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Synthesis of Dendritic Branches with Peripheral Fullerene Subunits

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Highly soluble dendritic branches with two, four, eight or 16 methanofullerene subunits at their peripheries and carboxylic acid functions at their focal points have been prepared by a convergent approach. Starting from a methanofullerene derivative possessing a *tert*-butyl ester function, the successive dendrimer generations were obtained by repetition of a reaction sequence involving cleavage of the *tert*-butyl ester moiety under acidic conditions, followed by a DCC-mediated esterification reaction with an A_2B building block possessing two benzylic alcohol functions and a *tert*-butyl ester group. This repetitive synthetic sequence is very efficient and allowed the dendritic growth up to the fifth-generation derivative, containing 16 peripheral fullerene subunits.

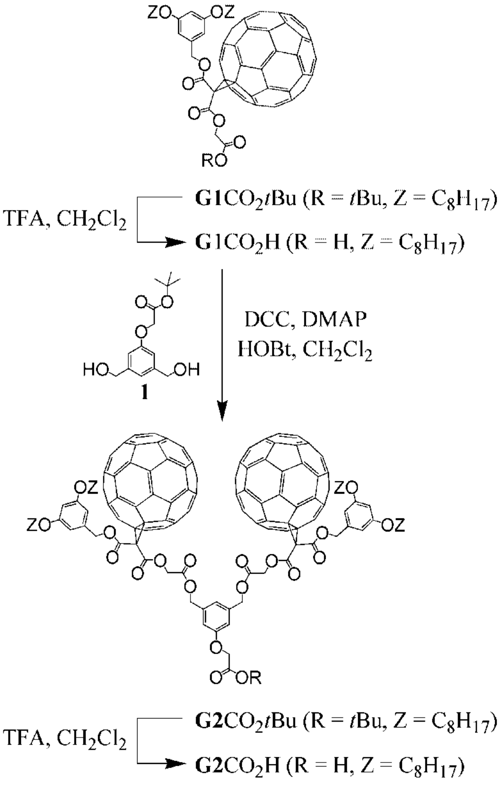
Introduction

Among the large number of functional groups used in dendrimer chemistry,[1] fullerene has proven to be particularly interesting.[2] Whereas dendrimers with fullerene cores have been widely studied,[3] the synthesis of fullerene-rich dendrimers has been considered to a lesser degree, mainly because of the difficulties encountered in their synthesis. The two major problems for the preparation of such dendrimers are the low solubilities of C_{60} derivatives and their chemical reactivity, limiting the range of reactions that can be used for the synthesis of branched structures bearing multiple C_{60} units. Over the past few years we have developed synthetic methodologies allowing the preparation of dendrons substituted with a few fullerene moieties.[4] These fullerodendrons are interesting building blocks for the preparation of monodisperse fullerene-rich macromolecules with intriguing properties[5] and fullerene-containing amphiphilic derivatives capable of forming stable Langmuir films at air/water interfaces.[6] However, the synthesis of high-generation dendritic branches from currently known building blocks remains difficult, either for solubility reasons or because of steric hindrance problems. This prompted us to explore the development of new fullerodendrons further, and in this paper we now report an efficient synthetic route to soluble dendritic branches with peripheral fullerene units and carboxylic acid functions at their focal points. The repetitive synthetic sequence used for their preparation is very efficient and allowed dendritic growth up to the fifth-generation derivative, containing 16 peripheral fullerene subunits.

Results and Discussions

Synthesis

The preparation of the first- and second-generation fullerene derivatives is depicted in Scheme 1. The starting ful-



Scheme 1. Synthesis of **G1**CO_2H and **G2**CO_2H.

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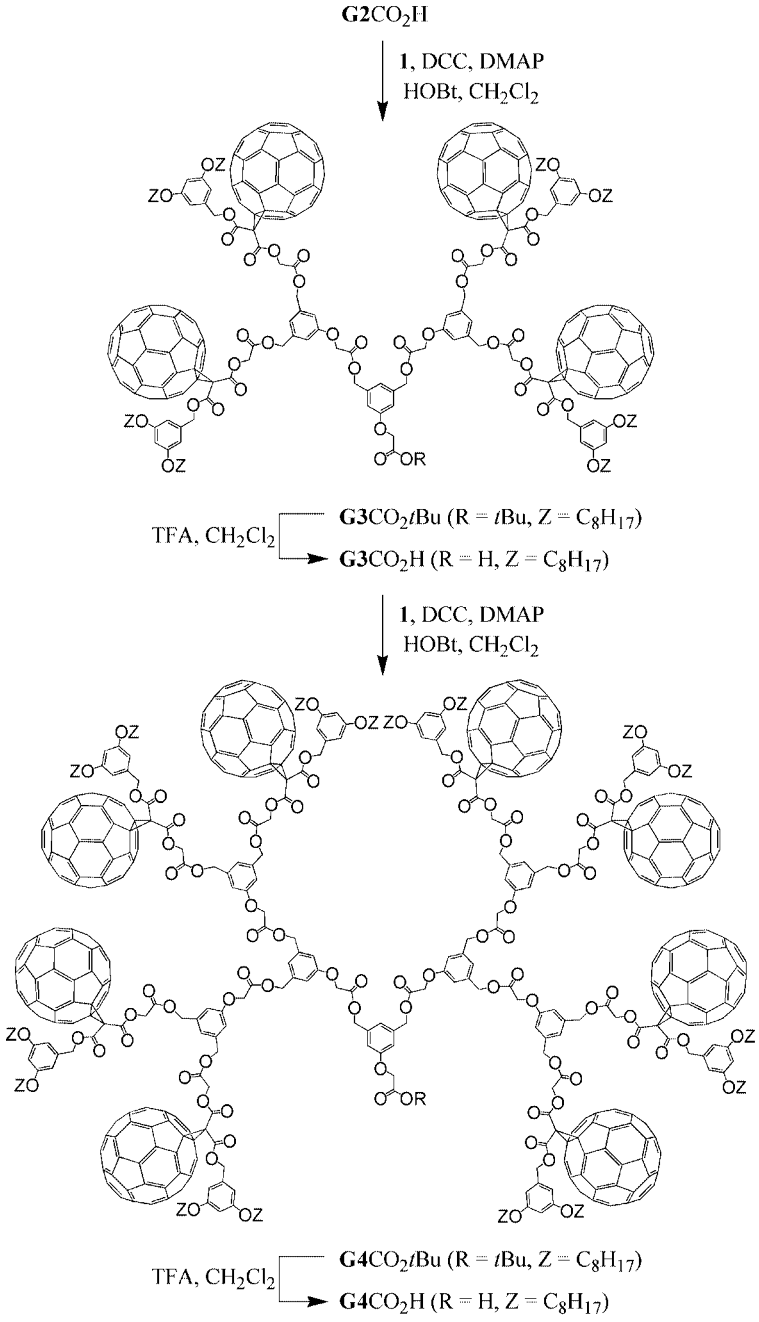
lerene derivative **G1**CO_2tBu was prepared by a previously described procedure.[4c] This compound is actually easily obtained on a multi-gram scale, is highly soluble in common organic solvents, thanks to the presence of the two long alkyl chains, and therefore appears to be a good candidate for the preparation of new fullerene-containing dendrimers. The iterative reaction sequence used for the preparation of the successive dendrimer generations is based on successive cleavage of a *tert*-butyl ester moiety under acidic conditions, followed by a DCC-mediated (DCC = *N*,*N*′-dicyclohexylcarbodiimide) esterification reaction with the A_2B building block **1**. This compound possessing two benzylic alcohol functions and a protected carboxylic acid function was obtained in six steps as already reported.[7]

Selective cleavage of the *tert*-butyl ester group in **G1**CO_2tBu was achieved by treatment with an excess of CF_3COOH (TFA)[8] in CH_2Cl_2 to afford **G1**CO_2H in a quantitative yield. Treatment of diol **1** with carboxylic acid **G1**CO_2H under esterification conditions in the presence of DCC, 4-(dimethylamino)pyridine (DMAP) and 1-hydroxybenzotriazole (HOBt) in CH_2Cl_2 gave the protected second-generation dendron **G2**CO_2tBu in 90% yield. Hydrolysis of



Scheme 2. Synthesis of **G3**CO_2H and **G4**CO_2H.

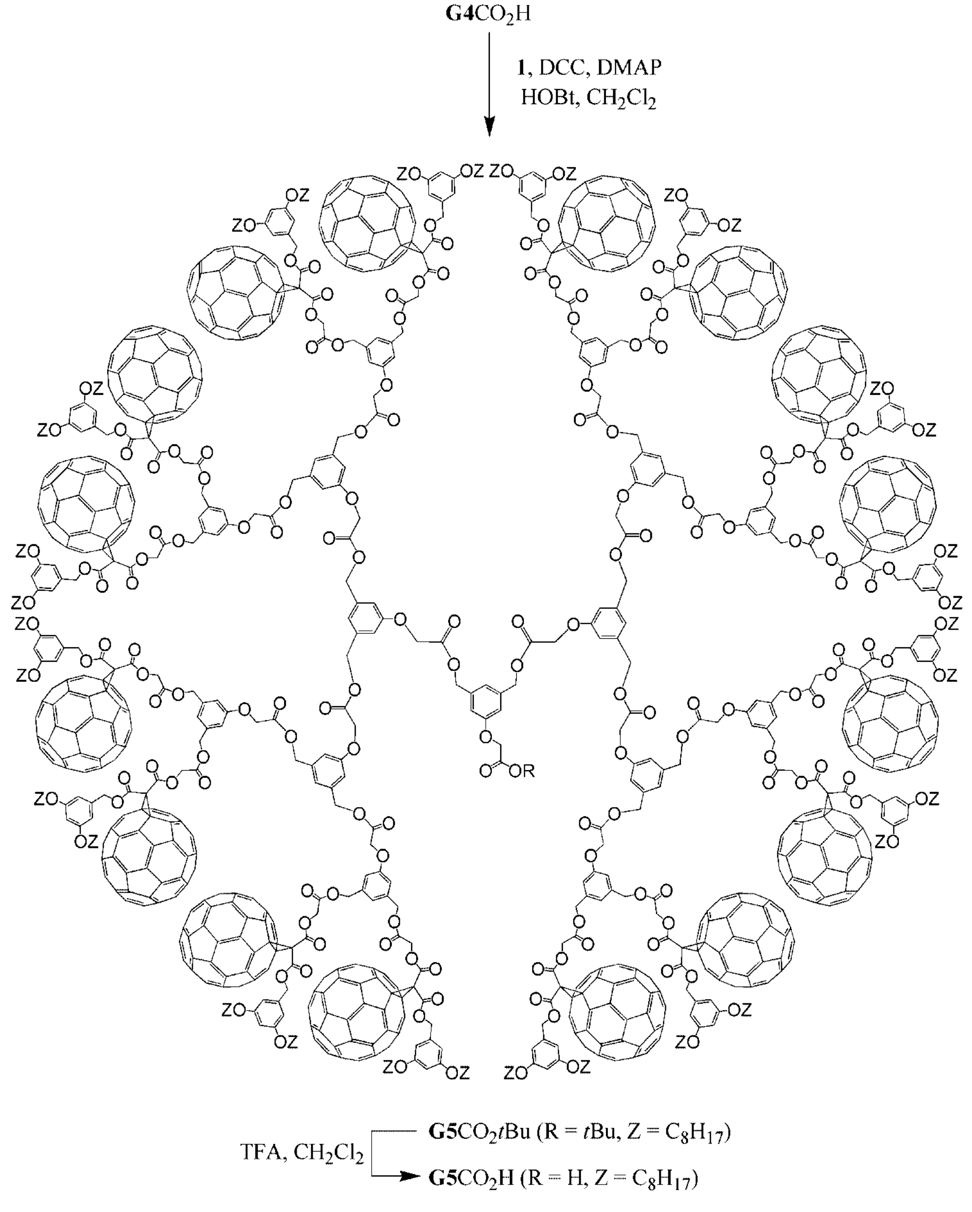
the *tert*-butyl ester moiety under acidic conditions then afforded the corresponding carboxylic acid **G2**CO_2H in quantitative yield.

Esterification of **G2**CO_2H with diol **1** (DCC, HOBt, DMAP) afforded the *tert*-butyl-protected fullerodendron **G3**CO_2*t*Bu in 87% yield (Scheme 2). Selective hydrolysis of the *tert*-butyl ester under acidic conditions afforded acid **G3**CO_2H in 99% yield. Subsequent treatment of **G3**CO_2H with the branching unit **1** in the presence of DCC, HOBt and DMAP afforded fullerodendron **G4**CO_2*t*Bu (95%), which after treatment with CF_3CO_2H gave **G4**CO_2H (97%).

By repetition of the same reaction sequence from **G4**CO_2H, the fifth-generation derivatives **G5**CO_2*t*Bu and **G5**CO_2H were also prepared (Scheme 3). It is important to highlight here that the time needed for complete consumption of all the reactants during the esterification step increased as the generation number increased, but *N*-acyldicyclohexylurea by-products resulting from the rearrangement of the activated acid intermediates[9] were quite limited even for the highest-generation compound, thus allowing the preparation of the fifth-generation protected dendron **G5**CO_2*t*Bu in a good yield (76%) under DCC-mediated esterification conditions. The synthetic methodology described here is therefore efficient for the preparation of fullerene-rich derivatives and does not suffer from the reduced accessibility of the reactive group located at the focal point of the dendritic structure as previously observed for dendrimers synthesized under similar esterification conditions.[10]

Characterization

Compounds **G1**–**G5**CO_2*t*Bu and **G1**–**G5**CO_2H are readily soluble in common organic solvents such as CH_2Cl_2,



Scheme 3. Synthesis of **G5**CO_2H.

$CHCl_3$ or THF, and complete spectroscopic characterization was easily achieved. In addition to the signals arising from the 3,5-dioctyloxybenzyl units, the ^1H NMR spectrum of **G1**CO_2H is characterized by two singlets at $\delta = 5.01$ and 5.45 ppm corresponding to the protons of the two methylene groups (H_a and H_b, see Figure 1 for the numbering). For **G2**CO_2*t*Bu, the ^1H NMR spectrum reveals the signals of the two equivalent **G1**CO_2 units as well as those corresponding to the central *tert*-butyl [3,5-bis(methylene)phenoxy]acetate core. In particular, a triplet and four singlets are seen for the different OCH_2 groups. Similarly, on going from the second to the third generation, the signals corresponding to the additional *tert*-butyl [3,5-bis(methylene)-phenoxy]acetate unit are clearly observable. As shown in Figure 1, the ^1H NMR spectrum of **G3**CO_2*t*Bu reveals six singlets and a triplet for the seven different OCH_2 units. It can be seen that the resonance of the methylenic protons H_d is shifted slightly downfield when the corresponding acetate unit is connected to a benzylic moiety ($\delta = 4.65$ ppm in **G3**CO_2*t*Bu) rather to a *tert*-butyl group ($\delta = 4.51$ ppm in **G2**CO_2*t*Bu). For **G4**CO_2*t*Bu, the eight expected singlets corresponding to the methylene groups $H_{a\text{–}h}$ are still clearly distinguishable in the 4.5–5.5 ppm region. In contrast, for the highest-generation *tert*-butyl ester, the ^1H NMR is slightly broadened and the signals arising from some of the methylenic groups overlap. It is important to emphasize, however, that the integration ratio of the five sets of signals is in perfect agreement with that expected for **G5**CO_2*t*Bu.

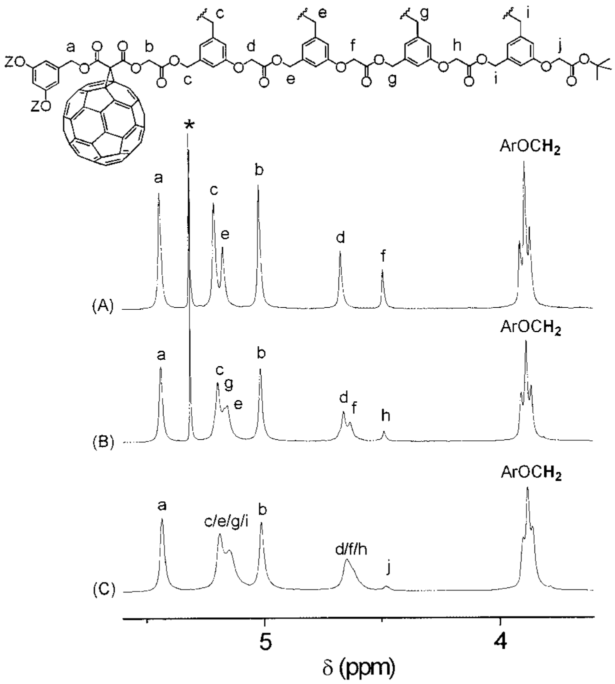


Figure 1. ^1H NMR spectra ($CDCl_3$, 300 MHz) of: A) **G3**CO_2*t*Bu, B) **G4**CO_2*t*Bu, and C) **G5**CO_2*t*Bu (* = CH_2Cl_2 impurity).

Fullerodendrons **G1**–**G5**CO_2*t*Bu and **G1**–**G5**CO_2H were also characterized by ^{13}C NMR spectroscopy. As typical examples, the ^{13}C NMR spectra of compounds **G2**CO_2*t*Bu and **G5**CO_2*t*Bu recorded in $CDCl_3$ are shown in Figure 2 and Figure 3. The spectrum of **G2**CO_2*t*Bu is in full accordance with the proposed molecular structure. As would be expected, four resonances are observed for the carbonyl C atoms ($\delta = 163.1$, 163.2, 166.4, and 167.6 ppm), five for the OCH_2 groups ($\delta = 62.7$, 65.8, 66.9, 68.3, and 69.3 ppm) and two for the *tert*-butyl unit ($\delta = 26.3$ and 82.7 ppm). Only 26 signals out of the 39 expected (31 for the fullerene sp^2 carbon atoms and eight for the aromatic rings) are observed in the typical aromatic and fullerene region. Indeed, the C_{60} unit of C_S-symmetrical methanofullerene derivatives substituted with different ester moieties generally possess a pseudo-C_{2v} symmetry. Actually, the resonances of the fullerene C atoms are usually observed in the ^{13}C NMR spectrum with a pattern almost identical to those of C_{2v}-symmetrical methanofullerene derivatives in which the two ester moieties are equivalent. Finally, the signals observed at $\delta =$ 51.4 and 71.3 ppm correspond to the methano bridge car-

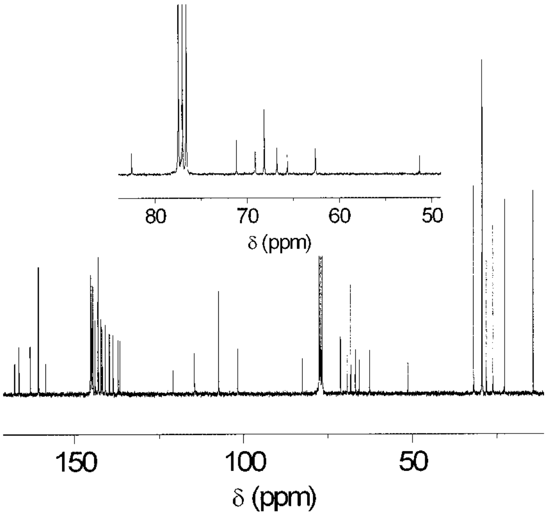


Figure 2. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **G2**CO_2*t*Bu.

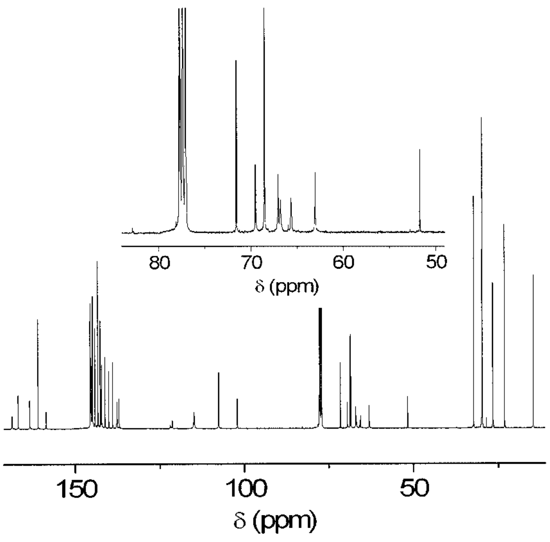


Figure 3. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of **G5**CO_2*t*Bu.

bons and to the fullerene sp^3 carbons, respectively. The ^{13}C NMR spectrum of fullerodendron **G5**CO$_2$*t*Bu shows the same characteristic features as **G2**CO$_2$*t*Bu with additional signals arising from the additional [3,5-bis(methylene)phenoxy]acetate units. Importantly, the spectrum clearly shows that all the 16 peripheral fullerene subunits are equivalent, as attested by a single resonance for the methano bridge carbons at δ = 51.4 ppm and a single signal for the fullerene sp^3 C atom at δ = 71.4 ppm. It can also be seen that the characteristic resonances of the *tert*-butyl group at the focal point are still observable (δ = 26.3 and 82.6 ppm) in spite of the large size of the dendritic structure.

Conclusions

Highly soluble dendritic branches with peripheral C_{60} subunits and carboxylic acid functions at their focal points have been prepared by a convergent approach. Starting from a methanofullerene derivative possessing a *tert*-butyl ester function, the synthesis is based on successive cleavage of a *tert*-butyl ester moiety under acidic conditions followed by a DCC-mediated esterification reaction with an A_2B building block. The successive dendrimer generations have thus been obtained in good yields and the efficient iterative reaction sequence allowed us to prepare the fifth-generation dendron, bearing 16 fullerene peripheral moieties.

Experimental Section

General: Reagents and solvents were purchased as reagent grade and were used without further purification. Compounds **G1**CO$_2$H[5a] and **1**[8] were prepared according to the literature. All reactions were performed in standard glassware. Evaporation and concentration were performed 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) from E. Merck. TLC: glass sheets coated with silica gel 60 F_{254} from E. Merck; visualization by UV light. UV/Vis spectra [λ_{max} in nm (ε)]: Hitachi U-3000 spectrophotometer. IR spectra (cm^{-1}): ATI Mattson Genesis Series FTIR instrument. NMR spectra: Bruker AM 300 (300 MHz); solvent peaks as reference; δ in ppm, *J* in Hz. Elemental analysis were performed by the analytical service at the Institut Charles Sadron (Strasbourg, France).

General Procedure for the Preparation of GnCO$_2$*t*Bu: DCC (2.1 equiv.) was added to a stirred solution of **1** (1 equiv.), the appropriate fullerenecarboxylic acid derivative (2.1 equiv.), DMAP (0.5 equiv.) and a catalytic amount of HOBt in CH_2Cl_2 at 0 °C. After 1 h, the mixture was allowed to warm slowly to room temp. and was then stirred at room temp. for 1 d (**G2**CO$_2$*t*Bu), 3 d (**G3**CO$_2$*t*Bu), 4 d (**G4**CO$_2$*t*Bu), or 5 d (**G5**CO$_2$*t*Bu). The produced solid was filtered off and the solvent was evaporated. The crude product was then purified as outlined below.

G2CO$_2$*t*Bu: This compound was prepared from **1** and **G1**CO$_2$H. Column chromatography on silica gel (CH_2Cl_2) and gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) yielded **G2**CO$_2$*t*Bu (1.59 g, 90%) as a dark red, glassy product. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7 Hz, 12 H), 1.22–1.43 (m, 40 H), 1.49 (s, 9 H), 1.72 (m, 8 H), 3.87 (t, *J* = 7 Hz, 8 H), 4.51 (s, 2 H), 5.00 (s, 4 H), 5.21 (s, 4 H), 5.30 (s, 2 H), 5.43 (s, 4 H), 6.38 (t, *J* = 2 Hz, 2 H), 6.58 (d, *J* = 2 Hz, 4 H), 6.85 (d, *J* = 2 Hz, 2 H), 7.00 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.3, 22.8, 26.3, 28.2, 29.4, 29.6, 32.0, 51.4, 62.7, 65.8, 66.9, 68.3, 69.3, 71.3, 82.7, 101.8, 107.4, 114.6, 120.9, 136.7, 137.2, 138.7, 139.8, 140.97, 141.03, 141.9, 142.0, 142.31, 142.34, 143.0, 143.1, 143.9, 144.0, 144.60, 144.62, 144.75, 144.77, 144.79, 144.81, 145.0, 145.1, 145.2, 145.28, 145.29, 145.31, 145.35, 145.4, 158.5, 160.6, 163.1, 163.2, 166.4, 167.6 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1747 (C=O) cm^{-1}. UV/Vis [CH_2Cl_2, nm (L mol^{-1} cm^{-1})]: λ_{max} (ε) = 258 (284200), 326 (86880), 426 (6980), 686 (440). $C_{190}H_{100}O_{19}$ (2686.8): C 84.93, H 3.75; found C 84.61, H 3.76.

G3CO$_2$*t*Bu: This compound was prepared from **1** and **G2**CO$_2$H. Column chromatography on silica gel (CH_2Cl_2) and gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) yielded **G3**CO$_2$*t*Bu (2.82 g, 87%) as a dark red, glassy product. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7 Hz, 24 H), 1.20–1.44 (m, 80 H), 1.48 (s, 9 H), 1.72 (m, 16 H), 3.87 (t, *J* = 7 Hz, 16 H), 4.47 (s, 2 H), 4.65 (s, 4 H), 5.00 (s, 8 H), 5.15 (s, 4 H), 5.19 (s, 8 H), 5.43 (s, 8 H), 6.38 (t, *J* = 2 Hz, 4 H), 6.57 (d, *J* = 2 Hz, 8 H), 6.83 (d, *J* = 2 Hz, 2 H), 6.85 (s, 4 H), 6.90 (s, 1 H), 7.01 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.3, 22.8, 26.3, 28.2, 29.4, 29.6, 32.0, 51.4, 62.7, 65.4, 65.7, 66.6, 66.8, 68.3, 69.2, 71.3, 82.7, 101.8, 107.4, 114.6, 114.8, 121.1, 121.4, 136.7, 137.28, 137.32, 138.6, 139.8, 140.91, 140.94, 141.8, 142.0, 142.3, 143.0, 143.1, 143.90, 143.92, 144.53, 144.57, 144.68, 144.73, 144.75, 144.97 145.05, 145.16, 145.23, 145.25, 145.30, 145.32, 158.3, 158.4, 160.6, 163.0, 163.1, 166.4, 167.6, 168.2 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1748 (C=O) cm^{-1}. UV/Vis [CH_2Cl_2, nm (L mol^{-1} cm^{-1})]: λ_{max} (ε) = 258 (568250), 326 (179980), 426 (17080), 686 (900). $C_{386}H_{200}O_{41}$ (5493.7): C 84.39, H 3.67; found C 84.06, H 3.67.

G4CO$_2$*t*Bu: This compound was prepared from **1** and **G3**CO$_2$H. Column chromatography on silica gel (CH_2Cl_2) and gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) yielded **G4**CO$_2$*t*Bu (1.60 g, 95%) as a dark red, glassy product. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7 Hz, 48 H), 1.18–1.44 (m, 160 H), 1.47 (s, 9 H), 1.71 (m, 32 H), 3.87 (t, *J* = 7 Hz, 32 H), 4.45 (s, 2 H), 4.62 (s, 4 H), 4.65 (s, 8 H), 5.00 (s, 16 H), 5.15 (m, 28 H), 5.43 (s, 16 H), 6.38 (t, *J* = 2 Hz, 8 H), 6.57 (d, *J* = 2 Hz, 16 H), 6.83 (br. s, 14 H), 6.90 (br. s, 3 H), 7.00 (s, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.3, 22.8, 26.3, 28.2, 29.4, 29.6, 32.0, 51.4, 62.7, 65.4, 65.7, 66.5 (br.), 66.8, 68.2, 69.2, 71.3, 82.6, 101.8, 107.4, 114.6, 114.7 (br.), 121.1, 136.7, 137.3, 137.5, 138.6, 139.8, 140.89, 140.92, 141.8, 142.0, 142.2, 143.0, 143.1, 143.9, 144.53, 144.55, 144.65, 144.70, 144.73, 144.9, 145.0, 145.16, 145.19, 145.22, 145.3, 158.2, 158.3, 158.4, 160.6, 163.0, 163.1, 166.4, 167.5, 168.2 (br.) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1747 (C=O) cm^{-1}. UV/Vis [CH_2Cl_2, nm (L mol^{-1} cm^{-1})]: λ_{max} (ε) = 258 (1145520), 326 (377910), 426 (40350), 686 (1960). $C_{778}H_{400}O_{85}$ (11107.45): C 84.13, H 3.63; found C 83.90, H 3.60.

G5CO$_2$*t*Bu: This compound was prepared from **1** and **G4**CO$_2$H. Column chromatography on silica gel (CH_2Cl_2) and gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) yielded **G5**CO$_2$*t*Bu (307 mg, 76%) as a dark red, glassy product. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7 Hz, 96 H), 1.18–1.44 (m, 320 H), 1.47 (s, 9 H), 1.71 (m, 64 H), 3.87 (t, *J* = 7 Hz, 64 H), 4.45 (s, 2 H), 4.62 (m, 28 H), 5.00 (s, 32 H), 5.15 (m, 56 H), 5.43 (s, 32 H), 6.38 (br. s, 16 H), 6.55 (br. s, 32 H), 6.83 (br. s, 32 H), 6.90 (br. m, 9 H), 7.00 (s, 8 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.3, 22.8, 26.3, 28.2, 29.4, 29.6, 32.0, 51.4, 62.7, 65.5, 65.8, 66.6, 66.9, 68.4, 69.3, 71.4, 82.6, 101.8, 107.4, 114.6, 114.8 (br.), 121.1, 121.6 (br.), 136.7, 137.3, 137.5, 138.6, 139.8, 140.9, 141.8, 142.0, 142.3, 143.0, 143.1, 143.9, 144.6, 144.67, 144.69, 144.74, 144.9, 145.05, 145.18, 145.23, 145.3, 158.2, 158.3, 160.6, 163.0, 163.1, 166.4, 168.2 (br.) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1747 (C=O) cm^{-1}. UV/Vis [CH_2Cl_2, nm ($L\,mol^{-1}\,cm^{-1}$)]: λ_{max} (ε) = 259 (2166900), 326 (712970), 426 (86010), 686 (4110). $C_{1562}H_{800}O_{173}$ (22335.0): C 84.00, H 3.61; found C 84.63, H 3.59.

General Procedure for the Preparation of GnCO$_2$H: The appropriate ester was dissolved in CH_2Cl_2 and TFA (100 equiv.) was added. The resulting solution was stirred at room temperature overnight, then extensively washed with water and dried ($MgSO_4$), and the solvents were evaporated.

G2CO$_2$H: This compound was prepared from **G2**CO$_2$*t*Bu. **G2**CO$_2$H (1.87 g, 96%) was obtained as a dark red, glassy product. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7 Hz, 12 H), 1.19–1.45 (m, 40 H), 1.72 (m, 8 H), 3.87 (t, J = 7 Hz, 8 H), 4.69 (s, 2 H), 5.01 (s, 4 H), 5.21 (s, 4 H), 5.29 (s, 2 H), 5.43 (s, 4 H), 6.38 (s, 2 H), 6.58 (s, 4 H), 6.85 (s, 2 H), 7.00 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.3, 22.8, 26.3, 29.4, 29.6, 32.0, 51.4, 62.8, 64.9, 66.7, 68.3, 69.3, 71.2, 101.8, 107.5, 114.4, 121.1, 136.7, 137.4, 138.6, 139.8, 140.9, 141.0, 141.9, 142.0, 142.28, 142.30, 143.0, 143.1, 143.93, 143.96, 144.5, 144.6, 144.72, 144.76, 144.78, 145.0, 145.07, 145.16, 145.26, 145.29, 145.34, 145.4, 158.1, 160.6, 163.1, 163.2, 166.5, 171.9 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1747 (C=O) cm^{-1}. UV/Vis [CH_2Cl_2, nm ($L\,mol^{-1}\,cm^{-1}$)]: λ_{max} (ε) = 259 (282680), 326 (88390), 426 (7250), 686 (425).

G3CO$_2$H: This compound was prepared from **G3**CO$_2$*t*Bu. **G3**CO$_2$H (1.73 g, 99%) was obtained as a dark red glassy product. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7 Hz, 24 H), 1.20–1.44 (m, 80 H), 1.72 (m, 16 H), 3.87 (t, J = 7 Hz, 16 H), 4.58 (s, 2 H), 4.65 (s, 4 H), 5.00 (s, 8 H), 5.15 (s, 4 H), 5.19 (s, 8 H), 5.43 (s, 8 H), 6.38 (t, J = 2 Hz, 4 H), 6.57 (d, J = 2 Hz, 8 H), 6.83 (s, 2 H), 6.85 (s, 4 H), 6.88 (s, 1 H), 7.00 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.3, 22.8, 26.3, 29.4, 29.6, 32.0, 51.4, 62.8, 64.9, 65.4, 66.4, 66.8, 68.3, 69.3, 71.3, 101.8, 107.4, 114.5, 121.0, 121.6, 136.7, 137.3, 137.5, 138.6, 139.8, 140.9, 141.0, 141.8, 142.0, 1452.26, 142.27, 143.0, 143.90, 143.92, 144.53, 144.58, 144.68, 144.73, 144.76, 144.97, 145.05, 145.16, 145.23, 145.26, 145.32, 145.33, 158.1, 158.3, 160.6, 163.0, 163.1, 166.5, 168.3, 170.4 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1748 (C=O) cm^{-1}. UV/Vis [CH_2Cl_2, nm ($L\,mol^{-1}\,cm^{-1}$)]: λ_{max} (ε) = 258 (571320), 326 (183110), 426 (17360), 686 (930).

G4CO$_2$H: This compound was prepared from **G4**CO$_2$*t*Bu. **G4**CO$_2$H (502 mg, 97%) was obtained as a dark red glassy product. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7 Hz, 48 H), 1.18–1.44 (m, 160 H), 1.71 (m, 32 H), 3.87 (t, J = 7 Hz, 32 H), 4.62 (m, 14 H), 5.00 (br. s, 16 H), 5.13 (br. s, 16 H), 5.43 (s, 16 H), 6.38 (br. s, 8 H), 6.57 (d, J = 2 Hz, 16 H), 6.80 (m, 14 H), 6.90 (br. s, 3 H), 7.00 (s, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.3, 22.8, 26.3, 29.4, 29.6, 32.0, 51.4, 62.7, 65.4, 66.3, 66.4, 66.7, 68.2, 69.2, 71.2, 101.8, 107.4, 114.6, 114.7 (br.), 121.0, 136.7, 137.3, 137.4, 138.6, 139.8, 140.89, 140.91, 141.8, 142.0, 142.2, 143.0, 143.1, 143.9, 144.52, 144.55, 144.65, 144.70, 144.73, 145.00, 145.04, 145.16, 145.22, 145.3, 158.2, 160.6, 163.08, 166.3, 166.4, 168.2, 168.4 (br.) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1747 (C=O) cm^{-1}. UV/Vis [CH_2Cl_2, nm ($L\,mol^{-1}\,cm^{-1}$)]: λ_{max} (ε) = 259 (1205680), 326 (382620), 426 (41280), 686 (1980).

G5CO$_2$H: This compound was prepared from **G5**CO$_2$*t*Bu. **G5**CO$_2$H (270 mg, 88%) was obtained as a dark red, glassy product. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7 Hz, 96 H), 1.18–1.44 (m, 320 H), 1.71 (m, 64 H), 3.87 (t, J = 7 Hz, 64 H), 4.45 (s, 2 H), 4.62 (m, 28 H), 5.00 (s, 32 H), 5.15 (m, 56 H), 5.43 (s, 32 H), 6.38 (br. s, 16 H), 6.55 (br. s, 32 H), 6.83 (br. s, 32 H), 6.90 (br. m, 9 H), 7.00 (s, 8 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.3, 22.8, 26.3, 29.4, 29.6, 32.0, 51.4, 62.7, 65.5, 65.8, 66.6, 66.9, 68.4, 69.3, 71.4, 101.8, 107.4, 114.6, 114.8 (br.), 121.1, 121.6 (br.), 136.7, 137.3, 137.5, 138.6, 139.8, 140.9, 141.8, 142.0, 142.3, 143.0, 143.1, 143.9, 144.6, 144.67, 144.69, 144.74, 144.9, 145.05, 145.18, 145.23, 145.3, 158.2, 158.3, 160.6, 163.0, 163.1, 166.4, 169.1 (br.) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 1750 (C=O) cm^{-1}. UV/Vis [CH_2Cl_2, nm ($L\,mol^{-1}\,cm^{-1}$)]: λ_{max} (ε) = 259 (2168530), 326 (713120), 426 (86320), 686 (4160).

Supporting Information Available (see footnote on the first page of this article): ^{1}H NMR spectra of **G1**–**G5**CO$_2$*t*Bu and **G1**–**G5**CO$_2$H.

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