

Electronic Supplementary Information

Unconventional U-shaped conformation of a bolaamphiphile embedded in a synthetic host

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General Methods. All the reagents and solvents were used as supplied without further purification. 1,12-dodecane diammonium hydrochloride salt was prepared by treating the corresponding amine with HCl. NMR data were recorded on a DRX500 spectrometer (Bruker). MALDI/TOF mass spectrometry was performed with a Reflex III mass spectrometer (Bruker). Isothermal titration calorimetry (ITC) was performed with a VP-ITC instrument (MicroCal, Inc.).

CB[8]•C₁₂DA²⁺ Complex. To a solution of C₁₂DA²⁺2Cl⁻ (1.1 mg, 4.0 μmol) in D₂O (2 mL), CB[8] (7.2 mg, 4.0 μmol) was added and the resulting solution was sonicated with occasional heating until all solid materials were dissolved. The formation of inclusion complex was confirmed by ¹H NMR and MALDI/TOF mass spectrometry. ¹H NMR (D₂O, 500 MHz, 25 °C) δ = 5.84 (d, *J* = 15.5 Hz, 16 H), 5.58 (s, 16 H), 4.27 (d, *J* = 15.5 Hz, 16 H), 2.79 (t, *J* = 8 Hz, 4 H), 1.14-1.21 (m, 4 H), 0.91-0.94 (m, 4 H), 0.83 (br s, 8 H), 0.79 (br s, 4 H); MS (MALDI/TOF): *m/z* 1528.6 [*M*]⁺.

2D NMR experiments. ¹H-¹H correlation spectroscopy (COSY) and rotating-frame Overhauser effect spectroscopy (ROESY) experiments have been performed on a Bruker DRX500 NMR spectrometer operating at the proton Larmor frequency of 500.23 MHz at 25 °C. DQF-COSY was used to assign the proton resonances of CB[8]•C₁₂DA²⁺ (Fig. S1). ROESY experiments for CB[8]•C₁₂DA²⁺ complex (Fig. S2) confirmed that the alkyl chain of the guest is included in a U-shaped conformation in the cavity of CB[8].

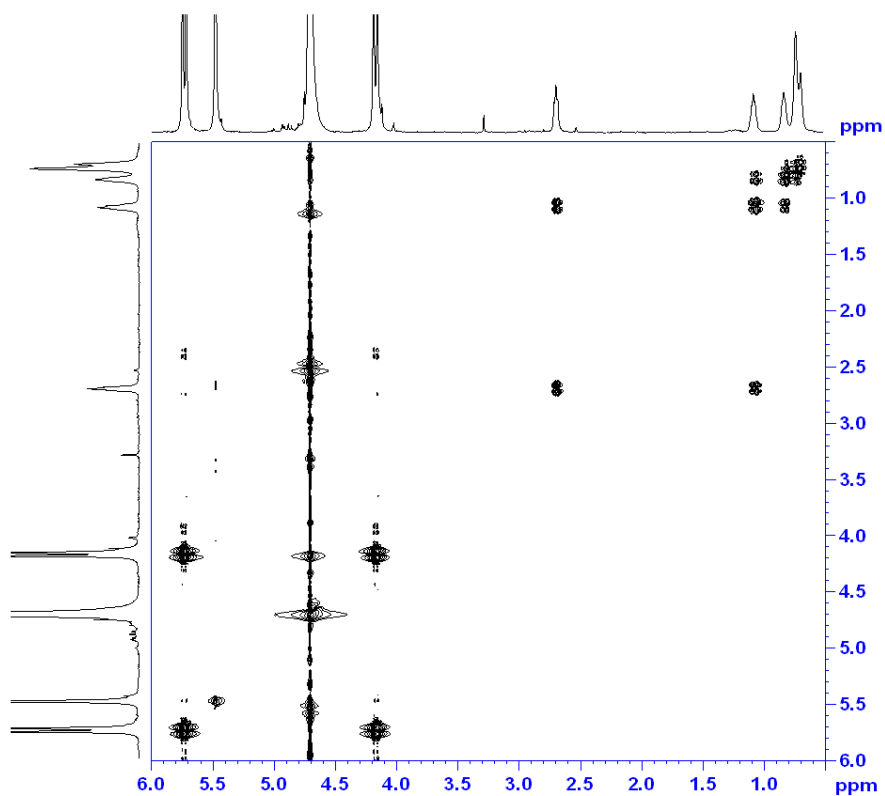


Fig. S1 ¹H-¹H DQF-COSY spectrum of CB[8]•C₁₂DA²⁺ complex in D₂O at 25 °C.

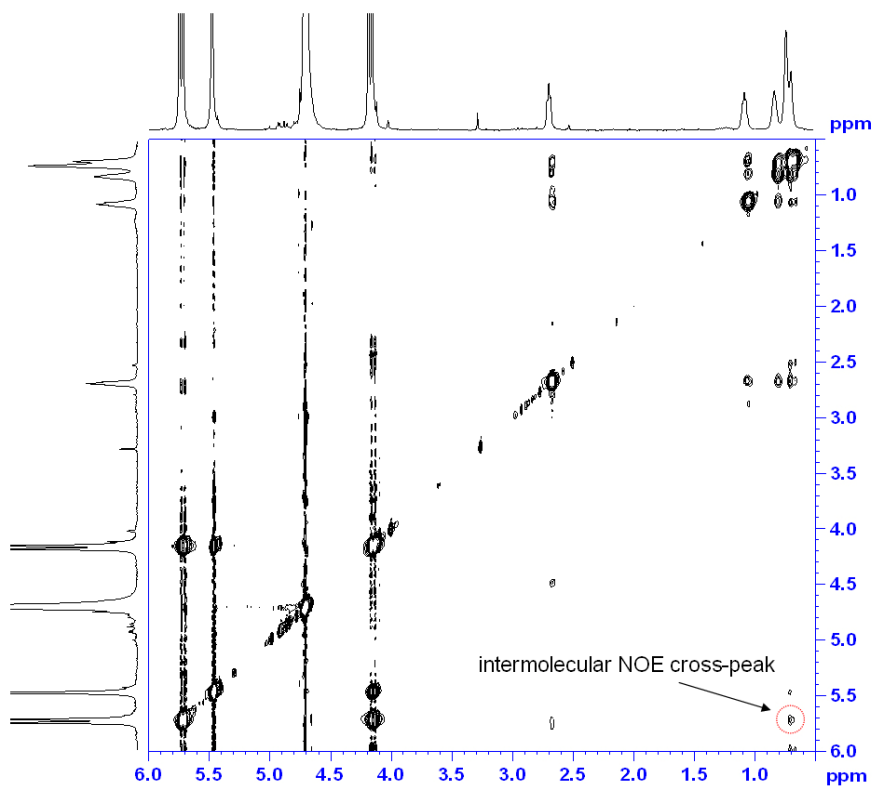


Fig. S2 ¹H-¹H ROESY spectrum of CB[8]•C₁₂DA²⁺ complex in D₂O at 25 °C

Isothermal titration calorimetry (ITC). The association constant and thermodynamic parameters for the inclusion complexation of C₁₂DA²⁺ with CB[8] were determined by isothermal titration calorimetry. All solutions were prepared in buffer (50 mM sodium acetate,

pH 4.74). All solutions were degassed prior to titration experiments according to the procedures provided by MicroCal, Inc. A solution (0.40 mM) of CB[8] was placed in a sample cell (1.4 mL). As a solution (6.1 mM) of the guest was added in a series of 24 injections (7 μ L), the heat evolved was recorded at $T=298.15$ K. The heat of dilution was corrected by injecting the guest solution into buffer (50 mM sodium acetate) and subtracting these data from those of the host–guest titration. The data were analyzed and fitted by the Origin software adapted for ITC data analysis (MicroCal, Inc.).

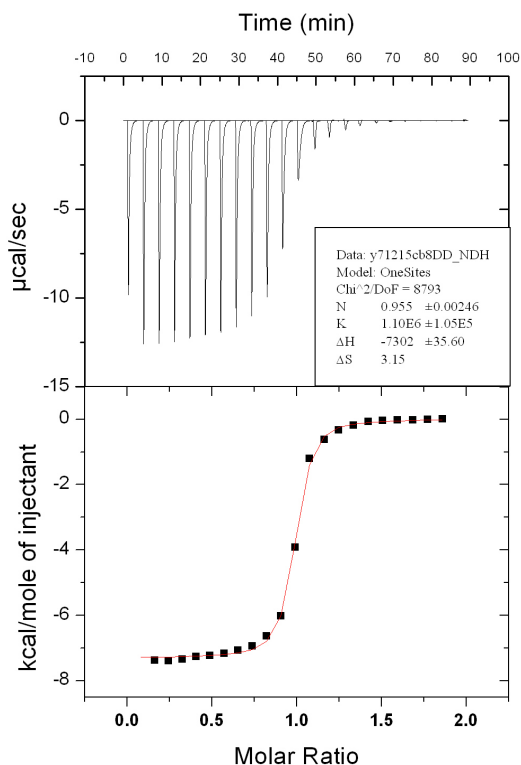


Fig. S3 ITC profile of CB[8] with 1,12-dodecane diammonium at 298.15 K: $K_a = 1.1(1) \times 10^6$ M^{-1} , $\Delta G = -34.5(3)$ $kJ mol^{-1}$, $\Delta H = -30.5(2)$ $kJ mol^{-1}$, $T\Delta S = 4.0(4)$ $kJ mol^{-1}$.