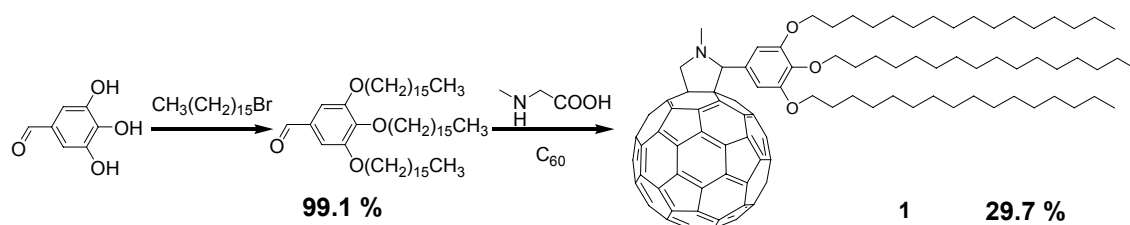


Supplementary Information

Hierarchical Supramolecular Fullerene Architectures with Controlled Dimensionality

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(A) Synthesis



Synthesis of 3,4,5-Trihexadecyloxybenzaldehyde. A mixture of 3,4,5-trihydroxybenzaldehyde (430 mg, 2.5 mmol), hexadecyl bromide (4.58 g, 15 mmol), K_2CO_3 (1.04 g, 7.5 mmol), KI (25 mg), and 15 mL of DMF was stirred at 70 °C for 14 hours. The reaction mixture was cooled to room temperature and mixed with water. The resulting aqueous layer was extracted with CHCl_3 . The organic layers were combined, then washed with brine and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the resulting crude product was purified by column chromatography (silica gel, eluent CHCl_3/n -hexane = 2/3) followed by recrystallization from $\text{CHCl}_3/\text{MeOH}$. The product was obtained as a white solid (2.05 g, 2.48 mmol, 99.1%).

^1H NMR (300 MHz, CDCl_3 , 20 °C, TMS): δ 9.83 (s, 1H), 7.08 (s, 2H), 4.06 (t, 2H, J = 6.6 Hz), 4.03 (t, 4H, J = 6.4 Hz), 1.87-1.70 (m, 6H), 1.47-1.26 (m, 78H), 0.88 (t, 9H, J = 6.8 Hz). FABMS: calcd for $\text{C}_{55}\text{H}_{102}\text{O}_4$ 826.8; found 827.9 [$\text{M}+\text{H}$]. Elemental analysis: calcd (%) for $\text{C}_{55}\text{H}_{102}\text{O}_4$; C 79.84, H 12.34; found C 79.64, H 12.48.

Synthesis of $\text{C}_{60}\text{Ph}_3,4,5\text{O}_3\text{C}_{16}$ (1**).** Dry toluene (800 mL), the benzaldehyde (827 mg, 1.0 mmol) from the previous reaction, C_{60} (720 mg, 1.0 mmol) and N -methylglycine (445

mg, 5.0 mmol) was refluxed for 21 hours. After cooling, the reaction mixture was chromatographed on silica gel with toluene then toluene/*n*-hexane (1/1) as eluent. The crude product was purified by recrystallization from 1,4-dioxane giving the desired product **1** (468 mg, 0.297 mmol, 29.7 %).

¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): δ 7.24-6.80 (br, 2H), 4.98 (d, 1H, *J* = 9.2 Hz), 4.81 (s, 1H), 4.24 (d, 1H, *J* = 9.4 Hz) 3.95 (m, 6H), 2.85 (s, 3H), 1.69 (m, 6H), 1.41-1.24 (m, 78H), 0.88 (t, 9H, *J* = 7.1 Hz). ¹³C NMR (75 MHz, CDCl₃, 20 °C, TMS): δ 156.2, 154.15, 153.97, 153.5, 147.37, 147.36, 147.08, 146.52, 146.37, 146.26, 146.20, 146.12, 146.00, 145.98, 145.81, 145.59, 145.55, 145.37, 145.31, 145.28, 145.21, 144.74, 144.73, 144.43, 143.20, 143.02, 142.74, 142.63, 142.61, 142.27, 142.19, 142.15, 142.11, 142.05, 141.91, 141.86, 141.71, 141.62, 140.24, 140.13, 139.70, 138.54, 136.61, 136.22, 135.79, 131.88, 83.74, 73.30, 70.07, 69.43, 68.98, 40.11, 31.96, 30.33, 29.75, 29.70, 29.64, 29.47, 29.40, 29.32, 26.13, 26.08, 22.72, 14.13, 14.11. IR (KBr, cm⁻¹): 2918.8, 2850.3, 2777.0, 1587.2, 1114.7. UV-vis (*n*-hexane, 1.0 × 10⁻⁵ M): λ_{max} (ε, mol⁻¹dm³cm⁻¹) = 210 (186605), 254.5 (130666), 309 (43051), 430 (5017), 701.5 (461). MALDI-TOF-MS (matrix, 2-Amino-5-nitropyridine): calcd for C₁₁₇H₁₀₇O₃N 1174.83; found 1174.96 [M⁺]. Elemental analysis: calcd (%) for C₁₁₇H₁₀₇O₃N·0.5H₂O: C 88.71, H 6.87, N 0.88; found C 88.68, H 7.02, N 0.85.

(B) Measurements

¹H and ¹³C NMR spectra were recorded at 20 °C on a JEOL model AL300, operating at 300 MHz and 75 MHz, respectively. FABMS spectra were recorded on a JEOL JMS-700. MALDI-TOF-MS spectra were recorded on an Applied Biosystems model Voyager-DE STR in reflector mode. UV-visible absorption spectra were recorded with a JASCO model V-570 UV/VIS/NIR spectrophotometer. FT-IR spectra were recorded on a NICOLET NEXUS 670FT-IR spectrometer. SEM images were obtained with a HITACHI S-4800 scanning electron microscope at acceleration voltages of 5 – 10 kV. Silicon (100) was used as substrate and a platinum coating was applied using a HITACHI E-1030 Ion Sputterer. TEM and HR-TEM images were obtained with JEOL model JEM-1010 and JEM-2100F transmission electron microscopes, respectively. One drop of a solution of the supramolecular objects was deposited on a carbon coated copper grid (Ouken Shoji, Elastic Carbon coated Cu 200-A mesh), left to dry under high vacuum, and the observation was performed at room temperature at voltages of 100 kV (TEM) and 200 kV (HR-TEM). No staining was used. AFM measurements were carried out using an SII E-Sweep with an SPI 4000 Probe Station in dynamic force mode (tapping mode). One

drop of a 1,4-dioxane solution of single bilayer disks was spin-coated on silicon (100) substrate with $r = 1200$ rpm. XRD measurements were examined using a RIGAKU RINT Ultima III X-ray diffractometer. DSC measurements were carried out using an SII DSC 6220 with an SII EXSTAR 6000 PC Station. All measurements were performed at 20.0 ± 0.5 °C.

(C) Additional data

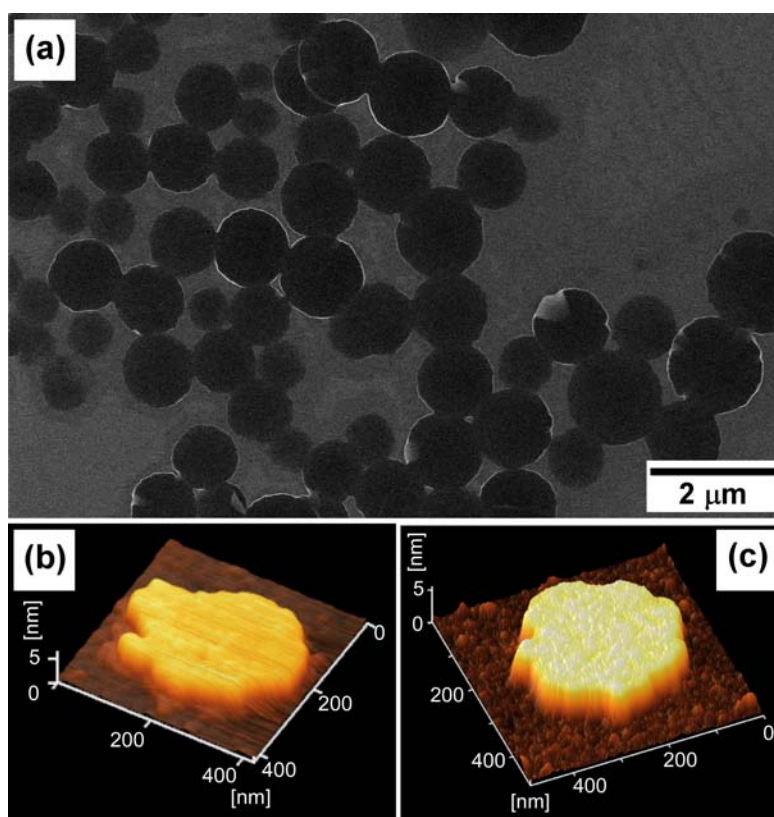


Figure S1. SEM (a) and AEM (b,c) images of single bilayer nano-disks of **1** from 1,4-dioxane at 20 °C. The top image proves the uniformity and high yield of the nano-disks.

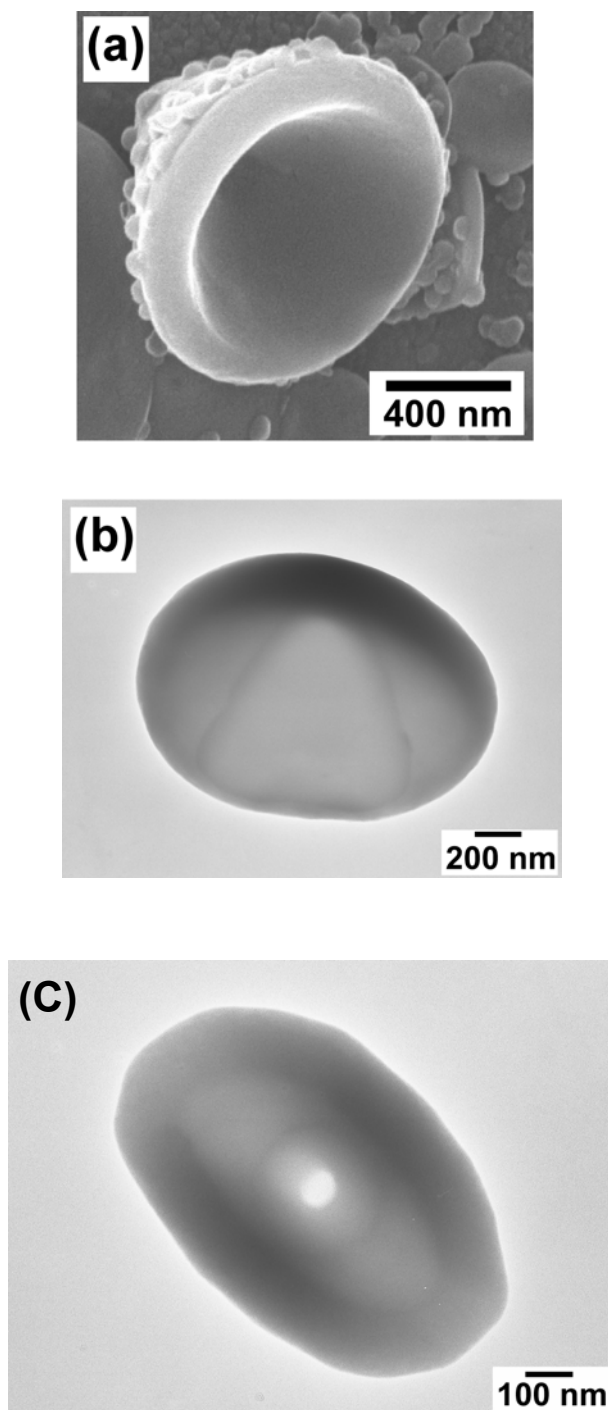


Figure S2. SEM (a) and TEM (b, c) images of conical objects of **1** from THF/H₂O (1/1) at 20 °C. These images prove the reproducibility of the nanostructures. The tip of the cone has a hole with a diameter of ca. 60 nm (c).

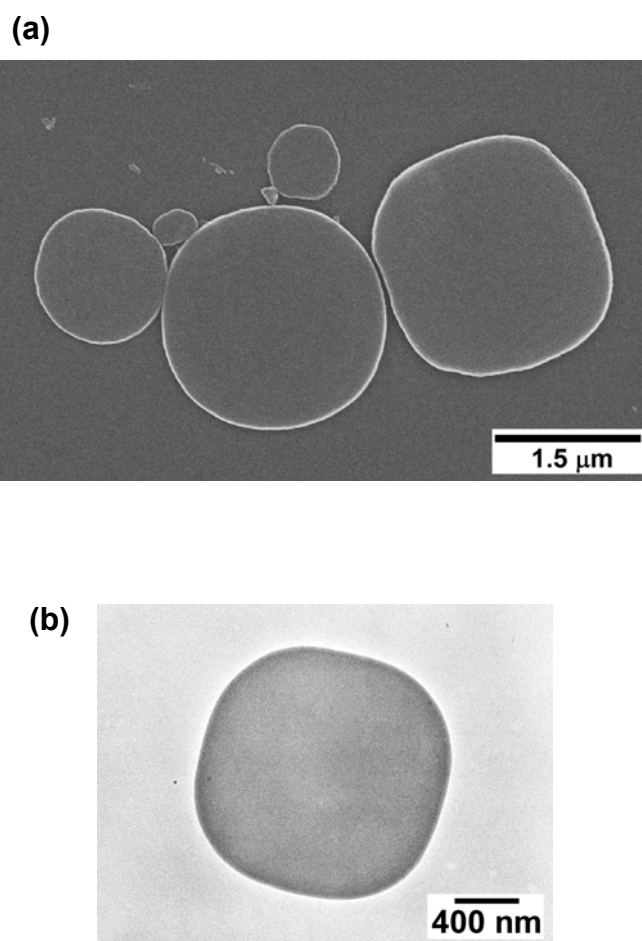


Figure S3. SEM (a) and TEM (b) images of disk-like sheets of **1** from mixture of THF/H₂O (1/1) at 20 °C.

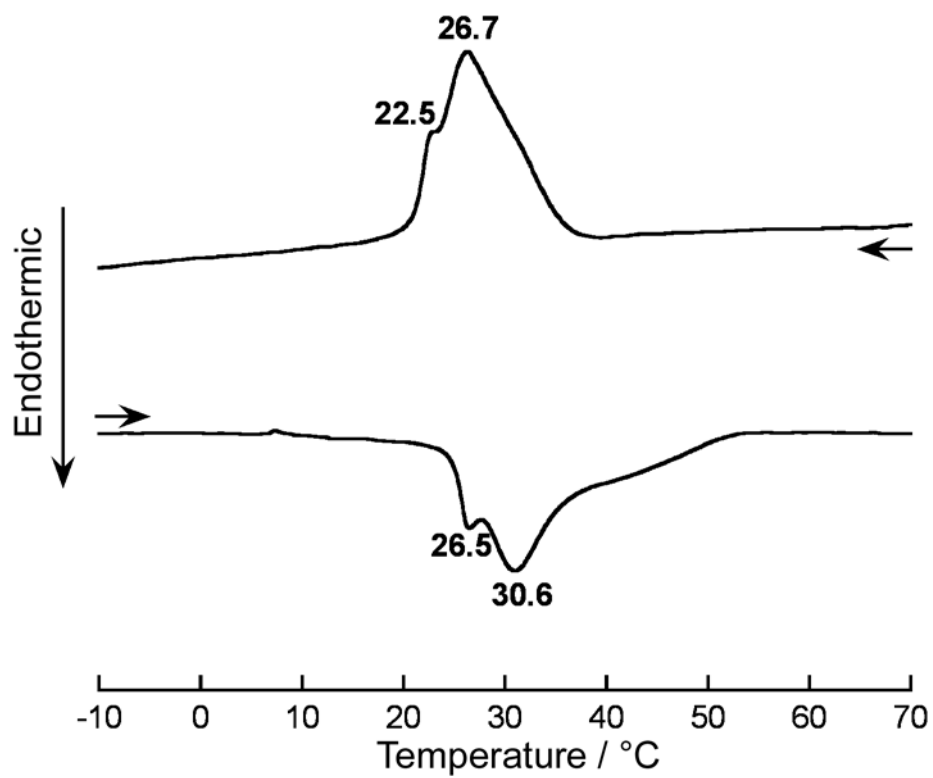


Figure S4. DSC heating and cooling traces of **1**.