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Synthesis of Oligophenylenevinylene Heptamers Substituted with Fullerene Moieties

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Oligophenylenevinylene (OPV) derivatives substituted with one or two fullerene subunits have been prepared starting from a fullerene carboxylic acid derivative and OPV heptamers bearing one or two alcohol functions. The electrochemical properties of the resulting C_{60}-OPV derivatives have been investigated by cyclic voltammetry. Whereas the fist reduction of both C_{60}–OPV conjugates is centered on the C_{60} unit, the oxidation is centered on the OPV rod.

Introduction

Following the preparation of the first photovoltaic devices from C_{60}–oligophenylenevinylene (OPV) conjugates,[1] a great deal of attention has been devoted to hybrid systems combining C_{60} with π-conjugated oligomers.[2–3] Among their potential use as active materials in photovoltaic devices, C_{60}-(π-conjugated oligomer) hybrid systems offers also interesting perspectives for optical limiting or photodynamic therapy applications.[4] The photophysical properties of these C_{60}-(π-conjugated oligomer) dyads have been extensively studied. A characteristic feature in all these dyads is an ultrafast energy transfer from the lowest singlet excited state of the conjugated system to populate the fullerene singlet.[2] This first event can be followed by an electron transfer depending on the donating ability of the oligomer, on structural factors and on the solvent polarity.[2] The peculiar electronic properties of C_{60}-(π-conjugated oligomer) dyads led also to the development of dendritic systems with interesting light harvesting properties[5] or for evidencing original dendritic effects.[6]

The C_{60}–OPV conjugates reported so far generally combine the fullerene accepting unit with relatively short OPV oligomers.[1,3] However, by increasing the length of the OPV conjugated backbone, its absorption can be extended to the red thus providing new hybrid materials with improved absorption properties for photovoltaic applications.[2] In addition, OPV derivatives with longer backbones are better electron donors, thus allowing electron transfer processes in the corresponding C_{60}-OPV systems. This has been demonstrated with an OPV heptamer derivative bearing two fullerene moieties.[7] In this paper, we now report in detail the synthesis of this compound. In addition, we also describe the preparation of the corresponding system substituted with one fullerene subunit as well as the electrochemical properties of the all series of compounds.

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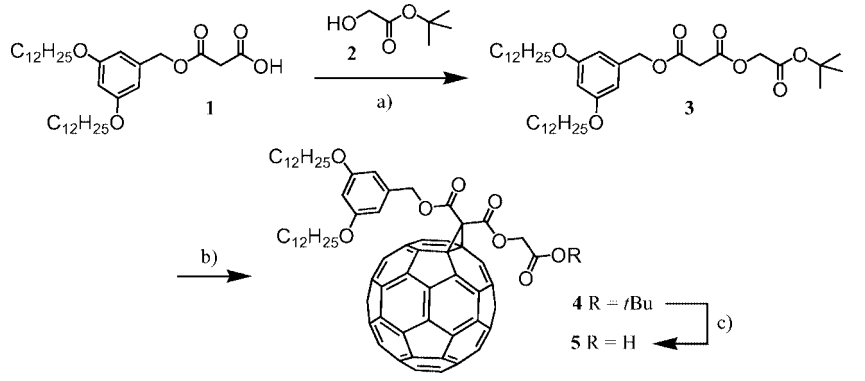
Results and Discussion

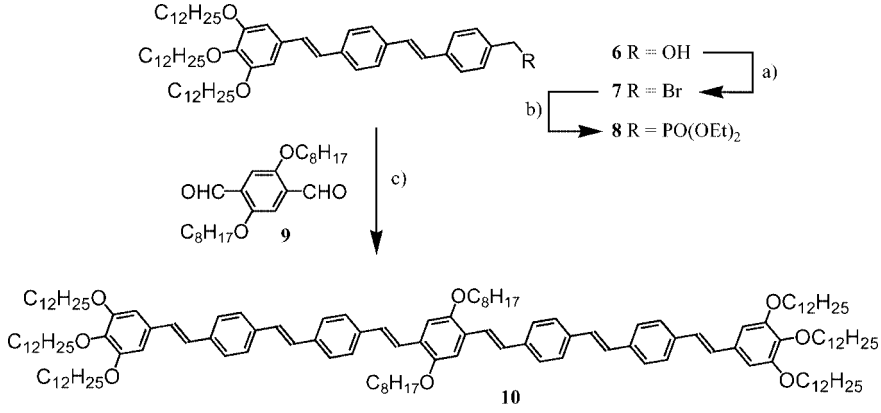
The synthesis of the C_{60}-OPV conjugate is based on the esterification reaction of a fullerene carboxylic acid building block with OPV heptamers bearing one or two hydroxy groups. To this end, we have first prepared methanofullerene derivative **5** (Scheme 1).

N,*N*′-Dicyclohexylcarbodiimide (DCC)-mediated esterification of *tert*-butyl 2-hydroxyacetate (**2**) with carboxylic acid **1**[8] yielded malonate **3**. The functionalization of C_{60} is based on the Bingel reaction.[9] Nucleophilic addition of a stabilized α-halocarbanion to the C_{60} core, followed by intramolecular nucleophilic substitution, leads to clean cyclopropanation of C_{60}. The α-halomalonate derivative is prepared in situ from the reaction of the malonate with iodine.[10] Treatment of C_{60} with **3**, iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded methanofullerene **4** in 52% yield. Subsequent hydrolysis of the *tert*-butyl ester group with CF_3CO_2H gave carboxylic acid **5** in 79% yield.

The synthetic approach to prepare the OPV heptamers relies upon reaction of terephthaldicarbaldehyde (benzene-1,4-dicarbaldehyde) derivatives and phosphonate **8** (Scheme 2). Actually, the Wadsworth–Emmons reaction has proven to be a powerful tool for the synthesis of OPV derivatives as the *trans* olefins are selectively produced from benzylic phosphonates.[11] The preparation of phosphonate **8** is depicted in Scheme 2. Compound **6** was obtained in nine steps from methyl 3,4,5-trihydroxybenzoate as previously



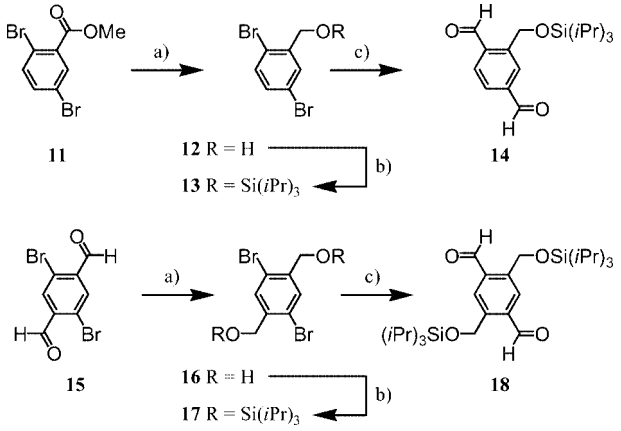
Scheme 1. Reagents and conditions: a) DCC, DMAP, CH_2Cl_2, 0 °C to room temp., 24 h (80%); b) C_{60}, DBU, I_2, PhMe, room temp., 3 h (52%); c) CF_3CO_2H, CH_2Cl_2, room temp., 4 h (79%).



Scheme 2. Reagents and conditions: a) TMSBr, $CHCl_3$, 0 °C, 3 h; b) $P(OEt)_3$, 150 °C, 12 h (88% from **6**); c) *t*BuOK, THF, 0 °C to room temp., 3 h (65%).

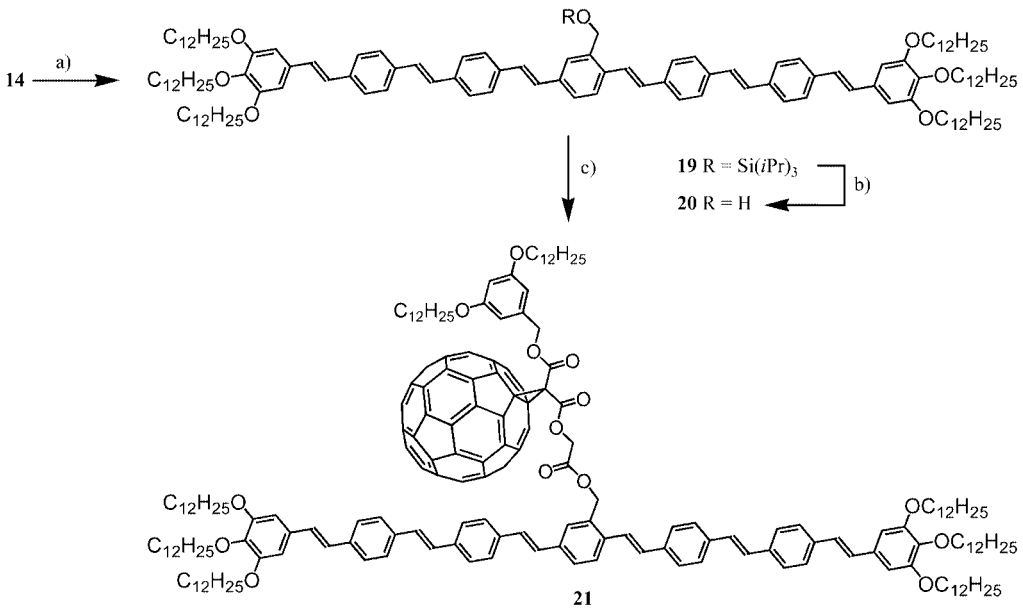
reported.[12] Treatment of **6** with trimethylsilyl bromide (TMSBr) in $CHCl_3$ yielded bromide **7**. It is worth noting that the choice of the appropriate conditions for the preparation of bromide **7** was the key to this synthesis. Actually, this intermediate was found to be unstable. Under bromination conditions using TMSBr, the volatile by-products can be eliminated by simple evaporation and no purification step was required. Therefore, the product could be used in the next step as received. Treatment of bromide **7** with $P(OEt)_3$ under Arbuzov conditions then gave phosphonate **8** in 88% yield. Reaction of **8** with dialdehyde **9**[13] in the presence of *t*BuOK in THF afforded the OPV model compound **10** in 65% yield. All the spectroscopic studies and elemental analysis results were consistent with the structure of **10**. In particular, coupling constants of ca. 16 Hz for the AB systems corresponding to the signals of the vinylic protons in the ^1H NMR spectrum confirmed the *E* stereochemistry of all the double bonds in **10**.

The preparation of the OPV heptamer substituted with one methanofullerene subunit is depicted in Schemes 3 and 4. Reduction of ester **11** with lithium aluminum hydride ($LiAlH_4$) in THF gave **12** in 91% yield. Subsequent treatment of **12** with triisopropylsilyl chloride (TIPSCl) in the presence of imidazole afforded protected derivative **13**. Reaction of **13** with an excess of *t*BuLi followed by treatment of the resulting organolithium derivative with *N*,*N*-dimethylformamide (DMF) gave **14** in 73% yield. The protected OPV heptamer **19** was then obtained from dialdehyde **14** and

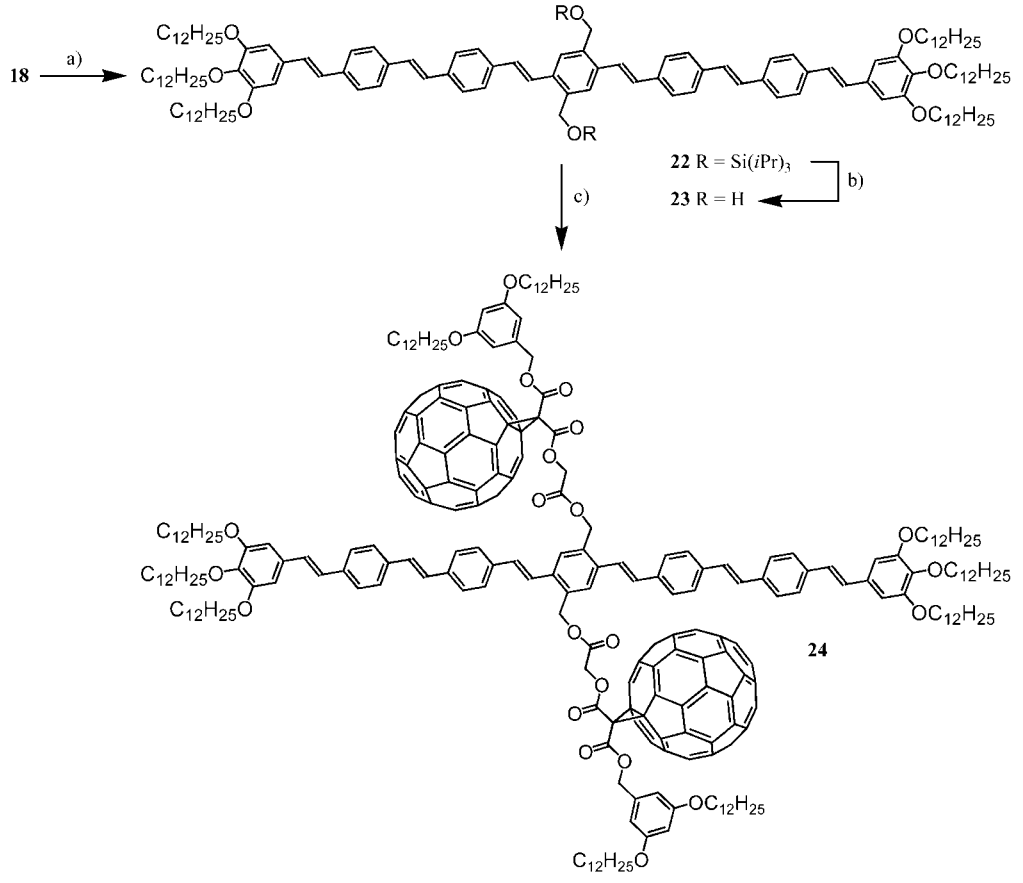


Scheme 3. Reagents and conditions: a) $LiAlH_4$, THF, 0 °C (**12**: 91%; **16**: 91%); b) TIPSCl, imidazole, DMF, 0 °C, 24 h (**13**: 90%; **17**: 87%); c) *t*BuLi, THF, –78 °C, 3 h then DMF, –78 to 0 °C, 3 h (**14**: 73%; **18**: 84%).

phosphonate **8** under Wadsworth–Emmons conditions (Scheme 4). Treatment of **19** with tetra-*n*-butylammonium fluoride (TBAF) in THF at 0 °C afforded alcohol **20**. Finally, the C_{60}–OPV conjugate **21** was prepared from **20** and carboxylic acid **5** under esterification conditions using DCC and 4-(dimethylamino)pyridine (DMAP).



Scheme 4. Reagents and conditions: a) **8**, *t*BuOK, THF, 0 °C to room temp., 3 h (40%); b) TBAF, THF, 0 °C, 2 h (93%); c) **5**, DCC, DMAP, CH_2Cl_2, 0 °C to room temp., 12 h (73%).



Scheme 5. Reagents and conditions: a) **8**, *t*BuOK, THF, 0 °C to room temp., 3 h (46%); b) TBAF, THF, 0 °C, 2 h (47%); c) **5**, DCC, DMAP, CH_2Cl_2, 0 °C to room temp., 12 h (71%).

Reduction of dialdehyde **15** with $LiAlH_4$ followed by treatment of the resulting **16** with TIPSCl in the presence of imidazole afforded protected derivative **17** (Scheme 3). Reaction of **17** with an excess of *t*BuLi in THF followed by quenching with DMF gave **18** in 84% yield. The protected OPV heptamer **22** was then prepared under Wadsworth–Emmons conditions from dialdehyde **18** and phosphonate **8** (Scheme 5). Diol **23** was finally obtained in 47% yield by treatment with TBAF in THF at 0 °C. The moderate yields for the two last steps are mainly associated with difficulties encountered during the purification of the OPV heptamer derivatives **22** and **23**. Reaction of diol **23** with carboxylic acid **5** under esterification conditions using DCC and DMAP afforded compound **24** in 71% yield.

The structure and purity of compounds **21** and **24** were confirmed by ^1H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. As a typical example, the ^1H NMR spectrum of **24** is depicted in Figure 1. Unambiguous assignment was achieved on the basis of 2D-COSY and NOESY spectra recorded at room temperature in $CDCl_3$. The spectrum shows the characteristic signals of the centrosymmetric OPV core. In particular, two sets of AB quartets (δ = 7.00 and 7.23 ppm) and a singlet (δ = 7.08 ppm) are seen for the vinylic protons, a singlet at δ = 6.72 ppm for the aromatic protons of the terminal trialkyloxyphenyl units (H_a), and a singlet at δ = 7.69 ppm for the aromatic protons of the central phenyl ring (H_l). The ^1H NMR spectrum reveals also two singlets at δ = 5.44 and 5.02 ppm corresponding to the resonances of the two different benzylic CH_2 groups (H_A and H_C), an A_2X system for the aromatic protons of the 3,5-didodecyloxyphenyl moiety (H_D and H_E) as well as the diagnostic signals of the alkyloxy groups.

The electrochemical properties of hybrid compounds **21** and **24** were investigated by cyclic voltammetry (CV). For the sake of comparison, electrochemical measurements were also carried out with model compounds **4**, **19** and **22**. All the experiments were performed at room temperature in CH_2Cl_2 solutions containing tetra-*n*-butylammonium tetrafluoroborate (0.1 M) as supporting electrolyte, with a Pt wire as the working electrode and a saturated calomel electrode (SCE) as a reference. Potential data for all of the compounds are collected in Table 1.

In the anodic region, model compound **4** presents an irreversible peak at ca. +1.7 V vs. SCE which can be likely attributed to the oxidation of the dialkyloxyphenyl unit.[14] In the cathodic region, compound **4** revealed the typical electrochemical response of methanofullerene derivatives

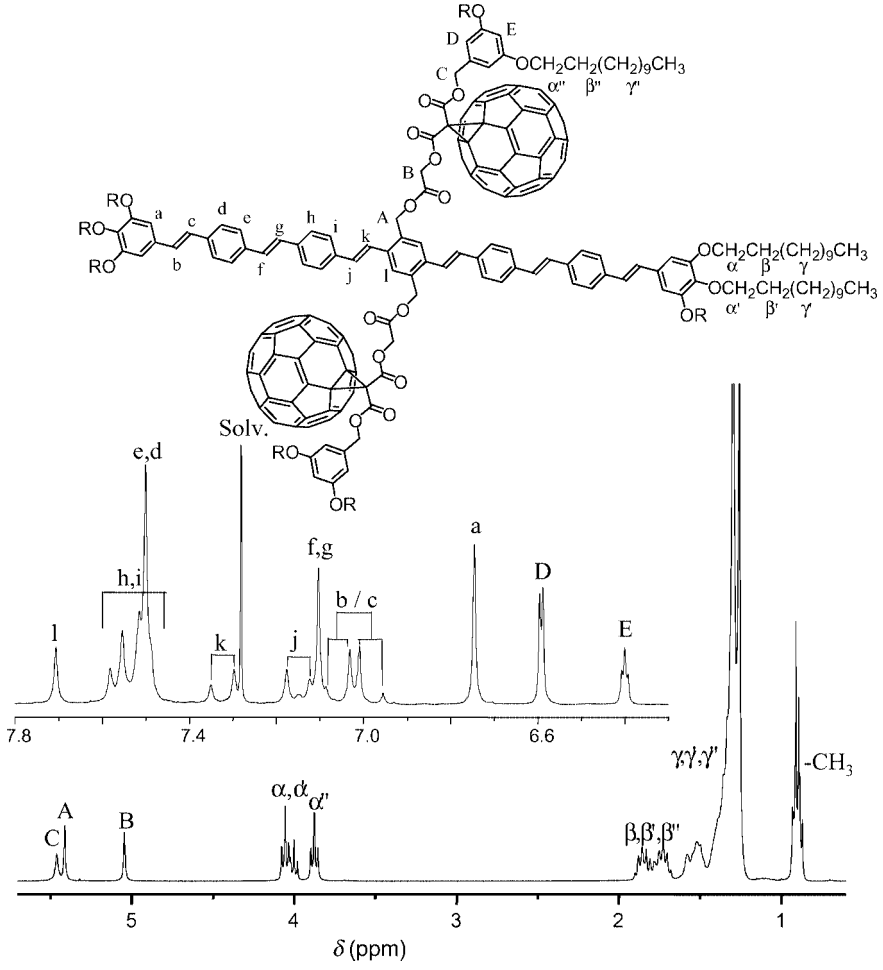


Figure 1. ^1H NMR spectrum ($CDCl_3$, 300 MHz) of compound **24**.

Table 1. Electrochemical data of **4**, **19**, **21**, **22** and **24** determined by CV on a Pt working electrode in CH_2Cl_2 + 0.1 M nBu_4NBF_4 at room temperature.

	Oxidation E_1	Reduction E_1	E_2	E_3
4	1.66[b]	–0.51 (75)[a]	–0.89[b]	–1.12[b]
19	0.96[b]	–1.74[b]		
21	0.96[b]	–0.50 (80)[a]	–0.88[b]	–1.10[b]
22	1.03[b]	–1.72[b]		
24	1.14[b]	–0.51 (80)[a,c]	–0.88[b]	–1.11[b]

[a] Values for $(E_{pa} + E_{pc})/2$ in V vs. SCE and ΔE_{pc} in mV (in parentheses) at a scan rate of 100 mVs^{-1}. [b] Peak potential value at a scan rate of 100 mVs^{-1}, irreversible process. [c] Bielectronic process.

and several reduction steps are seen. Whereas the first one is reversible, the second is irreversible at low scan rates but becomes partially reversible upon increasing the scan rate in accordance with already reported observations on other C_{60} derivatives.[15] The third wave gradually disappears when the second one becomes reversible, so that it probably implies reduction of the product formed after the second reduction. OPV heptamers **19** and **22** exhibit an irreversible one-electron transfer process both in the cathodic and in the anodic region. The cyclic voltammograms recorded for hybrid compounds **21** and **24** shows the characteristic electrochemical features of both constitutive units, i.e. methanofullerene and OPV. The comparison of the $E_{1/2}$ potentials of **21** and **24** with the corresponding model compounds clearly shows that, for both hybrid compounds, the three first reduction waves correspond to fullerene-centered processes, while the oxidation process is centered on the OPV unit. Comparison of the redox potentials of **21** with those of the corresponding model compounds **4** and **19** reveals no particular electronic interactions between the fullerene unit and the OPV moiety. In the case of **24**, the oxidation potential of the OPV core is shifted to more positive values. This shift could be a consequence of small electronic interactions between the OPV core and the C_{60} units, resulting in a more difficult oxidation for the OPV moiety. However, the different subunits are separated by rather long spacers and such effect is not observed for hybrid compound **21**. Therefore, it appears more reasonable to ascribe the observed potential shift to solvation effects resulting from the presence of the surrounding apolar fullerene groups.

Conclusions

In conclusion, we have developed novel OPV heptamers substituted with one or two alcohol groups allowing their further functionalization with fullerene subunits. The electrochemical properties of the resulting hybrid compounds have been investigated. Whereas the fist reduction of both C_{60}–OPV conjugates is centered on the C_{60} unit, the oxidation is centered on the OPV rod. Preliminary luminescence measurements reveal no emission from the OPV core in **21** or **24** indicating a strong quenching of the OPV fluorescence by the fullerene moiety in both **21** and **24** suggesting the occurrence of intramolecular photo-induced processes. Detailed photophysical studies are currently under investigation and special emphasis is placed on the detection of long-lived charge-separated states.

Experimental Section

General: Reagents and solvents were purchased as reagent grade and used without further purification. Compounds **1**,[8] **6**,[12] and **9**[13] were prepared according to the literature. THF was distilled from sodium benzophenone ketyl. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done 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. IR spectra [cm^{-1}] were measured on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AC 300 with solvent peaks as reference. MALDI-TOF-mass spectra (*m*/*z*; % relative intensity) were carried out on a Bruker BIFLEX™ matrix-assisted laser desorption time-of-flight mass spectrometer equipped with SCOUT™ High Resolution Optics, an X-Y multi-sample probe and a gridless reflector. Ionization is accomplished with the 337 nm beam from a nitrogen laser with a repetition rate of 3 Hz. All data were acquired at a maximum accelerating potential of 20 kV in the linear positive ion mode. The output signal from the detector was digitized at a sampling rate of 1 GHz. A saturated solution of 1,8,9-trihydroxyanthracene (dithranol Aldrich EC: 214–538–0) in CH_2Cl_2 was used as a matrix. Typically, a 1:1 mixture of the sample solution in CH_2Cl_2 was mixed with the matrix solution and 0.5 μL of the resulting mixture was deposited on the probe tip. Elemental analyses were performed by the analytical service at the Institut Charles Sadron, Strasbourg.

Compound 3: DCC (8.20 g, 0.04 mol) and DMAP (0.49 g, 4.00 mmol) were added to a solution of **1** (6.00 g, 0.01 mol) and **2** (1.28 g, 0.01 mol) in CH_2Cl_2 (300 mL) at 0 °C. After 1 h, the mixture was allowed to slowly warm to room temperature. After 24 h the mixture was filtered and the solvents evaporated. Column chromatography (SiO_2, CH_2Cl_2/cyclohexane, 1:1) gave **3** (5.42 g, 80%). Colourless glassy product. IR (neat): $\tilde{\nu}$ = 1747 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.47 (d, J = 2 Hz, 2 H), 6.40 (t, J = 2 Hz, 1 H), 5.10 (s, 2 H), 4.55 (s, 2 H), 3.92 (t, J = 6 Hz, 4 H), 3.54 (s, 2 H), 1.76 (m, 4 H), 1.49 (s, 9 H), 1.26 (m, 36 H), 0.88 (t, J = 6 Hz, 6 H) ppm. $C_{40}H_{68}O_8$ (676.98): calcd. C 70.97, H 10.12; found C 70.99, H 10.38.

Compound 4: DBU (0.26 mL, 1.74 mmol) was added to a stirred solution of C_{60} (500 mg, 0.69 mmol), I_2 (194 mg, 0.76 mmol) and **3** (331 mg, 0.69 mmol) in toluene (500 mL) at room temperature. The solution was stirred for 12 h, filtered through a short plug of SiO_2 (CH_2Cl_2) and the solvents evaporated. Column chromatography (SiO_2, CH_2Cl_2/Hexane, 1:9) yielded **4** (503 mg, 52%). Dark red glassy product. IR (neat): $\tilde{\nu}$ = 1747 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.61 (d, J = 2 Hz, 2 H), 6.39 (t, J = 2 Hz, 1 H), 5.47 (s, 2 H), 4.84 (s, 2 H), 3.89 (t, J = 6 Hz, 4 H), 1.73 (m, 4 H), 1.56 (s, 9 H), 1.28 (m, 36 H), 0.88 (t, J = 6 Hz, 6 H) ppm. $C_{100}H_{66}O_8$ (1395.62): calcd. C 86.06, H 4.77; found C 85.90, H 4.98.

Compound 5: A solution of **4** (667 mg, 0.48 mmol) and trifluoroacetic acid (25 mL) in CH_2Cl_2 (100 mL) was stirred at room temperature for 12 h. The mixture was then washed with water, dried

($MgSO_4$), filtered and the solvents evaporated. Recrystallization from CH_2Cl_2/hexane yielded **5** (510 mg, 79%). Dark red solid. IR (neat): $\tilde{\nu}$ = 1747 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.59 (d, J = 2 Hz, 2 H), 6.39 (t, J = 2 Hz, 1 H), 5.45 (s, 2 H), 5.00 (s, 2 H), 3.89 (t, J = 6 Hz, 4 H), 1.73 (m, 4 H), 1.28 (m, 36 H), 0.88 (t, J = 6 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 163.0, 162.9, 160.5, 145.3, 145.2, 145.1, 145.0, 144.9, 144.7, 144.5, 144.4, 143.9, 143.8, 143.1, 143.0, 142.95, 142.9, 142.2, 142.1, 141.9, 141.8, 140.9, 140.8, 139.7, 138.6, 136.5, 107.4, 101.7, 71.1, 69.2, 68.2, 62.0, 51.2, 31.9, 31.4, 31.0, 30.2, 29.7, 29.6, 29.5, 29.4, 29.3, 26.1, 25.7, 22.7, 14.1 ppm. $C_{96}H_{58}O_8$ (1339.51): calcd. C 86.08, H 4.36; found C 86.20, H 4.74.

Compound 8: TMSBr (0.1 mL, 0.69 mmol) was added to a stirred solution of **6** (500 mg, 0.58 mmol) in $CHCl_3$ (3 mL) at 0 °C. After 1 h, the mixture was warmed to room temperature (within 1 h), then stirred for 3 h, filtered and evaporated to give compound **7** as a yellow solid that was used as received in the next step. A solution of **7** in $P(OEt)_3$ (1 mL) was stirred at 150 °C for 12 h. After cooling, the resulting mixture was evaporated. Column chromatography (SiO_2, CH_2Cl_2/MeOH, 49:1) yielded **8** (502 mg, 88%). Yellow glassy product. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.49 (s, 4 H), 7.46 (d, J = 3 Hz, 2 H), 7.31 (dd, J = 2, J = 6.5 Hz, 2 H), 7.10 (s, 2 H), 7.10 (d, J = 16,5 Hz, 1 H), 6.99 (d, J = 16.5 Hz, 1 H), 6.72 (s, 2 H), 4.03 (t, J = 6.5 Hz, 6 H), 3.99 (t, J = 6.5 Hz, 4 H), 3.17 (d, J = 22 Hz, 2 H), 1.80 (m, 6 H), 1.32 (m, 60 H), 0.88 (t, J = 6 Hz, 9 H) ppm. $^{13}C\{^1H\}\{^{31}P\}$ NMR ($CDCl_3$, 75 MHz): δ = 153.3, 132.5, 131.0, 130.1, 128.8, 128.2, 128.0, 127.2, 126.8, 126.7, 126.6, 105.3, 73.5, 69.2, 62.2, 31.9, 30.4, 29.8, 29.75, 29.7, 29.65, 29.6, 29.5, 29.4, 29.35, 26.1, 22.7, 16.4, 14.1 ppm. $^{31}P\{^1H\}\{^{13}C\}$ NMR ($CDCl_3$, 162 MHz): δ = 27.4 ppm. $C_{63}H_{101}O_6P$ (985.47): calcd. C 76.79, H 10.33; found C 76.69, H 10.38.

Compound 10: *t*BuOK (73 mg, 0.65 mmol) was added to a stirred solution of **8** (600 mg, 0.56 mmol) and **9** (100 mg, 0.26 mmol) in THF (10 mL) at 0 °C. After 1 h, the mixture was allowed to slowly warm to room temperature (within 1 h), then stirred for 2 h, filtered and the solvents evaporated. Column chromatography (SiO_2, hexane/CH_2Cl_2, 3:1) followed by gel permeation chromatography (Biorad, Biobeads SX1, CH_2Cl_2) yielded **10** (350 mg, 65%). Orange glassy product. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.53 (s, 8 H), 7.50 (s, 8 H), 7.46 (d, J = 16 Hz, 2 H), 7.18 (d, J = 16 Hz, 2 H), 7.14 (AB, J = 16 Hz, 4 H), 7.05 (AB, J = 16 Hz, 4 H), 6.73 (s, 4 H), 4.03 (m, 12 H), 3.98 (t, J = 6.5 Hz, 4 H), 1.83 (m, 16 H), 1.27 (m, 128 H), 0.89 (t, J = 6 Hz, 24 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.3, 151.2, 138.4, 137.4, 136.8, 136.6, 136.5, 132.5, 128.8, 128.4, 128.2, 128.0, 127.3, 127.0, 126.9, 126.8, 126.7, 123.4, 110.6, 105.3, 73.5, 69.6, 69.2, 31.9, 31.8, 30.3, 29.8, 29.75, 29.7, 29.6, 29.5, 29.45, 29.4, 29.35, 29.3, 26.3, 26.1, 22.7, 14.1 ppm. $C_{142}H_{218}O_8$ (2053.29): calcd. C 83.06, H 10.66; found C 83.28, H 10.52.

Compound 12: A 1 M $LiAlH_4$ solution in THF (33 mL) was added to a stirred solution of **11** (8.04 g, 27.0 mmol) in dry THF (400 mL) at 0 °C under argon. After 2 h, MeOH was added, then water. The resulting mixture was filtered through celite and the solvents evaporated. Column chromatography (SiO_2, CH_2Cl_2/hexane, 1:1) yielded **12** (6.50 g, 91%). Colourless solid. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.66 (d, J = 2 Hz, 1 H), 7.40 (d, J = 8 Hz, 1 H), 7.29 (dd, J = 8 and 2 Hz, 1 H), 4.72 (d, J = 6 Hz, 2 H), 2.00 (t, J = 6 Hz, 1 H) ppm. $C_7H_6Br_2O$ (265.93): calcd. C 31.62, H 2.27; found C 31.70, H 2.28.

Compound 13: A mixture of TIPSCl (5 mL, 22.56 mmol), imidazole (3.10 g, 45.12 mmol) and **12** (5.00 g, 18.80 mmol) in DMF (50 mL) was stirred at room temperature for 12 h and the solvents evaporated. The residue was taken up with Et_2O, washed with brine, dried ($MgSO_4$), filtered and the solvents evaporated. Column chromatography (SiO_2, hexane) yielded **13** (7.14 g, 90%). Colourless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.70 (d, J = 2 Hz, 1 H), 7.34 (d, J = 8 Hz, 1 H), 7.25 (dd, J = 8 and 2 Hz, 1 H), 4.78 (s, 2 H), 1.13 (m, 21 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 142.6, 134.5, 133.3, 132.7, 131.0, 130.5, 121.7, 119.2, 64.4, 17.7, 12.2 ppm. $C_{16}H_{26}Br_2OSi$ (422.28): calcd. C 45.51, H 6.21; found C 44.98, H 5.82.

Compound 14: A 1.7 M *t*BuLi solution in THF (11 mL, 18.7 mmol) was added dropwise within 0.5 h to a solution of **13** (2.0 g, 4.73 mmol) in dry THF (80 mL) at –78 °C under Ar. The resulting mixture was stirred at –78 °C for 2 h, then warmed slowly to 0 °C (1 h) and cooled to –78 °C. DMF (2.2 mL, 28.38 mmol) was added and after 1 h at –78 °C, the mixture was warmed slowly to 0 °C. A 2 M aqueous HCl solution was then added. The THF was evaporated and Et_2O added. The organic layer was washed with a 2 M aqueous HCl solution, then with water, dried ($MgSO_4$) and the solvents evaporated. Column chromatography (SiO_2, hexane/CH_2Cl_2, 2:1) yielded **14** (1.11 g, 73%). Compound **14** was found to be quite unstable and was used as received in the next step. Colourless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 10.23 (s, 1 H), 10.14 (s, 1 H), 8.36 (br. s, 1 H), 7.98 (m, 2 H), 5.27 (s, 2 H), 1.19 (m, 21 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 192.7, 191.8, 145.5, 139.4, 136.2, 133.5, 128.4, 128.2, 127.3, 62.9, 18.04, 12.2 ppm.

Compound 16: A 2 M $LiAlH_4$ solution in THF (10 mL) was added to a stirred solution of **15** (1.00 g, 3.40 mmol) in dry THF (50 mL) at 0 °C under argon. After 2 h, MeOH was added, then water. The resulting mixture was filtered through celite and evaporated to yield **16** (0.92 g, 91%). Colourless solid. ^1H NMR (CD_3OD, 300 MHz): δ = 7.70 (s, 2 H), 4.63 (s, 4 H) ppm. $C_8H_8Br_2O_2$ (295.96): calcd. C 32.47, H 2.72; found C 32.56, H 2.71.

Compound 17: A mixture of TIPSCl (2.4 mL, 11.40 mmol), imidazole (1.55 g, 22.80 mmol) and **16** (1.40 g, 4.73 mmol) in DMF (20 mL) was stirred at room temperature for 12 h and the solvents evaporated. The residue was taken up with Et_2O, washed with brine, dried ($MgSO_4$), filtered and the solvents evaporated. Column chromatography (SiO_2, hexane) yielded **17** (2.50 g, 87%). Colourless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.73 (s, 2 H), 4.77 (s, 4 H), 1.12 (s, 36 H), 1.09 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 140.4, 130.7, 119.6, 64.3, 18.0, 12.0 ppm. $C_{26}H_{48}Br_2O_2Si_2$ (608.64): calcd. C 51.31, H 7.95; found C 51.47, H 8.08.

Compound 18: A 1.7 M *t*BuLi solution in THF (12 mL, 20.4 mmol) was added dropwise within 0.5 h to a solution of **17** (3.0 g, 4.90 mmol) in dry THF (80 mL) at –78 °C under Ar. The resulting mixture was stirred at –78 °C for 2 h, then warmed slowly to 0 °C (1 h) and cooled to –78 °C. DMF (2.2 mL, 28.38 mmol) was added and after 1 h at –78 °C, the mixture was warmed slowly to 0 °C. A 2 M aqueous HCl solution was then added. The THF was evaporated and Et_2O added. The organic layer was washed with a 2 M aqueous HCl solution, then with water, dried ($MgSO_4$) and the solvents evaporated. Column chromatography (SiO_2, hexane/CH_2Cl_2, 7:3) yielded **18** (2.10 g, 84%). Colourless solid. ^1H NMR ($CDCl_3$, 300 MHz): δ = 10.26 (s, 2 H), 8.35 (s, 2 H), 5.28 (s, 4 H), 1.13 (s, 36 H), 1.11 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 193.3, 143.0, 135.2, 131.9, 62.7, 18.0, 12.0 ppm. $C_{28}H_{50}O_4Si_2$ (506.87): calcd. C 66.35, H 9.94; found C 66.41, H 10.09.

Compound 19: *t*BuOK (170 mg, 1.55 mmol) was added to a stirred solution of **8** (1.40 g, 1.37 mmol) and **14** (200 mg, 0.62 mmol) in THF (10 mL) at 0 °C. After 1 h, the mixture was allowed to slowly warm to room temperature (within 1 h), then stirred for 2 h, filtered and the solvents evaporated. Column chromatography (SiO_2, hex-

ane/CH_2Cl_2, 1:1) followed by gel permeation chromatography (Biorad, Biobeads SX1, CH_2Cl_2) yielded **19** (480 mg, 40%). Orange glassy product. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.70 (br. s, 1 H), 7.65 (d, J = 8 Hz, 1 H), 7.52 (br. s, 8 H), 7.51 (br. s, 8 H), 7.43 (s, 1 H), 7.40 (d, J = 16 Hz, 2 H), 7.15–7.07 (m, 6 H), 7.05 (d, J = 16 Hz, 2 H), 6.97 (d, J = 16 Hz, 2 H), 6.72 (s, 4 H), 4.99 (s, 2 H), 4.03 (t, J = 6 Hz, 8 H), 3.98 (t, J = 6 Hz, 4 H), 1.81 (m, 12 H), 1.27 (m, 108 H), 1.14 (m, 21 H), 0.89 (t, J = 6 Hz, 18 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.3, 138.9, 138.4, 137.0, 136.9, 136.8, 136.7, 136.6, 136.5, 134.6, 132.5, 129.7, 128.8, 128.6, 128.5, 128.2, 128.2, 128.15, 128.1, 128.0, 127.2, 126.9, 126.8, 126.7, 125.6, 125.4, 125.3, 125.0, 105.2, 73.5, 69.2, 63.6, 63.5, 31.9, 30.4, 29.8, 29.75, 29.7, 29.6, 29.45, 29.4, 29.3, 26.1, 22.7, 18.1 ppm. $C_{136}H_{208}O_7Si$ (1983.23): calcd. C 82.37, H 10.57; found C 82.45, H 10.61.

Compound 20: A 1 M TBAF solution in THF (0.5 mL) was added to a stirred solution of **19** (300 mg, 0.15 mmol) in dry THF (6 mL) at 0 °C under argon. After 2 h, H_2O (10 mL) was added. The THF was evaporated and CH_2Cl_2 added. The organic layer was washed with water, dried ($MgSO_4$) and the solvents evaporated. Column chromatography (SiO_2, CH_2Cl_2/hexane, 1:1) followed by gel permeation chromatography (Biorad, Biobeads SX1, CH_2Cl_2) yielded **20** (250 mg, 93%). Orange glassy product. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.70 (s, 1 H), 7.65 (d, J = 8 Hz, 1 H), 7.52 (br. s, 8 H), 7.51 (br. s, 8 H), 7.43 (s, 1 H), 7.40 (d, J = 16 Hz, 2 H), 7.15–7.07 (m, 6 H), 7.05 (d, J = 16 Hz, 2 H), 6.97 (d, J = 16 Hz, 2 H), 6.73 (br. s, 4 H), 4.89 (s, 2 H), 4.03 (t, J = 6 Hz, 8 H), 3.98 (t, J = 6 Hz, 4 H), 1.81 (m, 12 H), 1.27 (m, 108 H), 0.89 (t, J = 6 Hz, 18 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.3, 138.4, 138.1, 137.0, 136.9, 136.7, 136.6, 136.5, 135.4, 132.5, 130.4, 128.9, 128.4, 128.3, 128.3, 128.2, 128.0, 127.95, 127.9, 127.2, 127.1, 127.0, 126.9, 126.8, 126.7, 126.5, 126.3, 126.1, 124.6, 116.1, 105.3, 73.6, 69.2, 63.7, 31.9, 30.3, 29.8, 29.75, 29.7, 29.6, 29.45, 29.4, 29.3, 26.1, 22.7, 14.13 ppm. $C_{127}H_{188}O_7$ (1826.89): calcd. C 83.50, H 10.37; found C 82.95, H 10.37.

Compound 21: DCC (54 mg, 0.26 mmol) and DMAP (5 mg, 0.04 mmol) were added to a solution of **20** (161 mg, 0.12 mmol) and **5** (200 mg, 0.11 mmol) in CH_2Cl_2 (15 mL) at 0 °C. After 1 h, the mixture was allowed to slowly warm to room temperature. After 24 h the mixture was filtered and the solvents evaporated. Column chromatography (SiO_2, CH_2Cl_2/cyclohexane, 1:1) followed by gel permeation chromatography (Biorad, Biobeads SX1, CH_2Cl_2) gave **21** (250 mg, 73%). Dark brown glassy product. IR (neat): $\tilde{\nu}$ = 1747 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.69 (d, J = 7 Hz, 1 H), 7.48 (m, 18 H), 7.32 (d, J = 16 Hz, 2 H), 7.15 (m, 6 H), 7.04 (d, J = 16 Hz, 2 H), 6.94 (d, J = 16 Hz, 2 H), 6.73 (br. s, 4 H), 6.57 (d, J = 2 Hz, 2 H), 6.38 (t, J = 2 Hz, 1 H), 5.47 (s, 2 H), 5.38 (s, 2 H), 5.04 (s, 2 H), 4.03 (t, J = 6 Hz, 8 H), 3.98 (t, J = 6 Hz, 4 H), 3.85 (t, J = 6 Hz, 4 H), 1.83 (m, 12 H), 1.70 (m, 4 H), 1.28 (m, 144 H), 0.88 (m, 24 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.4, 163.0, 160.4, 153.3, 145.2, 145.15, 145.1, 145.05, 144.95, 144.9, 144.6, 144.55, 144.5, 144.4, 143.8, 143.7, 143.0, 142.9, 142.8, 142.2, 142.1, 141.8, 141.7, 140.9, 140.8, 139.7, 138.4, 137.2, 136.9, 136.8, 136.6, 136.5, 136.45, 136.4, 136.35, 136.2, 132.5, 132.2, 131.1, 128.9, 128.8, 128.6, 128.4, 128.3, 128.0, 127.6, 127.3, 127.2, 127.1, 127.05, 127.0, 126.95, 126.9, 126.8, 126.7, 123.9, 107.3, 105.2, 101.6, 73.5, 71.1, 69.2, 68.1, 65.7, 62.7, 31.9, 30.3, 29.8, 29.7, 29.6, 29.5, 29.45, 29.4, 26.1, 22.7, 14.1 ppm. MALDI-TOF-MS: 3148.8 (M^+, calcd. for $C_{223}H_{244}O_{14}$: 3148.38). $C_{223}H_{244}O_{14}$ (3148.38): calcd. C 85.07, H 7.81; found C 84.61, H 7.58.

Compound 22: *t*BuOK (220 mg, 2.00 mmol) was added to a stirred solution of **8** (1.72 g, 1.75 mmol) and **18** (410 mg, 0.8 mmol) in THF (20 mL) at 0 °C. After 1 h, the mixture was allowed to slowly warm to room temperature (within 1 h), then stirred for 2 h, filtered and the solvents evaporated. Column chromatography (SiO_2, hexane/CH_2Cl_2, 1:1) followed by gel permeation chromatography (Biorad, Biobeads SX1, CH_2Cl_2) yielded **22** (800 mg, 46%). Orange glassy product. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.82 (s, 2 H), 7.52 (s, 8 H), 7.51 (s, 8 H), 7.40 (d, J = 16 Hz, 2 H), 7.13 (s, 4 H), 7.08 (d, J = 16 Hz, 2 H), 7.05 (d, J = 16 Hz, 2 H), 6.96 (d, J = 16 Hz, 2 H), 6.72 (s, 4 H), 5.00 (s, 4 H), 4.04 (t, J = 6 Hz, 8 H), 3.98 (t, J = 6 Hz, 4 H), 1.80 (m, 12 H), 1.32 (m, 108 H), 1.15 (m, 42 H), 0.89 (t, J = 6 Hz, 18 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.3, 138.4, 137.4, 136.5, 132.5, 128.8, 128.1, 127.3, 126.9, 126.7, 124.2, 105.3, 73.6, 69.2, 63.5, 31.9, 30.4, 29.7, 29.5, 29.4, 26.2, 22.7, 18.2, 17.7, 14.1, 12.2 ppm. $C_{146}H_{230}O_8Si_2 \cdot 0.5\,CH_2Cl_2$ (2212.06): calcd. C 79.55, H 10.53; found C 79.55, H 10.40.

Compound 23: A 1 M TBAF solution in THF (1.1 mL) was added to a stirred solution of **22** (740 mg, 0.34 mmol) in dry THF (15 mL) at 0 °C under argon. After 2 h, H_2O (10 mL) was added. The THF was evaporated and CH_2Cl_2 added. The organic layer was washed with water, dried ($MgSO_4$) and the solvents evaporated. Column chromatography (SiO_2, CH_2Cl_2/hexane, 1:1) followed by gel permeation chromatography (Biorad, Biobeads SX1, CH_2Cl_2) yielded **23** (303 mg, 47%). Orange glassy product. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.73 (s, 2 H), 7.53 (br. s, 8 H), 7.50 (br. s, 8 H), 7.40 (d, J = 16 Hz, 2 H), 7.13 (s, 4 H), 7.12 (d, J = 16 Hz, 2 H), 7.04 (d, J = 16 Hz, 2 H), 6.97 (d, J = 16 Hz, 2 H), 6.72 (s, 4 H), 4.91 (s, 4 H), 4.03 (t, J = 6 Hz, 8 H), 3.98 (t, J = 6 Hz, 4 H), 1.83 (m, 12 H), 1.32 (m, 108 H), 0.88 (t, J = 6 Hz, 18 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.7, 138.9, 137.3, 136.8, 131.0, 129.3, 128.8, 128.4, 127.7, 127.5, 127.2, 127.1, 126.4, 124.8, 105.7, 73.9, 69.6, 63.9, 32.3, 30.7, 30.15, 30.1, 30.0, 29.9, 29.85, 29.8, 29.7, 26.5, 23.1, 14.5 ppm. $C_{128}H_{190}O_8 \cdot 0.5\,CH_2Cl_2$ (1899.38): calcd. C 81.26, H 10.14; found C 81.60, H 10.10.

Compound 24: DCC (26 mg, 0.13 mmol) and DMAP (3 mg, 0.02 mmol) were added to a solution of **23** (98 mg, 0.05 mmol) and **5** (156 mg, 0.12 mmol) in CH_2Cl_2 (10 mL) at 0 °C. After 1 h, the mixture was allowed to slowly warm to room temperature. After 24 h the mixture was filtered and the solvents evaporated. Column chromatography (SiO_2, CH_2Cl_2/cyclohexane, 1:1) followed by gel permeation chromatography (Biorad, Biobeads SX1, CH_2Cl_2) gave **24** (160 mg, 71%). Dark brown glassy product. IR (neat): $\tilde{\nu}$ = 1747 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.69 (s, 2 H), 7.48 (m, 16 H), 7.32 (d, J = 16 Hz, 2 H), 7.15 (d, J = 16 Hz, 2 H), 7.08 (s, 4 H), 7.04 (d, J = 16 Hz, 2 H), 6.94 (d, J = 16 Hz, 2 H), 6.72 (s, 4 H), 6.57 (d, J = 1.5 Hz, 4 H), 6.38 (t, J = 1.5 Hz, 2 H), 5.44 (s, 4 H), 5.39 (s, 4 H), 5.02 (s, 4 H), 4.03 (t, J = 6 Hz, 8 H), 3.98 (t, J = 6 Hz, 4 H), 3.85 (t, J = 6 Hz, 8 H), 1.80 (m, 20 H), 1.32 (m, 180 H), 0.87 (m, 30 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.9, 163.4, 163.3, 160.9, 153.7, 145.6, 145.55, 145.5, 145.4, 145.35, 145.3, 145.0, 144.9, 144.85, 144.2, 143.4, 143.3, 142.5, 141.25, 141.2, 127.8, 127.4, 127.3, 127.1, 107.7, 105.7, 102.0, 73.9, 71.6, 69.6, 69.5, 68.6, 63.1, 51.7, 32.4, 30.8, 30.15, 30.1, 29.9, 29.8, 29.7, 26.6, 23.1, 14.6, 14.5 ppm. MALDI-TOF-MS: 4501 (MH^+, calcd. for $C_{320}H_{303}O_{22}$: 4500.91). $C_{320}H_{302}O_{22}$ (4499.90): calcd. C 85.41, H 6.76; found C 85.68, H 6.73.

Electrochemistry: The cyclic voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100. Experiments were performed at room temperature in a homemade airtight three–electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca 1 cm^2 apparent surface. The

working electrode was a Pt microdisk (0.5 mm diameter). The supporting electrolyte [nBu$_4$N][BF$_4$] (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. Dichloromethane was freshly distilled from CaH_2 prior to use. The solutions used during the electrochemical studies were typically 10^{-3} M in compound and 0.1 M in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar and the working electrode was polished with a polishing machine (Presi P230). Under these experimental conditions, Fc^+/Fc is observed at +0.54 ± 0.01 V vs. SCE.

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