Electronic Supplementary Information

Triptycene-derived oxacalixarene with expanded cavity: synthesis, structure and its complexation with fullerenes C_{60} and C_{70}

Shu-Zhen Hu and Chuan-Feng Chen*

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

E-mail: cchen@iccas.ac.cn

Content

1. Synthesis and characterization data of macrocycle 1

Under an argon atmosphere, a mixture of 2,7-dihydroxytriptycene (143 mg, 0.5 mmol), 2,7-Dichloro-1,8-naphthyridine (100 mg, 0.5 mmol), Cs_2CO_3 (488 mg, 1.5 mmol) in dry 1,4-dioxane (250 ml, 0.002 M) was stirred at reflux temperature for 48 h. The mixture was cooled down to room temperature and the solvent was completely removed. The crude residue was redissolved in a mixture of CH_2Cl_2 and water. The organic fraction was separated, washed with water, brine, dried over Na_2SO_4, filtered and evaporated to dryness. Purification by column chromatography over silica gel (200-300 mesh) (eluent: 1:100 ethyl acetate/CH_2Cl_2) afford **1** (76 mg, 37%) as a white solid. Mp: > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.23 (s, 2H), 5.41 (s, 2H), 6.94-7.00 (m, 16H), 7.30-7.37 (m, 8H), 8.00 (d, J = 8.7 Hz, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 163.5, 153.3, 150.6, 146.6, 145.8, 145.1, 141.3, 140.9, 125.1, 124.9, 124.3, 123.7, 123.4, 117.2, 116.6, 116.1, 112.2, 52.1, 51.4.

MALDI-TOF MS: *m/z* 825.5 $[M+H]^+$, 847.5 $[M+Na]^+$, 863.4 $[M+K]^+$. Anal. Calcd for $C_{56}H_{32}N_4O_4 \cdot 2CH_2Cl_2 \cdot 0.5H_2O$: C 69.40, H 3.72, N 5.58; found C 69.66, H 3.81, N 5.59.

2. Variable-temperature ^{1}H NMR experiments of macrocycle 1

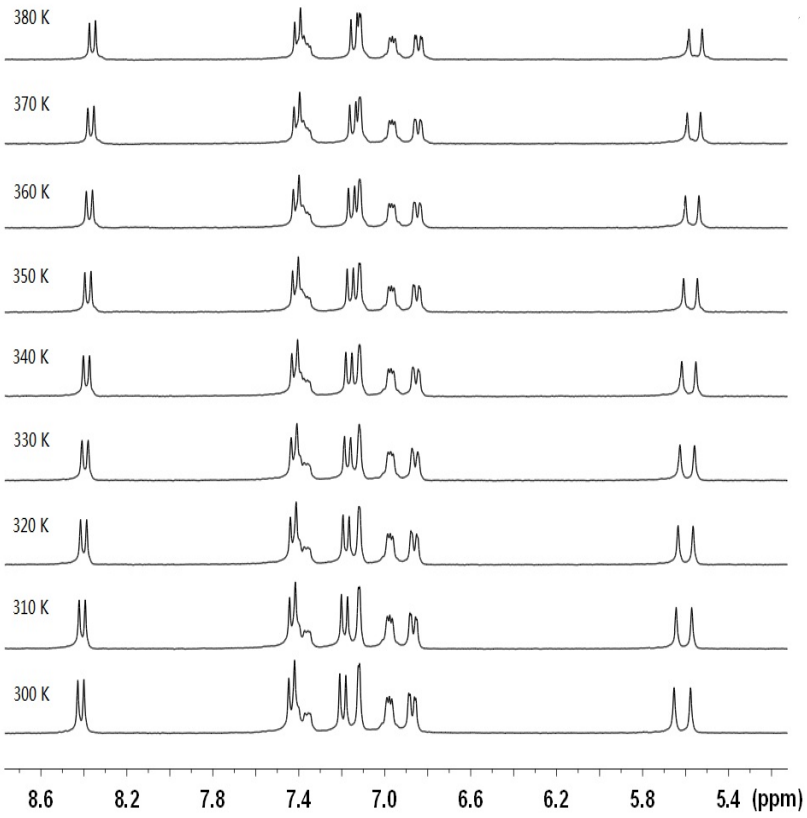

Fig. S1 Partial ^{1}H NMR spectra of **1** (DMSO-d_6, 300 MHz) at various temperatures.

3. Job plot for the complex 1•C_{60}

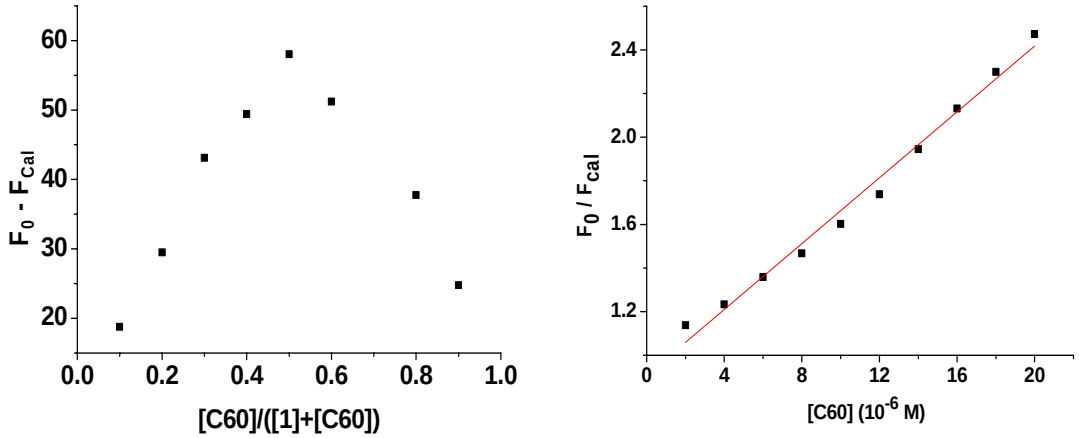

Fig. S2 Left: the Job plot for the complex **1**•C_{60} in toluene solution ([**1**]+[C_{60}]= 2×10^{-5} mol dm^{-3}). Right: the variation of fluorescence intensity F_0/F_{cal} of **1** with increasing C_{60} concentration.

4. Fluorescence titration spectra of 1 with C_{70}

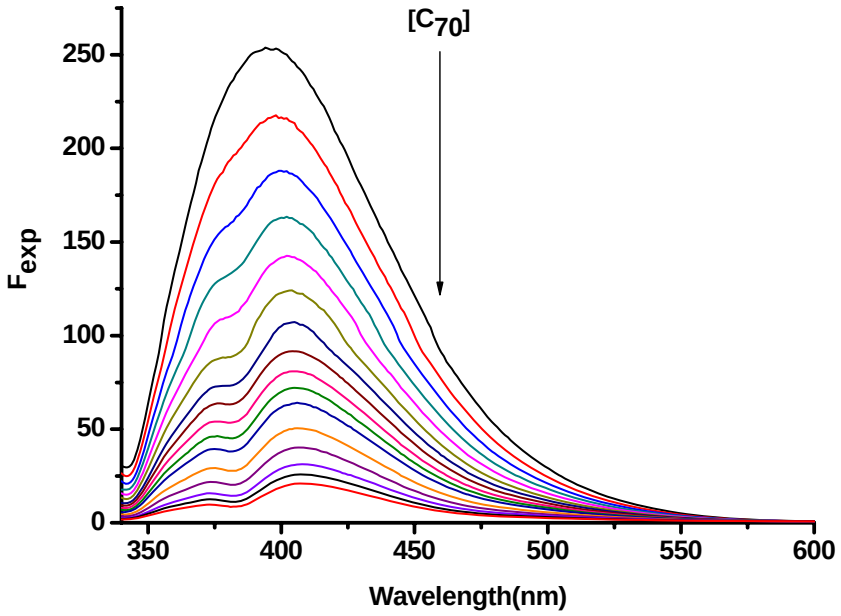

Fig. S3 Emission spectra (λ_{ex} = 330 nm) of **1** (2×10^{-5} mol dm^{-3}) in the presence of C_{70} (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 equiv.) in toluene.

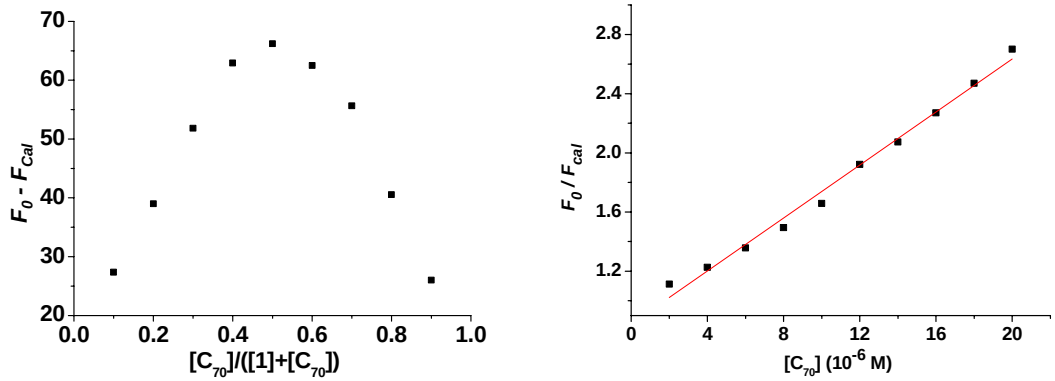

Fig. S4 Left: the Job plot for the complex **1**•C_{70} in toluene solution ([**1**]+[C_{70}]= 2×10^{-5} mol dm^{-3}). Right: the variation of fluorescence intensity F_0/F_{cal} of **1** with increasing C_{70} concentration.

5. Copies of ^{1}H NMR and ^{13}C NMR spectra of macrocycle 1

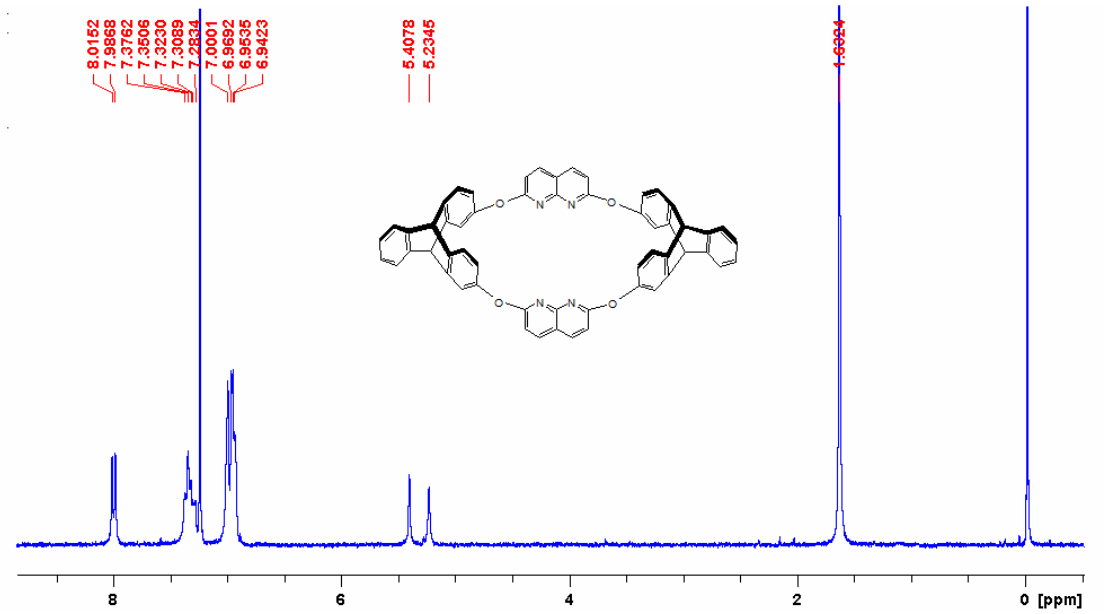

Fig. S5 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **1**.

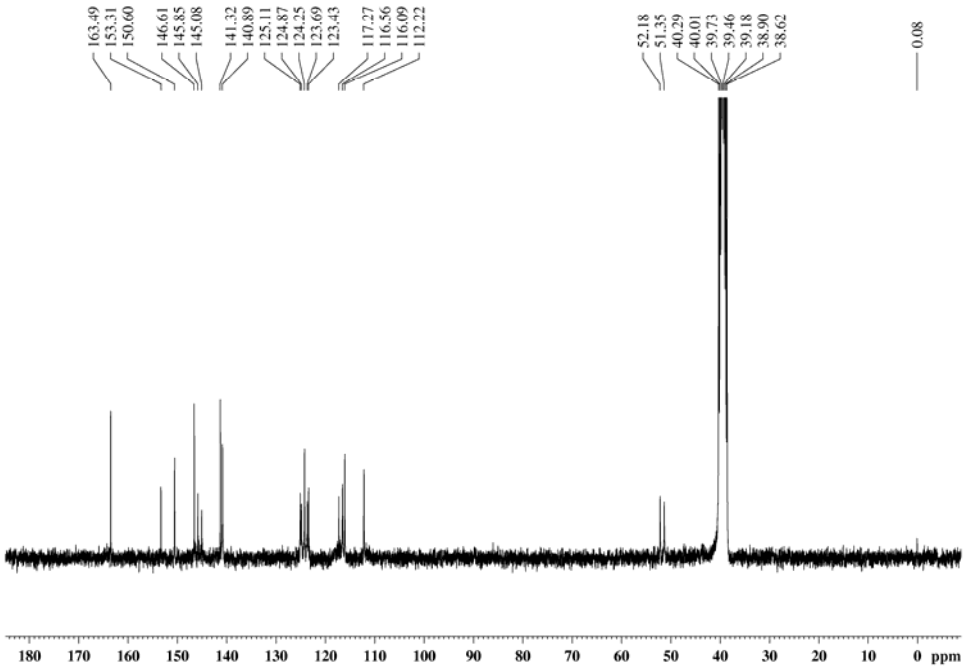

Fig. S6 ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of **1**.

6. Crystal structure of 1

X-ray structural analysis was performed on a Rigaku MM007HF + CCD (Saturn 724+) diffractometer. Data collection: CrystalClear (Rigaku Inc., 2008). Structure solution and structure refinement: SHELX-97 (Sheldrick, 1997). SQUEEZE in PLATON was used to remove disordered solvents.

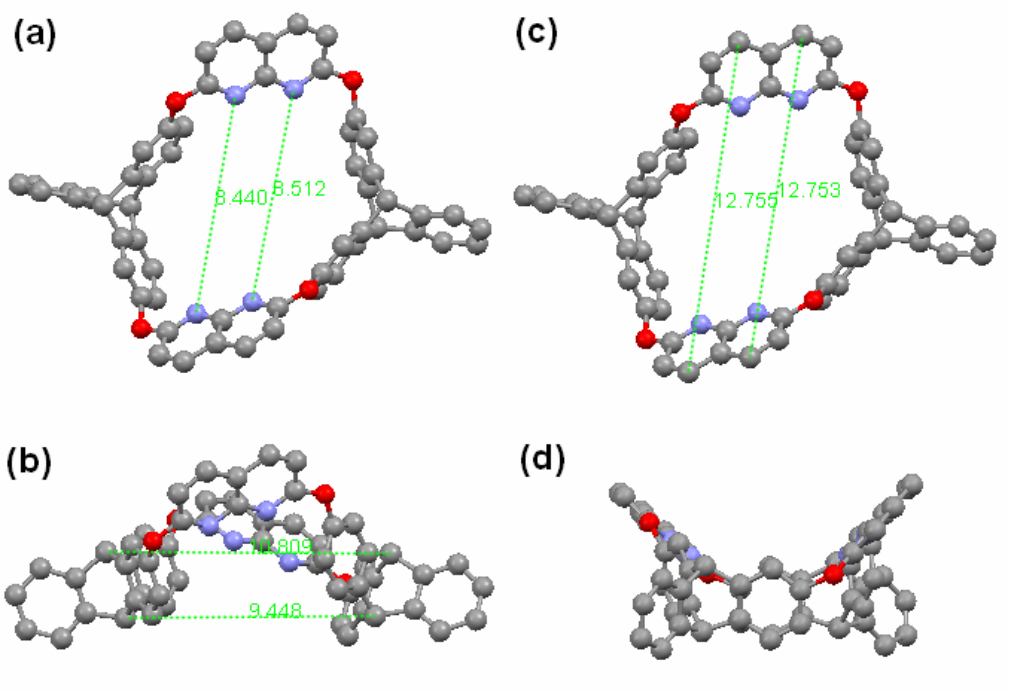

Fig. S7 Crystal structures (a, c) top view and (b, d) side view of **1** that adopts a distorted 1,3-alternate conformation. Solvent molecules and hydrogen atoms are omitted for clarity.