Electronic Supplementary Information

Aromatic single-walled organic nanotubes self-assembled from *NH*-bridged azacalix[2]triptycene[2]pyridine

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Contents

1. Synthesis of *NH*-bridged azacalix[2]triptycene[2]pyridine

General methods: Melting points, taken on an electrothermal melting point apparatus, are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a DMX300 NMR. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. Elemental analyses were performed by the Analytical Laboratory of Institute of Chemistry, CAS. Materials obtained commercially were used without further purification.

***NH*-bridged azacalix[2]triptycene[2]pyridine (1):** By the coupling reaction of 3,5-dicyano-2,6-dichloropyridine (40 mg, 0.2 mmol) and 2,7-diaminotriptycene (57 mg, 0.2 mmol) in dry acetonitrile (30 mL) in the presence of DIPEA (66 mg, 0.5 mmol) under a dry argon atmosphere, after refluxing for 7 days, the product **1** (26 mg, 16%) was obtained via a silica gel column with ethyl acetate/dichloromethane (1:30, v/v) as the eluent. Mp > 300 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.37 (s, 2H), 5.51 (s, 2H), 6.95-7.03 (m, 4H), 7.08 (s, 4H), 7.15 (d, J = 7.9 Hz, 4H), 7.42 (d, J = 7.9 Hz, 4H), 7.36-7.46 (m, 4H), 8.22 (s, 2H), 9.24 (s, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 51.9, 52.4, 81.9, 116.2, 118.9, 122.0, 122.6, 123.3, 123.4, 124.8, 124.9, 133.9, 141.3, 144.5, 145.2, 145.7, 149.0, 156.7. IR (KBr, cm^{-1}): 2212.0, 3300.6, 3403.7. MALDI TOF-MS: *m/z* 819.6 $[M+H]^+$, 841.5 $[M+Na]^+$, 857.5 $[M+K]^+$. Anal. Calcd for $C_{54}H_{30}N_{10}$: C, 79.20; H, 3.69; N, 17.10. Found: C, 79.32; H, 3.61; N, 17.07.

2. ^{1}H NMR and ^{13}C NMR spectra of 1

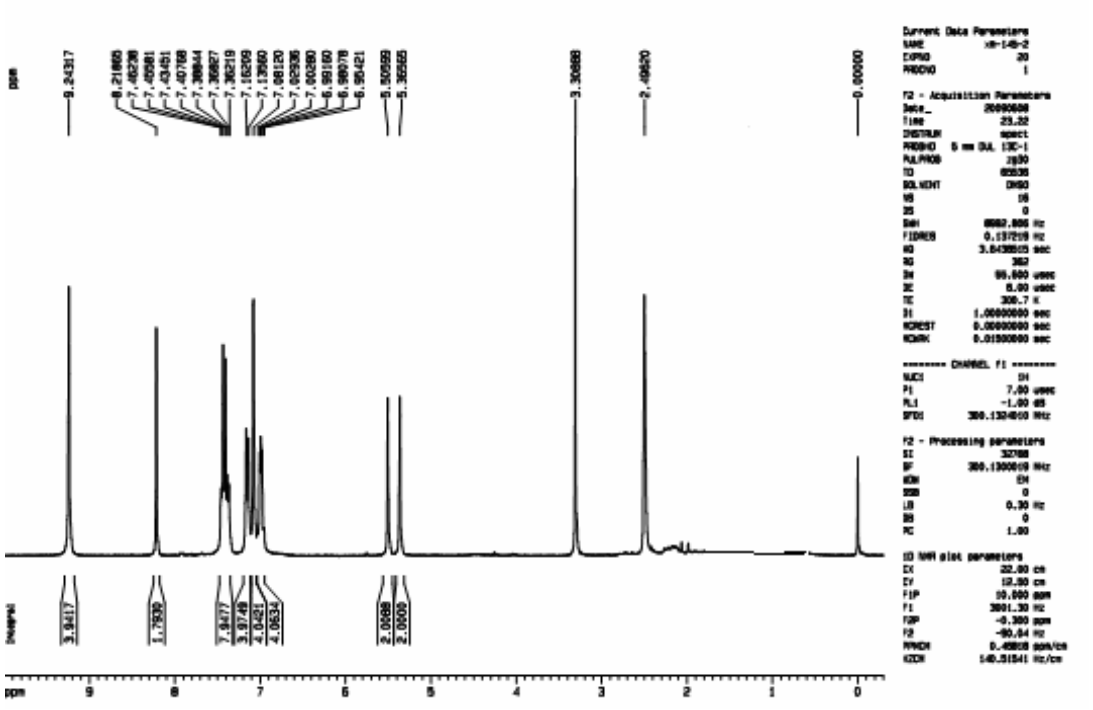

Figure S1. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1**.

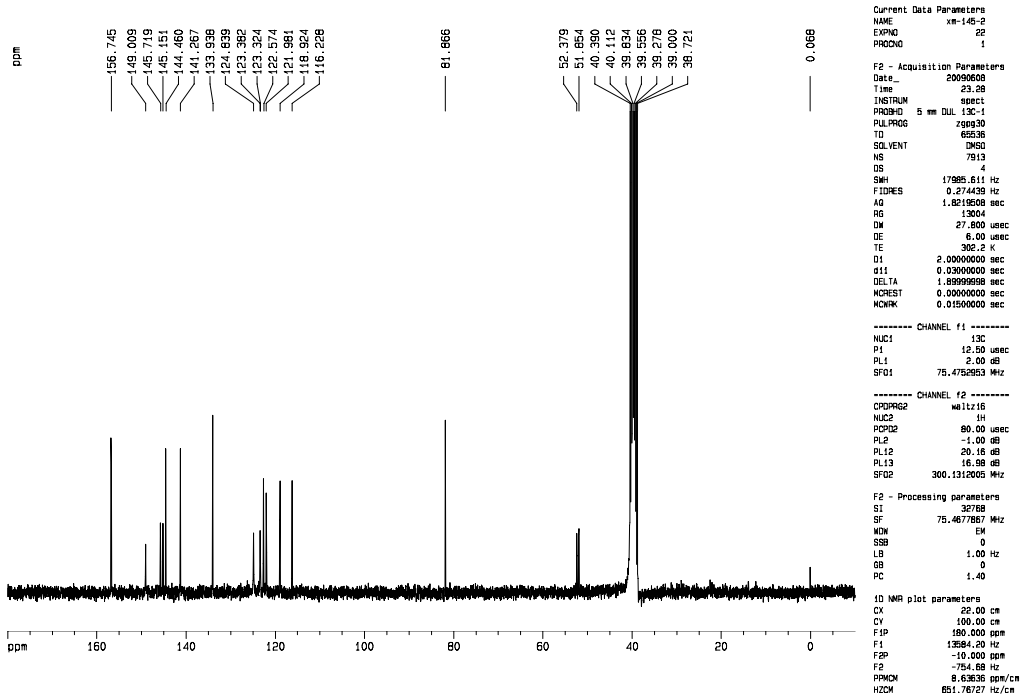

Figure S2. ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of **1**.

3. X-ray crystal structures and/or packing of 1

Data for structure **1** were collected on a Rigaku Saturn724 CCD X-ray diffractometer with graphite-monochromator Mo-Kα radiation (λ = 0.71073 Å) at 173 K. Intensities were corrected for absorption effects using the multi-scan technique. The structures were solved by direction methods and refined by a full matrix least squares technique based on F^2 using SHELXL 97 program. All non-hydrogen atoms were refined anisotropically and H atoms were placed in calculated positions and refined using the riding model. Data for **1** were given three times, **1-1** (CCDC 742049) is depicted in article with the solvents of THF-methanol squeezed, **1-2** (CCDC 742050) is described here within disordered solvents of THF-methanol, and **1-3** (CCDC 798301) is also described here within disordered solvents of acetone-methanol.

Crystallographic data for **1** with solvents of THF-methanol: $C_{81}H_{45}N_{15}O_5$, M_r = 1308.32, 0.52 × 0.14 × 0.14 mm^3, triclinic, a = 17.478(4), b = 20.112(4), c = 22.165(4) Å, α = 65.87(3), β = 80.27(3), γ = 79.76(3), V = 6957(2) Å^3, space group *P-1*, Z = 4, ρ_{calcd} = 1.249, $\lambda(Mo_{Ka})$ = 0.71073 Å, T = 173(2) K, 71381 reflections, 24494 unique (19000 observed, R_{int} = 0.074), R_1 = 0.1474, wR_2 = 0.3829.

Crystallographic data for **1** with solvents of acetone-methanol: $C_{115.04}H_{99.74}N_{20}O_{12.82}$, M_r = 1967.42, 0.10 × 0.08 × 0.04 mm^3, triclinic, a = 17.445(4), b = 20.049(4), c = 22.132(4) Å, α = 65.99(3), β = 79.88(3), γ = 79.54(3), V = 6909(2) Å^3, space group *P-1*, Z = 2, ρ_{calcd} = 0.946, $\lambda(Mo_{Ka})$ = 0.71073 Å, T = 113(2) K, 48620 reflections, 24235 unique (16236 observed, R_{int} = 0.0563), R_1 = 0.0998, wR_2 = 0.3227.

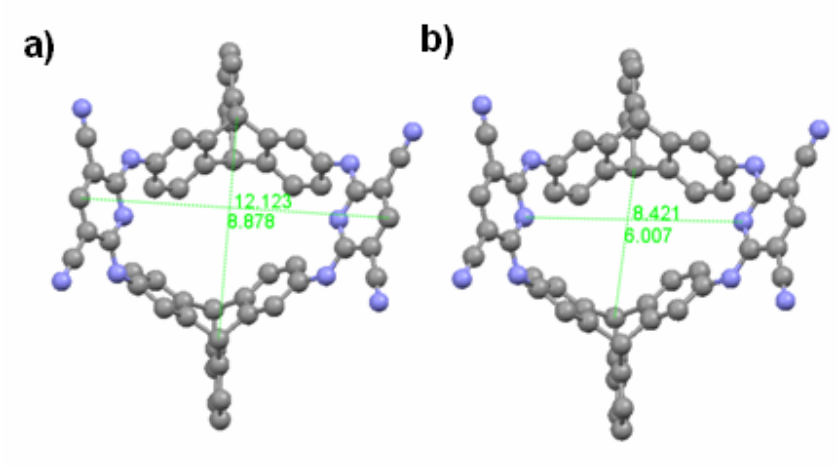

Figure S3. Crystal structure of **1A** showing (a) 8.81×12.84 Å of the upper rim, and (b) 6.17×8.67 Å of the lower rim.

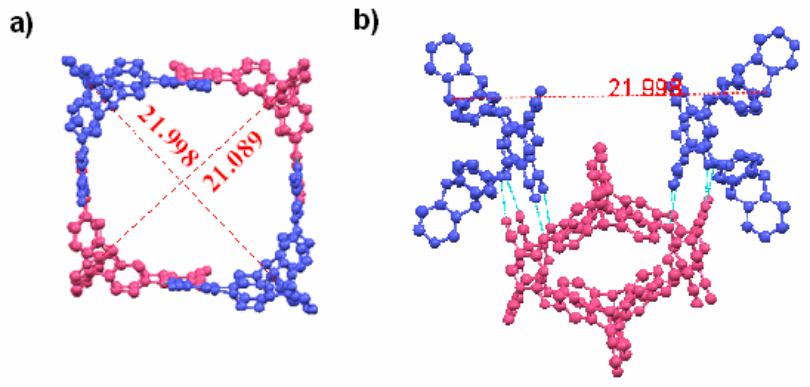

Figure S4. (a) Top view and (b) side view of the tetramer showing the diagonal length.

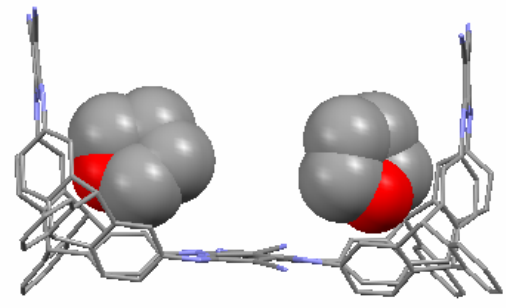

Figure S5. Crystal structure of host **1** and THF guest.

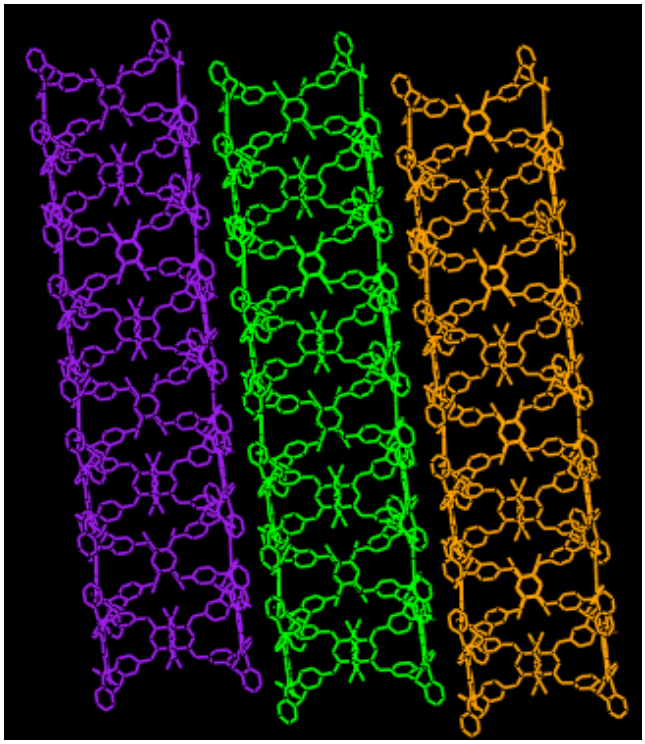

Figure S6. Self-assembled organic nanotubes viewed along the crystallographic *b* axis.

Hydrogen atoms are omitted for clarity.

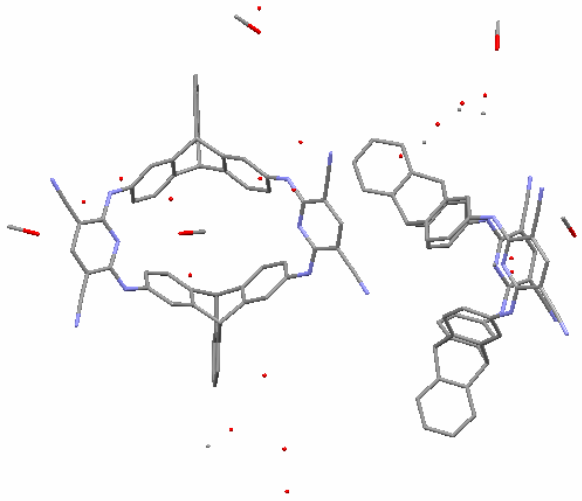

Figure S7. Crystal structure of host **1** and disordered acetone-methanol.