Electronic Supplementary Information

Kinetic trapping of the host-guest association intermediate and its transformation into thermodynamic inclusion complex.

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Adrenaline((-)-Epinephrine), anhydrous $MgCl_2$ (≥98 %) and $MgCl_2 \cdot 6H_2O$ (99.0-102.0%) were purchased from Sigma-Aldrich. CB6 was synthesized according to the literature procedure [A. Day *et al*, *J. Org. Chem*. **2001**, *66*, 8094-8100].

Synthesis of complexes 1 and 2: $CB6 \cdot 10H_2O$ (10 mg, 8.5 μmol) and $MgCl_2 \cdot 6H_2O$ (173 mg, 0.85 mmol) were dissolved in distilled water (1 ml) upon gentle heating. The solution of adrenaline (3.1mg, 17 μmol) in 1ml of 0.1M HCl was carefully layered upon solution of CB6 to create an interface. The diffraction quality needle-like crystals of complex **1** were formed at the interface overnight. The crystals of complex 1 kept in mother solution underwent spontaneous dissolution and recrystallized as prismatic crystals of complex **2** during several days.

Synthesis of complex 3: $CB6 \cdot 10H_2O$ (10 mg, 8.5 μmol) and $MgCl_2 \cdot 6H_2O$ (173 mg, 0.85 mmol) were dissolved in distilled water (2 ml) upon gentle heating. The adrenaline (3.1mg, 17 μmol) was added to the warm CB6 solution and dissolved under stirring. The needle-like yellowish crystals appeared after several hours.

Synthesis of complex 4: CB6·10H_2O (10 mg, 8.5 μmol) and adrenaline (3.1mg, 17 μmol) were dissolved in 2ml of 5M hydrochloric acid. The solution was left for slow evaporation, block-shaped crystals appeared after one week.

General comments on crystallographic data: The crystals of all complexes were found to be sensitive to the lost of crystallization water when out of mother solution. The crystals were selected under Paratone-N oil, mounted on the nylon loops and positioned in the cold stream on the diffractometer. The X-ray data for complexes **1**, **2** and **4** were collected at 100(2)K on a Nonius KappaCCD diffractometer using Mo*Kα* radiation (λ = 0.71073 Å). The data were processed with *HKL2000*.[1] The X-ray data for complex **3** were collected at 100(2)K on a SuperNova Agilent diffractometer using Cu*Kα* radiation (λ = 1.54184 Å). The data were processed with *CrysAlisPro*.[2] Structures were solved by direct methods and refined using *SHELXL-97*.[3] The figures were prepared using *X-Seed*[4]/ *POV-Ray*.

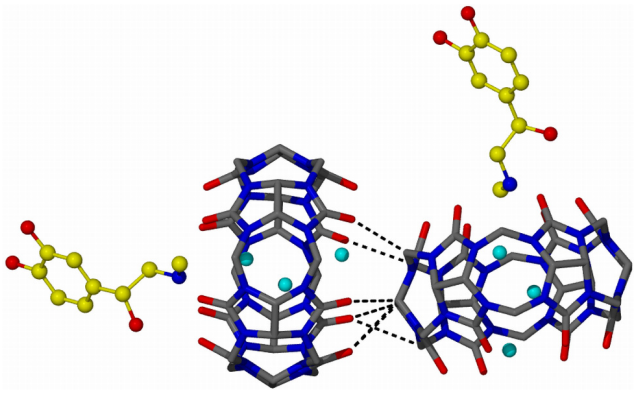

Fig. ESI-1. The mutual arrangement of neighboring complexes 1 in the crystal lattice showing the role of multiple cucurbituril-cucurbituril CH···O interactions in the solid state host-guest assembly.

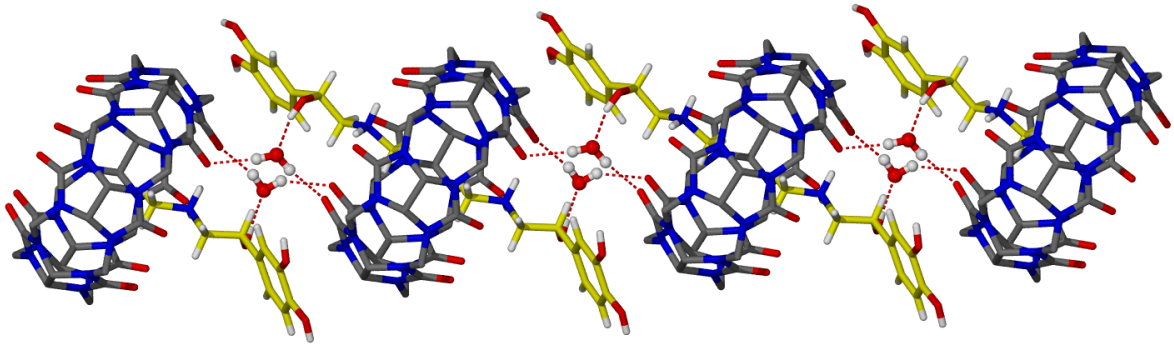

Fig. ESI-2. The supramolecular chain of CB6/protonated adrenaline units connected by hydrogen bonding through bridging water molecules in complex 2.

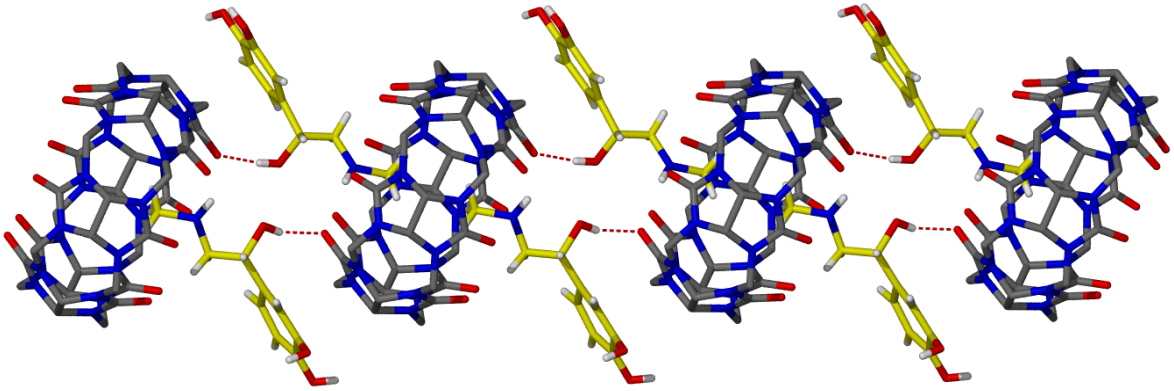

Fig. ESI-3. The supramolecular chain of CB6/neutral adrenaline units connected by direct hydrogen bonding between hydroxyl groups of adrenaline molecules and carbonyl oxygen atoms of CB6 in complex 3.

^{1}H NMR spectra were recorded on a Varian (400 MHz) instrument. The chemical shifts (δ) are given in ppm.

NMR measurements:

a) CB6

CB6 (10 mg, 8.5 μmol) was dissolved in D_2O (0.6 mL) in the presence of anhydrous $MgCl_2$ (81 mg, 0.85 mmol) under gentle heating. The obtained solution was left to cool to the room temperature, placed into NMR tube and NMR spectrum was recorded. The spectrum is shown on Fig. ESI-4.

b) Adrenaline

Adrenaline (3.1 mg, 17 μmol) was dissolved in D_2O (0.6 mL) in the presence of anhydrous $MgCl_2$ (81 mg, 0.85 mmol) by adding 35% DCl/D_2O (2.5 μL). The spectrum is shown on Fig. ESI-4.

c) CB6+adrenaline

CB6 (10 mg, 8.5 μmol) was dissolved in D_2O (0.4 mL) in the presence of anhydrous $MgCl_2$ (81 mg, 0.85 mmol) under gentle heating. The obtained solution was left to cool to the room temperature and placed into NMR tube. Adrenaline (3.1 mg, 17 μmol) was dissolved in D_2O (0.2 mL) by adding 35% DCl/D_2O (2.5 μL). The adrenaline solution was added to the CB6 solution

and stirred. The crystallization of complex **I** started immediately. The NMR spectra were recorded at time intervals shown on Fig. ESI-4.

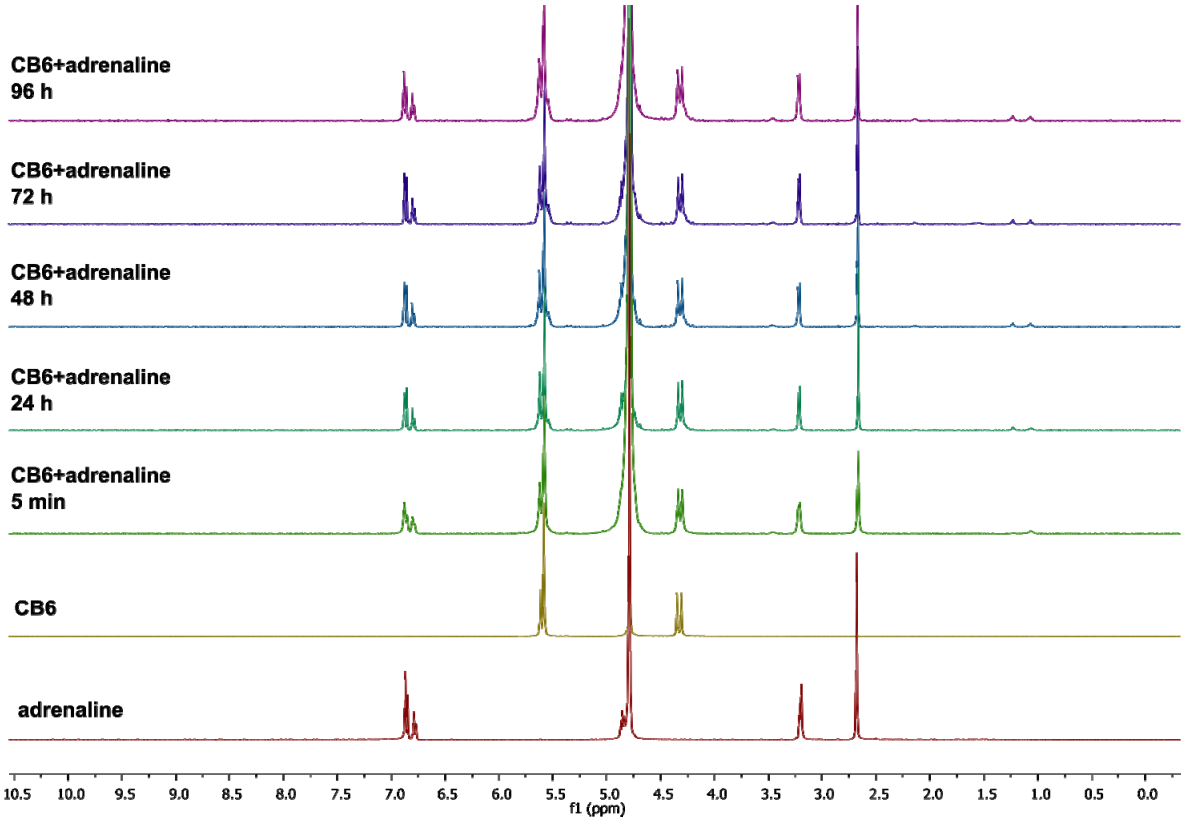

Fig. ESI-4. NMR spectra of adrenaline, CB6 and their mixture.

[1] Z. Otwinowski, W. Minor, *Methods Enzymol*. **1997**, 276, 307-326.
[2] Agilent Technologies, *CrysAlisPro*, Version 1.171.35.21b.
[3] G. M. Sheldrick, *Acta Cryst*. **2008**, 64A, 112-122.
[4] L. J. Barbour, *J. Supramol. Chem.* **2001**, *1*, 189-191.