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Bismalonates Constructed on a Hexaphenylbenzene Scaffold for the Synthesis of *Equatorial* Fullerene Bisadducts

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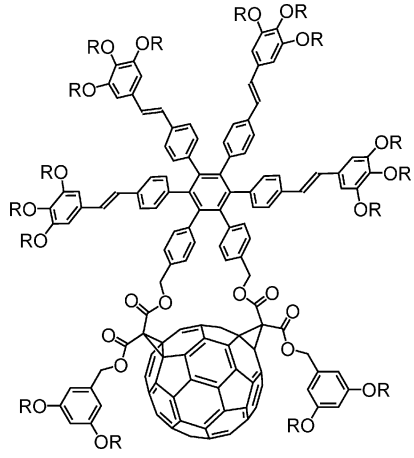
Hexaphenylbenzene derivatives bearing two aldehyde groups were prepared by reaction of 4,4′-(ethyne-1,2-diyl)dibenzaldehyde with bisarylalkynes in the presence of a catalytic amount of $Co_2(CO)_8$. These synthetic intermediates were used to produce the corresponding bismalonates. Finally, macrocyclization of the bismalonates with C_{60} afforded *equatorial* fullerene bisadducts. The relative position of the two cyclopropane rings on the C_{60} core was determined on the basis of the molecular symmetry (C_1) deduced from the ^1H and ^{13}C NMR spectra and further confirmed by the characteristic features seen in their UV/Vis spectra.

Introduction

The use of C_{60} as an energy and/or electron acceptor in photochemical molecular devices has generated tremendous research efforts in the past few years.[1] In particular, the carbon sphere has been combined with π-conjugated oligomers for the construction of donor-fullerene arrays.[2] Such hybrid compounds have shown excited-state interactions making them excellent candidates for fundamental photophysical studies.[2] Furthermore, C_{60}–(π-conjugated oligomer) dyads have been used as the active layer in organic photovoltaic cells.[3] Fullerene derivatives have also shown great potential for optical-limiting applications.[4] Effectively, the transmission of fullerene solutions decreases by increasing the light intensity. For short pulses (ps), the limiting action is ascribed to pure reverse saturable absorption (RSA), whereas for longer pulses (ns–μs) additional mechanisms of mainly thermal origin are invoked.[5] Several strategies have been developed to improve the optical limiting properties of fullerene derivatives.[6,7] One is the preparation of hybrid compounds combining the fullerene with an excited-state multiphoton absorption (MPA) chromophore.[7] As part of this research, we have reported a preliminary communication on the excited-state properties of compound **1** assembling C_{60} with a branched oligophenylenevinylene (OPV)-based MPA chromophore.[7] Interestingly, compound **1** shows enhanced optical-limiting properties when compared to a 1:1 mixture of the separated components. When the two moieties are covalently linked, deactivation of the lowest singlet excited state of the conjugated system occurs by OPV→C_{60} singlet–singlet energy transfer, thus populating the lowest fullerene singlet excited state. As the latter possesses a larger cross-section than the ground state, it is itself involved in the nonlinear behavior. For this reason, the combination of a MPA chromophore with C_{60} leads to improved optical limiting properties. In this paper, we now report in detail the synthesis of this fullerene bisadduct as well as our efforts to unambiguously assign its regiochemistry.



1 R = $C_{12}H_{25}$

Results and Discussion

The preparation of the functionalized hexaphenylbenzene core required for the synthesis of compound **1** is based on a metal-catalyzed cyclotrimerization[8] involving two different bisarylalkynes. The synthesis of alkyne building

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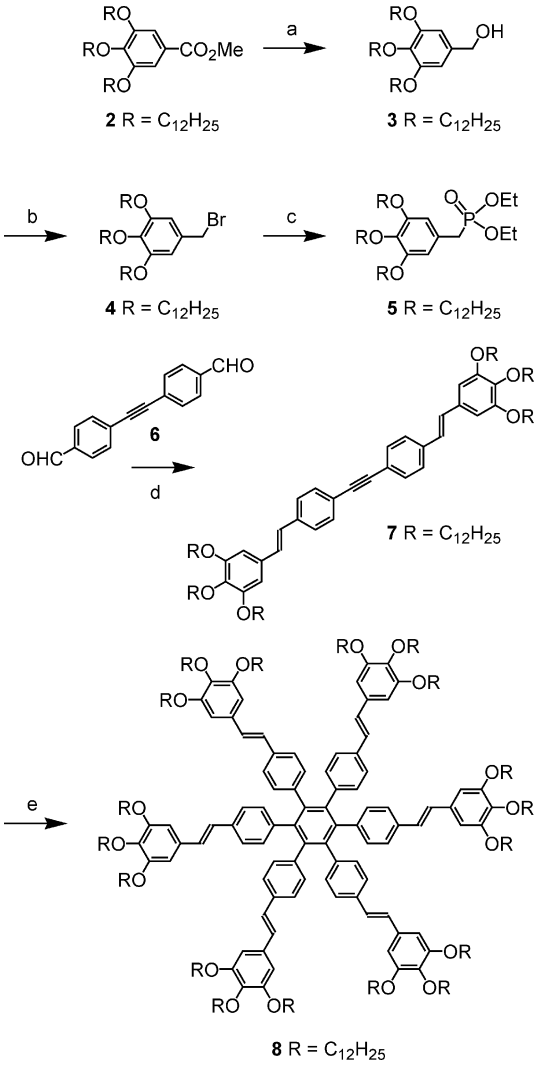
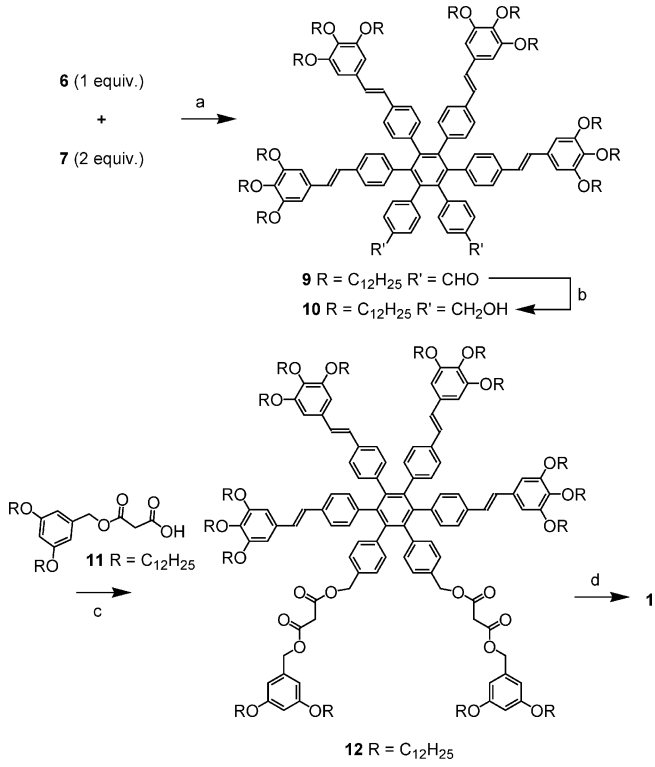
block **7** is depicted in Scheme 1. Reduction of ester **2**[9] with $LiAlH_4$ gave benzylic alcohol **3** in 94% yield. Bromination of **3** by using trimethylsilyl bromide (TMSBr) followed by treatment of resulting bromide **4** with $P(OEt)_3$ under Arbuzov conditions afforded **5** in an overall 80% yield. Reaction of **5** with bisaldehyde **6**[10] under Wadsworth–Emmons conditions gave compound **7** in 77% yield. All the spectroscopic studies and elemental analysis results were consistent with the structure of **7**. In particular, the coupling constant of ca. 17 Hz for the AB system corresponding to the signal of the vinylic protons in the ^1H NMR spectrum confirmed the *E* stereochemistry of the two equivalent double bonds in **7**.



Scheme 1. Reagents and conditions: (a) $LiAlH_4$, THF, 0 °C, 3 h (94%); (b) TMSBr, $CHCl_3$, 0 °C to room temperature, 4 h (99%); (c) $P(OEt)_3$, 150 °C, 4 h (81%); (d) *t*BuOK, THF, 0 °C, 4 h (77%); (e) $Co_2(CO)_8$, dioxane, room temperature, 17 h (78%).

The reaction conditions for the cyclotrimerization were first optimized with compound **7**. We found that $Co_2(CO)_8$ is an efficient catalyst[8,11] for the preparation of compound **8** from alkyne **7**. Under optimized conditions, treatment of **7** with a catalytic amount of $Co_2(CO)_8$ in dioxane at room temperature for 17 h afforded **8** in 78% yield. The ^1H NMR spectrum of **8** is quite simple and shows that all the six peripheral stilbene subunits are equivalent. Further conclusive evidence for the formation of the homotrimer came from the comparison of the ^{13}C NMR spectra of **7** and **8**. In particular, the characteristic signal corresponding to the sp C atom detected at 90.5 ppm for compound **7** is not anymore present for **8**, whereas an additional resonance is detected at 140.1 ppm in the spectrum of **8**. The latter signal is attributed to the six equivalent sp^2 C atoms of the central phenyl core of **8**. The structure of **8** was also confirmed by MALDI-TOF mass spectrometry showing the expected molecular ion peak at m/z = 4463 $[M + H]^+$ (calcd. for $C_{306}H_{499}O_{18}$ 4462.81).

The reaction conditions developed for the preparation of **8** from building block **7** were adapted for the preparation of **9** starting from alkynes **6** and **7**. Treatment of **6** (1 equiv.) and **7** (2 equiv.) with a catalytic amount of $Co_2(CO)_8$ in dioxane at room temperature for 24 h gave a mixture of hetero- and homotrimers from which targeted heterotrimer **9** was isolated by column chromatography. Compound **9** was thus obtained in 53% yield. It is worth noting that the choice of the appropriate pairs of alkyne building blocks for the preparation of a heterotrimer such as **9** was the key to this synthesis. Actually, both alkyne precursors must have a similar reactivity towards the catalyst. Indeed, the first reactions were attempted from **7** and the bisalcohol derived from bisaldehyde **6**. Reaction of **7** with this diol in

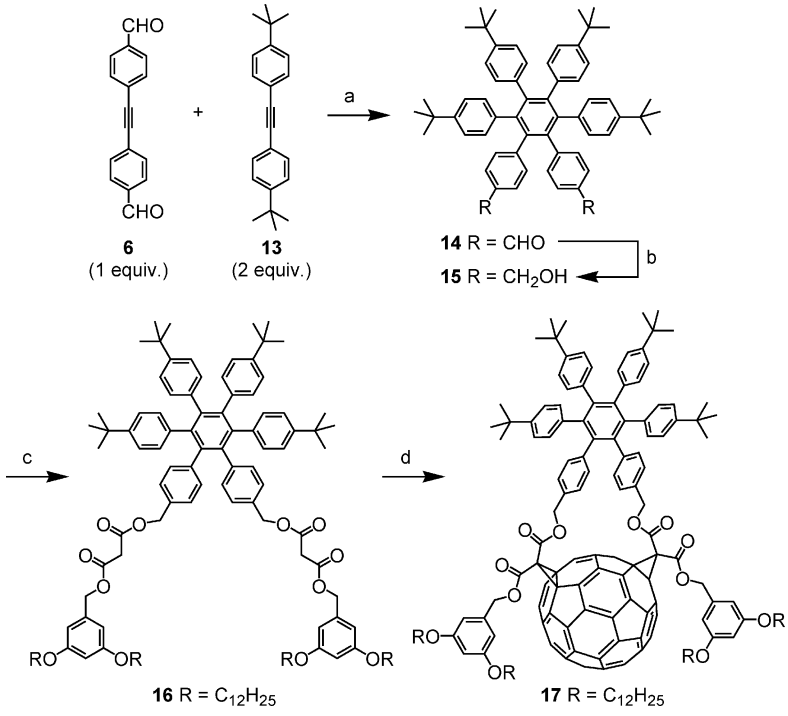


Scheme 2. Reagents and conditions: (a) $Co_2(CO)_8$, dioxane, room temperature, 24 h (53%); (b) $LiAlH_4$, THF, 0 °C, 4 h (76%); (c) DCC, DMAP, CH_2Cl_2, 0 °C to room temperature, 29 h (75%); (d) C_{60}, DBU, I_2, PhMe, room temperature, 3 h (32%).

the presence of a catalytic amount of $Co_2(CO)_8$ yielded mainly the two homotrimers; no heterotrimers could be detected in the reaction mixture. The latter result is due to the difference in reactivity between the two alkyne building blocks under these conditions. Effectively, by following the reaction by TLC, it appeared that compound **7** was consumed much faster than the other alkyne derivative (Scheme 2).

Reduction of dialdehyde **9** with $LiAlH_4$ in THF gave **10** in 76% yield. Reaction of diol **10** with carboxylic acid **11**[12] under esterification conditions with the use of *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) in CH_2Cl_2 afforded compound **12** in 75% yield. Fullerene derivative **1** was then prepared by taking advantage of the versatile regioselective reaction developed in the group of Diederich,[13] which led to macrocyclic bisadducts of C_{60} by a cyclization reaction at the C sphere with bismalonate derivatives in a double Bingel[14] cyclopropanation. Reaction of **12** with C_{60}, I_2, and DBU in toluene at room temperature afforded the corresponding cyclization product **1**. Fullerene derivative **1** was characterized by ^1H and ^{13}C NMR, UV/Vis, and IR spectroscopy. In addition, its structure was confirmed by MALDI-TOF mass spectrometry, showing the expected molecular ion peak at *m*/*z* = 5021 $[M]^+$ (calcd. for $C_{348}H_{454}O_{24}$ 5021.42). The molecular symmetry (C_1) deduced from the ^1H and ^{13}C NMR spectra of **1** suggests that this bisadduct could be the *equatorial* regioisomer. This is also consistent with molecular modeling studies. For fullerene derivatives bearing two malonate addends, the relative position of the two cyclopropane rings on the C_{60} core suggested by the molecular symmetry is usually confirmed by UV/Vis spectroscopy. Effectively, the absorption spectra of C_{60} bisadducts are highly dependent on the addition pattern and characteristic for each of the regioisomers.[13,15] In the case of **1**, however, the strong absorption of the π-conjugated chromophore in the 300–450 nm region partially covers the characteristic features of the fullerene bisadduct moiety, which thus prevents unambiguous structural assignment. This prompted us to prepare model compound **17** with a simpler hexaphenylbenzene bridging unit (Scheme 3).

Reaction of **6** (1 equiv.) and **13** (2 equiv.) with a catalytic amount of $Co_2(CO)_8$ in dioxane at room temperature for 12 h gave compound **14** in 49% yield. Reduction of dialdehyde **14** with $LiAlH_4$ followed by treatment of resulting **15** with acid **11** in the presence of DCC and DMAP afforded bismalonate **16**. Compound **17** was then obtained in 25% yield by reaction of **16** with C_{60}, I_2, and DBU in toluene at room temperature. The structure of compound **17** was confirmed by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. The ^1H NMR spectrum of **17** is depicted in Figure 1. In addition to the signals corresponding to the hexaphenylbenzene bridging moiety, the spectrum is characterized by four sets of AB quartets for the four different diastereotopic benzylic CH_2 groups and two AX_2 systems for the aromatic protons of the two nonequivalent peripheral didodecyloxyphenyl moieties. As observed for compound **1**, NMR spectroscopy shows that compound **17** is C_1 symmetric. The absorption spectrum of bisadduct **17** reveals two distinct bands (λ_{max} = 252 and 320 nm) in the UV region. In the visible spectral region, the spectrum is broad with two shoulders (395 and 408 nm),



Scheme 3. Reagents and conditions: (a) $Co_2(CO)_8$, dioxane, room temperature, 12 h (49%); (b) $LiAlH_4$, THF, 0 °C, 3 h (68%); (c) **11**, DCC, DMAP, CH_2Cl_2, 0 °C to room temperature, 26 h (53%); (d) C_{60}, DBU, I_2, PhMe, room temperature, 12 h (25%).

and the band corresponding to the lowest-allowed singlet transition, which is very sharp and well distinguishable for C_{60},[16] is barely detectable at ca. 420 nm. Importantly, the UV/Vis spectrum of **17** clearly shows the characteristic features previously reported for analogous *equatorial* bisadducts[13,15] and unambiguously confirms the addition pattern deduced from the ^1H and ^{13}C NMR spectra.

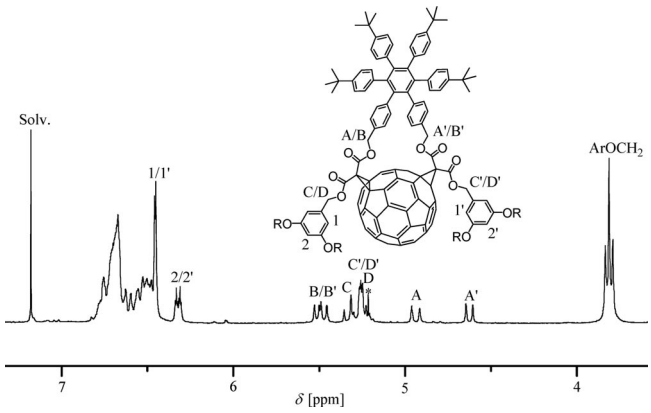


Figure 1. ^1H NMR spectrum (300 MHz, $CDCl_3$) of compound **17** (* = CH_2Cl_2 impurity).

Conclusions

Hexaphenylbenzene derivatives **9** and **14** substituted with two aldehyde groups were easily obtained by reaction of bisaldehyde **6** with bisarylalkynes **8** and **13**, respectively, in the presence of a catalytic amount of $Co_2(CO)_8$. These precursors were used to produce the corresponding bismalonates **10** and **14**. Finally, *equatorial* fullerene bisadducts **1** and **17** were prepared by the direct macrocyclization of **10** and **14**, respectively, with the C_{60} sphere. The construction of fullerene derivative **1** already illustrates the advantage of the molecular design reported in this paper: multiple derivatizations can be easily performed on the hexaphenylbenzene bridging unit. Indeed, the easy access to functionalized hexaphenylbenzene derivatives should find multiple applications in supramolecular devices, which rely on control of geometry for the expression of function.

Experimental Section

General: Reagents and solvents were purchased as reagent grade and used without further purification. Compounds **2**,[9] **6**,[10] **11**,[12] and **13**[10] were prepared according to the literature. THF and dioxane were 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 was performed with silica gel 60 (230–400 mesh, 0.040–0.063 mm) purchased from E. Merck. Thin-layer chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from E. Merck with visualization by UV light. IR spectra were measured with an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded with a Bruker AC 300 with solvent peaks as reference. MALDI-TOF mass spectra were carried out with a Bruker BIFLEX™ matrix-assisted laser desorption time-of-flight mass spectrometer equipped with SCOUT™ high-resolution optics, an X-Y multisample probe, and a gridless reflector. Ionization was 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: A 1 M $LiAlH_4$ solution in THF (4.5 mL, 4.5 mmol) was added dropwise to a stirred solution of **2** (4.00 g, 5.81 mmol) in dry THF (30 mL) at 0 °C. The resulting mixture was stirred for 3 h at 0 °C, then MeOH was carefully added. The resulting mixture was filtered (Celite) and evaporated to yield **3** (3.62 g, 94%) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.5 Hz, 9 H, CH_3), 1.20–1.80 (m, 60 H, CH_2), 3.95 (m, 9 H, OCH_2), 4.59 (s, 2 H, $ArCH_2$), 6.56 (s, 2 H, Ar-H) ppm. $C_{43}H_{80}O_4$ (661.11): calcd. C 78.12, H 12.20; found C 78.34, H 12.41.

Compound 4: TMSBr (0.9 mL, 6.56 mmol) was added dropwise to a stirred solution of **3** (3.62 g, 5.46 mmol) in $CHCl_3$ (25 mL) at 0 °C. The resulting solution was stirred for 1 h at 0 °C, then 3 h at room temperature. The resulting mixture was evaporated to yield **4** (3.90 g, 5.39 mmol, 99%) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (m, 9 H, CH_3), 1.2–1.8 (m, 60 H, CH_2), 3.95 (m, 9 H, OCH_2), 4.43 (s, 2 H, CH_2Br), 6.57 (s, 2 H, Ar-H) ppm. $C_{43}H_{79}BrO_3$ (724.00): calcd. C 71.34, H 11.00; found C 71.45, H 10.98.

Compound 5: A mixture of $P(OEt)_3$ (0.92 mL, 5.39 mmol) and **4** (3.90 g, 5.39 mmol) was heated at 150 °C for 4 h. After cooling to room temperature, the mixture was dried under high vacuum. Column chromatography (SiO_2; CH_2Cl_2/MeOH, 99:1) yielded **5** (3.40 g, 81%) as a pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (m, 9 H, CH_3), 1.20–1.80 (m, 66 H, CH_2), 3.04 (d, $J_{P,H}$ = 21 Hz, 2 H, CH_2-P), 3.94 (m, 10 H, OCH_2), 6.49 (d, $J_{P,H}$ = 3 Hz, 2 H, Ar-H) ppm. $C_{47}H_{89}O_6P$ (781.19): calcd. C 72.26, H 11.48; found C 72.36, H 11.59.

Compound 7: A mixture of **6** (423 mg, 1.81 mmol), *t*BuOK (447 mg, 3.98 mmol), and **5** (3.39 g, 4.34 mmol) in dry THF (30 mL) was stirred at 0 °C for 4 h. A saturated aqueous NH_4Cl solution was then added, and the THF evaporated. The aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with water, dried ($MgSO_4$), and filtered, and the solvent was then evaporated to dryness. Column chromatography (SiO_2; hexane/CH_2Cl_2, 1:1) gave **7** (2.08 g, 77%) as a pale yellow solid. M.p. 85 °C. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 229 (37600), 372 (92000) nm. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 18 H, CH_3), 1.20–1.60 (m, 108 H, CH_2), 1.80 (m, 12 H, CH_2), 4.00 (m, 12 H, OCH_2), 6.72 (s, 4 H, Ar-H), 7.00 (AB, J = 17 Hz, 4 H, CH=CH), 7.47 (d, J = 7 Hz, 4 H, Ar-H), 7.51 (d, J = 7 Hz, 4 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.1, 29.4, 29.6, 29.7, 30.4, 31.9, 69.2, 73.6, 90.5, 105.3, 122.1, 126.3, 129.8, 131.9, 132.2, 137.4, 138.6, 153.3 ppm. $C_{102}H_{166}O_6$ (1488.44): calcd. C 82.31, H 11.24; found C 82.32, H 11.32.

Compound 8: A mixture of $Co_2(CO)_8$ (5 mg, 0.015 mmol) and **7** (200 mg, 0.134 mmol) in dry dioxane (5 mL) was stirred at room temperature for 17 h, and the solvent was then evaporated. Column chromatography (SiO_2; CH_2Cl_2/hexane, 1:1) yielded **7** (156 mg,

78%) as a yellow solid. M.p. 274 °C. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 338 (172000) nm. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (m, 54 H, CH_3), 1.10–1.60 (m, 324 H, CH_2), 3.94 (m, 36 H, OCH_2), 6.59 (s, 12 H, Ar-H), 6.79 (m, 24 H, CH=CH and Ar-H), 7.00 (d, J = 7 Hz, 12 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.1, 29.3, 29.4, 29.7, 30.3, 31.9, 69.1, 73.4, 76.4, 105.0, 125.0, 127.7, 128.0, 131.7, 132.6, 134.1, 138.1, 139.8, 140.1, 153.2 ppm. MS (MALDI-TOF): m/z = 4463 $[M+H]^+$. $C_{306}H_{498}O_{18}$ (4465.31): calcd. C 82.31, H 11.24; found C 82.25, H 11.23.

Compounds 8 and 9: A mixture of $Co_2(CO)_8$ (21 mg, 0.061 mmol), **6** (111 mg, 0.47 mmol), and **7** (1.35 g, 0.91 mmol) in dry dioxane (25 mL) was stirred at room temperature for 24 h, and the solvent was then evaporated. Two successive column chromatography (SiO_2; CH_2Cl_2/hexane, 1:1 then 7:3) yielded **8** (343 mg, 17%) and **9** (770 mg, 53%).

9: Yellow glassy product. IR (neat): $\tilde{\nu}$ = 1704 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (m, 36 H, CH_3), 1.10–1.50 (m, 216 H, CH_2), 1.75 (m, 24 H, CH_2), 3.94 (m, 24 H, OCH_2), 6.60 (s, 8 H, Ar-H), 6.72 (d, J = 17 Hz, 2 H, =CH), 6.78 (AB, J = 17 Hz, 4 H, CH=CH), 6.80 (m, 8 H, Ar-H), 6.2 (d, J = 17 Hz, 2 H, =CH), 7.05 (m, 12 H, Ar-H), 7.41 (d, J = 8 Hz, 4 H, Ar-H), 9.78 (s, 2 H, CHO) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 30.3, 32.0, 69.1, 73.5, 105.1, 125.1, 127.3, 127.5, 128.3, 128.4, 128.6, 131.5, 131.9, 132.4, 132.5, 133.7, 134.5, 134.7, 138.3, 138.7, 139.0, 139.1, 140.1, 141.0, 147.0, 153.2, 191.9 ppm. MS (MALDI-TOF): m/z = 3210 $[M+H]^+$. $C_{220}H_{342}O_{14}$ (3211.13): calcd. C 82.29, H 10.74; found C 82.45, H 11.01.

Compound 10: A 1 M $LiAlH_4$ solution in THF (0.6 mL, 0.6 mmol) was added to a stirred solution of **9** (740 mg, 0.23 mmol) in dry THF (20 mL) at 0 °C. The resulting mixture was stirred for 4 h at 0 °C, then MeOH was carefully added. The resulting mixture was filtered (Celite), and the solvent was evaporated. Column chromatography (SiO_2, CH_2Cl_2) gave **10** (560 mg, 76%) as a yellow glassy product. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 233 (106800), 338 (150200) nm. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (m, 36 H, CH_3), 1.1–1.5 (m, 216 H, CH_2), 1.75 (m, 24 H, CH_2), 3.94 (m, 24 H, OCH_2), 4.46 (s, 4 H, $ArCH_2$), 6.59 (m, 4 H, Ar-H), 6.60 (s, 4 H, Ar-H), 6.72 (d, J = 17 Hz, 2 H, =CH), 6.80 (m, 20 H, CH=CH and Ar-H), 6.84 (d, J = 17 Hz, 2 H, =CH), 7.04 (m, 8 H, Ar-H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 30.3, 31.9, 65.1, 69.1, 73.5, 105.0, 124.9, 125.4, 127.8, 128.0, 131.7, 132.6, 134.2, 138.2, 139.8, 140.2, 153.2 ppm. MS (MALDI-TOF): m/z = 3214 $[M+H]^+$. $C_{220}H_{346}O_{14}$ (3215.16): calcd. C 82.19, H 10.85; found C 82.25, H 11.11.

Compound 12: DCC (72 mg, 0.35 mmol) was added to a stirred solution of **10** (470 mg, 0.15 mmol), **11** (271 mg, 0.48 mmol), and DMAP (7 mg, 0.06 mmol) in CH_2Cl_2 (30 mL) at 0 °C. After 1 h, the mixture was allowed to slowly warm to room temperature (within 1 h), then stirred for 28 h, and filtered, and the solvent was then evaporated. Column chromatography (SiO_2; hexane/CH_2Cl_2, 1:1) yielded **12** (470 mg, 75%) as a yellow glassy product. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (m, 48 H, CH_3), 1.10–1.60 (m, 288 H, CH_2), 1.74 (m, 32 H, CH_2), 3.39 [s, 4 H, $CH_2(CO_2R)_2$], 3.92 (m, 32 H, OCH_2), 4.96 (s, 4 H, Ar-CH_2), 5.00 (s, 4 H, Ar-CH_2), 6.38 (s, 2 H, Ar-H), 6.42 (s, 4 H, Ar-H), 6.59 (s, 8 H, Ar-H), 6.78 (m, 24 H, CH=CH and Ar-H), 7.00 (2d, J = 8 Hz, 8 H, Ar-H) ppm.

Compound 1: DBU (0.08 mL, 0.55 mmol) was added to a stirred solution of C_{60} (79 mg, 0.109 mmol), I_2 (61 mg, 0.24 mmol), and **12** (470 mg, 0.109 mmol) in toluene (200 mL) at room temperature. The solution was stirred for 3 h, filtered through a short plug of SiO_2 (toluene then CH_2Cl_2), and the solvent was then evaporated. Column chromatography (SiO_2; hexane/CH_2Cl_2, 7:3) followed by gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) yielded **1** (155 mg, 32%) as a dark brown glassy product. IR (CH_2Cl_2): $\tilde{\nu}$ = 1749 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 228 (295900), 328 (196750) nm. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (m, 48 H, CH_3), 1.10–1.60 (m, 288 H, CH_2), 1.75 (m, 32 H, CH_2), 3.93 (m, 32 H, OCH_2), 4.90 (d, J = 12 Hz, 1 H, Ar-CH), 5.10 (d, J = 12 Hz, 1 H, Ar-CH), 5.34 (d, J = 12 Hz, 1 H, Ar-CH), 5.40 (s, 2 H, Ar-CH_2), 5.50 (d, J = 12 Hz, 1 H, Ar-CH), 5.60 (d, J = 12 Hz, 1 H, Ar-CH), 5.65 (d, J = 12 Hz, 1 H, Ar-CH), 6.3–7.1 (m, 46 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 14.1, 22.6, 26.0, 26.1, 29.2, 29.3, 29.35, 29.4, 29.45, 29.5, 29.6, 29.7, 30.3, 31.9, 68.1, 69.1, 73.4, 101.7, 105.1, 105.15, 106.9, 124.9, 127.6, 128.0, 128.1, 131.0, 131.2, 131.4, 131.6, 131.9, 132.0, 132.5, 134.1, 136.4, 136.5, 138.2, 138.3, 138.5, 139.1, 139.3, 139.4, 139.6, 140.2, 140.3, 140.6, 141.4, 141.6, 141.9, 142.1, 142.6, 142.7, 142.9, 142.95, 143.3, 143.4, 143.5, 143.6, 143.7, 143.8, 144.0, 144.1, 144.2, 144.4, 144.6, 144.7, 144.8, 144.9, 145.0, 145.2, 145.5, 145.7, 146.0, 146.1, 146.3, 146.4, 146.9, 147.2, 148.5, 153.2, 153.5, 160.4, 163.0, 163.1, 163.3, 163.4 ppm. MS (MALDI-TOF): m/z = 5021 $[M]^+$. $C_{348}H_{454}O_{24}$ (5021.42): calcd. C 83.24, H 9.11; found C 82.99, H 9.41.

Compound 14: A mixture of $Co_2(CO)_8$ (170 mg, 0.5 mmol), **6** (390 mg, 1.65 mmol), and **13** (960 mg, 3.30 mmol) in dry dioxane (100 mL) was stirred at room temperature for 12 h, and the solvent was then evaporated. Two successive column chromatography (SiO_2; CH_2Cl_2/hexane, 1:1) yielded **14** (660 mg, 49%). Yellow glassy product. IR (neat): $\tilde{\nu}$ = 1705 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.09 (s, 36 H, *t*Bu), 6.73 (AA′XX′, J_{AX} = 7 Hz, 8 H, Ar-H), 6.74 (AA′XX′, J_{AX} = 7 Hz, 8 H, Ar-H), 7.19 (AA′XX′, J_{AX} = 7 Hz, 8 H, Ar-H), 9.76 (s, 2 H, CHO) ppm. MS (MALDI-TOF): m/z = 815 $[M+H]^+$. $C_{60}H_{62}O_2$ (815.15): calcd. C 88.41, H 7.67; found C 88.29, H 7.73.

Compound 15: A 1 M $LiAlH_4$ solution in THF (2.4 mL, 2.4 mmol) was added to a stirred solution of **14** (660 mg, 0.81 mmol) in dry THF (25 mL) at 0 °C. The resulting mixture was stirred for 3 h at 0 °C, then MeOH was carefully added. The resulting mixture was filtered (Celite). The solvent was then evaporated to give **15** (450 mg, 68%) as a pale yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.07 (s, 18 H, *t*Bu), 1.09 (s, 18 H, *t*Bu), 4.43 (s, 4 H, Ar-CH_2), 6.66 (m, 8 H, Ar-H), 6.80 (m, 16 H, Ar-H) ppm. $C_{60}H_{66}O_2$ (819.18): calcd. C 87.97, H 8.12; found C 87.75, H 8.43.

Compound 16: DCC (270 mg, 1.32 mmol) was added to a stirred solution of **15** (450 mg, 0.55 mmol), **11** (680 mg, 1.21 mmol), and DMAP (27 mg, 0.22 mmol) in CH_2Cl_2 (30 mL) at 0 °C. After 1 h, the mixture was allowed to slowly warm to room temperature (within 1 h), then stirred for 24 h, and filtered, and the solvent was then evaporated. Column chromatography (SiO_2; hexane/CH_2Cl_2, 1:1) yielded **16** (550 mg, 53%) as a yellow glassy product. IR (neat): $\tilde{\nu}$ = 1739 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, J = 7 Hz, 12 H, CH_3), 1.10 (s, 36 H, *t*Bu), 1.27 (m, 72 H, CH_2), 1.76 (m, 8 H, CH_2), 3.39 [s, 4 H, $CH_2(CO_2R)_2$], 3.91 (m, 8 H, OCH_2), 4.95 (s, 4 H, Ar-CH_2), 5.06 (s, 4 H, Ar-CH_2), 6.43 (m, 2 H, Ar-H), 6.64 (m, 4 H, Ar-H), 6.80 (m, 24 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 26.0, 26.9, 29.2, 29.3, 29.4, 29.55, 29.6, 29.65, 31.1, 31.9, 33.9, 34.0, 41.3, 67.0, 67.1, 68.0, 101.1, 106.4, 123.0, 123.2, 126.3, 130.9, 131.0, 131.7, 131.75, 137.2, 137.5, 137.7, 139.2, 140.3, 140.9, 141.0, 147.4, 147.6, 160.4, 166.0, 166.2 ppm. $C_{128}H_{178}O_{12}$ (1908.81): calcd. C 80.54, H 9.40; found C 80.25, H 9.40.

Compound 17: DBU (0.16 mL, 1.04 mmol) was added to a stirred solution of C_{60} (187 mg, 0.260 mmol), I_2 (145 mg, 0.57 mmol), and

16 (500 mg, 0.26 mmol) in toluene (500 mL) at room temperature. The solution was stirred for 12 h and then filtered through a short plug of SiO_2 (toluene then CH_2Cl_2). The solvent was then evaporated. Column chromatography (SiO_2; hexane/CH_2Cl_2, 3:2) followed by gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) yielded **17** (170 mg, 25%) as a dark brown glassy product. IR (CH_2Cl_2): $\tilde{\nu}$ = 1745 (C=O) cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 252 (220000), 320 (140000), 395 (sh., 8000), 408 (sh., 6000), 420 (4800), 475 (4900) nm. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7 Hz, 12 H, CH_3), 1.13–1.07 (m, 36 H, *t*Bu), 1.26 (m, 72 H, CH_2), 1.75 (m, 8 H, CH_2), 3.90 (t, J = 6 Hz, 8 H, OCH_2), 4.61 (d, J = 13 Hz, 1 H, Ar-CH), 4.95 (d, J = 13 Hz, 1 H, Ar-CH), 5.30 (AB, J = 13 Hz, 2 H, Ar-CH_2), 5.35 (AB, J = 13 Hz, 2 H, Ar-CH_2), 5.48 (d, J = 13 Hz, 1 H, Ar-CH), 5.52 (d, J = 13 Hz, 1 H, Ar-CH), 6.40 (t, J = 2 Hz, 1 H, Ar-H), 6.42 (t, J = 2 Hz, 1 H, Ar-H), 6.84–6.54 (m, 28 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.0, 26.1, 29.2, 29.25, 29.3, 29.4, 29.45, 29.6, 29.7, 31.1, 31.2, 31.9, 33.9, 34.0, 34.1, 51.4, 53.7, 67.0, 68.1, 68.7, 68.8, 70.2, 71.4, 71.4, 71.5, 101.6, 101.7, 106.8, 106.9, 122.9, 123.2, 124.1, 127.6, 127.9, 130.6, 130.7, 130.8, 130.9, 131.1, 131.4, 131.5, 131.9, 136.4, 136.5, 137.4, 137.5, 137.6, 138.5, 138.55, 138.6, 139.0, 139.2, 139.3, 140.1, 140.3, 140.5, 140.6, 140.8, 141.0, 141.3, 141.4, 141.6, 141.8, 142.0, 142.1, 142.2, 142.5, 142.7, 142.8, 142.9, 143.2, 143.4, 143.5, 143.6, 143.65, 143.7, 143.8, 143.9, 144.0, 144.2, 144.3, 144.5, 144.6, 144.65, 144.7, 144.8, 144.9, 144.95, 145.0, 145.05, 145.1, 145.4, 145.6, 145.9, 146.0, 146.2, 146.3, 146.35, 146.9, 147.1, 147.2, 147.4, 147.45, 147.6, 147.7, 148.5, 160.4, 162.9, 163.1, 163.3, 163.4 ppm. MALDI-MS: *m*/*z* = 2626 [M + H]$^+$. $C_{188}H_{174}O_{12}$ (2625.44): calcd. C 86.01, H 6.68; found C 85.69, H 6.69.

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