Electronic Supplementary Material for Chemical Communications

Synthesis and excited state properties of a [60]fullerene derivative bearing a star-shaped multi-photon absorption chromophore

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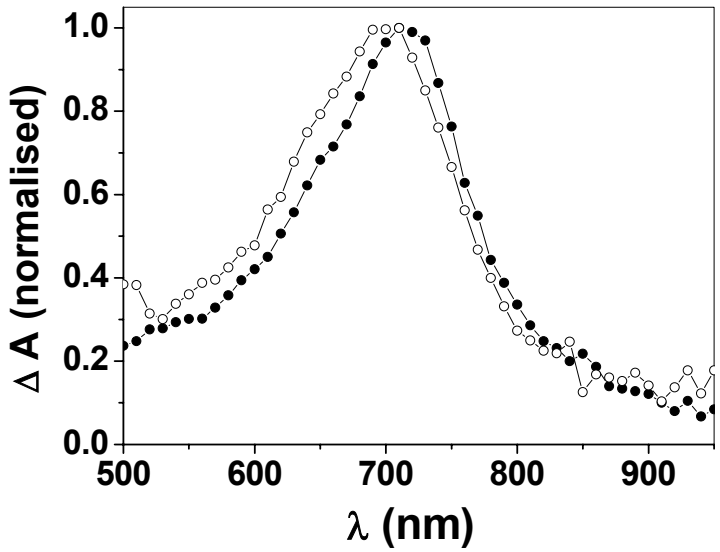


Figure S1. Transient absorption spectra recorded at 530 μs following laser excitation at 355 nm in toluene of fullerene reference compound **4** (●) and dyad **1** (○).

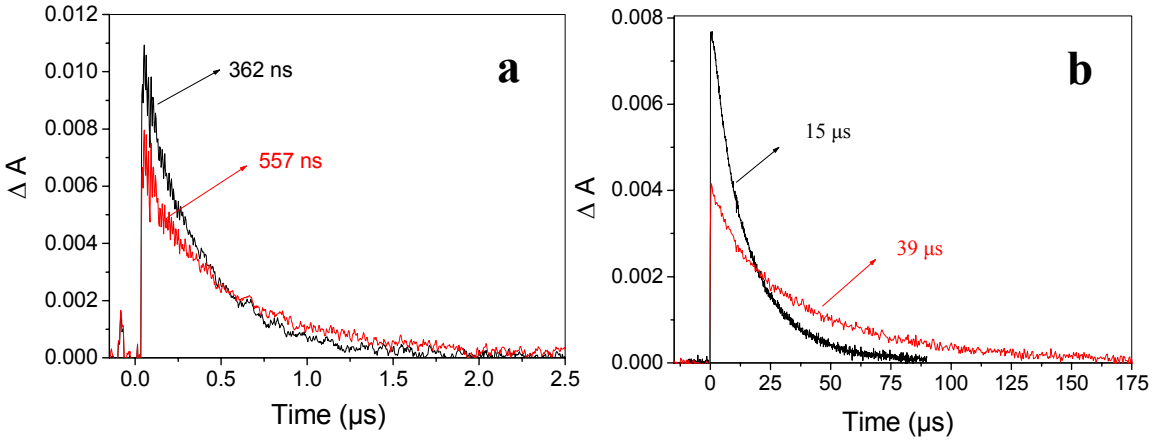


Figure S2. Transient absorption kinetics of fullerene reference compound **4** (black) and dyad **1** (red) recorded in aerated (a) and (b) deaerated toluene. λ_{ex} = 532 nm, λ_{em} = 900 nm (no ground state absorption).

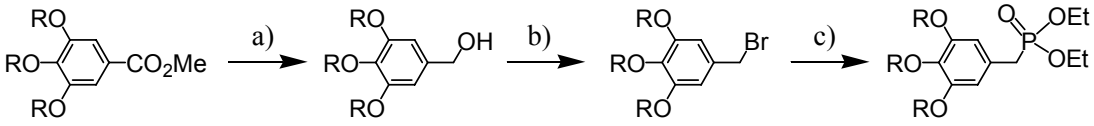
Model parameters for the fitting of the optical limiting behavior of 2 in Figure 3.
Ground state absorption: $\sigma^{(1)}= 2.19\ 10^{-19}$ cm^2; excited sate ES-TPA $\sigma^{(2)}= 1.58\ 10^{-43}$ cm^4 s ph^{-1} mol^{-1}; relaxation constant for the first excited state $k_1= 7.9\ 10^8$ s^{-1}; relaxation constant for the second excited state $k_2= 5.6\ 10^{13}$ s^{-1}.

Table S1 Values of the parameters of the fitting of the non linear absorption of **4** and **1.**

Compound	**4**	**1**
ground state absorption $\sigma_{GS}^{(1)}$/ cm^2	$7.0\ 10^{-18}$	$8.9\ 10^{-18}$
lowest triplet state absorption $\sigma_{T1}^{(1)}$/ cm^2	$1.58\ 10^{-17}$	$1.80\ 10^{-17}$
first triplet state absorption $\sigma_{T2}^{(1)}$/ cm^2	$1.58\ 10^{-15}$	$2.0\ 10^{-15}$
relaxation first singlet state k_{S1}/ s^{-1}	$1.58\ 10^{9}$	$1.6\ 10^{9}$
intersystem crossing k_{IC}/ s^{-1}	$9.0\ 10^{8}$	$9.98\ 10^{8}$
relaxation first triplet state k_{T1}/ s^{-1}	$3.16\ 10^{11}$	$2.0\ 10^{11}$
relaxation second triplet state k_{T2}/ s^{-1}	$1.0\ 10^{13}$	$1.0\ 10^{13}$
relaxation lowest triplet state k_{T0}/ s^{-1}	$1.0\ 10^{5}$	$1.0\ 10^{5}$

Experimental

General. All reagents were used as purchased from commercial sources without further purification. Compounds **3**,[1] **5**,[2] and **9**[3] have been prepared according to previously reported procedures. Solvents were dried using standard techniques prior to use. All reactions were performed in standard glassware under an inert argon atmosphere. Evaporation was done using water aspirator and drying *in vacuo* at 10^{-2} Torr. Column chromatography: Merck silica gel 60, 40-63 μm (230-400 mesh). TLC: Precoated glass sheets with silica gel 60 F_{254} (Merck), visualization by UV light. Melting points were determined on a Electrothermal Digital Melting Point apparatus and are uncorrected. UV/Vis spectra (λ_{max} in nm (ε)) were measured on a Hitachi U-3000 spectrophotometer. IR spectra (cm^{-1}) were determined on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AM 300 (300 MHz) with solvent signal as reference. FAB-mass spectra (*m/z*; % relative intensity) were taken on a *ZA HF* instrument with 4-nitrobenzyl alcohol as matrix. MALDI-TOF mass spectra were taken on a on a Brucker BIFLEX™ matrix-assisted laser desorption time-of-flight mass spectrometer (MALD-TOF) equipped with the SCOUT™ High Resolution Optics with a X-Y multi-sample probe and a gridless reflector, a saturated solution of 1, 8, 9– trihydroxyanthracene (dithranol ALDRICH EC: 214-538-0) in CH_2Cl_2 was used as a matrix.



5 R = $C_{12}H_{25}$ **6** R = $C_{12}H_{25}$ **7** R = $C_{12}H_{25}$ **8** R = $C_{12}H_{25}$

Scheme S1. Reagents and conditions: a) $LiAlH_4$, THF, 3 h, 94%; b) TMSBr, $CHCl_3$, 4 h, 99%; c) $P(OEt)_3$, Δ, 4 h, 81%.

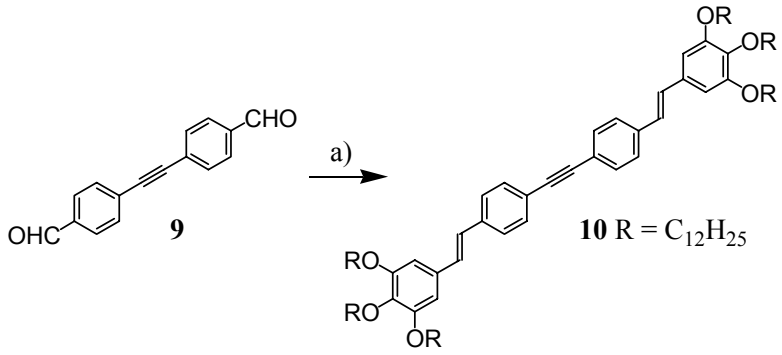
Compound **6**. A 1 M $LiAlH_4$ solution in THF (4.5 mL, 4.5 mmol) was added dropwise to a stirred solution of **5** (4.00 g, 5.81 mmol) in dry THF (30 mL) at 0°C. The resulting mixture was stirred for 3 h at 0°C, then MeOH was carefully added. The resulting mixture was filtered (Celite) and evaporated to

[1] D. Felder, M. Gutiérrez Nava, M. del Pilar Carreon, J.-F. Eckert, M. Luccisano, C. Schall, P. Masson, J.-L. Gallani, B. Heinrich, D. Guillon, J.-F. Nierengarten, *Helv. Chim. Acta* **2002**, *85*, 288.
[2] G. Zerban, H. Z. Meier, *Naturforsch. Teil B* **1993**, *48*, 171.
[3] M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth, P.A. Grieco, *Org. Let.* **2002***, 4,* 3199.

yield **6** (3.62 g, 94%) as a colorless solid. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.88 (m, 9H), 1.2-1.8 (m, 60H), 3.95 (m, 6H), 4.59 (s, 2H), 6.56 (s, 2H). Anal. calc. for $C_{43}H_{80}O_4$: C 78.12, H 12.20; found: C 78.34, H 12.41.

Compound **7**. TMSBr (0.9 mL, 6.56 mmol) was added dropwise to a stirred solution of **6** (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 **7** (3.90 g, 5.39 mmol, 99%) as a colorless solid. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.88 (m, 9H), 1.2-1.8 (m, 60H), 3.95 (m, 6H), 4.43 (s, 2H), 6.57 (s, 2H). Anal. calc. for $C_{43}H_{79}BrO_3$: C 71.34, H 11.00; found: C 71.45, H 10.98.

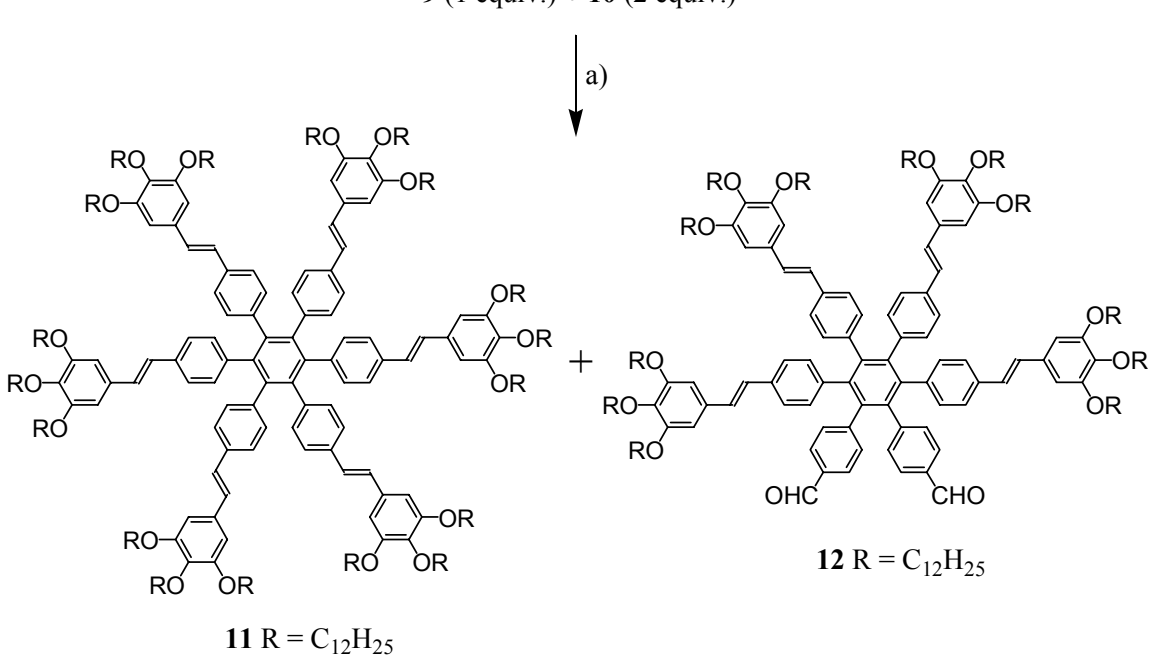
Compound **8**. A mixture of $P(OEt)_3$ (0.92 mL, 5.39 mmol) and **7** (3.90 g, 5.39 mmol) was heated at 150°C for 4 h. After cooling to room temperature, the mixture was dried under high vacuum. Column chromatography (SiO_2, CH_2Cl_2/MeOH 99:1) yielded **8** (3.40 g, 81%). Pale yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.88 (m, 9H), 1.2-1.8 (m, 60H), 3.04 (d, ^2J = 21 Hz, 2H), 3.94 (m, 10H), 6.49 (d, ^4J = 3 Hz, 2H). Anal. calc. for $C_{47}H_{89}PO_6$: C 72.26, H 11.48; found: C 72.36, H 11.59.



Scheme S2. Reagents and conditions: a) **8**, *t*-BuOK, THF, 4 h, 77%.

Compound **10**. A mixture of **9** (423 mg, 1.81 mmol), *t*-BuOK (447 mg, 3.98 mmol) and **8** (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 resulting mixture was concentrated. The aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with water, dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, hexane/CH_2Cl_2 1:1) gave **10** (2.08 g, 77%) as a pale yellow solid (mp. 85°C). UV/Vis (CH_2Cl_2): 229 (37600), 372 (92000). ^{1}H-NMR ($CDCl_3$, 300

MHz): 0.86 (m, 18H), 1.2-1.6 (m, 108H), 1.80 (m, 12H), 4.00 (m, 12H), 6.72 (s, 4H), 7.00 (AB, ^3J = 17 Hz, 4H), 7.47 (d, ^3J = 8 Hz, 4H), 7.51 (d, ^3J = 8 Hz, 4H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 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. Anal. calc. for $C_{102}H_{166}O_6$: C 82.31, H 11.24; found: C 82.32, H 11.32.



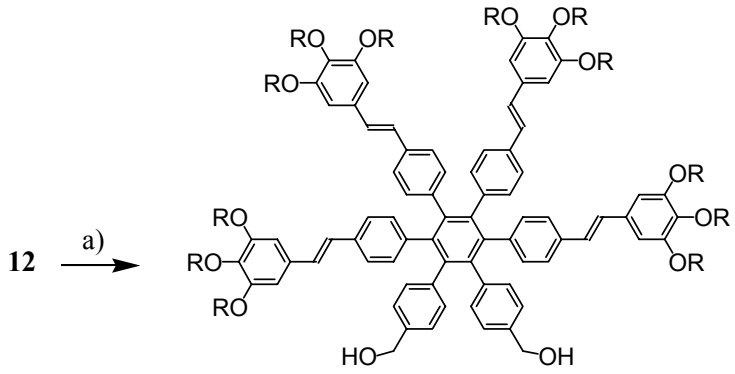
Scheme S3. Reagents and conditions: a) $Co_2(CO)_8$, dioxane, 20 h, **11**: 17%, **12**: 53%.

Compounds **11** and **12**. A mixture of $Co_2(CO)_8$ (21 mg, 0.061 mmol), **9** (111 mg, 0.47 mmol) and **10** (1.35 g, 0.91 mmol) in dry dioxane (25 mL) was stirred at room temperature for 17 h and evaporated. Two successive column chromatography (SiO_2) yielded **11** (CH_2Cl_2/hexane 1:1; 343 mg, 17%) and **12** (CH_2Cl_2/hexane 7:3; 770 mg, 53%).

11. Yellow solid (mp. 274°C). UV/Vis (CH_2Cl_2): 338 (172000). ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.88 (m, 54H), 1.1-1.6 (m, 324H), 3.94 (m, 36H), 6.59 (s, 12H), 6.79 (m, 24H), 7.00 (m, 12H). ^{13}C-NMR ($CDCl_3$, 50 MHz) : 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. MALDI-TOF MS: 4463 (MH^+, calc. for $C_{306}H_{499}O_{18}$: 4462.81). Anal. calc. for $C_{306}H_{498}O_{18}$: C 82.31, H 11.24; found: C 82.25, H 11.23.

12. Yellow glassy product. IR (neat): 1704 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.88 (m, 36H), 1.1-1.5 (m, 216H), 1.75 (m, 24H), 3.94 (m, 24H), 6.60 (s, 8H), 6.72 (d, ^3J = 17 Hz, 2H), 6.78 (AB, ^3J =

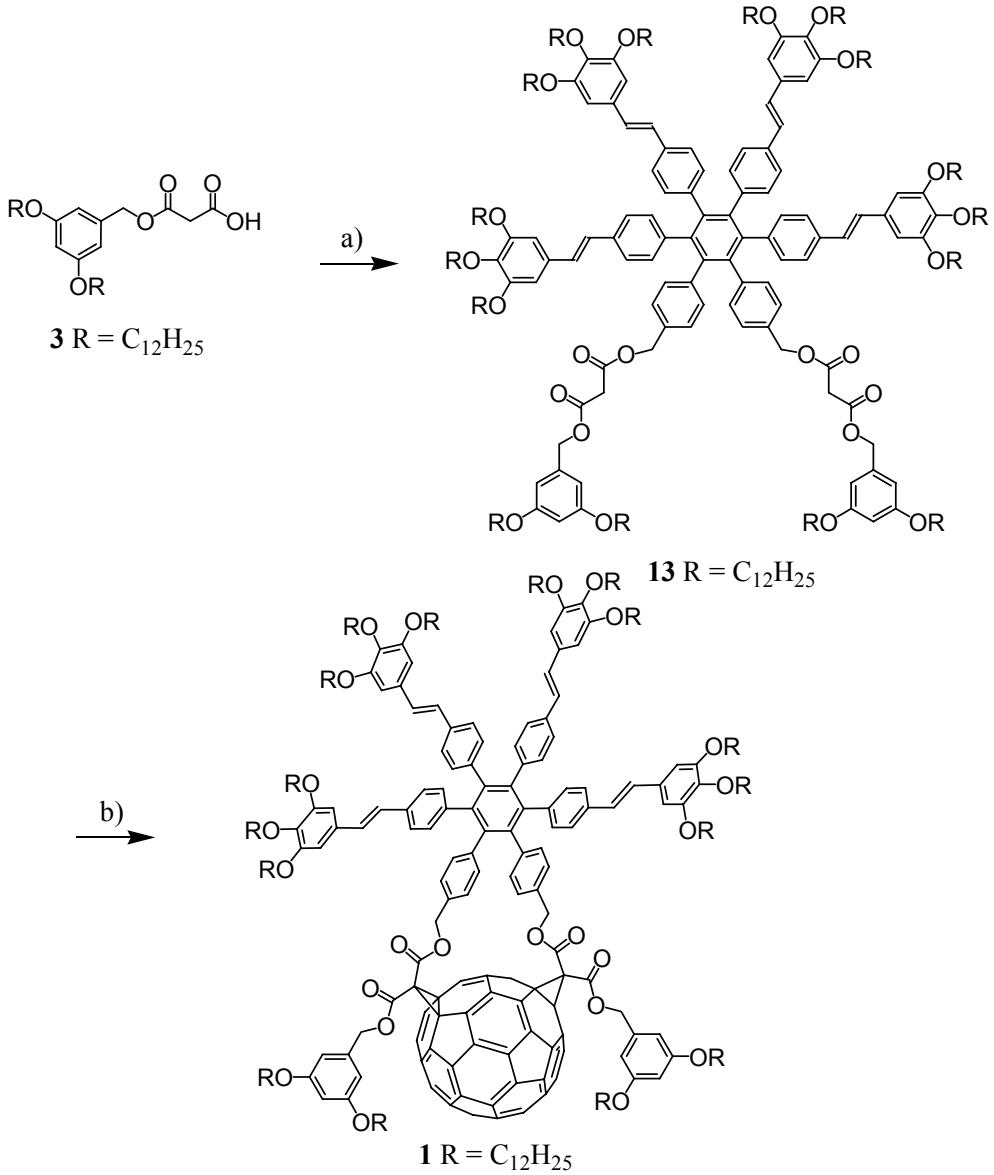
17 Hz, 4H), 6.80 (m, 8H), 6.2 (d, ^3J = 17 Hz, 2H), 7.05 (m, 12H), 7.41 (d, ^3J = 8 Hz, 4H), 9.78 (s, 2H). ^{13}C-NMR ($CDCl_3$, 300 MHz): 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 30.3, 32.0, 69.1, 73.5, 105.1, 125.1, 127.3, 127.5, 128.3, 128.4, 128.6, 131.5, 131.9, 132.4, 132.5, 133.7, 134.5, 134.7, 138.3, 138.7, 139.0, 139.1, 140.1, 141.0, 147.0, 153.2, 191.9. MALDI-TOF MS: 3210 (MH^+, calc. for $C_{220}H_{343}O_{14}$: 3209.61). Anal. calc. for $C_{220}H_{342}O_{14}$: C 82.29, H 10.74; found: C 82.45, H 11.01.



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

Scheme S4. Reagents and conditions: a) $LiAlH_4$, THF anhydre, 4 h, 76%.

Compound **2**. A 1 M $LiAlH_4$ solution in THF (0.6 mL, 0.6 mmol) was added to a stirred solution of **12** (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 evaporated. Column chromatography (SiO_2, CH_2Cl_2) gave **2** (560 mg, 76%) as a yellow glassy product. UV/Vis (CH_2Cl_2): 233 (106800), 338 (150200). ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.85 (m, 36H), 1.1-1.5 (m, 216H), 1.75 (m, 24H), 3.94 (m, 24H), 4.46 (s, 4H), 6.59 (m, 4H), 6.60 (s, 4H), 6.72 (d, ^3J = 17 Hz, 2H), 6.80 (m, 20H), 6.84 (d, ^3J = 17 Hz, 2H), (m, 8H). ^{13}C-NMR ($CDCl_3$, 300 MHz): 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. MALDI-TOF MS: 3214 (MH^+, calc. for $C_{220}H_{347}O_{14}$: 3213.64. Anal. calc. for $C_{220}H_{346}O_{14}$: C 82.19, H 10.85; found: C 82.25, H 11.11.



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

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

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

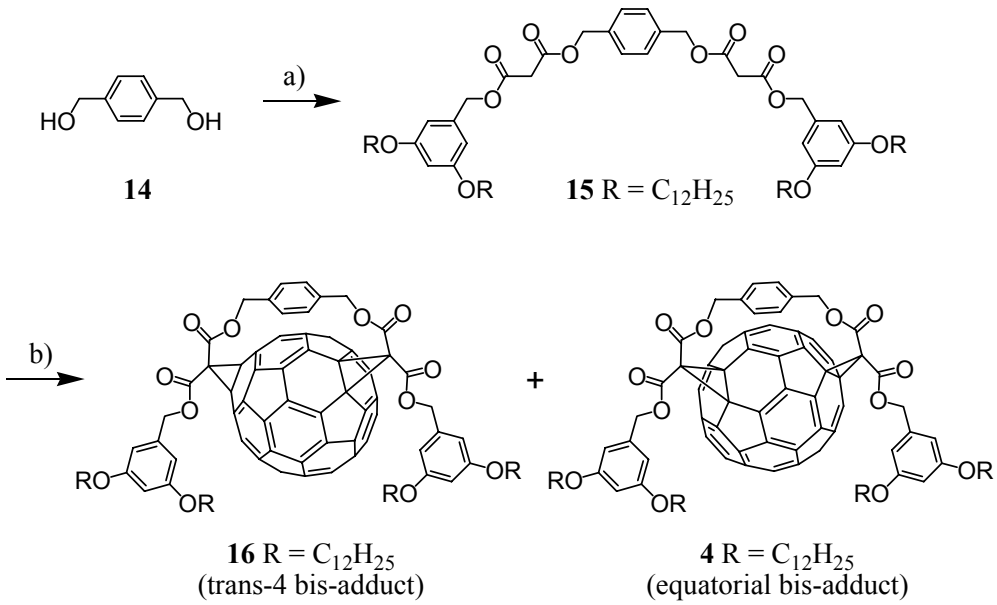
Scheme S5. Reagents and conditions: a) DCC, DMAP, CH_2Cl_2, 30 h, 75%; b) C_{60}, I_2, DBU, PhMe, 3 h, 32%.

Compound **13**. DCC (72 mg, 0.35 mmol) was added to a stirred solution of **2** (470 mg, 0.15 mmol), **3** (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, filtered and evaporated. Column chromatography (SiO_2, hexane/CH_2Cl_2 1:1) yielded **13** (470 mg, 75%) as a yellow glassy product. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.88 (m, 48H), 1.1-1.6 (m, 288H), 1.74 (m, 32H), 3.39

(s, 4H), 3.92 (m, 32H), 4.96 (s, 4H), 5.00 (s, 4H), 6.38 (s, 2H), 6.42 (s, 4H), 6.59 (s, 8H), 6.78 (m, 24H), 7.00 (2d, ^3J = 8Hz, 8H).

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 **13** (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 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): 1749 (C=O). UV/Vis (CH_2Cl_2): 228 (295900), 328 (196750). ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.88 (m, 48H), 1.1-1.6 (m, 288H), 1.75 (m, 32H), 3.93 (m, 32H), 4.90 (d, ^2J = 12 Hz, 1H), 5.10 (d, ^2J = 12 Hz, 1H), 5.34 (d, ^2J = 12 Hz, 1H), 5.40 (s, 2H), 5.50 (d, ^2J = 12 Hz, 1H), 5.60 (d, ^2J = 12 Hz, 1H), 5.65 (d, ^2J = 12 Hz, 1H), 6.3-7.1 (m, 46H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.08, 14.11, 22.68, 26.07, 26.14, 29.24, 29.28, 29.36, 29.41, 29.44, 29.46, 29.64, 29.69, 30.34, 31.92, 68.14, 69.16, 73.45, 101.68, 105.06, 105.11, 106.99, 124.91, 127.62, 128.03, 128.12, 131.03, 131.24, 131.45, 131.61, 131.99, 132.09, 132.54, 134.18, 136.43, 136.46, 138.23, 138.28, 138.55, 139.18, 139.33, 139.48, 139.64, 140.21, 140.31, 140.68, 141.47, 141.69, 141.90, 142.17, 142.65, 142.68, 142.91, 142.95, 143.36, 143.45, 143.59, 143.61, 143.72, 143.79, 144.00, 144.06, 144.27, 144.41, 144.61, 144.71, 144.81, 144.94, 145.02, 145.18, 145.49, 145.66, 146.03, 146.14, 146.27, 146.37, 146.96, 147.20, 148.54, 153.22, 153.52, 160.47, 163.00, 163.14, 163.32, 163.38. MALDI-TOF MS: 5021 (M^+, calc. for $C_{348}H_{454}O_{24}$: 5021.42). Anal. calc. for $C_{348}H_{454}O_{24}$: C 83.24, H 9.11; found: C 82.99, H 9.41.

Compound **15**. DCC (1.61 g, 7.78 mmol) was added to a stirred solution of **3** (4.27 g, 7.60 mmol), **14** (500 mg, 3.62 mmol) and DMAP (120 mg, 1.09 mmol) in CH_2Cl_2 (100 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, filtered and evaporated. Column chromatography (SiO_2, hexane/CH_2Cl_2 1:1) yielded **15** (2.14 mg, 48%) as a colorless glassy product. IR (CH_2Cl_2): 1753 (C=O). ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.89 (m, 12H), 1.27 (m, 72H), 1.76 (m, 8H), 3.48 (s, 4H), 3.92 (t, ^3J = 6.5 Hz), 5.10 (s, 4H), 5.17 (s, 4H), 6.41 (t, ^4J = 2 Hz, 2H), 6.47 (d, ^4J = 2 Hz, 4H), 7.33 (s, 4H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.09, 22.65, 26.02, 29.21, 29.32, 29.60, 31.87, 41.43, 66.76, 67.3, 68.03, 101.10, 106.40, 128.42, 135.44, 137.10, 160.43, 166.13. Anal. calc. for $C_{76}H_{122}O_{12}$: C 74.35, H 10.02; found: C 74.30, H 10.11.



Scheme S6. Reagents and conditions: a) DCC, DMAP, CH_2Cl_2, 26 h, 48%; b) C_{60}, I_2, DBU, PhMe, 3 h, **16**: 43%, **4**: 16%.

Compounds **4** and **16**. DBU (0.2 mL, 1.39 mmol) was added to a stirred solution of C_{60} (200 mg, 0.28 mmol), I_2 (178 mg, 0.70 mmol) and **13** (375 mg, 0.31 mmol) in toluene (500 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 evaporated. Column chromatography (SiO_2) yielded **4** (hexane/CH_2Cl_2 1:1; 89 mg, 16%) and **16** (CH_2Cl_2/hexane 1:1; 232 mg, 43%).

4. Dark red glassy product. IR (CH_2Cl_2): 1749 (C=O). UV/Vis (CH_2Cl_2): 252 (158900), 306 (72000), 357 (26800), 395 (8500), 408 (5700), 420 (4800), 474 (5600). ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.88 (m, 12H), 1.1-1.6 (m, 72H), 1.79 (m, 8H), 3.92 (t, ^3J = 6.5 Hz, 4H), 3.96 (t, ^3J = 6.5 Hz, 4H), 4.89 (d, ^2J = 12 Hz, 1H), 5.08 (d, ^2J = 12 Hz, 1H), 5.38 (AB, ^2J = 12 Hz, 2H), 5.45 (AB, ^2J = 12 Hz, 2H), 5.74 (d, ^2J = 12 Hz, 1H), 5.86 (d, ^2J = 12 Hz, 1H), 6.41 (t, ^4J = 2 Hz, 1H), 6.46 (t, ^4J = 2 Hz, 1H), 6.58 (d, ^4J = 2 Hz, 2H), 6.60 (d, ^4J = 2 Hz, 2H), 6.93 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1H), 7.04 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1H), 7.62 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1H), 7.66 (dd, ^3J = 7 Hz, ^4J = 2 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 14.12, 22.68, 26.09, 29.25, 29.35, 29.41, 29.61, 29.66, 31.90, 51.95, 52.68, 68.11, 68.63, 68.87, 70.39, 70.71, 70.91, 71.77, 101.38, 101.51, 106.53, 106.78, 128.53, 130.00, 130.19, 132.65, 135.28, 136.46, 136.72, 137.33, 138.09, 138.31, 139.11, 140.90, 140.96, 141.09, 141.34, 141.51, 141.60, 141.79, 142.02, 142.17, 142.24, 142.65, 142.82, 142.88, 142.94, 143.04, 143.20, 143.38, 143.45, 143.53, 143.61, 143.89, 144.03, 144.30, 144.41, 144.59, 144.70, 144.77, 145.37, 145.49, 145.72, 145.88, 145.97, 146.32, 146.39, 146.45, 146.64, 147.15, 160.48, 162.28, 162.79, 163.50. FAB MS:

1944 (MH^+, calc. for $C_{136}H_{119}O_{12}$: 1943.87). Anal. calc. for $C_{136}H_{118}O_{12}$: C 84.01, H 6.12; found: C 83.99, H 6.39.

16. Dark brown glassy product. IR (CH_2Cl_2): 1749 (C=O). UV/Vis (CH_2Cl_2): 314 (61500), 416 (6650), 466 (4100), 631 (900), 696 (560). ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.89 (m, 12H), 1.1-1.6 (m, 72H), 1.79 (m, 8H), 3.97 (t, ^3J = 6.5 Hz, 8H), 5.03 (d, ^2J = 12 Hz, 2H), 5.46 (s, 4H), 6.02 (d, ^2J = 12 Hz, 1H), 6.48 (t, ^4J = 2 Hz, 2H), 6.64 (d, ^4J = 2 Hz, 4H), 7.19 (broad s, 2H), 7.37 (broad s, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz):14.12, 22.68, 26.11, 29.28, 29.35, 29.44, 29.63, 31.90, 48.91, 68.16, 68.28, 68.80, 70.39, 70.68, 101.67, 106.71, 130.53, 131.45, 131.81, 135.73, 136.49, 138.35, 140.87, 140.98, 141.06, 141.16, 141.35, 141.41, 141.92, 142.08, 142.21, 142.72, 142.92, 143.10, 144.09, 144.29, 144.70, 145.02, 142.11, 145.28, 145.72, 145.91, 146.34, 146.90, 148.15, 160.54, 163.69, 163.91. FAB MS: 1944 (MH^+, calc. for $C_{136}H_{119}O_{12}$: 1943.87). Anal. calc. for $C_{136}H_{118}O_{12}$: C 84.01, H 6.12; found: C 84.15, H 6.11.