

## Electronic Supplementary Information

# Self-assembly of a ternary architecture driven by cooperative Hg<sup>2+</sup> ion binding between cucurbit[7]uril and crown ether macrocyclic hosts

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## 1. Materials and equipment

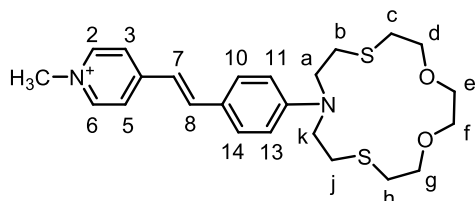
All reagents and solvents were obtained from commercial sources and used as received. Preparation of the dye **1** solution and all experiments were carried out in a laboratory environment of red light.

The absorption spectra measurements were performed using a Varian-Cary 100 spectrophotometer.

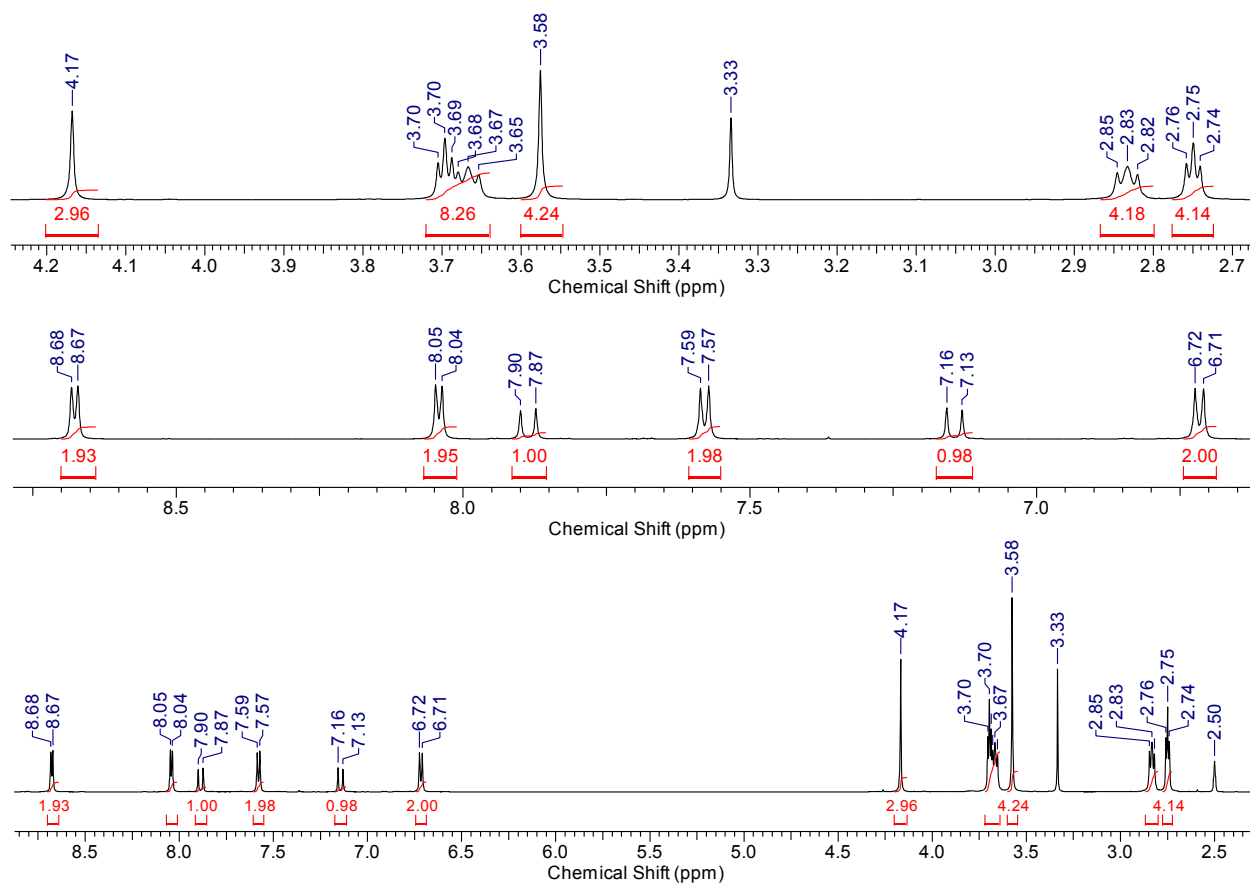
The NMR experiments were carried out using a Bruker Avance<sup>TM</sup> spectrometer operating at 600.22 MHz for <sup>1</sup>H and 150.93 MHz for <sup>13</sup>C. The spectrometer was equipped with an inverse gradient probe-head. All 1D <sup>1</sup>H and <sup>13</sup>C as well as 2D experiments (COSY, ROESY, HSQC, HMBC) were performed at 298 K using standard pulse sequences from the Bruker library. Chemical shifts were determined with an accuracy of 0.01 ppm (<sup>1</sup>H) and 0.1 ppm (<sup>13</sup>C) and are given relative to the residual signal of the solvent that was used as internal reference. Spin-spin coupling constants were determined with an accuracy of 0.1 Hz.

## 2. Synthesis

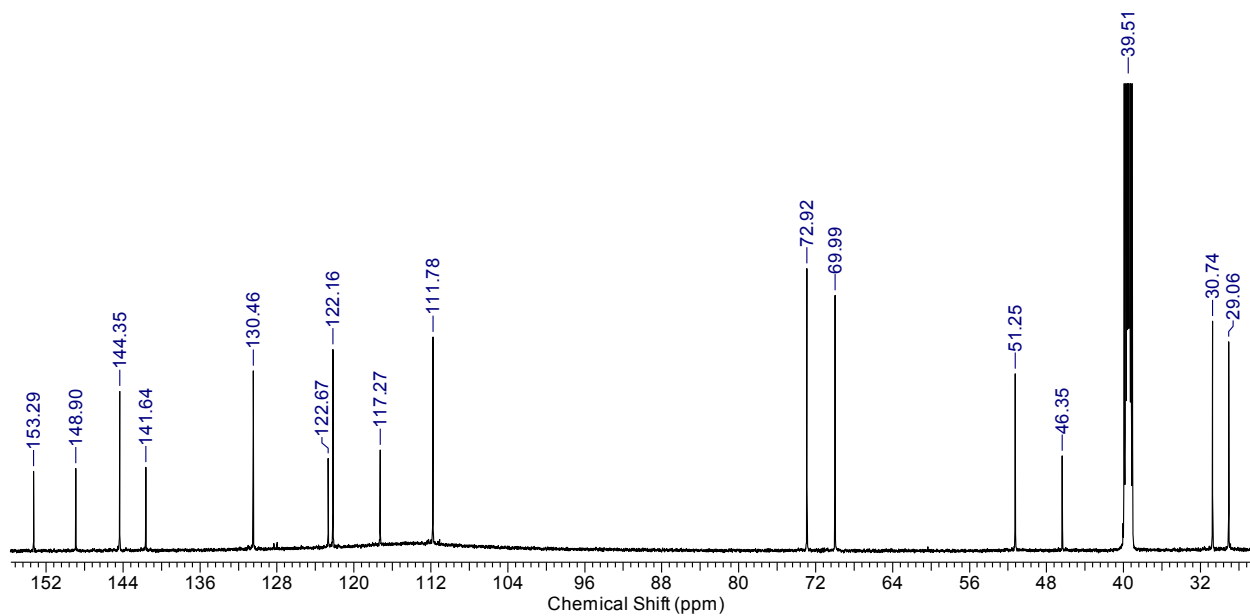
Cucurbit[7]uril was synthesized according to known procedures<sup>1,2</sup>.



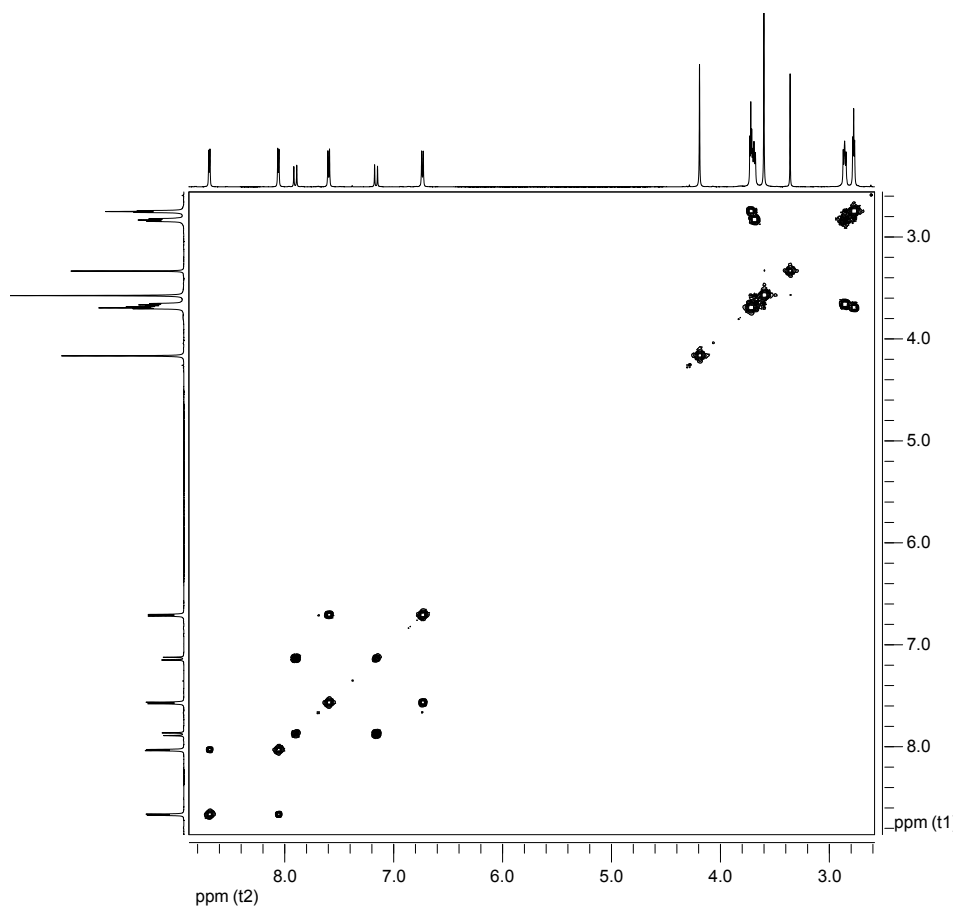
Compound **1**. (E)-4-(4-(1,4-dioxo-7,13-dithia-10-azacyclopentadecan-10-yl)styryl)-1-methylpyridinium perchlorate (**1**) was synthesized according to the reported methods from 1,4-dimethylpyridinium perchlorate and 4-(1,4-dioxo-7,13-dithia-10-azacyclopentadecan-10-yl)benzaldehyde in 71% yield<sup>3</sup>. M.p. 232 °C; <sup>1</sup>H-NMR (600 MHz, DMSO-*d*<sub>6</sub>, *J* [Hz]): 2.75 (m, 4H, H-c, H-h), 2.83 (m, 4H, H-b, H-j), 3.58 (s, 4H, H-e, H-f), 3.67 (m, 4H, H-a, H-k), 3.70 (m, 4H, H-d, H-g), 4.17 (s, 3H, CH<sub>3</sub>), 6.72 (d, 2H, H-11, H-13, <sup>3</sup>*J*=8.9), 7.15 (d, 1H, H-8, <sup>3</sup>*J*=15.9), 7.58 (d, 2H, H-10, H-14, <sup>3</sup>*J*=8.7), 7.89 (d, 1H, H-7, <sup>3</sup>*J*=16.1), 8.05 (d, 2H, H-3, H-5, <sup>3</sup>*J*=6.9), 8.68 (d, 2H, H-2, H-6, <sup>3</sup>*J*=6.9); <sup>13</sup>C-NMR (600 MHz, DMSO-*d*<sub>6</sub>, δ [ppm]): 29.1 (C-b, C-j), 30.7 (C-c, C-h), 46.4 (CH<sub>3</sub>), 51.3 (C-a, C-k), 70.0 (C-e, C-f), 72.9 (C-d, C-g), 111.8 (C-11, C-13), 117.3 (C-8), 122.2 (C-3, C-5), 122.7 (C-9), 130.5 (C-10, C-14), 141.6 (C-7), 144.4 (C-2, C-6), 148.9 (C-12), 153.3 (C-4); elemental analysis calcd. (%) for C<sub>24</sub>H<sub>33</sub>ClN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: C 52.88, H 6.10, N 5.14; found: C 53.04, H 5.98, N 5.06; ESI-MS in MeCN *m/z*: 445.2 [**1**<sup>+</sup>].



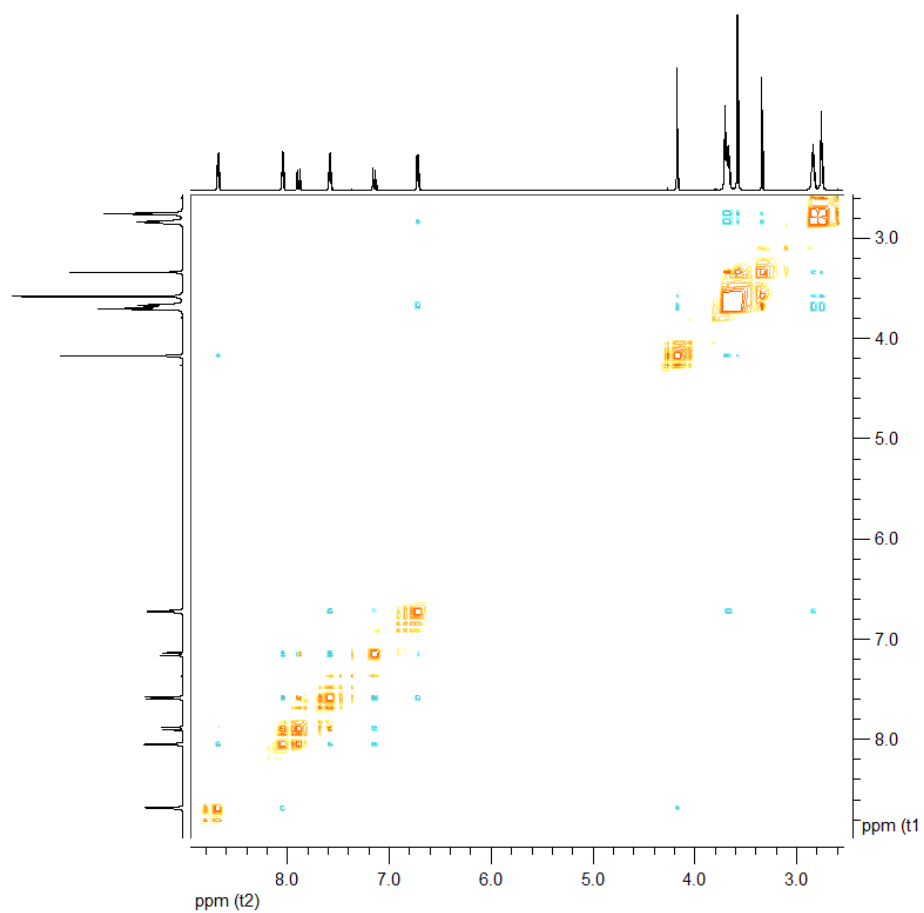
**Fig. S1**  $^1\text{H-NMR}$  spectrum of **1** in  $\text{DMSO-}d_6$



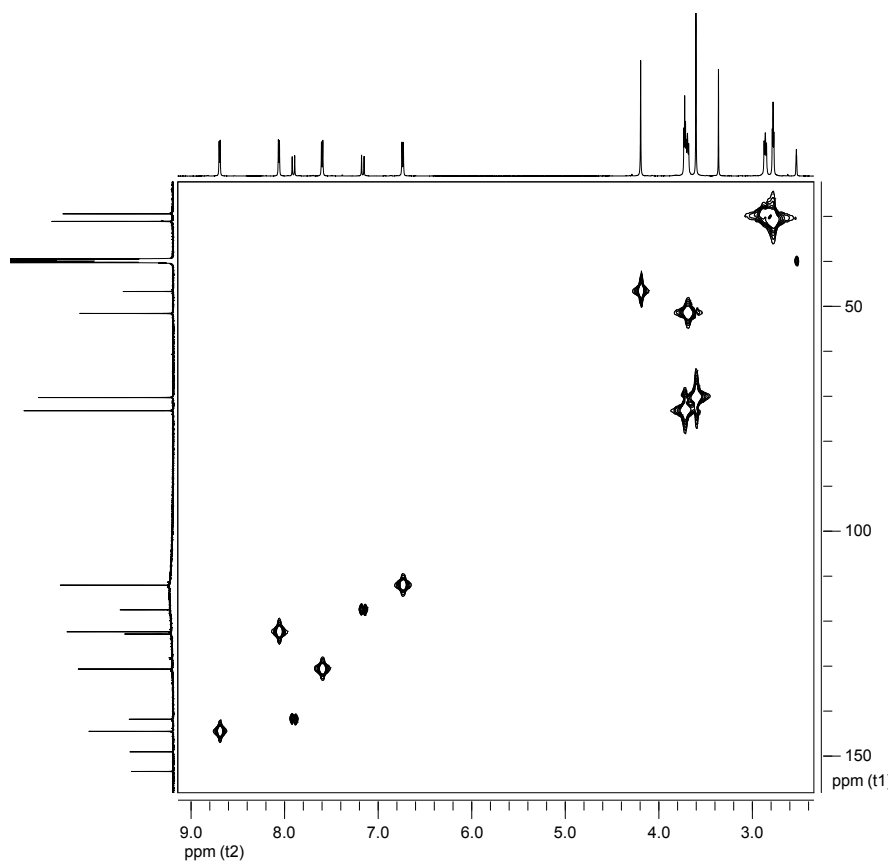
**Fig. S2**  $^{13}\text{C-NMR}$  spectrum of **1** in  $\text{DMSO-}d_6$



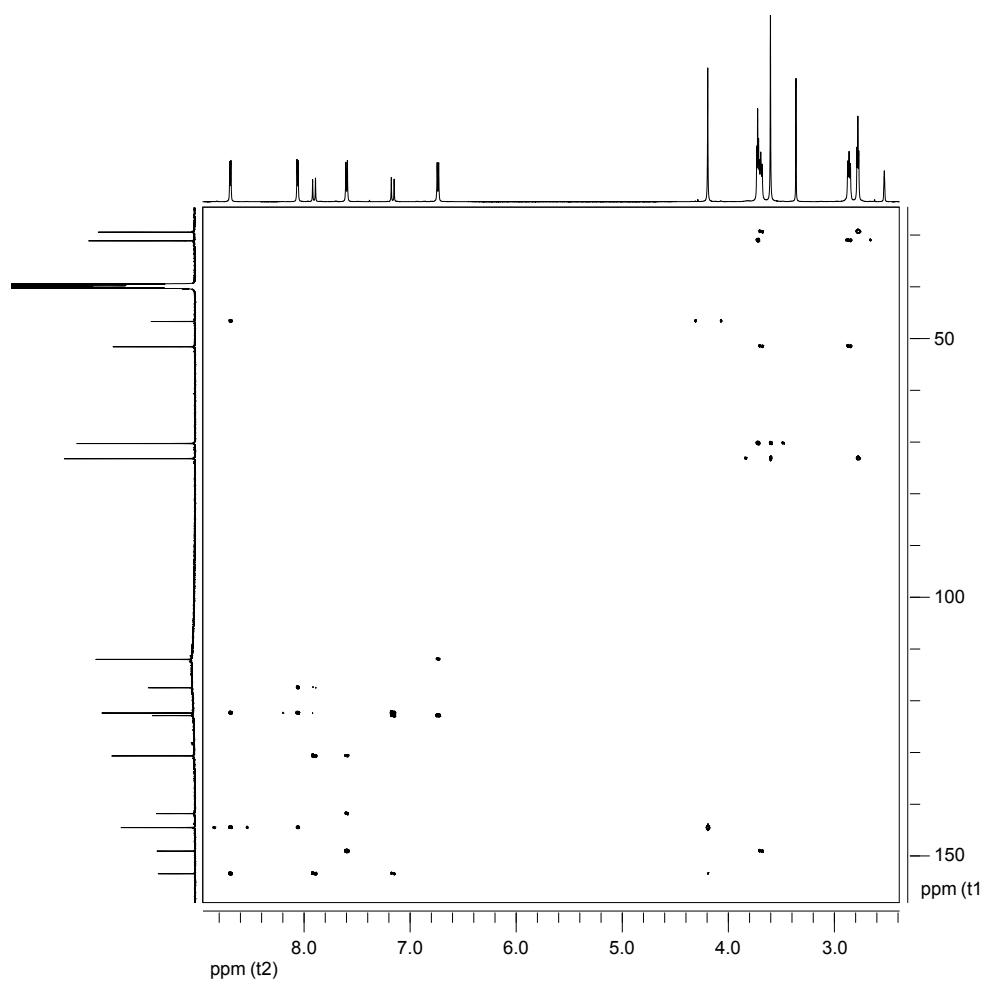
**Fig. S3** {1H, 1H}-COSY spectrum of **1** in DMSO-*d*<sub>6</sub>.



**Fig. S4** {1H, 1H}-ROESY spectrum of **1** in DMSO-*d*<sub>6</sub>.

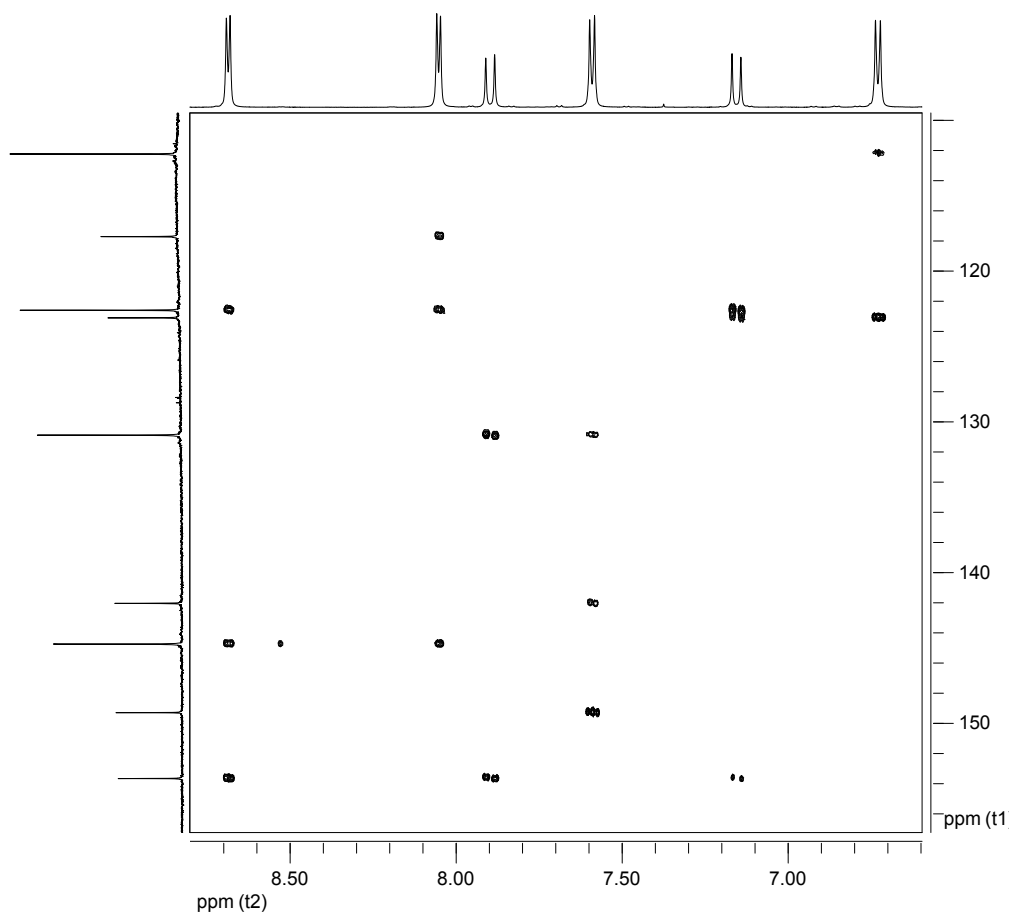


**Fig. S5** HMPC spectrum of **1** in DMSO-*d*<sub>6</sub>.

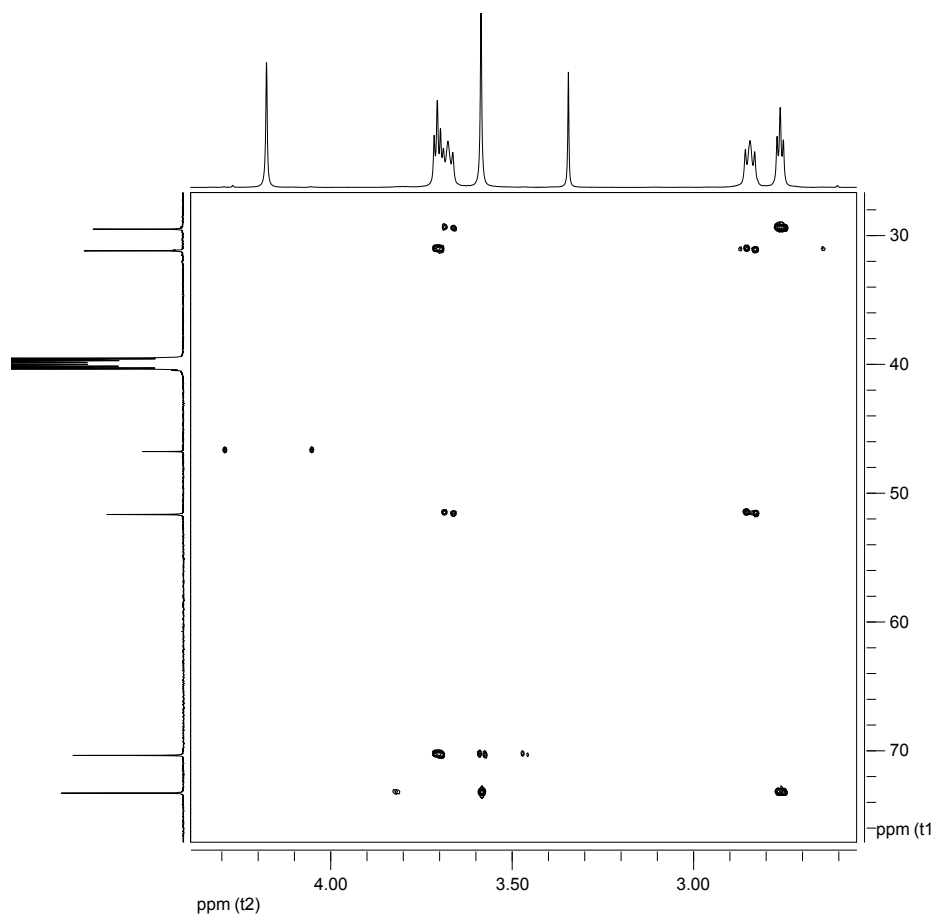


**Fig. S6** HMBC spectrum of **1** in DMSO-*d*<sub>6</sub>.





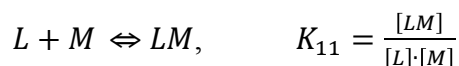
**Fig. S6** HMBC spectrum of **1** in DMSO-*d*<sub>6</sub> (expansion of aromatic region).



**Fig. S6** HMBC spectrum of **1** in DMSO-*d*<sub>6</sub> (expansion of aliphatic region).

### 3. Stability constants determination

**Stability constant of CB[7]•1 complex.** Complex formation of dye **1** with CB[7] in H<sub>2</sub>O+CH<sub>3</sub>CN (1-2%) at 20 ± 1 °C was studied by spectrophotometric titration. The ratio of dye **1** to CB[7] was varied by adding aliquots of a solution containing known concentrations of **1** and CB[7] to a solution of **1** alone of the same concentration. The absorption spectrum of each solution was recorded and the stability constants of the complexes were determined using the «SPECFIT/32» program (Spectrum Software Associates, PMB 361, 197M Boston Post Road, West Marlborough, MA 01752, U.S.A.). One equilibrium was considered in the fitting (L = dye **1**; M = CB[7]):

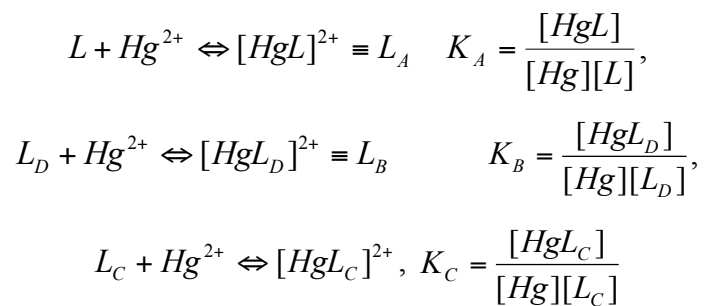


**Relative stability constants of 1•Hg<sup>2+</sup>•CB[7] and 1•Hg<sup>2+</sup> complexes.** Ratio of the ternary complex stability constant to the binary complex stability constant  $K_B/K_A$  was determined by competitive spectrophotometric titration with phenyl-dithia-dioxa-monoaza crown ether **2** as competitor.

To achieve this goal the titration of 1•Hg<sup>2+</sup> and 1•Hg<sup>2+</sup>•CB[7] complexes with increasing competitor concentration were carry out as illustrated in scheme:



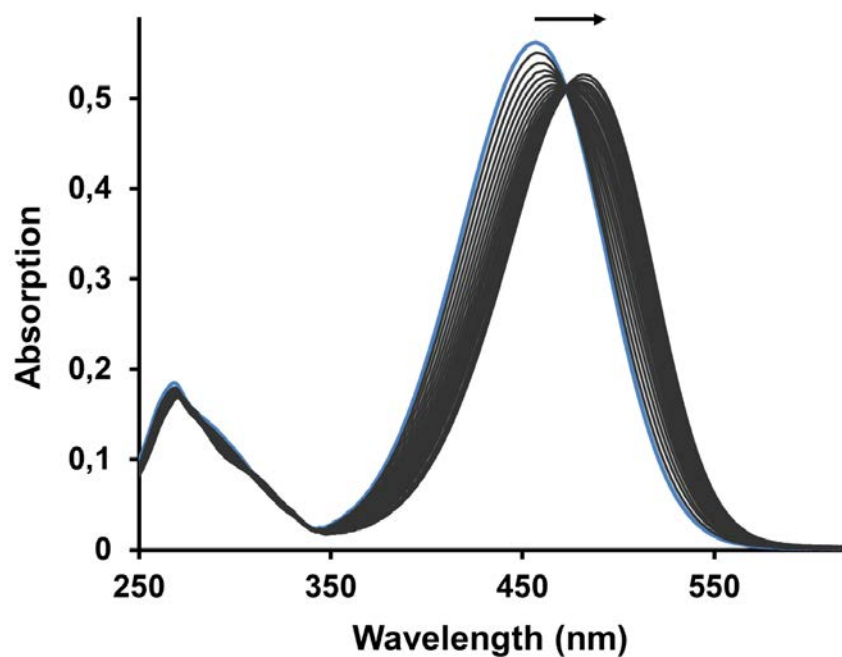
Specifically, the competition for  $\text{Hg}^{2+}$  ions in a solution containing **1** and competitor or CB[7]•**1** and competitor, is described by three equilibria, given below:



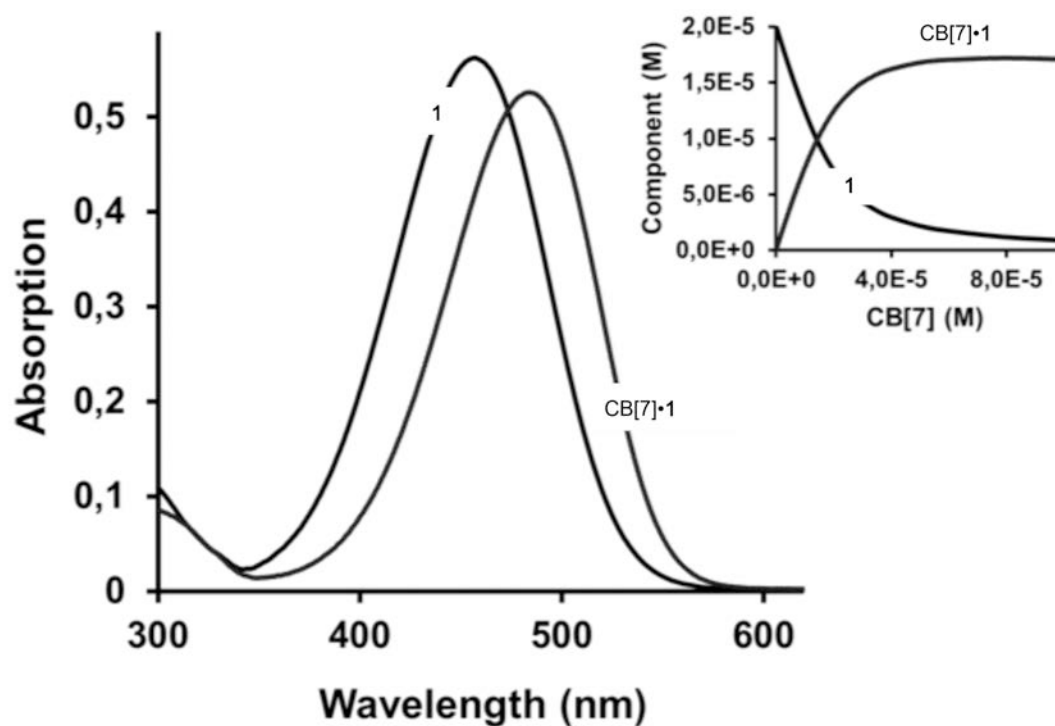
where L – dye **1**,  $L_B$  – **1**• $\text{Hg}^{2+}$ •CB[7] complex,  $L_A$  – **1**• $\text{Hg}^{2+}$  complex,  $L_C$  – phenyl-dithia-dioxo-monoaza crown ether **2**,  $L_D$  – CB[7]•**1** complex.

Ratio of the stability constant  $K_B/K_A$  was determined using the «SPECFIT/32» program.

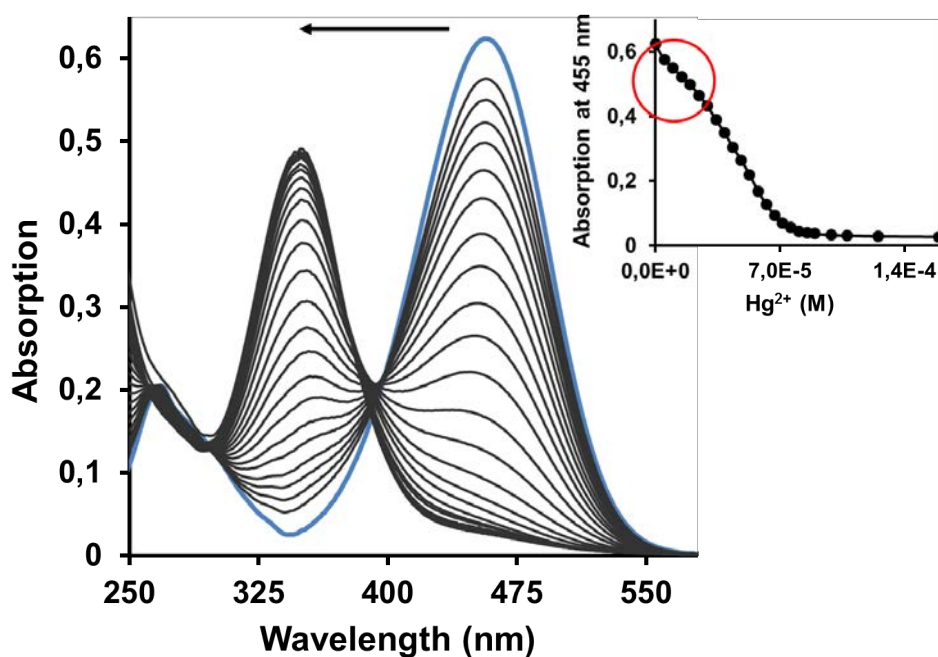
#### 4. UV-Vis spectroscopy data



**Fig. S6** UV-Vis spectra of dye **1** ( $2.0 \times 10^{-5}$  M) with increasing CB[7] concentration ( $0-1.0 \times 10^{-4}$  M) in  $H_2O$ .

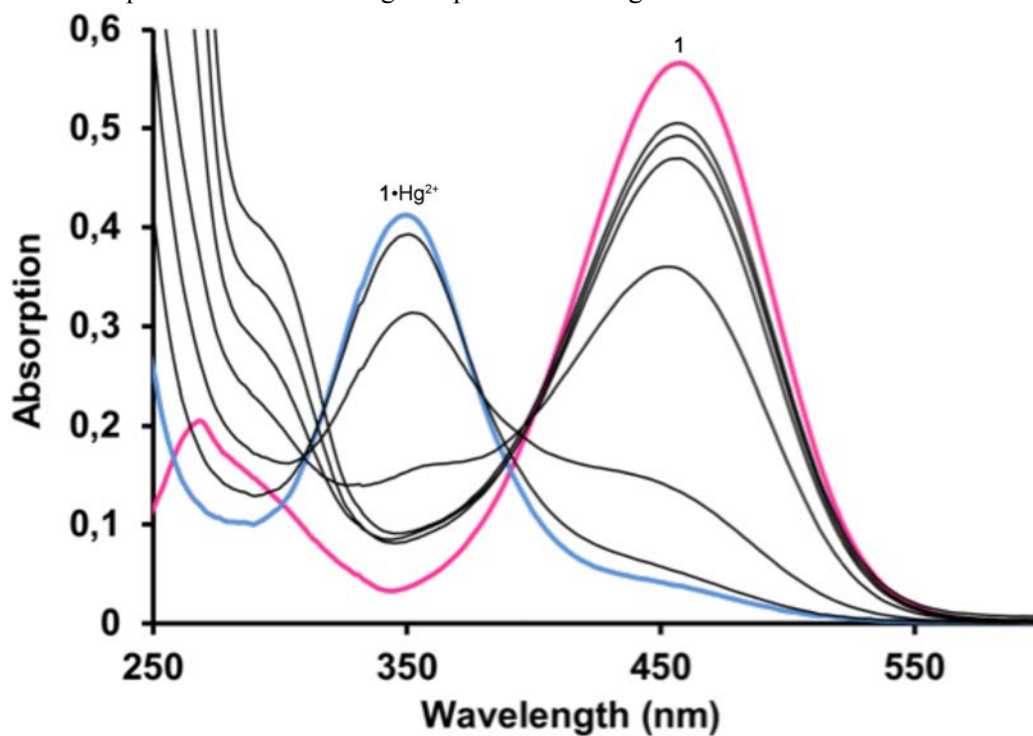


**Fig. S7** Electronic absorption spectra of dye **1** and complex CB[7]•**1** obtained by a global fit of the spectrophotometric titration data using the SpecFit/32 program. Concentration of dye **1** and complex CB[7]•**1** in the system (**1**+CB[7]) as a function of [CB[7]] (inset).

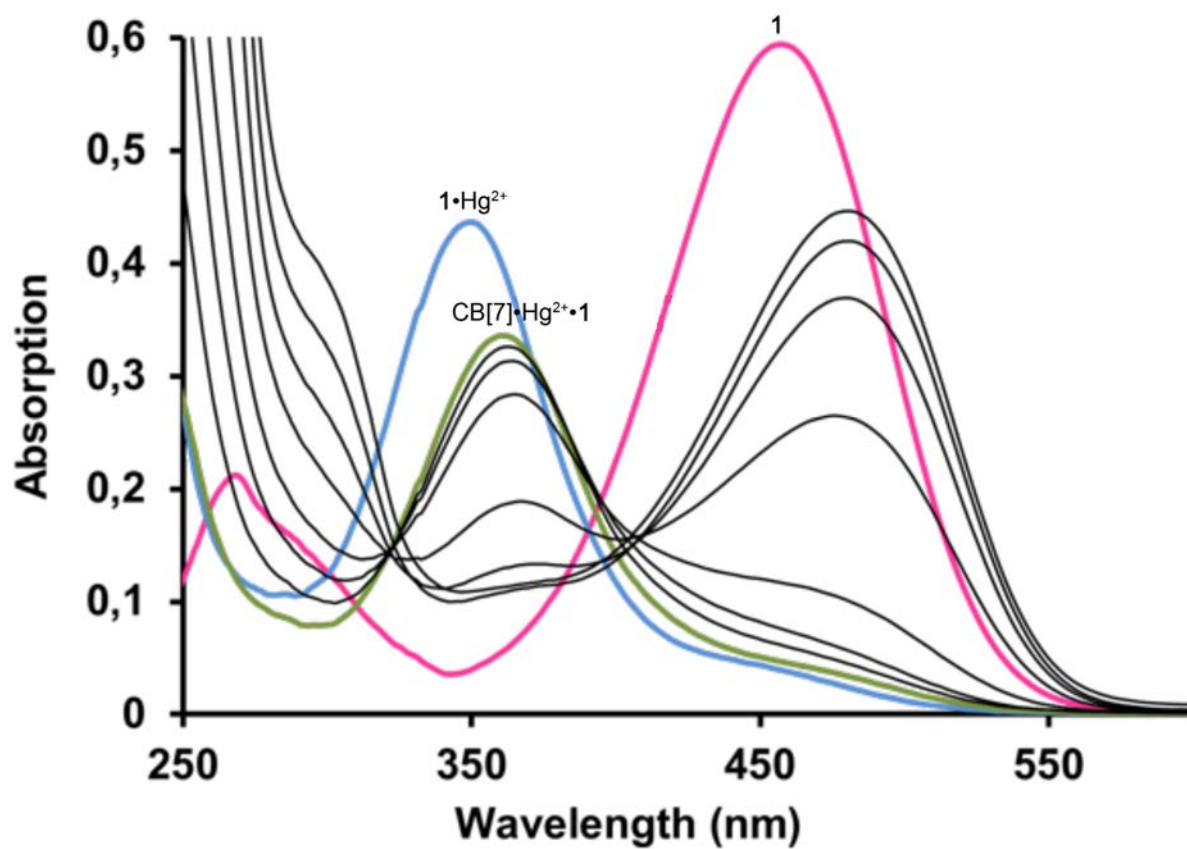


**Fig. S8** UV-Vis spectra of dye **1** ( $2.0 \times 10^{-5}$  M) with increasing  $\text{Hg}(\text{ClO}_4)_2$  concentration ( $0 - 1.6 \times 10^{-4}$  M) in  $\text{H}_2\text{O}$ . Absorption of dye **1** at 455 nm in the system ( $1+\text{Hg}^{2+}$ ) as a function of  $[\text{Hg}^{2+}]$  (inset).\*

\*The distortion of an isosbestic point and ambiguous UV-Vis binding curves (see red ring) were observed upon titration indicating complicated binding model.



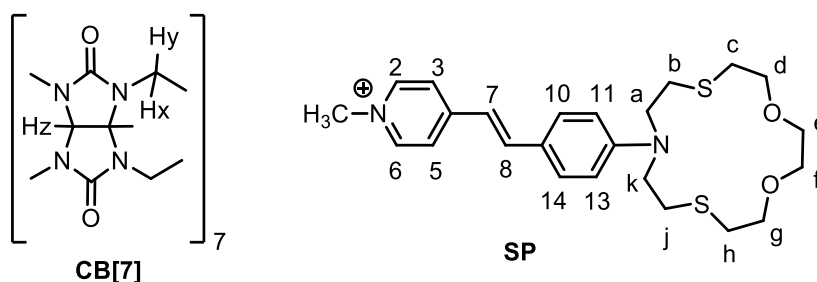
**Fig. S9** UV-Vis spectra of  $1 \cdot \text{Hg}^{2+}$  complex ( $[1] = 2.0 \times 10^{-5}$  M,  $[\text{Hg}^{2+}] = 1.0 \times 10^{-4}$  M) with increasing concentration of **2** ( $0 - 3.2 \times 10^{-4}$  M) in  $\text{H}_2\text{O}$ .



**Fig. S10** UV-Vis spectra of CB[7]·Hg<sup>2+</sup>·1 complex ( $[1] = 2.0 \times 10^{-5}$  M,  $[\text{Hg}^{2+}] = 1.0 \times 10^{-4}$  M,  $[\text{CB}[7]] = 1 \times 10^{-4}$  M) with increasing concentration of 2 ( $0 - 3.2 \times 10^{-4}$  M) in H<sub>2</sub>O.

## 5. Study of complex formation by NMR spectroscopy

$^1\text{H}$  NMR spectra of free dye **1** and **1**• $\text{Hg}^{2+}$ ,  $\text{CB}[7]\cdot\mathbf{1}$ ,  $\text{CB}[7]\cdot\text{Hg}^{2+}\cdot\mathbf{1}$  complexes in  $\text{D}_2\text{O}$ :



**Dye 1.**  $^1\text{H}$ -NMR ( $\text{D}_2\text{O}$ ,  $\delta$  [ppm],  $J$  [Hz]): 2.74 (m, 4H, H-c, H-h), 2.88 (m, 4H, H-b, H-j), 3.63 (s, 4H, H-e, H-f), 3.70 (m, 4H, H-d, H-g), 3.71 (m, 4H, H-a, H-k), 4.10 (s, 3H,  $\text{CH}_3$ ), 6.76 (d, 2H, H-11, H-13,  $^3J=8.8$ ), 7.00 (d, 1H, H-8,  $^3J=16.1$ ), 7.54 (d, 2H, H-10, H-14,  $^3J=8.6$ ), 7.64 (d, 1H, H-7,  $^3J=16.1$ ), 7.80 (d, 2H, H-3, H-5,  $^3J=6.9$ ), 8.32 (d, 2H, H-2, H-6,  $^3J=6.6$ ).

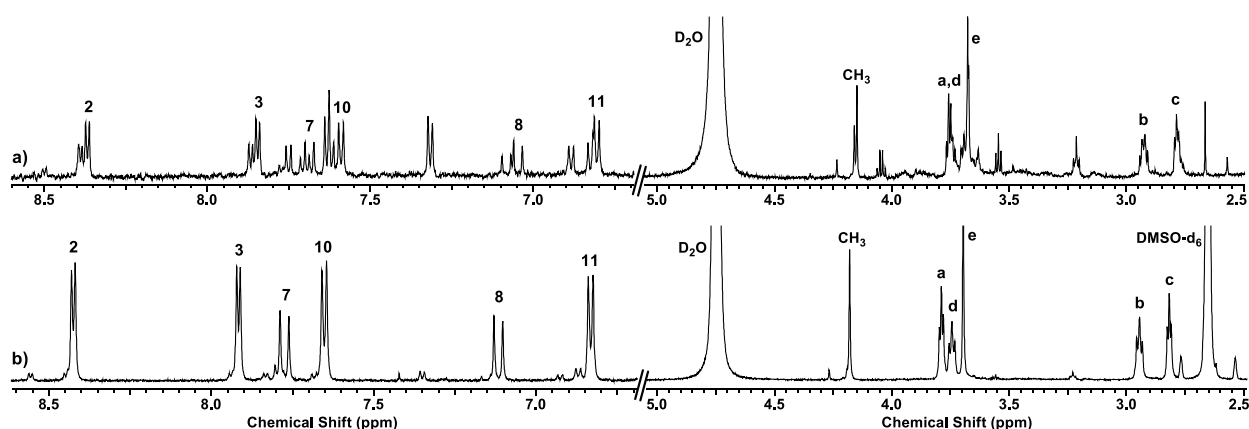
**Dye 1 in the presence of the 1.1 eq. CB[7].**  $^1\text{H}$ -NMR ( $\text{D}_2\text{O}$ ,  $\delta$  [ppm],  $J$  [Hz]): 2.82 (m, 4H, H-c, H-h), 3.07 (m, 4H, H-b, H-j), 3.70 (s, 4H, H-e, H-f), 3.77 (m, 4H, H-d, H-g), 3.85 (m, 4H, H-a, H-k), 4.09 (d, 14H, H-y,  $J=15.4$ ), 4.13 (s, 3H,  $\text{CH}_3$ ), 5.39 (s, 14H, H-z), 5.63 (d, 14H, H-x,  $J=15.4$ ), 6.38 (d, 1H, H-8,  $J=16.0$ ), 6.91 (d, 1H, H-7,  $J=16.0$ ), 7.08 (d, 2H, H-11, H-13,  $^3J=7.9$ ), 7.26 (m, 2H, H-10, H-14), 7.48 (m, 2H, H-3, H-5), 8.08 (m, 2H, H-2, H-6).

**Dye 1 in the presence of the 1.6 eq.  $\text{Hg}(\text{ClO}_4)_2$ .**  $^1\text{H}$ -NMR ( $\text{D}_2\text{O}$ ,  $\delta$  [ppm],  $J$  [Hz]): 3.08-3.67 (m, 16H, H-a, H-b, H-c, H-d, H-g, H-h, H-j, H-k), 3.88 (s, 4H, H-e, H-f), 4.19 (s, 3H,  $\text{CH}_3$ ), 7.50 (d, 2H, H-11, H-13,  $^3J=8.2$ ), 7.27 (d, 1H, H-8,  $^3J=16.3$ ), 7.71 (d, 1H, H-7,  $^3J=16.3$ ), 7.78 (d, 2H, H-10, H-14,  $^3J=8.5$ ), 7.96 (d, 2H, H-3, H-5,  $^3J=6.7$ ), 8.49 (d, 2H, H-2, H-6,  $^3J=6.7$ ).

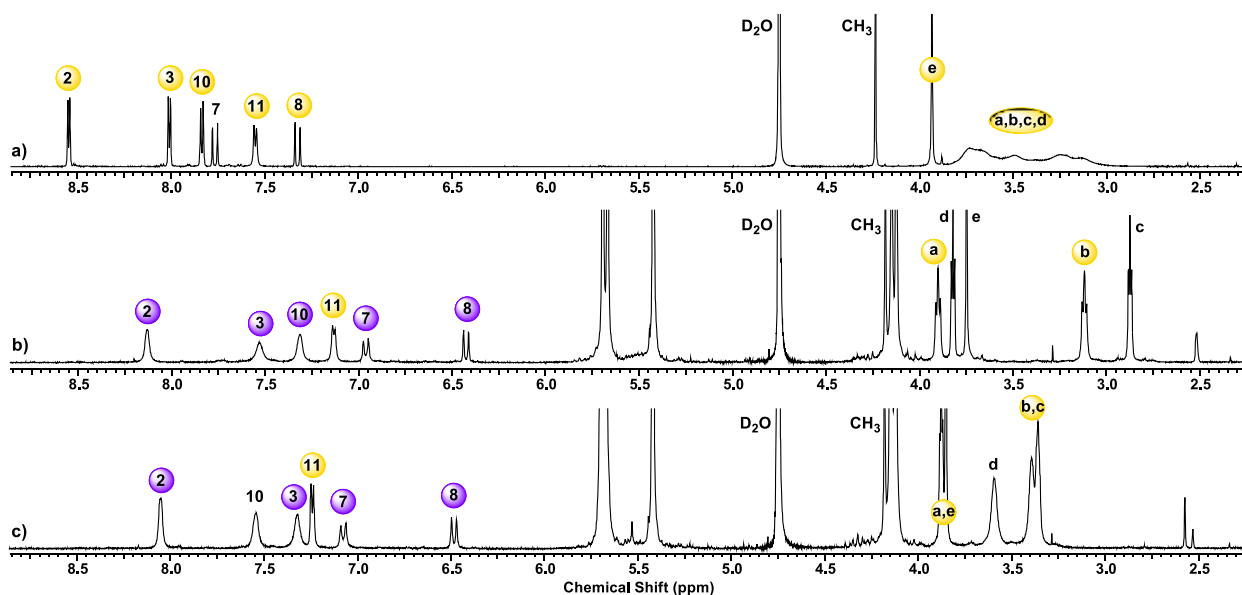
**Dye 1 in the presence of the 1 eq. CB[7] and 1.3 eq.  $\text{Hg}(\text{ClO}_4)_2$ .**  $^1\text{H}$ -NMR ( $\text{D}_2\text{O}$ ,  $\delta$  [ppm],  $J$  [Hz]): 3.31 (m, 4H, H-c, H-h), 3.34 (m, 4H, H-b, H-j), 3.54 (m, 4H, H-d, H-g), 3.80 (s, 4H, H-e, H-f), 3.83 (m, 4H, H-a, H-k), 4.08 (d, 14H, H-y,  $J=15.4$ ), 4.13 (s, 3H,  $\text{CH}_3$ ), 5.37 (s, 14H, H-z), 5.63 (d, 14H, H-x,  $J=15.4$ ), 6.38 (d, 1H, H-8,  $^3J=15.9$ ), 6.91 (d, 1H, H-7,  $^3J=15.9$ ), 7.19 (d, 2H, H-11, H-13,  $^3J=8.2$ ), 7.27 (m, 2H, H-3, H-5), 7.49 (m, 2H, H-10, H-14), 8.00 (m, 2H, H-2, H-6).



The complexity in study of the complex formation by NMR spectroscopy is consisted in extremely poor solubility of free dye **1** in aqueous solution. Despite the fact that the NMR spectrum of dye **1** in DMSO-*d*<sub>6</sub> reveals high purity of the obtained sample (Fig. S1), <sup>1</sup>H-NMR spectrum of **1** in D<sub>2</sub>O represents two combinations of proton signals. We assumed that the second family of proton signals may be associated with dye **1** in the form of tosylate, which could remain after the synthesis in an amount less than 5% due to higher solubility of tosylates in water. To identify correctly the proton signals of dye **1** in the form of perchlorate in D<sub>2</sub>O and make conclusions about the chemical shifts that occur upon complexation with CB[7] and Hg(ClO<sub>4</sub>)<sub>2</sub>, the NMR spectrum of dye **1** was recorded in a mixture of D<sub>2</sub>O/DMSO-*d*<sub>6</sub> at a ratio of 5/2 (Fig. S11). This impurity is only apparent when the <sup>1</sup>H NMR spectrum is measured in D<sub>2</sub>O alone where the impurity is more soluble than the compound itself. Under the conditions used in the rest of the paper where complexation with Hg<sup>2+</sup> and/or CB[7] are involved homogenous solutions are obtained so we are confident that our results are not affected.



**Fig. S11** <sup>1</sup>H-NMR spectra of dye **1** in the D<sub>2</sub>O (a) and in the mixture of D<sub>2</sub>O and DMSO-*d*<sub>6</sub>, the ratio D<sub>2</sub>O: DMSO-*d*<sub>6</sub> = 5:2 (b).



**Fig. S12**  $^1\text{H-NMR}$  spectra (600MHz,  $\text{D}_2\text{O}$ ) of dye **1** in the presence of: a) 1.6 eq. of  $\text{Hg}(\text{ClO}_4)_2$ , b) 1.1 eq. of  $\text{CB}[7]$ , and c) 1 eq. of  $\text{CB}[7]$  and 1.3 eq. of  $\text{Hg}(\text{ClO}_4)_2$ .\*

\* violet color – upfield shift, yellow color – downfield shift.

**Table S1.** Change in the chemical shift in  $^1\text{H-NMR}$  spectra of protons resonance for dye **1** in the presence of  $\text{CB}[7]$  and  $\text{Hg}(\text{ClO}_4)_2$  in  $\text{D}_2\text{O}$ .

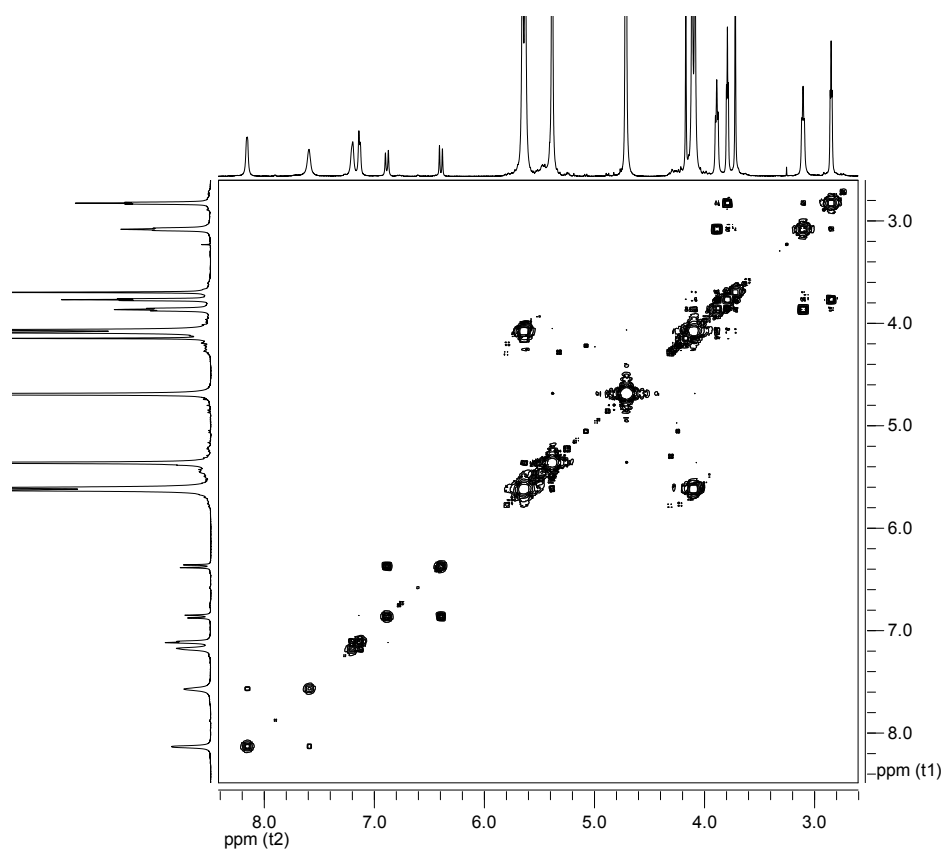
a) Aromatic part

Systems	$\Delta\delta_{\text{H}}$ , ppm ( $\Delta\delta_{\text{H}} = \delta_{\text{complex}} - \delta_{\text{L}}$ )						
	$\text{CH}_3$	H-2,6	H-3,5	H-7	H-8	H-10,14	H-11,13
$\text{CB}[7]\cdot\mathbf{1}$	0.03	-0.24	-0.32	-0.73	-0.62	-0.28	0.32
$\mathbf{1}\cdot\text{Hg}^{2+}$	0.09	0.17	0.16	0.07	0.27	0.24	0.74
$\text{CB}[7]\cdot\text{Hg}^{2+}\cdot\mathbf{1}$	0.03	-0.32	-0.53	-0.62	-0.57	-0.05	0.43

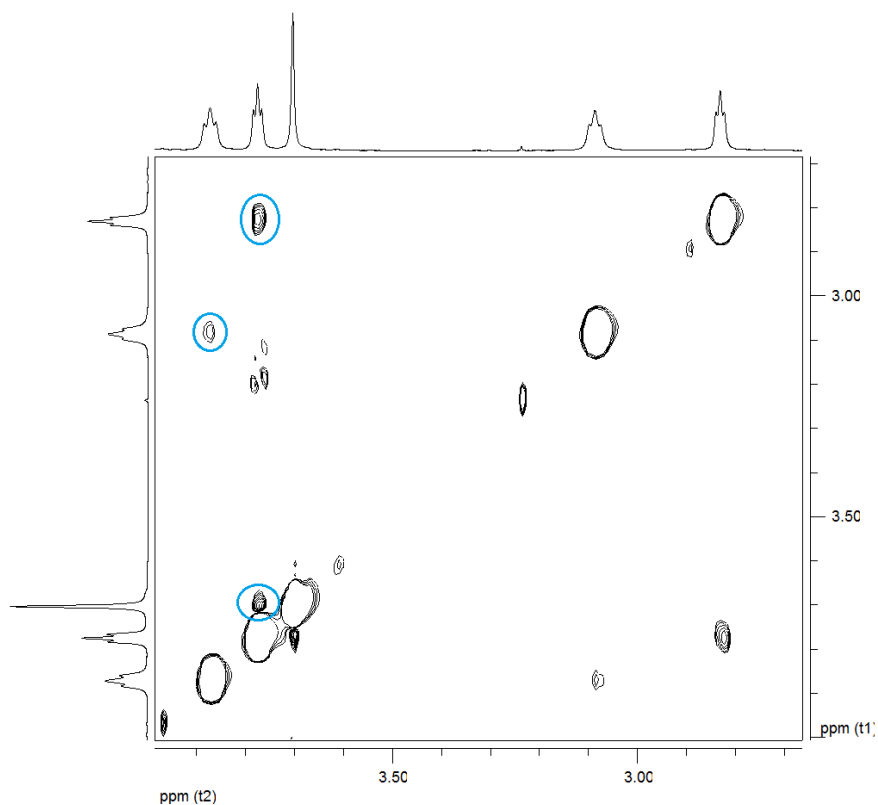
b) Aliphatic part

Systems	$\Delta\delta_{\text{H}}$ , ppm ( $\Delta\delta_{\text{H}} = \delta_{\text{complex}} - \delta_{\text{L}}$ )				
	H-a,k	H-b,j	H-c,h	H-d,g	H-e,f
$\text{CB}[7]\cdot\mathbf{1}$	0.14	0.19	0.08	0.07	0.07
$\mathbf{1}\cdot\text{Hg}^{2+}$	broadened signals; $\Delta\delta_{\text{H}}$ up to 0.34				0.25
$\text{CB}[7]\cdot\text{Hg}^{2+}\cdot\mathbf{1}$	0.13	0.46	0.57	-0.16	0.17

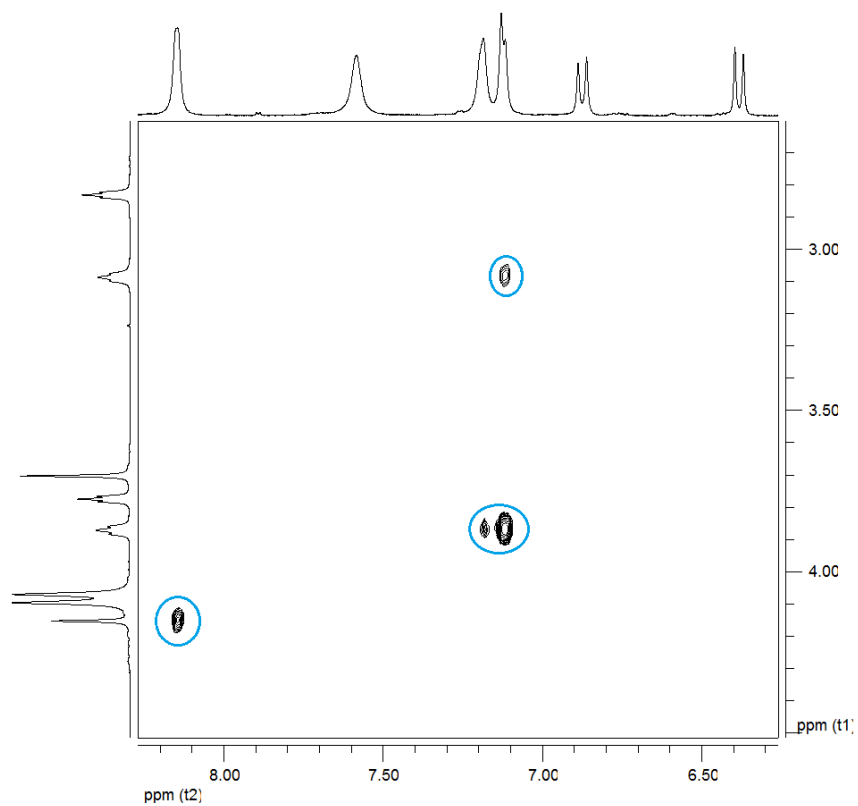
The 2D NMR spectra of the discussed complexes are presented below. The ROESY-signals, which are relevant to the molecular structure, are marked with blue color.



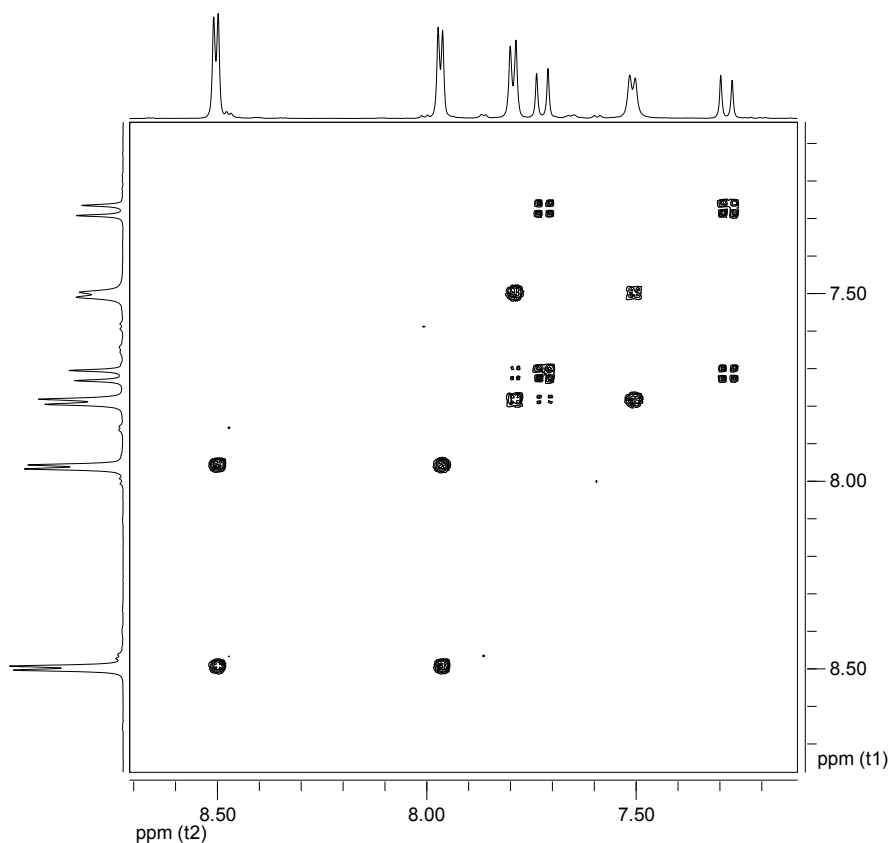
**Fig. S13**  $\{^1\text{H}, ^1\text{H}\}$ -COSY spectrum of dye **1** in the presence of 1.1 eq. of CB[7] in  $\text{D}_2\text{O}$ .



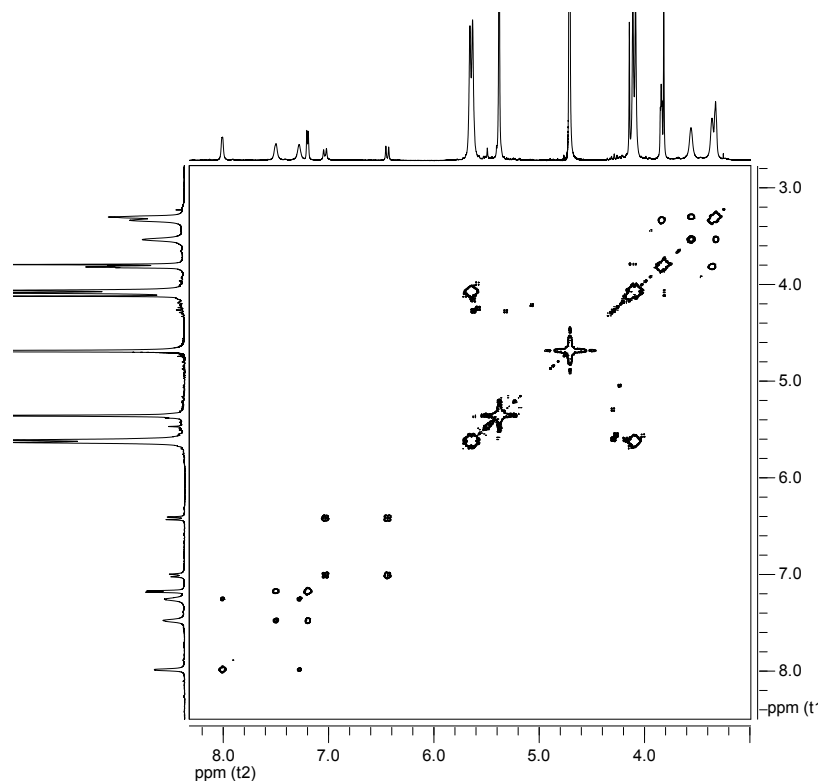
**Fig. S14** {<sup>1</sup>H, <sup>1</sup>H}-ROESY spectrum of dye **1** in the presence of 1.1 eq. of CB[7] in D<sub>2</sub>O (aliphatic part).



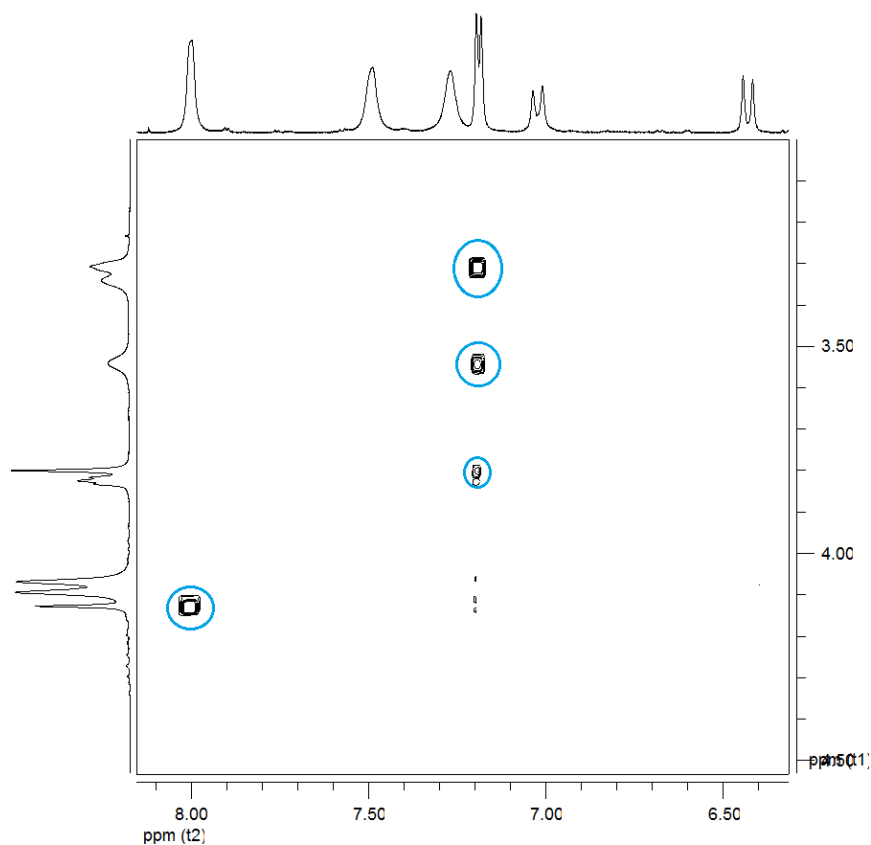
**Fig. S15** {<sup>1</sup>H, <sup>1</sup>H}-ROESY spectrum of dye **1** in the presence of 1.1 eq. of CB[7] in D<sub>2</sub>O (aliphatic-aromatic part).



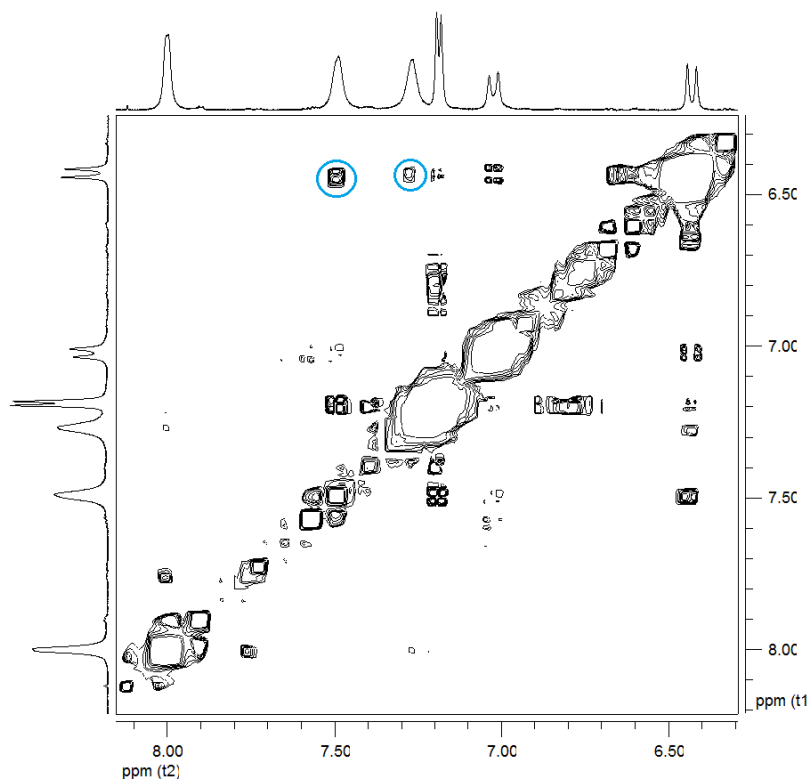
**Fig. S16** {<sup>1</sup>H, <sup>1</sup>H}-COSY spectrum of dye **1** in the presence of 1.6 eq. of Hg(ClO<sub>4</sub>)<sub>2</sub> in D<sub>2</sub>O (aromatic part).



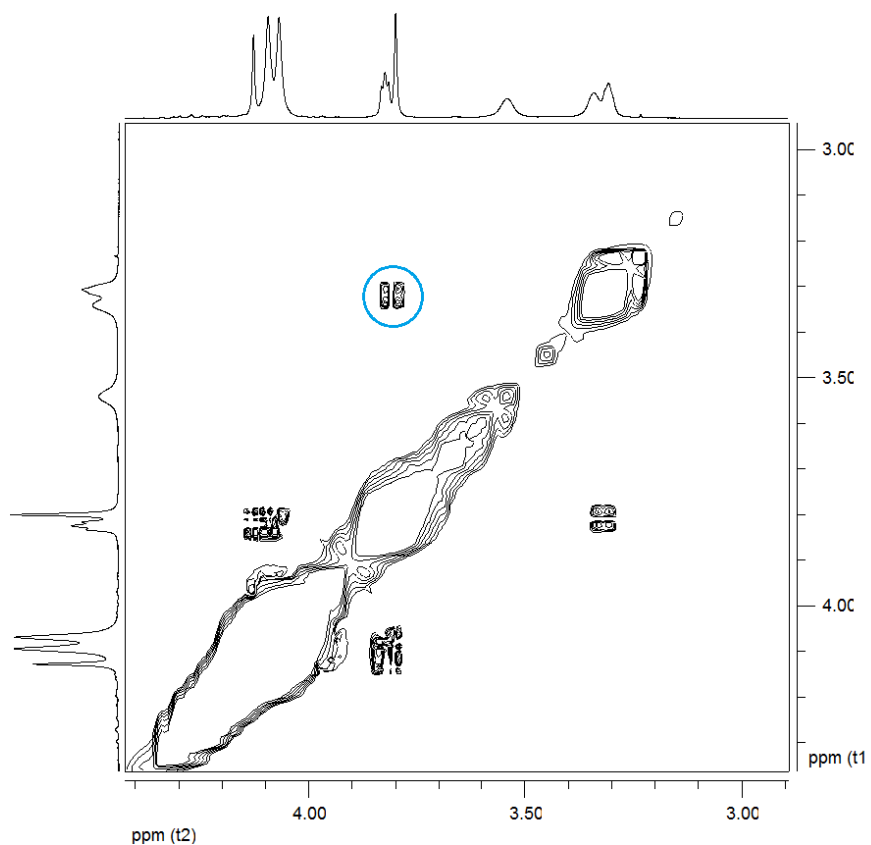
**Fig. S17** {<sup>1</sup>H, <sup>1</sup>H}-COSY spectrum of dye **1** in the presence of 1 eq. of CB[7] and 1.3 eq. of Hg(ClO<sub>4</sub>)<sub>2</sub> in D<sub>2</sub>O.



**Fig. S18** {<sup>1</sup>H, <sup>1</sup>H}-ROESY spectrum of dye **1** in the presence of 1 eq. of CB[7] and 1.3 eq. of Hg(ClO<sub>4</sub>)<sub>2</sub> in D<sub>2</sub>O (aliphatic-aromatic part).



**Fig. S19** {<sup>1</sup>H, <sup>1</sup>H}-ROESY spectrum of dye **1** in the presence of 1 eq. of CB[7] and 1.3 eq. of Hg(ClO<sub>4</sub>)<sub>2</sub> in D<sub>2</sub>O (aromatic part).



**Fig. S20** {1H, 1H}-ROESY spectrum of dye **1** in the presence of 1 eq. of CB[7] and 1.3 eq. of Hg(ClO<sub>4</sub>)<sub>2</sub> in D<sub>2</sub>O (aliphatic part).

## 6. References

- <sup>1</sup> A. Day, A.P. Arnold, R.J. Blanch, B. Snushall, *J. Org. Chem.*, 2001, **66**, 8094.
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