHz): δ = 25.32, 27.88, 29.47, 32.65, 33.81, 55.16, 69.78, 72.44, 113.64, 129.12, 130.58, 159.01. $C_{14}H_{21}O_2Br$ (301.23): calcd C 55.82, H 7.03; found C 55.86, H 7.02.

Compound 4. A mixture of **3** (6.3 g, 20.91 mmol), 3,5-dihydroxybenzyl alcohol (1.37 g, 9.96 mmol), and K_2CO_3 (5.78 g, 41.82 mmol) in DMF (150 mL) was stirred for 20 h at 80 °C. After cooling, the resulting mixture was filtered and evaporated to dryness. The brown residue was taken up in Et_2O. The organic layer was washed with a saturated aqueous NaCl solution (2 ×), dried ($MgSO_4$), filtered and evaporated. Column chromatography (SiO_2, CH_2Cl_2–AcOEt 8 : 2) yielded **4** (3.00 g, 52%). Colorless oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.45–1.78 (m, 16H), 3.47 (t, J = 6 Hz, 4H), 3.80 (s, 6H), 3.95 (t, J = 6 Hz, 4H), 4.42 (s, 4H), 4.60 (s, 2H), 6.37 (t, J = 2 Hz, 1H), 6.50 (d, J = 2 Hz, 2H), 6.90 (d, J = 8 Hz, 4H), 7.27 (d, J = 8 Hz, 4H); ^{13}C-NMR ($CDCl_3$, 50 MHz): δ = 25.72, 25.80, 29.03, 29.49, 55.04, 64.93, 67.66, 69.81, 72.32, 100.20, 104.76, 113.54, 129.06, 130.29, 143.29, 158.90, 160.21; IR (CH_2Cl_2): ν = 3599 cm^{-1} (OH). $C_{35}H_{48}O_7 \cdot 0.5\ H_2O$ (589.77). calcd C 71.28, H 8.37; found C 71.55, H 8.33.

Compound 5. A mixture of **4** (3.00 g, 5.16 mmol) and Meldrum's acid (0.75 g, 5.16 mmol) was heated at 110–120 °C for 3 h. After cooling, drying (10^{-2} torr, 24 h) provided **5** (3.40 g, 99%), which was used without further purification. Pale yellow oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.44–1.80 (m, 16H), 3.47 (t, J = 6 Hz, 4H), 3.48 (s, 2H), 3.80 (s, 6H), 3.93 (t, J = 6 Hz, 4H), 4.46 (s, 4H), 5.14 (s, 2H), 6.40 (t, J = 2 Hz, 1H), 6.48 (d, J = 2 Hz, 2H), 6.87 (d, J = 8 Hz, 4H), 7.26 (d, J = 8 Hz, 4H); ^{13}C-NMR ($CDCl_3$, 50 MHz): δ = 25.71, 25.76, 28.96, 29.38, 40.83, 55.10, 67.12, 67.80, 69.77, 72.28, 101.18, 106.14, 113.83, 129.24, 130.23, 137.10, 159.00, 160.27, 166.53, 169.40.

Compound 6. DCC (1.05 g, 5.10 mmol) and DMAP (0.10 g, 0.85 mmol) were added to **5** (3.40 g, 5.10 mmol) and *tert*-butyl 2-hydroxyacetate (0.56 g, 4.25 mmol) in CH_2Cl_2 (50 mL) at 0 °C. The mixture was allowed to slowly warm to room temperature (1 h) and, after stirring for 24 h, filtered and evaporated. Column chromatography (SiO_2, CH_2Cl_2) yielded **6** (3.03 g, 91%). Colorless oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 1.33 (s, 9H), 1.33–1.78 (m, 14H), 3.43 (t, J = 6 Hz, 4H), 3.51 (s, 2H), 3.80 (s, 6H), 3.93 (t, J = 6 Hz, 4H), 4.41 (s, 4H), 4.55 (s, 2H), 5.10 (s, 2H), 6.36 (t, J = 2 Hz, 1H), 6.46 (d, J = 2 Hz, 2H), 6.90 (d, J = 8 Hz, 4H), 7.27 (d, J = 8 Hz, 4H); ^{13}C-NMR ($CDCl_3$, 50 MHz): δ = 25.77, 25.86, 27.84, 29.05,

29.56, 40.86, 55.10, 61.73, 67.16, 67.77, 69.85, 72.38, 82.54, 100.99, 106.29, 113.58, 129.08, 130.55, 137.06, 158.95, 160.26, 165.66, 166.04; IR (CH_2Cl_2): $\nu = 1748\ cm^{-1}$ (C=O).

Compound 7. DBU (0.084 mL, 0.582 mmol) was added at room temperature to a solution of **6** (0.2 g, 0.254 mmol), C_{60} (0.168 g, 0.232 mmol), and I_2 (0.074 g, 0.291 mmol) in toluene (200 mL), and the mixture was stirred for 6 h. Filtration through a short plug of silica (CH_2Cl_2) followed by column chromatography (SiO_2, CH_2Cl_2–1% AcOEt) yielded **7** (106 mg, 30%). Dark red glassy product; ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 1.23$–1.78 (m, 16H), 1.53 (s, 9H), 3.43 (t, $J = 6$ Hz, 4H), 3.80 (s, 6H), 3.88 (t, $J = 6$ Hz, 4H), 4.42 (s, 4H), 4.82 (s, 2H), 5.47 (s, 2H), 6.38 (t, $J = 2$ Hz, 1H), 6.60 (d, $J = 2$ Hz, 2H), 6.87 (d, $J = 8$ Hz, 4H), 7.27 (d, $J = 8$ Hz, 4H); ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 26.02$, 28.09, 29.23, 29.72, 51.80, 55.26, 63.11, 67.96, 69.13, 70.00, 71.25, 72.53, 83.09, 101.65, 107.37, 113.73, 129.21, 130.68, 136.61, 138.21, 139.88, 140.85, 141.85, 142.16, 142.97, 143.80, 144.45, 144.62, 144.91, 145.19, 159.05, 160.37, 163.07, 165.35; IR (CH_2Cl_2): $\nu = 1747\ cm^{-1}$ (C**2**O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (108 000), 326 (33 200), 425 (2150), 482 (1210), 686 nm (140). $C_{104}H_{58}O_{12} \cdot 0.5CH_2Cl_2$ (1542.1): calcd C 81.39, H 3.86; found C 81.30, H 3.95.

Compound 1. DDQ (220 mg, 0.968 mmol) was added to a solution of **7** (660 mg, 0.44 mmol) in 18 : 1 CH_2Cl_2–H_2O (50 mL) and the mixture was stirred for 1 h. The resulting CH_2Cl_2 solution was washed with an aqueous $NaHCO_3$ solution, then with a saturated aqueous NaCl solution, dried ($MgSO_4$), filtered and evaporated. Column chromatography (SiO_2, CH_2Cl_2–2% MeOH) yielded **1** (462 mg, 84%). Dark red glassy product; ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 1.40$–1.77 (m, 16H), 1.58 (s, 9H), 3.68 (t, $J = 6$ Hz, 4H), 3.90 (t, $J = 6$ Hz, 4H), 4.85 (s, 2H), 5.50 (s, 2H), 6.40 (t, $J = 2$ Hz, 1H), 6.62 (d, $J = 2$ Hz, 2H); ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 25.48$, 25.86, 28.00, 29.12, 32.57, 51.30, 62.72, 63.03, 67.84, 69.01, 71.15, 83.05, 101.57, 107.25, 136.56, 138.15, 139.77, 140.72, 140.80, 141.69, 141.79, 142.07, 142.75, 142.90, 143.67, 143.74, 144.35, 144.53, 144.76, 144.85, 145.09, 160.24, 162.82, 162.96, 165.31; IR (CH_2Cl_2): $\nu = 3600$ (OH), 1748 cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 257 (136 000), 326 (40 600), 425 (2850), 482 (1540), 686 nm (200). $C_{88}H_{42}O_{10}$ (1259.3): calcd C 83.93, H 3.36; found C 83.55, H 3.46.

Compound 9. A mixture of K_2CO_3 (41.5 g, 300 mmol), 3,5-dihydroxybenzyl alcohol (10 g, 71.36 mmol) and 1-bromooctane (35.6 g, 142.78 mmol) in DMF (150 mL) was heated at 70 °C for 41 h, then cooled to room temperature. After filtration through celite (CH_2Cl_2) and evaporation, the residue was taken up in Et_2O. The organic layer was washed with a saturated aqueous NaCl solution (2 ×), dried ($MgSO_4$), filtered and evaporated. Column chromatography (SiO_2, CH_2Cl_2–hexane 1 : 1) yielded **9** (23.48 g, 90%). Colorless oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.89$ (t, $J = 6.5$ Hz, 6H), 1.30 (m, 20H), 1.73 (m, 4H), 3.93 (t, $J = 6.5$ Hz, 4H), 4.60 (br s, 2H), 6.38 (t, $J = 2$ Hz, 1H), 6.49 (d, $J = 2$ Hz, 2H); ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 14.05$, 22.61, 26.00, 29.22, 29.31, 31.77, 65.28, 67.99, 110.45, 104.96, 143.19, 160.43; IR (CH_2Cl_2): $\nu = 3604\ cm^{-1}$ (OH). $C_{23}H_{40}O_3$ (364.6): calcd C 75.78, H 11.06; found C 75.72, H 11.20.

Compound 10. A mixture of **9** (11 g, 30.16 mmol) and Meldrum's acid (4.35 g, 30.16 mmol) was heated at 110–120 °C for 3 h. After cooling, drying (10^{-2} torr, 24 h) provided **10** (13.55 g, 99%), which was used without further purification. Pale yellow oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.89$ (t, $J = 6$ Hz, 6H), 1.30 (m, 20H), 1.76 (m, 4H), 3.50 (s, 2H), 3.91 (t, $J = 6$ Hz, 4H), 5.14 (s, 2H), 6.42 (t, $J = 2$ Hz, 1H), 6.48 (d, $J = 2$ Hz, 2H); ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 14.05$, 22.61, 25.99, 29.18, 29.31, 31.77, 40.73, 67.52, 68.05, 101.25, 106.42, 136.87, 160.42, 166.49, 171.22; IR (CH_2Cl_2): $\nu = 1747\ cm^{-1}$ (C=O).

Compound 11. DCC (4.58 g, 22.19 mmol) and DMAP (450 mg, 3.69 mmol) were added to *tert*-butyl 2-hydroxyacetate (2.44 g, 18.49 mmol) and **10** (10 g, 22.19 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The mixture was allowed to slowly warm to room temperature (1 h) and, after stirring for 24 h, filtered and evaporated. Column chromatography (SiO_2, CH_2Cl_2) yielded **11** (9.77 g, 93%). Colorless oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.89$ (t, $J = 6$ Hz, 6H), 1.35 (m, 20H), 1.49 (s, 9H), 1.77 (m, 4H), 3.53 (s, 2H), 3.91 (t, $J = 6$ Hz, 4H), 4.55 (s, 2H), 5.10 (s, 2H), 6.41 (t, $J = 2$ Hz, 1H), 6.46 (d, $J = 2$ Hz, 2H); ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 13.99$, 22.54, 25.93, 27.83, 29.12, 29.23, 31.70, 40.87, 61.71, 67.14, 67.90, 82.49, 101.00, 106.26, 137.09, 160.31, 165.66, 166.02; IR (CH_2Cl_2): $\nu = 1748\ cm^{-1}$ (C=O). $C_{32}H_{52}O_8$ (564.8): calcd C 68.06, H 9.28; found C 68.27, H 9.40.

Compound 12. DBU (0.310 mL, 2.08 mmol) was added at room temperature to a solution of **11** (516 mg, 0.915 mmol), C_{60} (600 mg, 0.832 mmol), and I_2 (264 mg, 1.04 mmol) in toluene (600 mL), and the mixture was stirred for 6 h. Filtration through a short plug of silica (toluene) followed by column chromatography (SiO_2, toluene) yielded **12** (470 mg, 44%). Dark red glassy product; ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.89$ (t, $J = 6$ Hz, 6H), 1.28 (m, 20H), 1.54 (s, 9H), 1.74 (m, 4H), 3.90 (t, $J = 6$ Hz, 4H), 4.84 (s, 2H), 5.48 (s, 2H), 6.40 (t, $J = 2$ Hz, 1H), 6.62 (d, $J = 2$ Hz, 2H); ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 14.12$, 22.67, 26.09, 28.07, 29.25, 29.38, 29.66, 31.80, 51.80, 63.08, 68.09, 69.12, 71.25, 83.06, 101.64, 107.34, 136.58, 138.22, 139.84, 140.84, 141.79, 141.88, 142.15, 142.85, 142.94, 143.77, 143.83, 144.42, 144.46, 144.61, 144.85, 144.92, 145.20, 160.40, 162.92, 163.05, 165.32; IR (CH_2Cl_2): $\nu = 1748\ cm^{-1}$ (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (107 000), 326 (35 300), 425 (2320), 482 (1310), 688 nm (170); ESMS: see Fig. 3. $C_{92}H_{50}O_8$ (1283.4): calcd C 86.10, H 3.93; found C 86.56, H 3.83.

Compound 8. A mixture of **12** (2.00 g, 1.56 mmol) and CF_3CO_2H (25 mL) in CH_2Cl_2 (100 mL) was stirred at room temperature for 1 h. The reaction mixture was then washed with water (until pH was near neutrality), dried ($MgSO_4$), filtered and evaporated to yield **8** (1.86 g, 97%). Dark red glassy product; ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.88$ (t, $J = 6$ Hz, 6H), 1.28 (m, 20H), 1.75 (m, 4H), 3.90 (t, $J = 6$ Hz, 4H), 5.01 (s, 2H), 5.45 (s, 2H), 6.41 (t, $J = 2$ Hz, 1H), 6.60 (d, $J = 2$ Hz, 2H); IR (CH_2Cl_2): $\nu = 1748\ cm^{-1}$ (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (115 200), 325 (35 600), 425 (3260), 488 (1855), 687 nm (180). $C_{88}H_{42}O_8$ (1227.3): calcd C 86.12, H 3.45; found C 86.09, H 3.71.

Compound 13. DCC (143 mg, 0.694 mmol) and DMAP (13.58 mg, 0.111 mmol) were added to **8** (852 mg, 0.694 mmol), **1** (350 mg, 0.277 mmol), and HOBt (catalytic amount) in CH_2Cl_2 (150 mL) at 0 °C. The mixture was allowed to slowly warm to room temperature (1 h) and, after stirring for 24 h, filtered and evaporated. Column chromatography (SiO_2, CH_2Cl_2) yielded **13** (720 mg, 70%). Dark red glassy product; ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.88$ (t, $J = 6$ Hz, 12H), 1.20–1.43 (m, 52H), 1.53 (s, 9H), 1.77 (m, 12H), 3.86 (t, $J = 6$ Hz, 4H), 3.90 (t, $J = 6$, 8H), 4.22 (t, $J = 6$ Hz, 4H), 4.84 (s, 2H), 4.94 (s, 4H), 5.46 (s, 6H), 6.33 (t, $J = 2$ Hz, 1H), 6.40 (t, $J = 2$ Hz, 2H), 6.57 (d, $J = 2$ Hz, 2H), 6.60 (d, $J = 2$ Hz, 4H); ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 14.14$, 22.65, 25.56, 25.82, 26.09, 28.05, 28.46, 29.10, 29.25, 29.37, 31.77, 51.22, 51.23, 62.57, 63.05, 65.71, 67.73, 68.05, 69.02, 71.12, 71.18, 83.02, 101.54, 107.15, 107.28, 136.52, 136.65, 138.12, 138.39, 139.73, 139.84, 140.83, 141.72, 141.82, 142.10, 142.75, 142.81, 142.91, 143.68, 143.76, 144.32, 144.40, 144.55, 144.79, 144.88, 145.10,

145.23, 160.24, 160.38, 162.89, 165.28, 166.40; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (340 000), 327 (107 700), 425 (9500), 482 (4500), nm 689 (570); ESMS: see Fig. 4. $C_{264}H_{122}O_{24}$ (3677.9): calcd C 86.22, H 3.34; found C 86.07, H 3.36.

Compound 14. A mixture of **13** (680 mg, 0.184 mmol) and CF_3CO_2H (25 mL) in CH_2Cl_2 (100 mL) was stirred at room temperature for 1 h. The reaction mixture was then washed with water (until pH was near neutrality), dried ($MgSO_4$), filtered and evaporated to yield **14** (660 mg, 98%). Dark red glassy product; ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 0.88 (t, J = 6 Hz, 12H), 1.27–1.43 (m, 52H), 1.70 (m, 12H), 3.87 (t, J = 6 Hz, 4H), 3.89 (t, J = 6 Hz, 8H), 4.24 (t, J = 6 Hz, 4H), 4.95 (s, 4H), 4.98 (s, 2H), 5.43 (s, 2H), 5.46 (s, 4H), 6.35 (t, J = 2 Hz, 1H), 6.40 (t, J = 2 Hz, 2H), 6.59 (d, J = 2 Hz, 2H), 6.61 (d, J = 2 Hz, 4H); ^{13}C-NMR ($CDCl_3$, 50 MHz): δ = 14.15, 22.67, 25.51, 25.80, 26.11, 28.44, 29.09, 29.25, 29.37, 29.58, 31.80, 51.10, 51.18, 62.09, 62.62, 65.79, 67.78, 68.08, 69.05, 71.09, 101.56, 107.17, 136.52, 136.65, 138.40, 138.50, 139.74, 140.80, 141.72, 141.81, 142.10, 142.81, 142.92, 143.76, 144.39, 144.55, 144.79, 144.89, 145.11, 160.27, 160.37, 162.77, 162.88, 162.97, 166.65; IR (CH_2Cl_2): ν = 1748 cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (276 000), 326 (90 700), 425 (8880), 480 (4000) 686 nm (530); ESMS (negative mode): m/z = 1207.4 ([M^{3-}]), 1810.8 ([M^{3-} + H^+]).

Compound 15. DCC (11.4 mg, 0.055 mmol) and DMAP (1 mg) were added to **14** (200 mg, 0.055 mmol), **1** (27.8 mg, $2.20.10^{-2}$ mmol) and HOBt (catalytic amount) in CH_2Cl_2 (50 mL) at 0 °C. The mixture was allowed to slowly warm to room temperature (1 h) and, after stirring for 24 h, filtered and evaporated. Column chromatography (SiO_2, $CHCl_3$) yielded **15** (70 mg, 37%). Dark red glassy product; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 0.88 (t, J = 6 Hz, 24H), 1.20–1.46 (m, 116H), 1.54 (s, 9H), 1.56–1.79 (m, 28H), 3.85 (t, J = 6 Hz, 4H), 3.86 (t, J = 6 Hz, 8H), 3.91 (t, J = 6 Hz, 16H), 4.23 (t, J = 6 Hz, 4H), 4.24 (t, J = 6 Hz, 8H), 4.85 (s, 2H), 4.94 (s, 12H), 5.45 (s, 2H), 5.47 (s, 12H), 6.33 (t, J = 2 Hz, 1H), 6.35 (t, J = 2 Hz, 2H), 6.42 (t, J = 2 Hz, 4H), 6.56 (d, J = 2 Hz, 4H), 6.58 (d, J = 2 Hz, 2H), 6.61 (d, J = 2 Hz, 8H); ^{13}C-NMR ($CDCl_3$, 50 MHz): δ = 14.16, 22.68, 25.59, 25.87, 26.12, 28.10, 28.50, 29.26, 29.28, 29.40, 29.66, 31.80, 51.24, 51.50, 62.63, 65.74, 67.78, 68.09, 69.05, 71.15, 83.06, 101.56, 107.18, 136.56, 136.66, 138.12, 138.42, 138.43, 139.76, 139.77, 140.81, 140.82, 141.72, 141.84, 142.13, 142.83, 142.85, 142.94, 143.79, 144.71, 144.43, 144.57, 144.82, 144.91, 145.13, 160.30, 160.41, 162.89, 166.43; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (550 000), 326 (190 000), 425 (19 600), 690 nm (2000); ESMS: see Fig. 4. $C_{608}H_{266}O_{56}\cdot 3\ CHCl_3$ (8824.9): calcd C 83.16, H 3.07; found C 83.09, H 3.18.

Compound 16. A mixture of **15** (25 mg, 2.96×10^{-3} mmol) and CF_3CO_2H (10 mL) in CH_2Cl_2 (50 mL) was stirred at room temperature for 3 h. The reaction mixture was then washed with water (until pH was near neutrality), dried ($MgSO_4$), filtered and evaporated to yield **16** (20 mg, 80%). Dark red glassy product; ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 0.88 (t, J = 6 Hz, 24H), 1.26 (m, 116H), 1.74 (m, 28H), 3.92 (m, 28H), 4.22 (m, 12H), 4.94 (br s, 14H), 5.46 (br s, 14H), 6.33 (m, 3H), 6.40 (t, J = 2 Hz, 4H), 6.55 (m, 6H), 6.60 (d, J = 2 Hz, 8H); ^{13}C-NMR ($CDCl_3$, 50 MHz): δ = 14.18, 22.70, 25.60, 25.88, 26.15, 28.51, 29.30, 29.42, 29.89, 31.83, 51.80, 62.66, 65.82, 67.83, 68.12, 69.10, 71.15, 101.60, 107.22, 136.59, 136.60, 138.44, 138.46, 139.81, 140.85, 141.76, 141.88, 142.16, 142.95, 142.96, 142.97, 143.82, 144.45, 144.60, 144.85, 144.94, 145.15, 160.33, 160.43, 162.96, 162.98, 166.54, 166.56, 166.59; IR (CH_2Cl_2): ν = 1748 cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 259 (546 000), 326 (187 700), 425 (23 830), 684 (1900) nm.

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