Supporting Information

Enhancement of metal−metal interactions inside a large-cavity synthetic host in water

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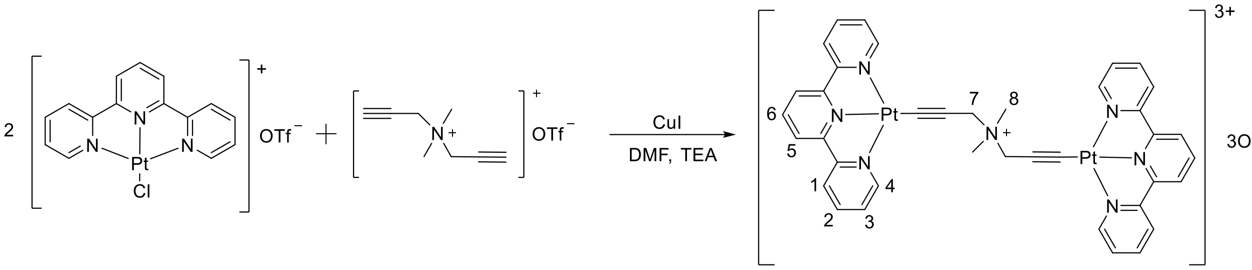
General Experimental Section.

CB[7], CB[8], CB[10], guest **1**, **2**, **3** and new compound **4** were prepared by the corresponding literature procedures.[1-5] All ^1H NMR spectra were collected on Agilent 600 MHz DD2. Mass spectrometry was performed using a Bruker Agilent 1290-micrOTOF Q II. Elemental analyses were performed on an Elementar Vario MACRO cube. UV/Vis were performed on a SHIMADZU UV-3600 instrument with 1 cm pathlength cells at 298 K. Fluorescence spectra were collected on a PerkinElmer LS-55 machine (solid-state fluorescence spectrum was collected on Hitachi F-7000 Fluorescence Spectrophotometer). Dynamic Light Scattering (DLS) experiments were carried out by Malvern Zeta SIZER NANO ZS90. The X-ray intensity data were measured on a Bruker APEX DUO system (Data collection temperature was 150 K).

Synthesis of compound 4



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[Pt(tpy)Cl][OTf] (80 mg, 0.13 mmol) was dissolved in degassed DMF (10mL) containing triethylamine (4mL), followed by the addition of $[(HC\equiv CCH_2)_2NMe_2][OTf]$ (17.6 mg, 0.065 mmol) and copper(I) iodide (3.9 mg, 0.02 mmol). The reaction mixture was stirred overnight under N_2 at room temperature, and then diethyl ether (80 mL) was added and stirred for 10 min. The product was isolated by filtration, washed with diethyl ether and acetonitrile, and dried to afford **4** as a yellow solid. Yield: 42 mg (45%). ^1H NMR (600MHz, D_2O): δ (ppm) = 3.32 (s, 6H; $-NMe_2$), 4.54 (s, 4H; $-CH_2-$), 7.52 (t, *J* = 7.9 Hz, 4H; tpy), 7.91 (d, *J* = 7.9 Hz, 4H; tpy), 7.98 (d, *J* = 8.1Hz, 4H; tpy), 8.05 (t, *J* = 8.1Hz, 4H; tpy), 8.26 (t, *J* = 8.1 Hz, 2H; tpy), 8.82 (d, *J* = 8.1 Hz, 4H; tpy). ^{13}C NMR (150 MHz, D_2O): δ (ppm) = 50.62, 123.73, 125.30, 129.34, 142.15, 142.80, 153.29, 154.78, 157.18. Elemental analysis calcd. (%) for $C_{41}H_{32}N_7F_9O_9Pt_2S_3\cdot 2H_2O$: C 33.73, H 2.49, N 6.72; found: C 33.99, H 3.38, N 6.89. ESI-MS (positive-ion): m/z 1274.6 [**4**-OTf$^-$]$^+$ (calcd. $C_{40}H_{32}F_6N_7O_6Pt_2S_2^+$ 1274.1).

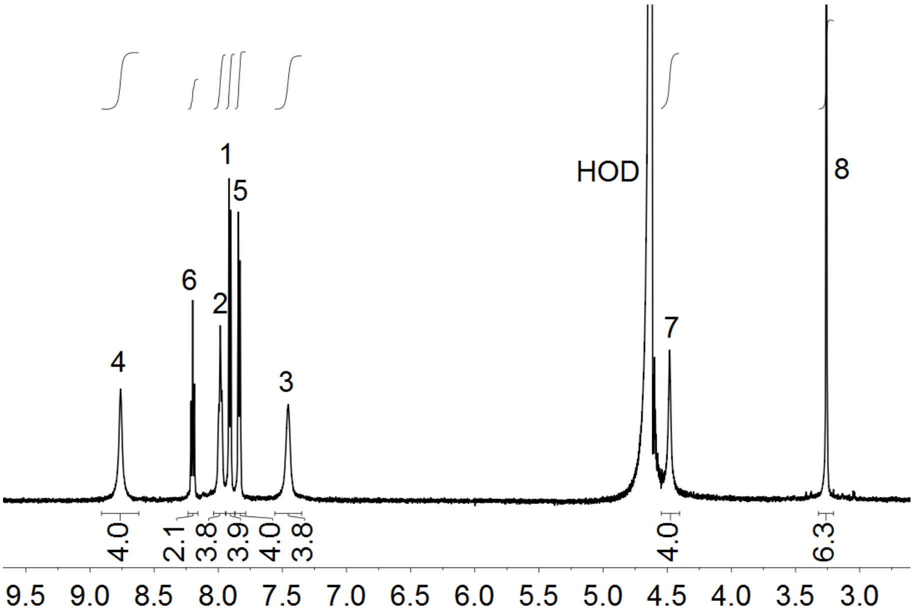

Fig. S1 ^{1}H NMR (600 MHz, D_2O) spectrum of compound **4**.

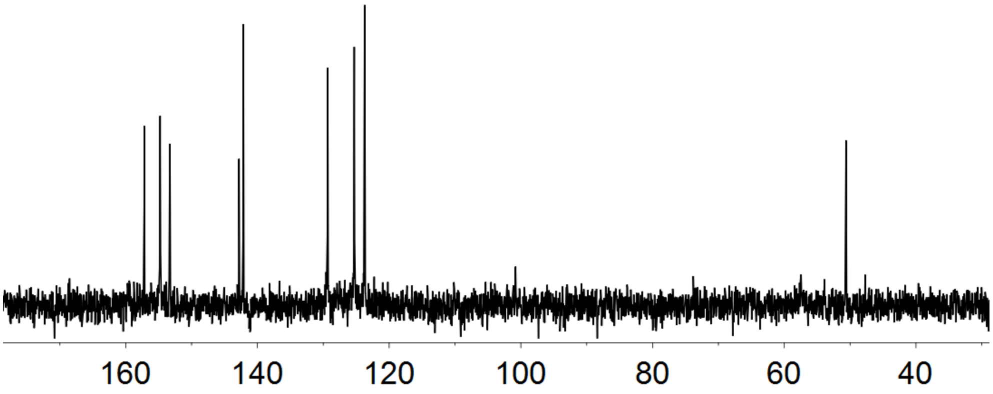

Fig. S2 ^{13}C NMR (150 MHz, D_2O) spectrum of compound **4**.

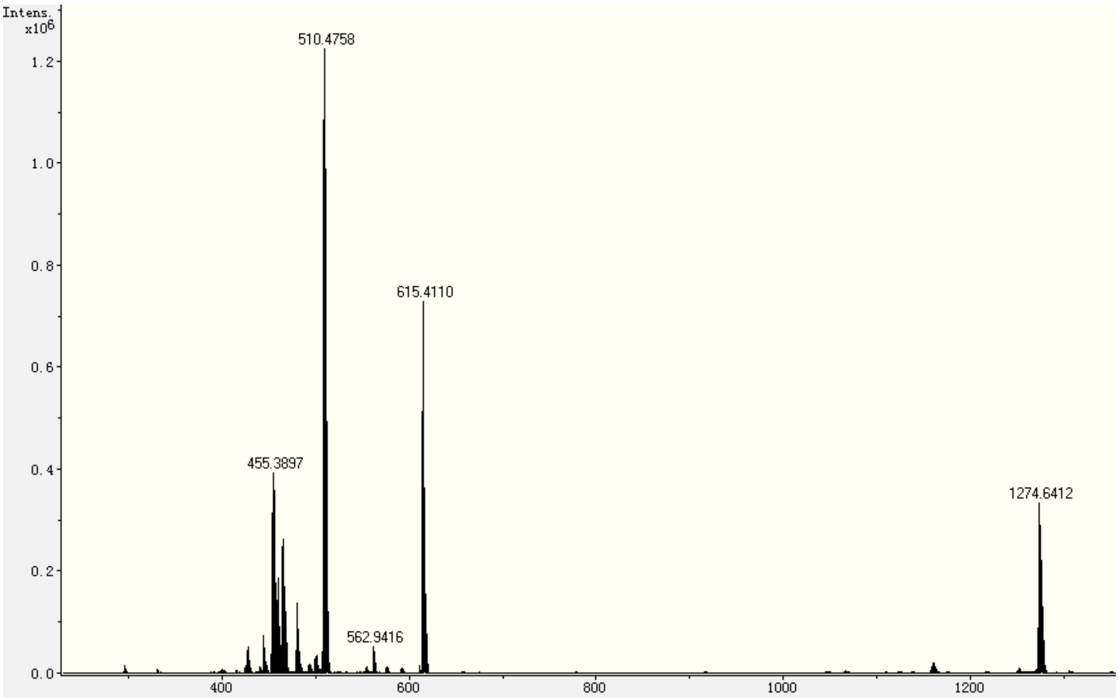

Fig. S3 ESI-MS spectrum of compound **4**.

References

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2. X. Yang, Z. Zhao, X. Zhang and S. Liu, *Sci. China Chem.*, 2018, doi: 10.1007/ s11426-017-9173-4.
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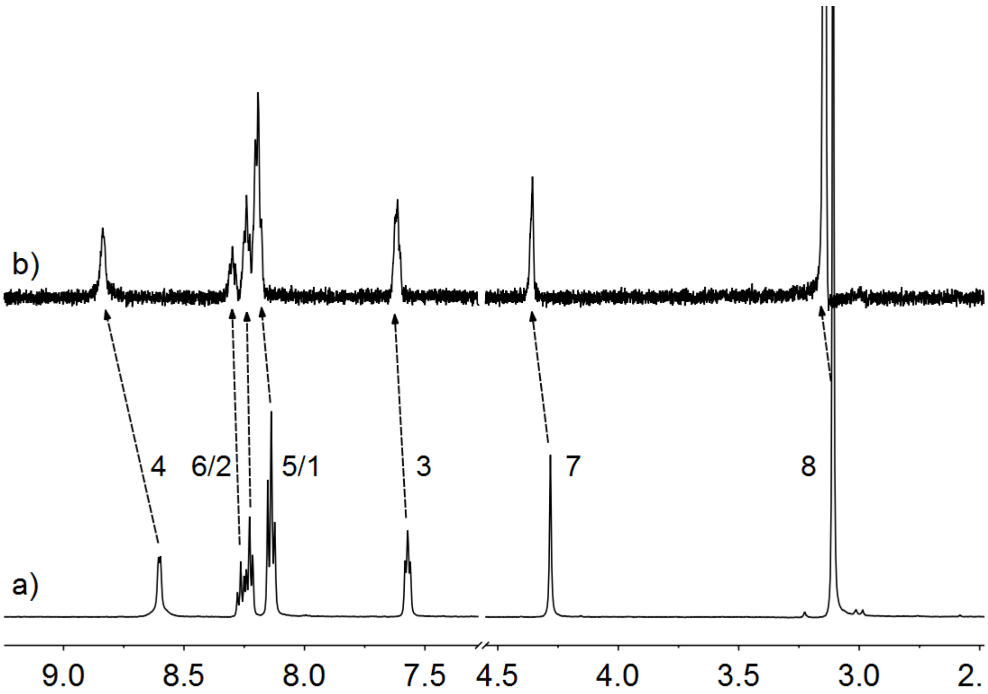

Fig. S4 ^{1}H NMR (600 MHz, D_2O) spectra of compound **1** at the concentration of: a) 1.0 mM; b) 0.1 mM. Dilution NMR proves that weak π-π stacking of compound **1** exits (more diluted, less π-π stacking).

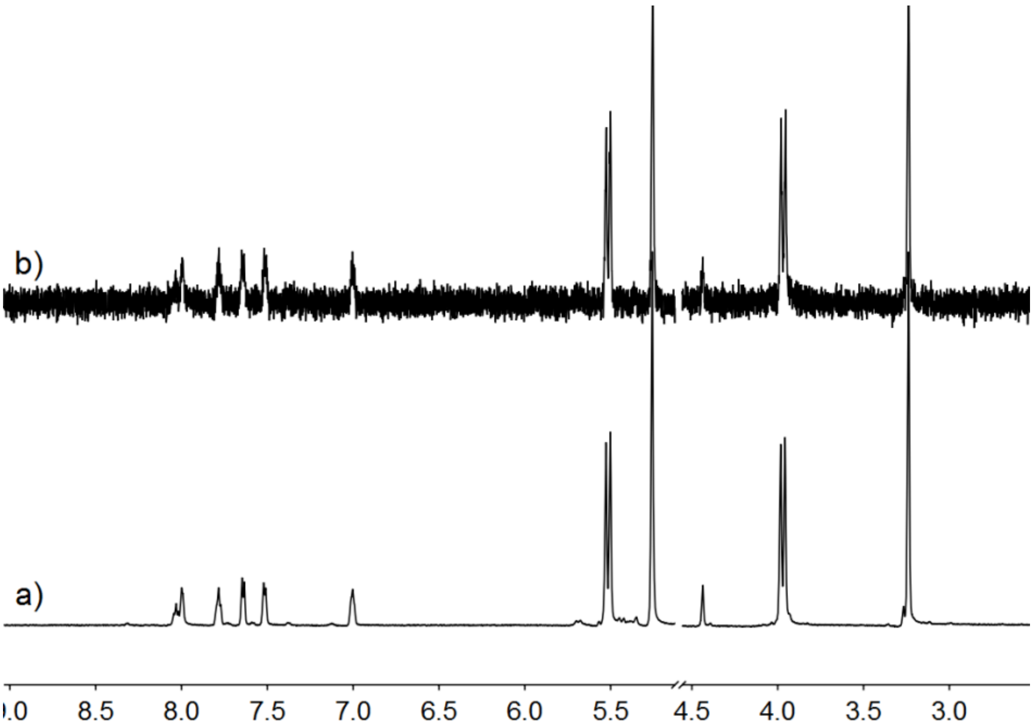

Fig. S5 ^{1}H NMR (600 MHz, D_2O) spectra for CB[10]·$\mathbf{1}_2$ at the concentration of: a) 1.0 mM; b) 0.02 mM.

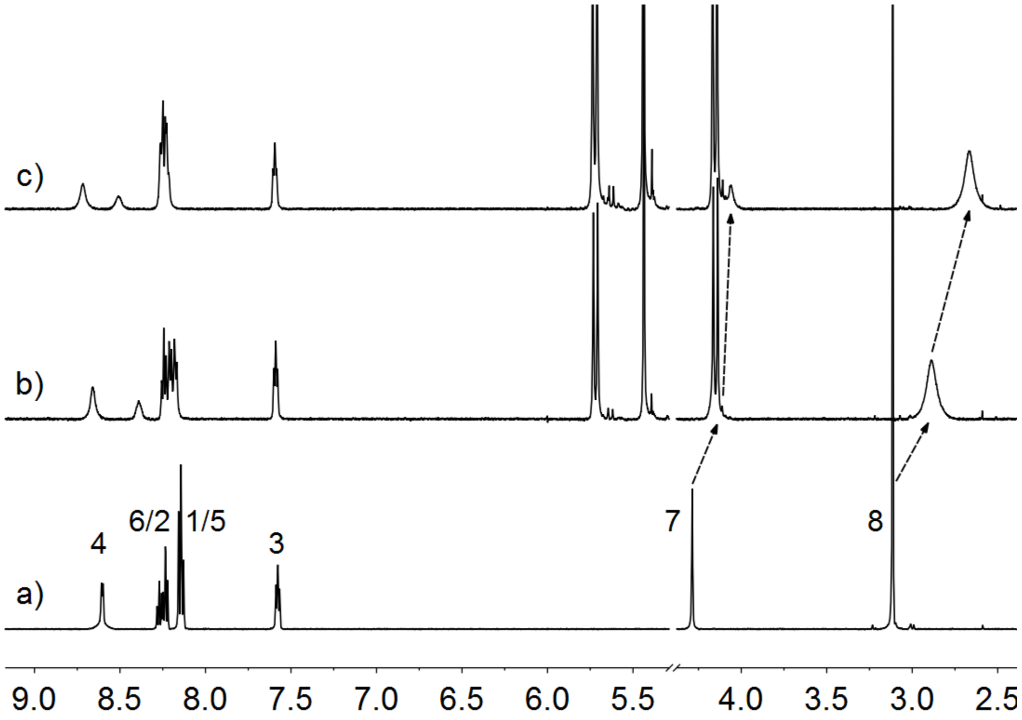

Fig. S6 ^{1}H NMR spectra (600 MHz, D_2O) of: a) free **1** (1.0 mM); b) 2:1 mixture of guest **1** and CB[7]; c) 1:1 mixture of guest **1** and CB[7]. Encapsulation by CB[7] weakened the π-π stacking of compound **1**, leading to the downfield of H_4 proton.

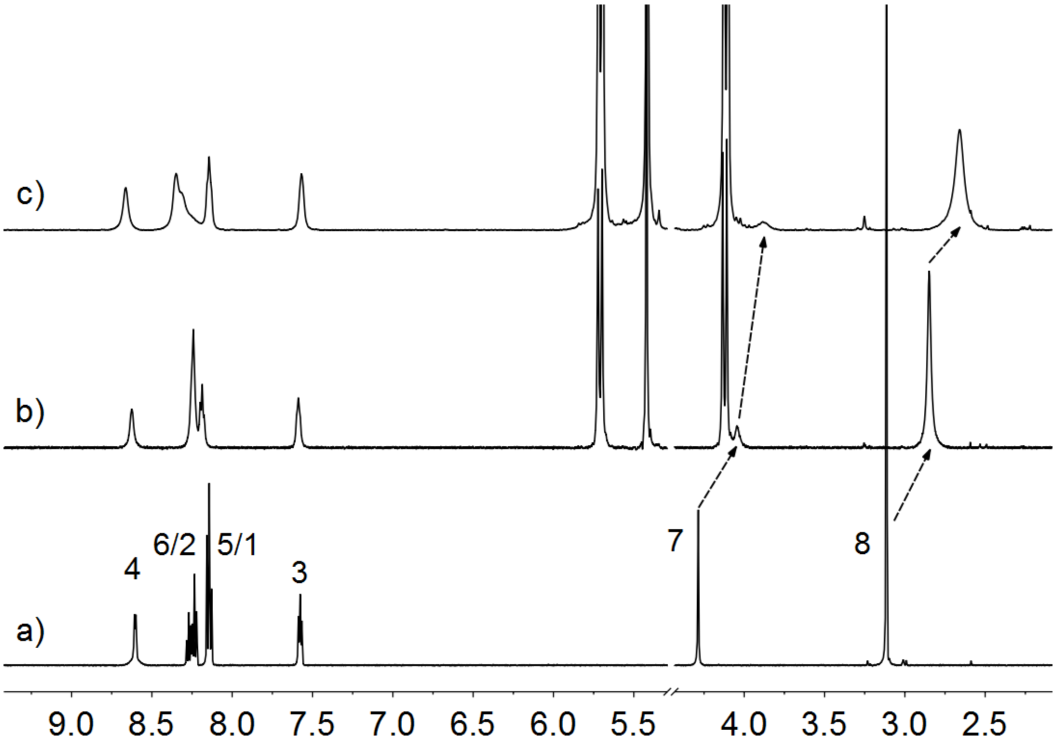

Fig. S7 ^{1}H NMR spectra (600 MHz, D_2O) of: a) free **1** (1.0 mM); b) 1:0.6 mixture of guest **1** and CB[8]; c) 1:1.2 mixture of guest **1** and CB[8].

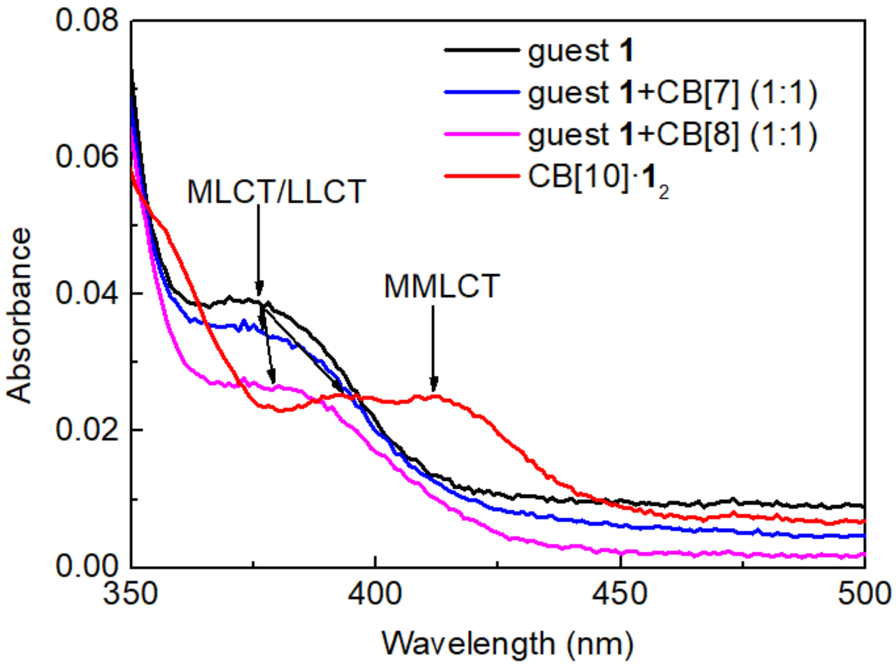

Fig. S8 UV/Vis spectra recorded for guest **1** in the presence of CB[*n*] (*n* = 7, 8, 10) in pure H_2O. The concentration of guest **1** was held constant at 0.01 mM.

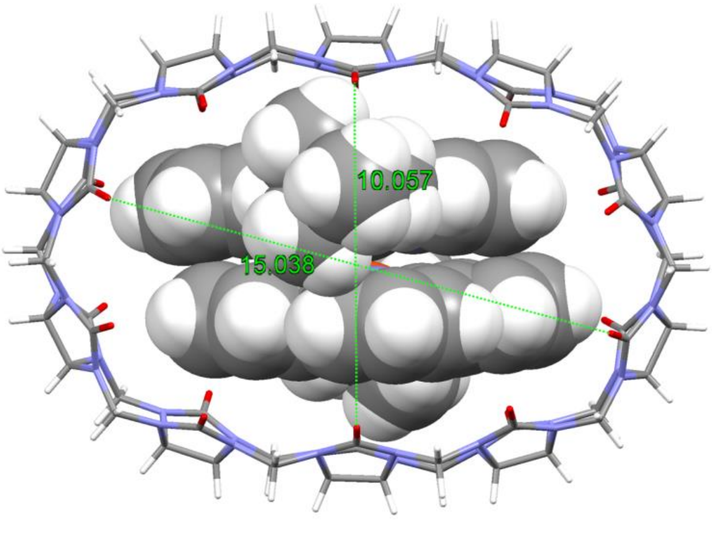

Fig. S9 X-ray crystal structure of the inclusion complex CB[10]•$\mathbf{1}_2$ (mode **α**), showing huge deformation of CB[10] upon encapsulating two molecules of **1**.

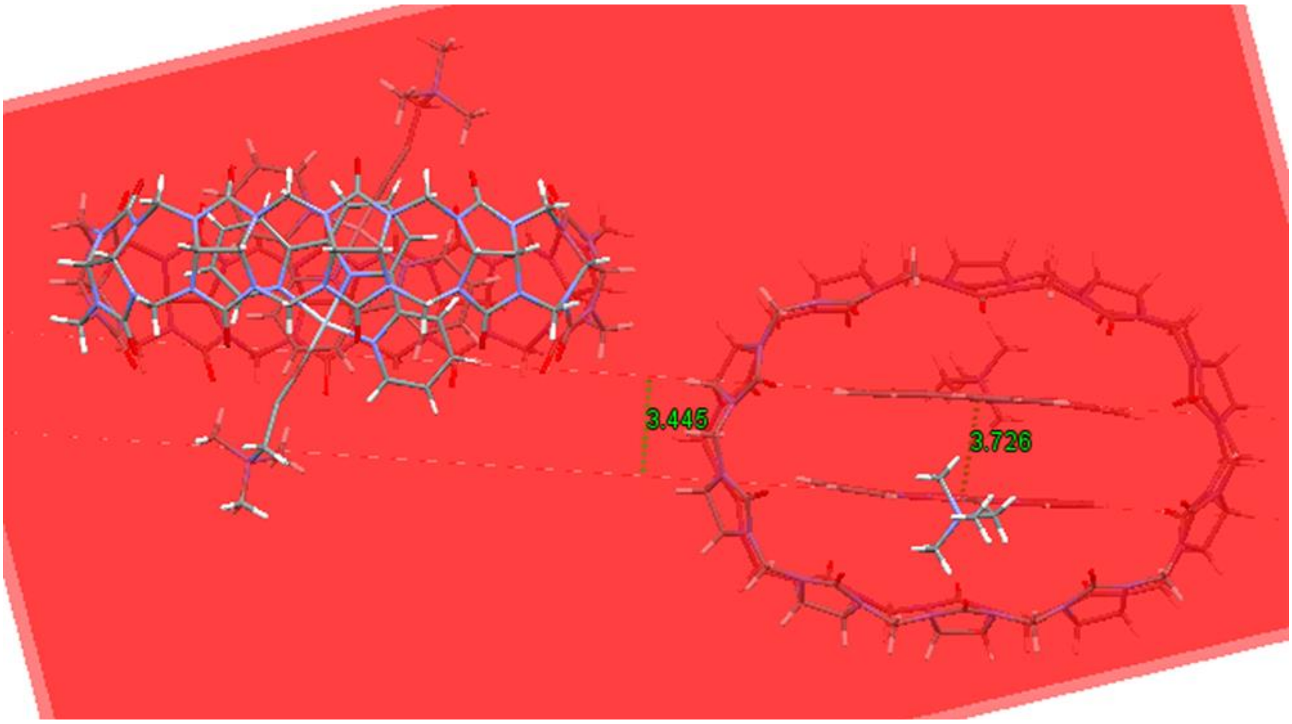

Fig. S10 X-ray crystal structure of the inclusion complex CB[10]•$\mathbf{1}_2$ (mode **α**). In mode **α**, the distance of two parallel planes composed from two encapsulated guest **1** is 3.445 Å.

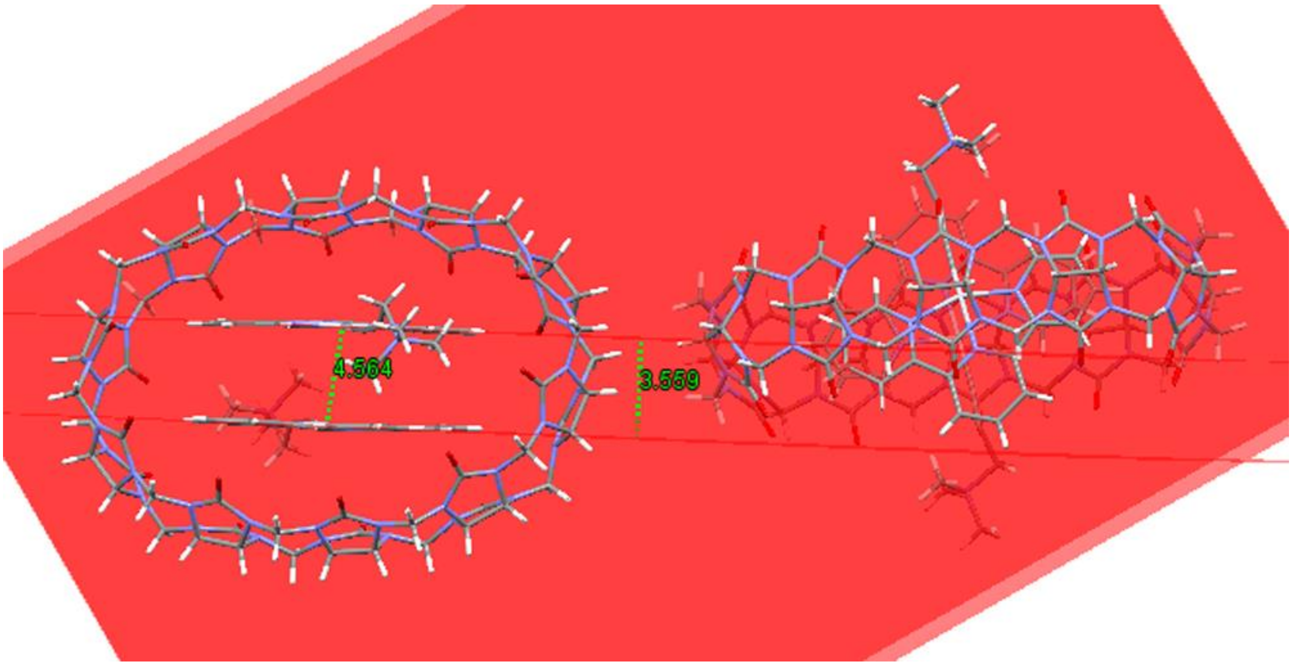

Fig. S11 X-ray crystal structure of the inclusion complex CB[10]•$\mathbf{1}_2$ (mode **β**). In mode **β**, the distance of two parallel planes composed from two encapsulated guest **1** is 3.559 Å.

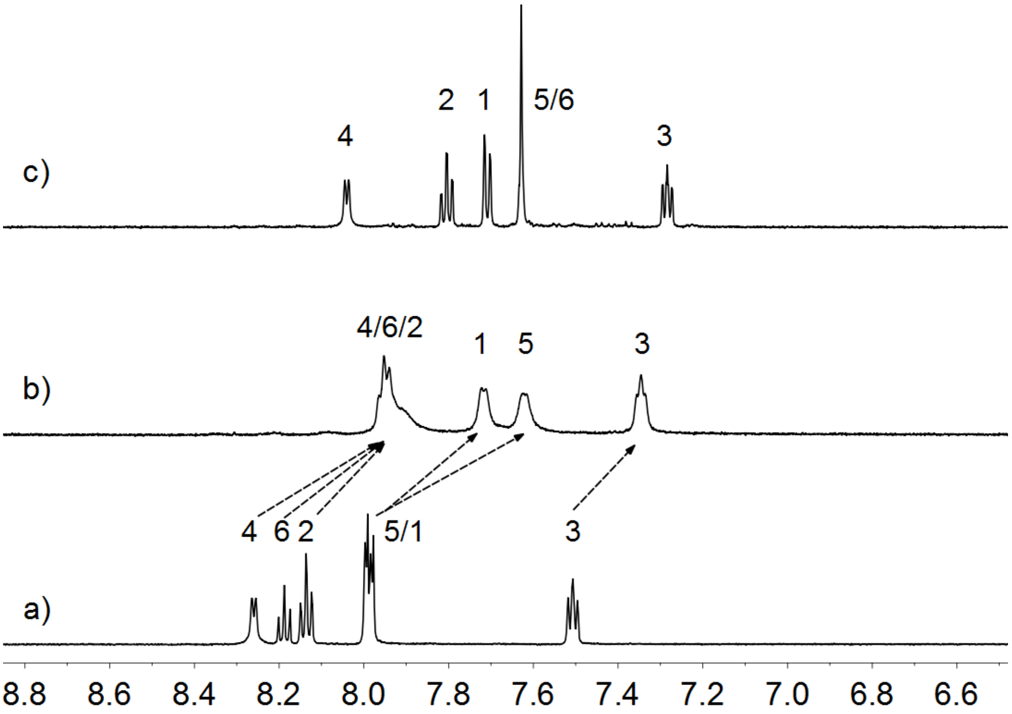

Fig. S12 ^{1}H NMR spectra (600 MHz, D_2O) of: a) free **2** (1.0 mM); b) 4:1 mixture of **2** and CB[10]; c) CB[10]·$\mathbf{2}_2$.

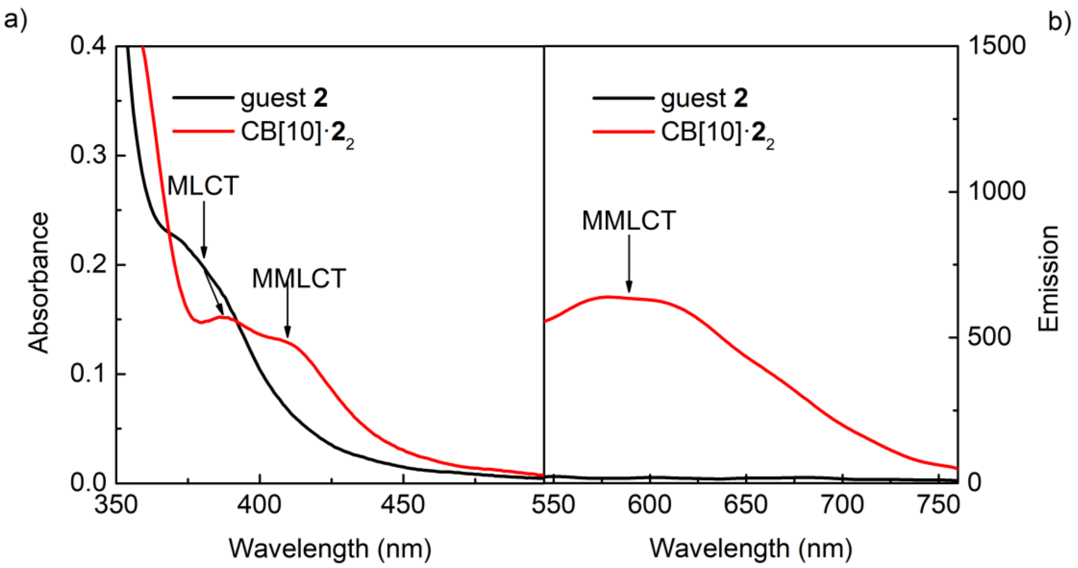

Fig. S13 a) UV/Vis spectra recorded for guest **2** with CB[10] in pure H_2O. b) Fluorescence spectra recorded for **2** with CB[10] at an excitation wavelength of 400 nm in pure H_2O. The excitation and emission monochrometer bandpasses were set at 2.5 nm and 20nm, respectively. The concentration of **2** was held constant at 0.1 mM.

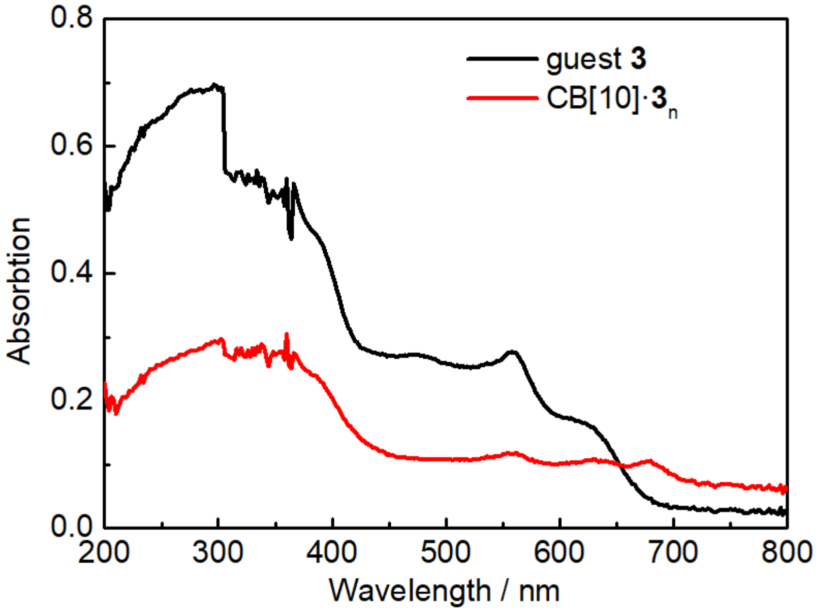

Fig. S14 Solid-state UV/Vis spectra recorded for guest **3** and CB[10]·$\mathbf{3}_n$.

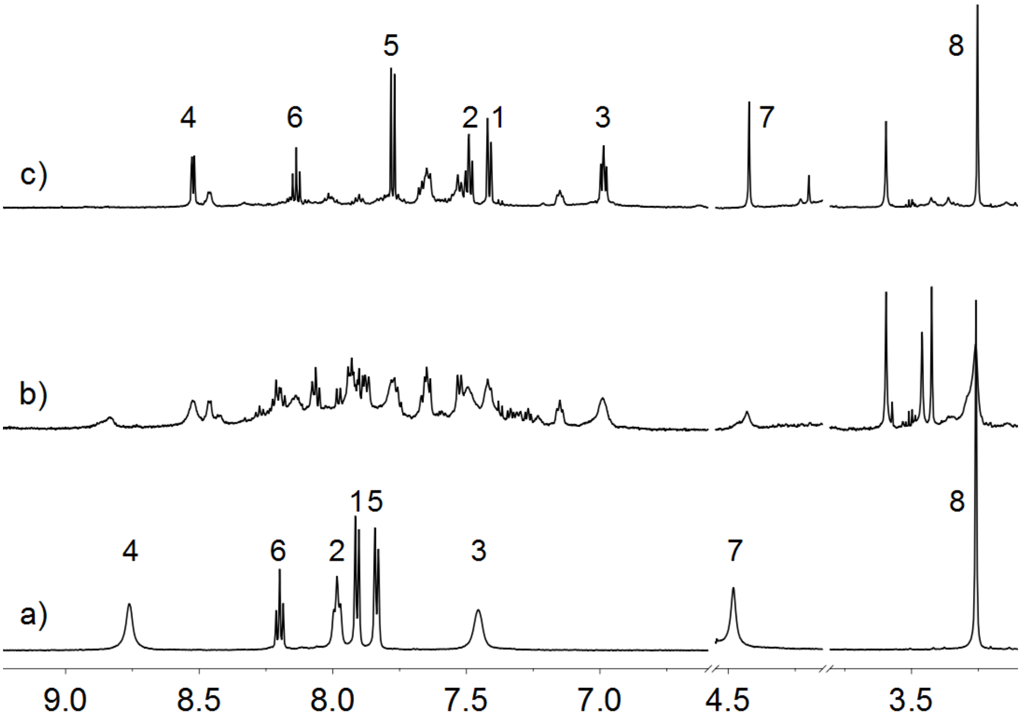

Fig. S15 ^1H NMR spectra (600 MHz, D_2O) of: a) free **4** (1.0 mM); b) 2:1 mixture of **4** and CB[10]; c) **4** and excess CB[10] (excess CB[10] wasn't soluble) after 2 days. Integration from spectrum c) indicated the ration of CB[10] to **4** was 1:1.

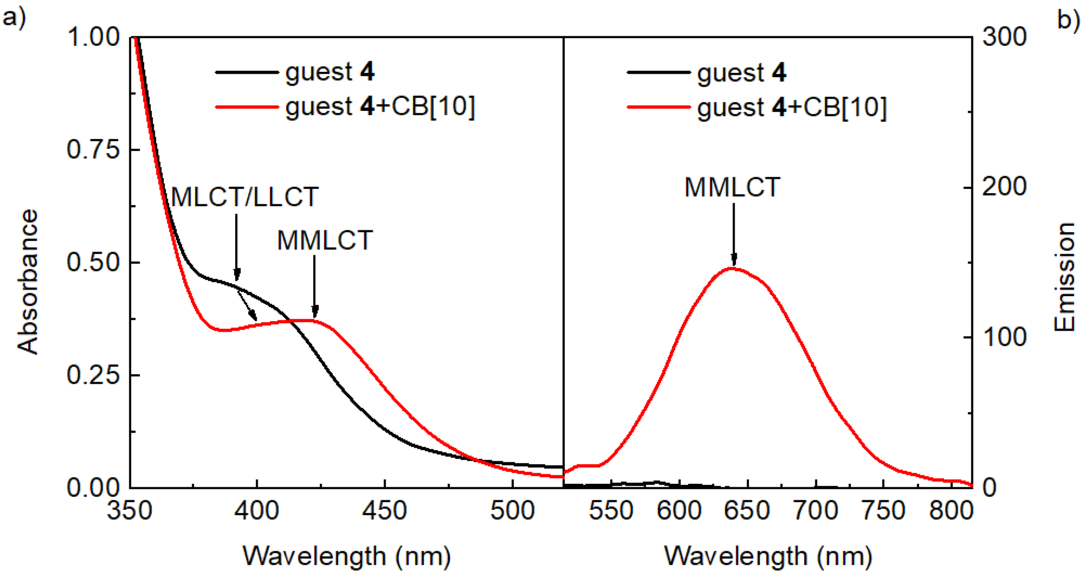

Fig. S16 a) UV/Vis spectra recorded for guest **4** with CB[10] in pure H_2O after 2 days. b) Fluorescence spectra recorded for **4** with CB[10] at an excitation wavelength of 423nm in pure H_2O after 2 days. The excitation and emission monochrometer bandpasses were set at 2.5 nm and 8.0 nm, respectively. The concentration of guest **4** was held constant at 0.1 mM.