

# Photoinduced Guest Transformation Promotes Translocation of Guest from Hydroxypropyl- $\beta$ -Cyclodextrin to Cucurbit[7]uril

## SUPPORTING INFORMATION

By Yuri V. Fedorov,<sup>\*,a</sup> Sergey V. Tkachenko,<sup>a</sup> Ekaterina Yu. Chernikova,<sup>a</sup> Ivan A. Godovikov,<sup>a</sup> Olga A. Fedorova,<sup>a</sup> and Lyle Isaacs<sup>\*,b</sup>

<sup>a</sup>A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences,  
28 Vavilova Str., Moscow, 119991 Russia

<sup>b</sup>Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA

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## Experimental section

### *Materials.*

The solvents used for absorption and emission analysis are as follows: acetonitrile (ACN), distilled water (18.2 M $\Omega$ ), phosphate buffer solution. All the solvents employed (with the exception of distilled water) were Aldrich or Fluka spectroscopic grade. The absorption and fluorescence of all solvents were checked for impurities and have been subtracted from the sample spectra. Reagents for synthesis were purchased from commercial suppliers and used without further purification. The 2-hydroxypropyl- $\beta$ -cyclodextrin HP- $\beta$ -CD was purchased from Aldrich (catalog number 332606, degree of substitution = 0.8 per sugar). Anhydrous Ba(ClO<sub>4</sub>)<sub>2</sub>, Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> (Aldrich) were used as received. Cucurbit[7]uril was synthesized according to the literature procedures.[1] Compounds **1** and **2** were synthesized according to the literature procedures.[2,3] The photochemical synthesis of compounds **3** and **4** has been published previously.[4,5]

### *General Techniques.*

All melting points were taken on a «Mel-temp II». The NMR experiments were carried out using a Bruker Avance 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 experiments as well as 2D experiments (COSY, ROESY, HSQC, HMBC) were performed at 298 K using standard pulse sequences from the Bruker library. The chemical shifts and spin-spin coupling constants were determined with an accuracy of 0.01 ppm and 0.1 Hz, respectively. Microanalyses were performed by the Service of Microanalysis of A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS). Steady-state UV-vis spectra were recorded with a Varian-Cary 100 UV-Vis spectrophotometer or Specord M40 spectrophotometer (Carl Zeiss JENA, DDR) connected with a computer. The spectrophotometer was controlled, data were collected, and the simplest computer simulation of the spectra was performed using the SPECORD standard program (version 2.0, Etalon). Acquisition of electronic absorption spectra under continuous irradiation of samples was performed using an «Avantes» spectrophotometer. The fluorescence quantum yield measurements were performed

using FluoroLog-3-221 (Jobin Yvon) spectrofluorimeter. All measured fluorescence spectra were corrected for the non-uniformity of detector spectral sensitivity. Quinine sulfate solution in 0.5 M H<sub>2</sub>SO<sub>4</sub> ( $\Phi_{fl} = 0.55$ ) and coumarin 6 in ethanol ( $\Phi_{fl} = 0.78$ ) were used as reference for the fluorescence quantum yield measurements.[6]  $\Phi_F$  values were determined by applying the following equation:

$$\Phi_{F,x} = \Phi_{F,r} \frac{(1 - 10^{-A_r})D_x}{(1 - 10^{-A_x})D_r},$$

where  $\Phi_{F,x}$  and  $\Phi_{F,r}$  are the fluorescence quantum yields of the analyte and the standard, respectively,  $A_x$  and  $A_r$  are the absorbances of the analyte and the standard solutions, respectively, and  $D_x$  and  $D_r$  are the integrated area of the emission fluorescence spectra, corrected for the solvent blank, of the analyte and the standard solutions, respectively.

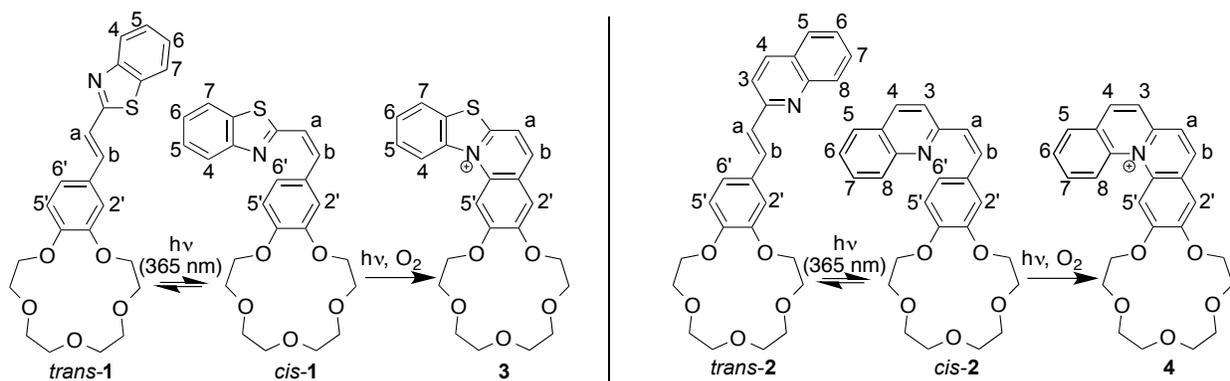
Solution preparations and measurements were carried out in red light.

## Procedures

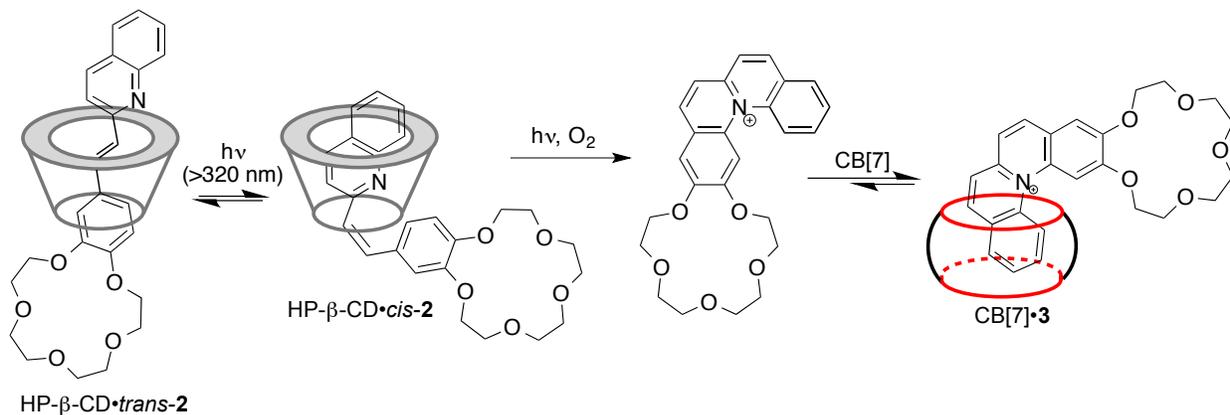
Stock solutions of  $2 \times 10^{-3}$  M **1** or **2** were prepared in MeCN and kept in the dark to avoid photoisomerization. These solutions were diluted to obtain  $2 \times 10^{-5}$  M working solutions for spectroscopic studies.  $10^{-1}$  M stock solution of HP- $\beta$ -CD and  $2 \times 10^{-3}$  M stock solution of CB[7] were prepared in distilled water. The general procedure was to add in the cuvette 20  $\mu$ l of the ligand stock solution to 2.0 ml of the HP- $\beta$ -CD/CB[7] initial solution or to 2.0 ml of pure ethanol, cyclohexane, dimethyl sulfoxide or distilled water. Thus, a  $2 \times 10^{-5}$  M concentration of ligand and concentrations of HP- $\beta$ -CD equal to those of the stock solutions were obtained in all cases. For all working aqueous solutions, the water-MeCN ratio was 100:1, v/v.

10 mM phosphate buffer solution was prepared from Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> (Aldrich) and distilled water according to known methods. pH of solution was measured using a pH-meter and set to 7.00 by addition of small amounts of concentrated aqueous solutions of NaOH (1 M) or HClO<sub>4</sub> (1 M).

### Scheme S1



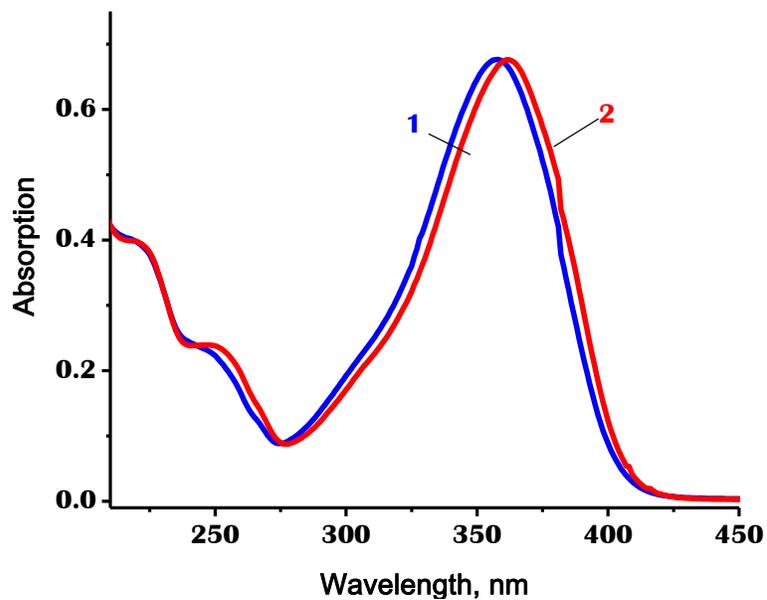
### Scheme S2



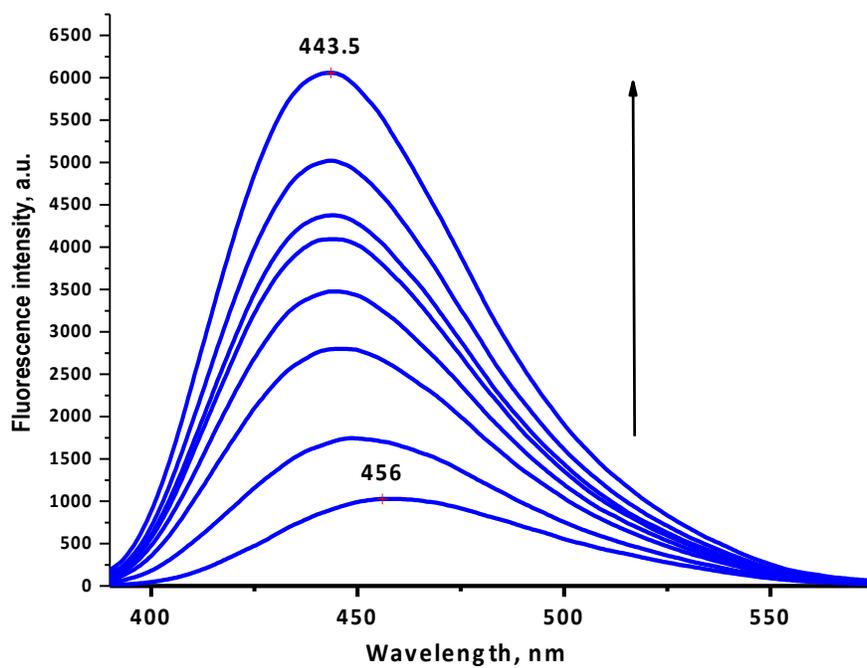
**Table S1.** Steady-State Absorption and Fluorescence Data and Equilibrium Constants for Dyes **1-4** and their Complexes with HP- $\beta$ -CD and CB[7] in H<sub>2</sub>O.

compound	$\lambda_{\text{abs}}$ (nm)	$\Delta\lambda_{\text{abs}}$ (nm) <sup>a</sup>	$\epsilon \times 10^{-4}$ (L·mol <sup>-1</sup> ·cm <sup>-1</sup> )	log K (M <sup>-1</sup> or M <sup>-2</sup> )	$\lambda_{\text{n}}$ (nm)	$\Delta\lambda_{\text{n}}$ (nm) <sup>b</sup>	$\phi_{\text{n}} \times 10^2$
<b>1</b>	358	-	3.4	-	463	-	0.78
(HP- $\beta$ -CD) <b>1</b>	362	4	3.4	logK <sub>11</sub> = 3.58 ± 0.01	445	-18	7.78
(HP- $\beta$ -CD) <sub>2</sub> <b>1</b>				logK <sub>21</sub> = 4.70 ± 0.15			
<b>3</b>	399	-	1.5	-	442	-	2.66
(CB[7]) <b>3</b>	404	5	1.1	logK <sub>11</sub> = 3.14 ± 0.01	439	-3	2.53
<b>2</b>	357	-	2.9	-	487	-	4.07
(HP- $\beta$ -CD) <b>2</b>	358	1	2.9	logK <sub>11</sub> = 3.04 ± 0.06	460	-27	11.84
<b>4</b>	431	-	0.28	-	488	-	33.42
(CB[7]) <b>4</b>	440	9	0.25	logK <sub>11</sub> = 2.47 ± 0.15	484	-4	33.21

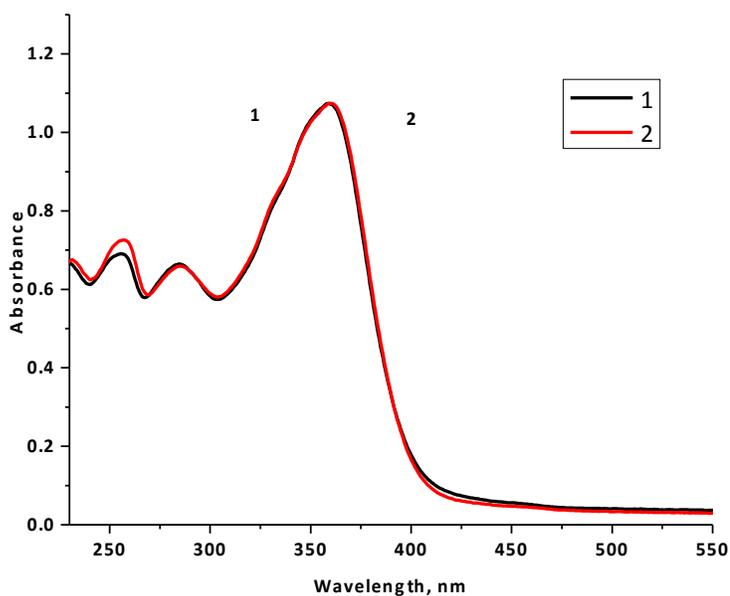
## UV-Vis, Fluorescence and NMR data



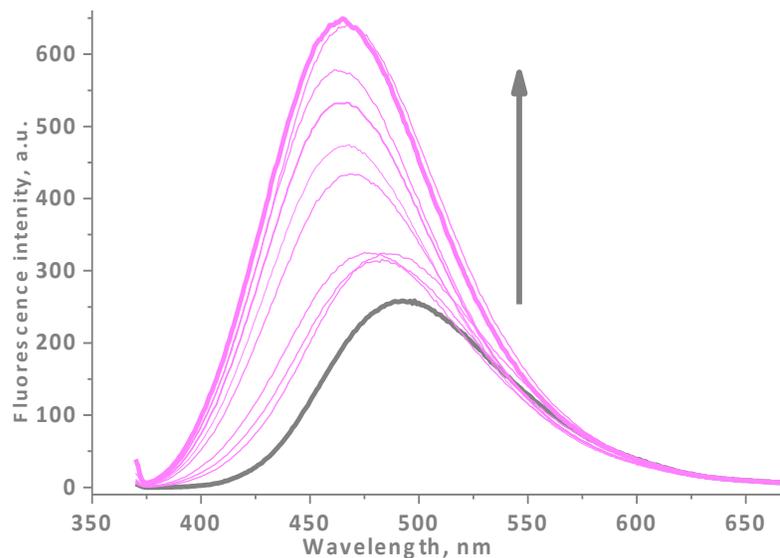
**Figure S1.** UV-Vis spectra of 1) *trans*-1 and 2) 1-HP- $\beta$ -CD in H<sub>2</sub>O,  $C_1 = 2 \cdot 10^{-5}$  M,  $C_{\text{HP-}\beta\text{-CD}} = 4 \cdot 10^{-3}$  M.



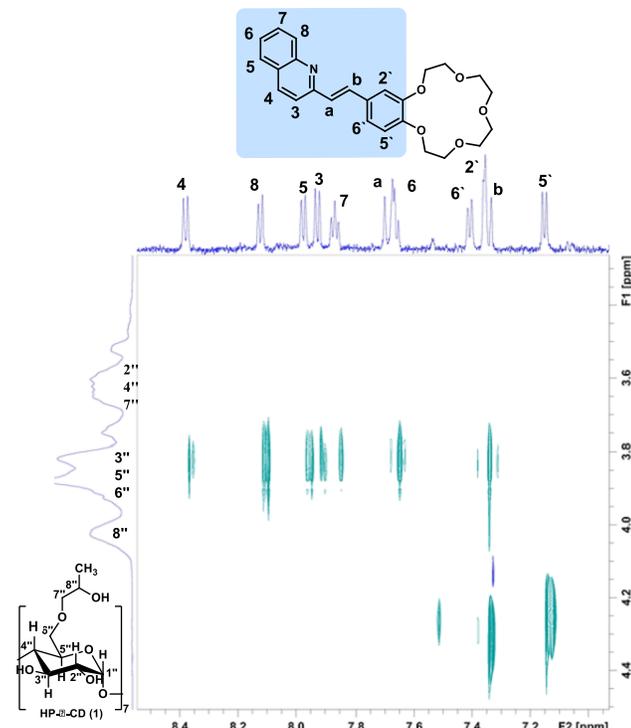
**Figure S2.** Changes in fluorescence spectra of *trans*-1 upon addition of HP- $\beta$ -CD in H<sub>2</sub>O, 20°C:  $C_1 = 2 \cdot 10^{-5}$  M,  $C_{\text{HP-}\beta\text{-CD}} = 0 - 0.1$  M,  $\lambda_{\text{ex}} = 366$  nm.



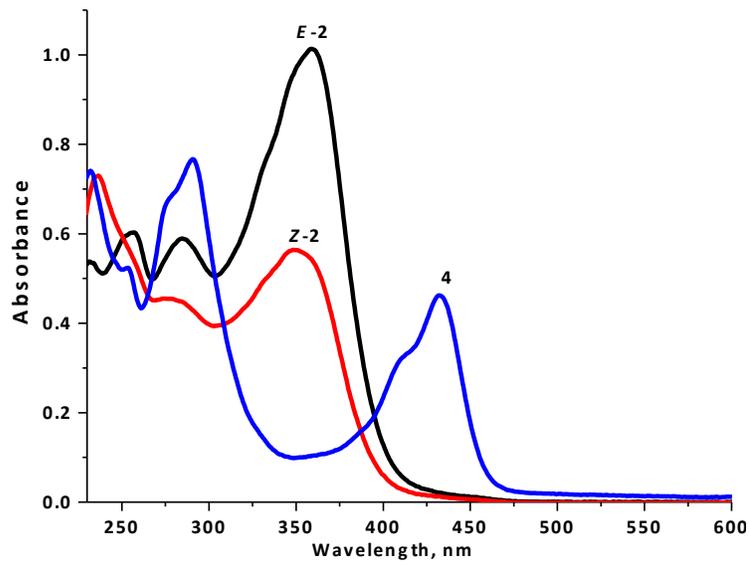
**Figure S3.** UV-Vis spectra of 1) *trans-2* and 2)  $2 \cdot \text{HP-}\beta\text{-CD}$  in  $\text{H}_2\text{O}$ ,  $C_2 = 4 \cdot 10^{-5} \text{ M}$ ,  $C_{\text{HP-}\beta\text{-CD}} = 4 \cdot 10^{-3} \text{ M}$ .



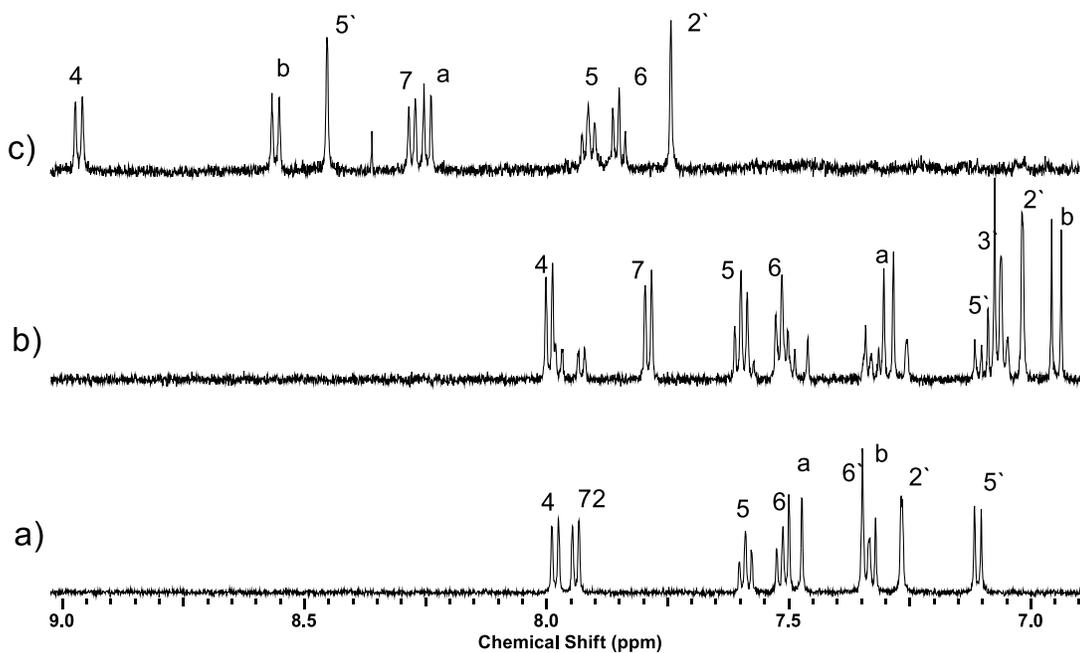
**Figure S4.** Changes in fluorescence spectra of *trans-2* upon addition of  $\text{HP-}\beta\text{-CD}$  in  $\text{H}_2\text{O}$ ,  $20^\circ\text{C}$ :  $C_2 = 1 \cdot 10^{-5} \text{ M}$ ,  $C_{\text{HP-}\beta\text{-CD}} = 0 - 1 \cdot 10^{-3} \text{ M}$ ,  $\lambda_{\text{ex}} = 366 \text{ nm}$ .



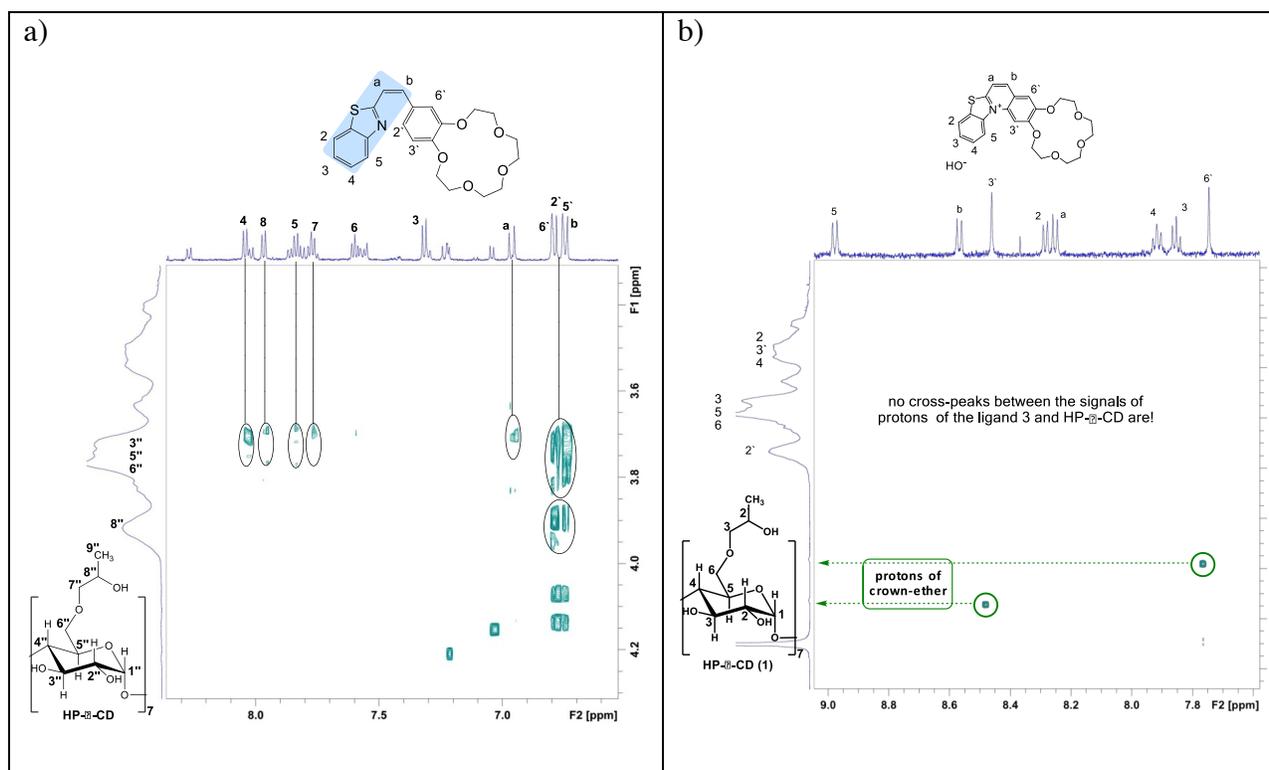
**Figure S5.** ROESY spectrum (600 MHz, D<sub>2</sub>O) of *trans-2*+HP-β-CD ( $C_2 = 2 \cdot 10^{-4}$  M,  $C_{\text{HP-}\beta\text{-CD}} = 0.01$  M).



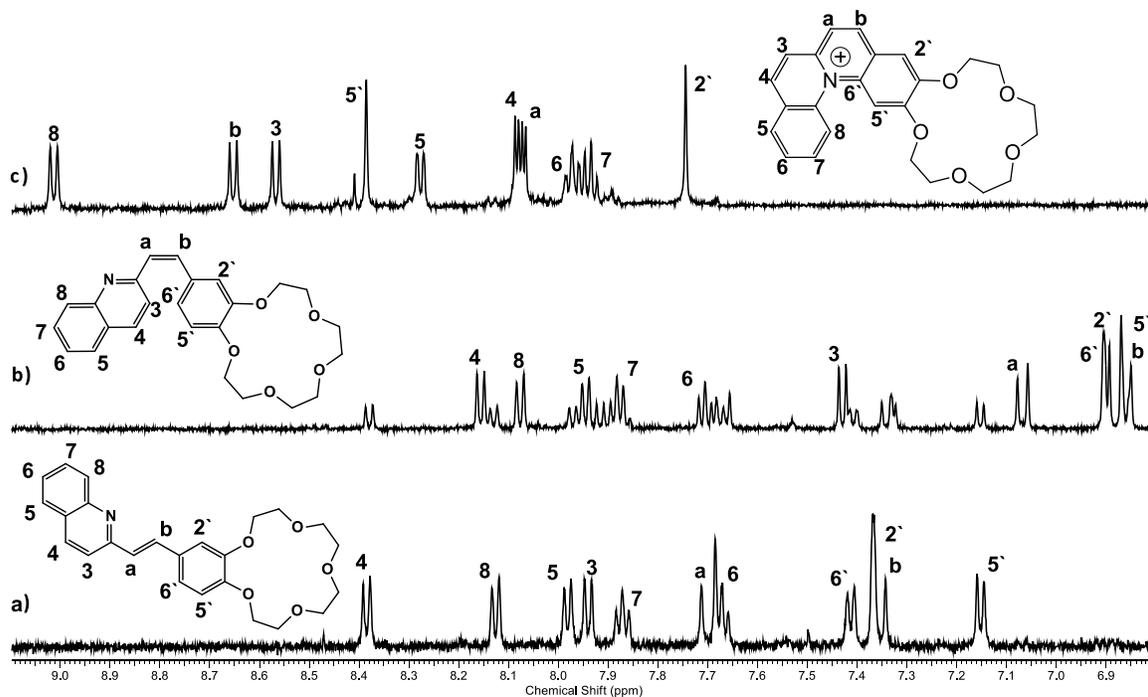
**Figure S6.** UV-Vis spectra of: 1) *trans-2*-HP-β-CD; 2) *cis-2*-HP-β-CD and 3) **4** in H<sub>2</sub>O;  $C_2 = C_4 = 2 \cdot 10^{-5}$  M.



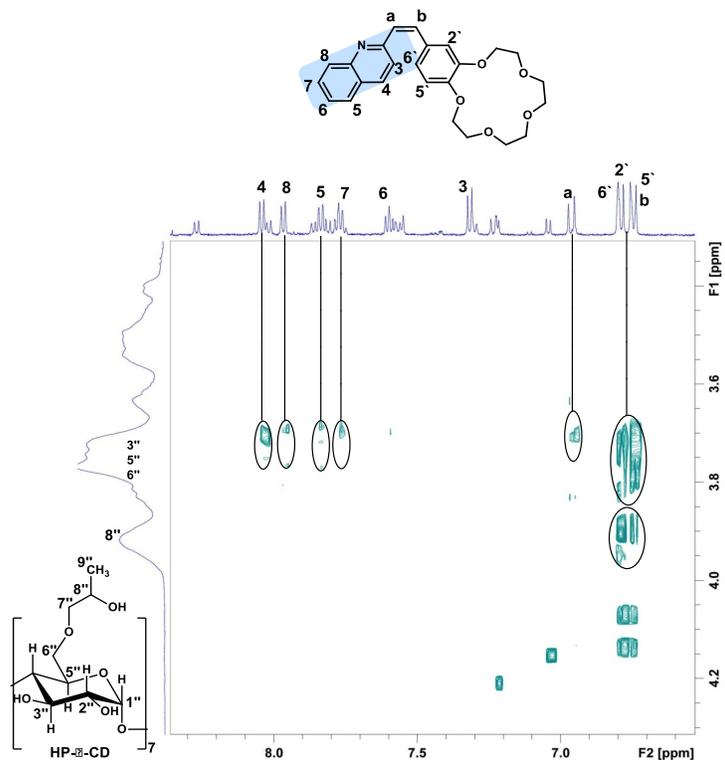
**Figure S7.**  $^1\text{H}$  NMR spectra of a) *trans*-1+HP- $\beta$ -CD; b) *cis*-1+HP- $\beta$ -CD; c) **3** in  $\text{D}_2\text{O}$ .



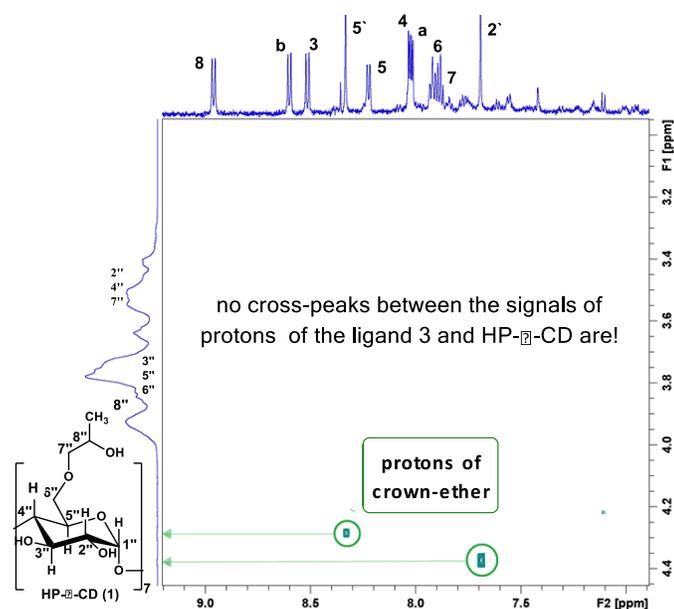
**Figure S8.** ROESY spectra of a) *cis*-1+HP- $\beta$ -CD; b) **3**+HP- $\beta$ -CD in  $\text{D}_2\text{O}$ .



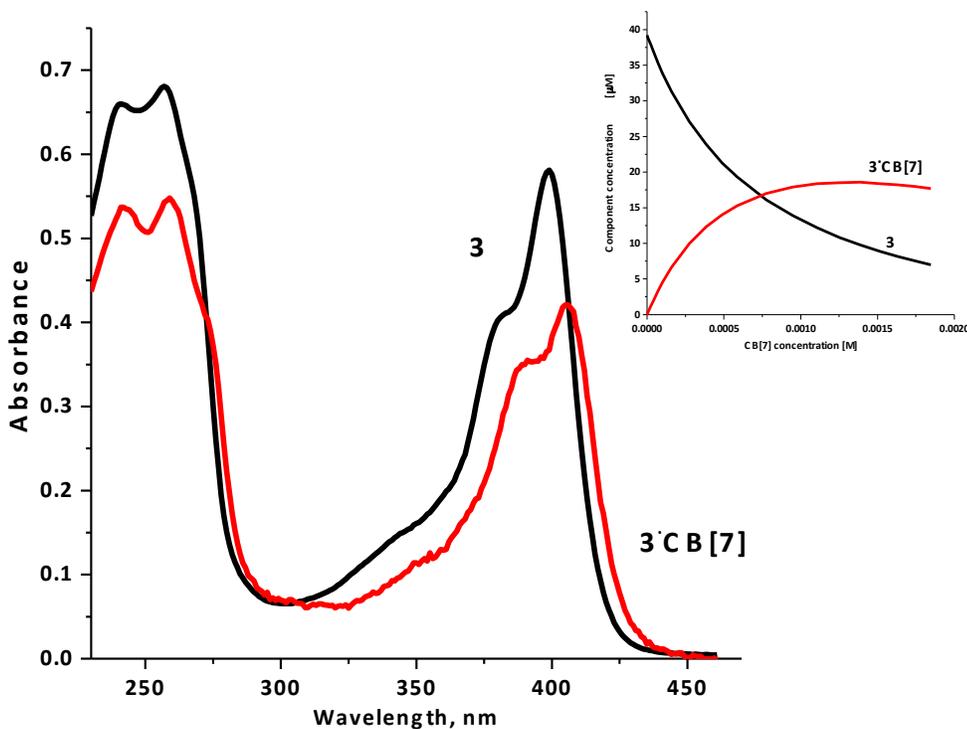
**Figure S9.**  $^1\text{H}$  NMR spectra of a) *trans*-2+HP- $\beta$ -CD; b) *cis*-2-HP- $\beta$ -CD; c) **4**.



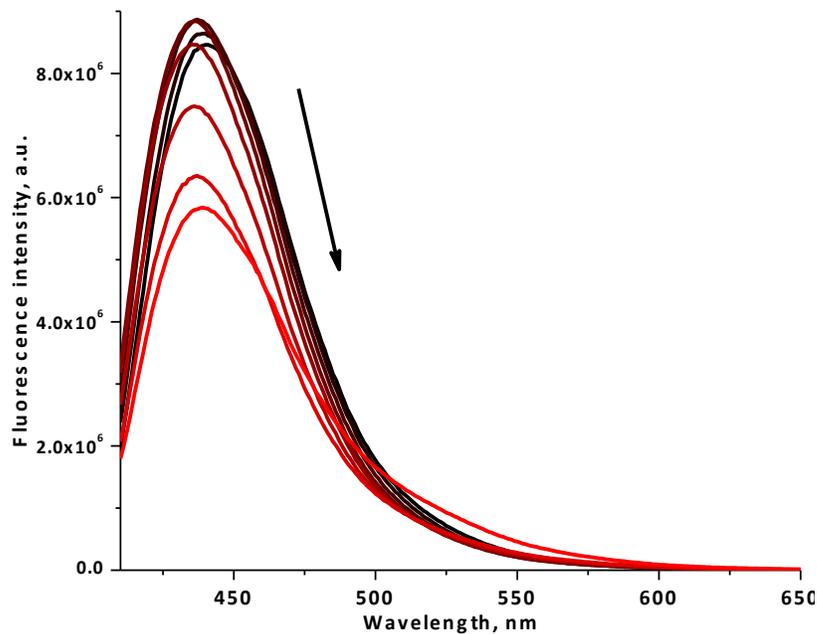
**Figure S10.** ROESY spectrum (600 MHz,  $\text{D}_2\text{O}$ ) of *cis*-2+HP- $\beta$ -CD,  $C_2 = 2 \cdot 10^{-4}$  M,  $C_{\text{HP-}\beta\text{-CD}} = 10$  mM.



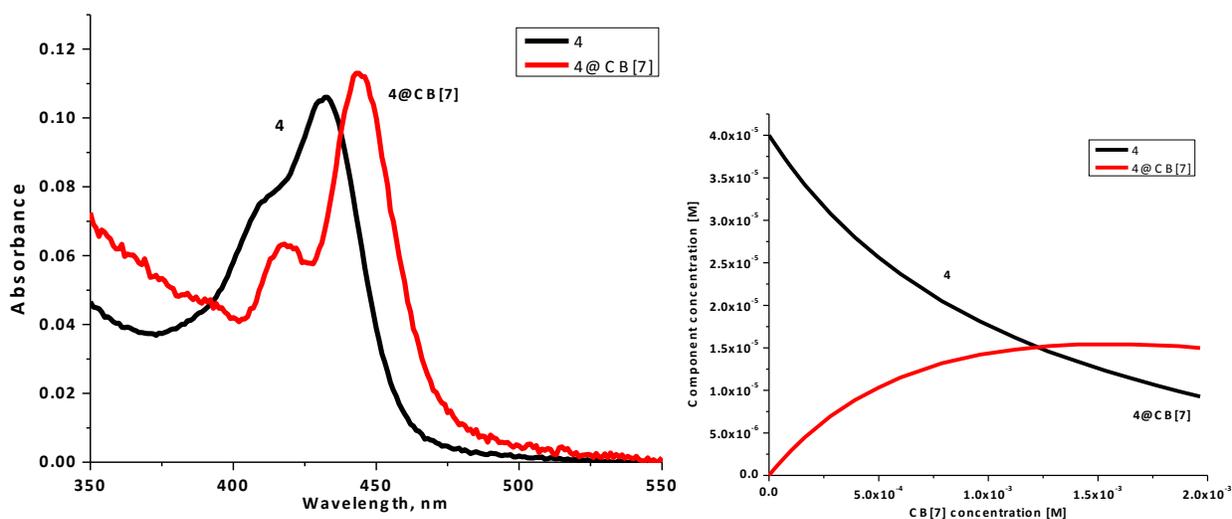
**Figure S11.** ROESY spectrum (600 MHz, D<sub>2</sub>O) of 4+HP-β-CD, C<sub>4</sub> = 2·10<sup>-4</sup> M, C<sub>HP-β-CD</sub> = 0.01 M.



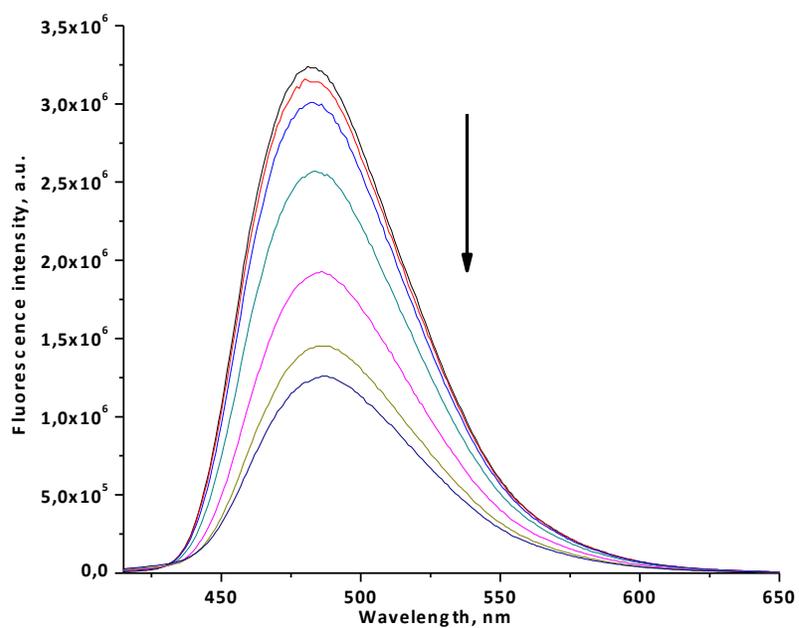
**Figure S12.** UV-Vis spectra of 3 and 3·CB[7] (C<sub>3</sub> = 3.9·10<sup>-4</sup> M, C<sub>3·CB7</sub> = 3.9·10<sup>-4</sup> M in H<sub>2</sub>O); changes in concentration of 3 and 3·CB7 upon the increase of C<sub>CB7</sub> = 0-0.01M are shown in the inset.



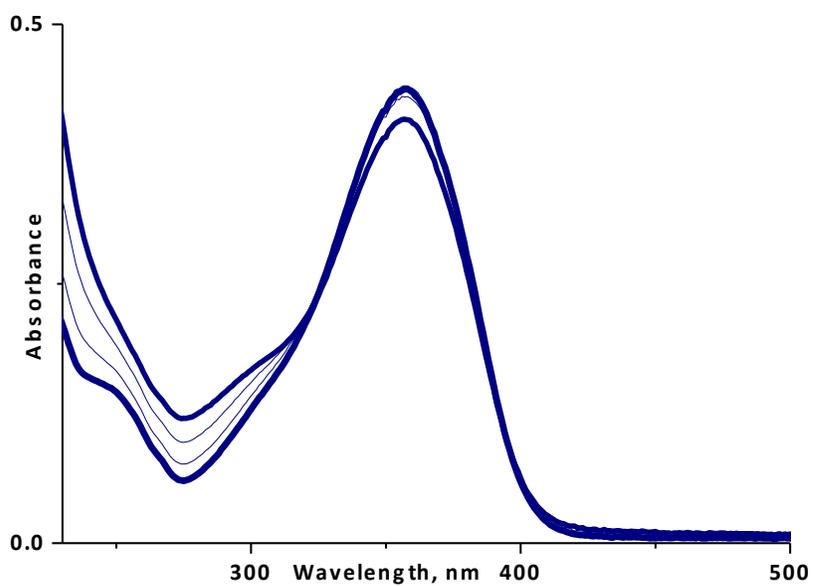
**Figure S13.** Changes in fluorescence spectra of **3** upon the addition of CB[7],  $C_3 = 1 \cdot 10^{-5}$  M,  $C_{CB[7]} = 1, 2.5, 8.5, 20, 50, 100$  and  $200 \times 10^{-4}$  M in  $D_2O$ ,  $\lambda_{exc} = 399$  nm.



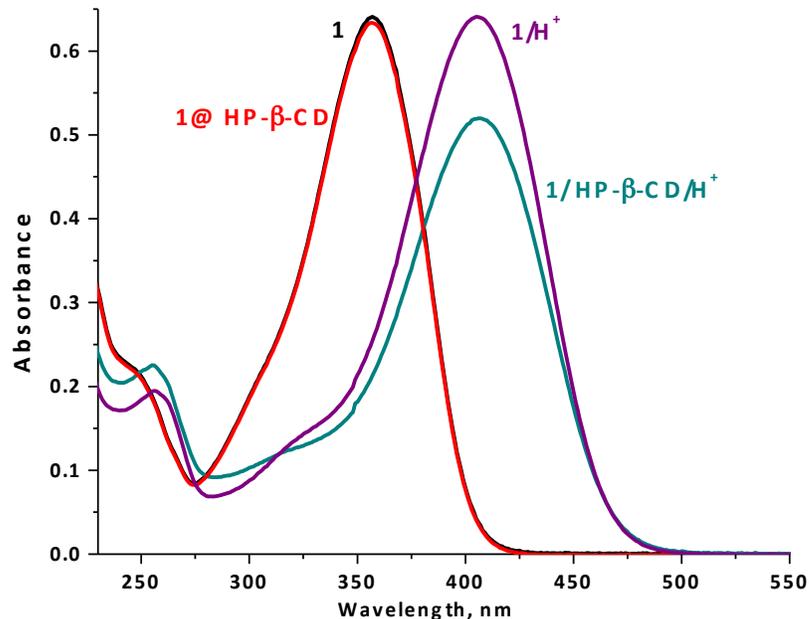
**Figure S14.** UV-Vis spectra of **4** and **4**·CB[7] ( $C_4 = 4 \cdot 10^{-5}$  M,  $C_{CB[7]} = 0 - 1.85 \times 10^{-3}$  M in  $D_2O$ ); changes in concentration of **4** and **4**·CB7 upon the increase of  $C_{CB[7]} = 0 - 1.85 \times 10^{-3}$  are shown in the inset.



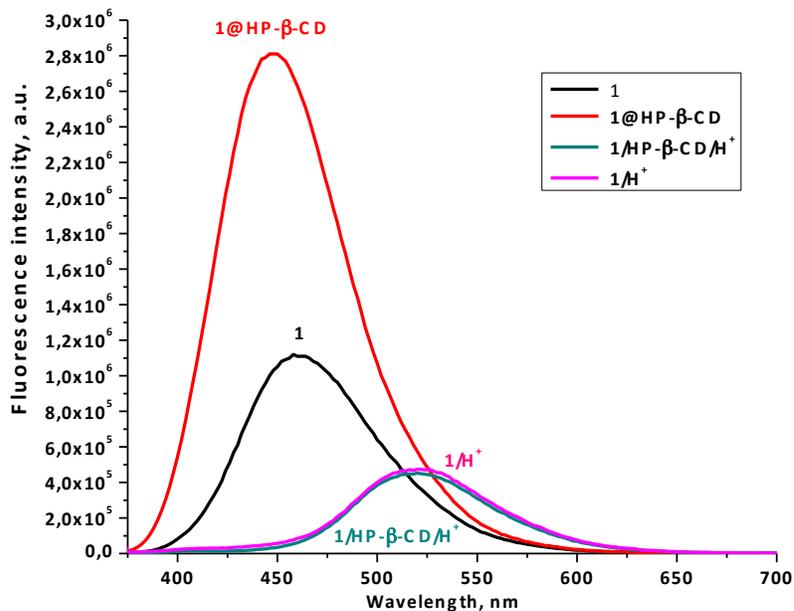
**Figure S15.** Changes in fluorescence spectra of **4** upon the addition of CB[7],  $C_4 = 4 \cdot 10^{-5}$  M,  $C_{CB[7]} = 0, 1, 5, 10, 20, 50$  and  $100 \times 10^{-4}$  M in  $D_2O$ ,  $\lambda_{exc} = 406$  nm.



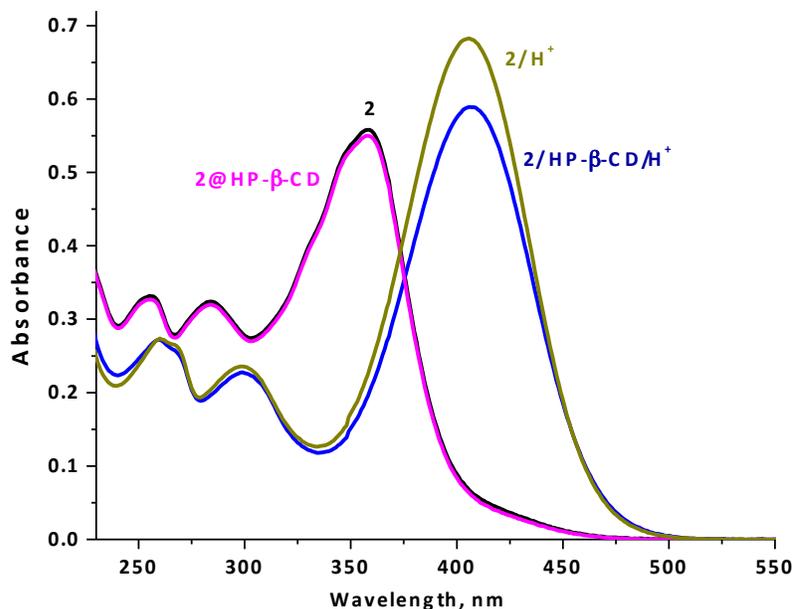
**Figure S16.** Changes in absorption spectra upon the spectrophotometric titration of the solution of *trans-1* by CB[7] in phosphate buffer solution at 25 °C,  $C_1 = 1 \cdot 10^{-5}$  M,  $C_{CB7} = 0 - 0.4 \cdot 10^{-3}$  M



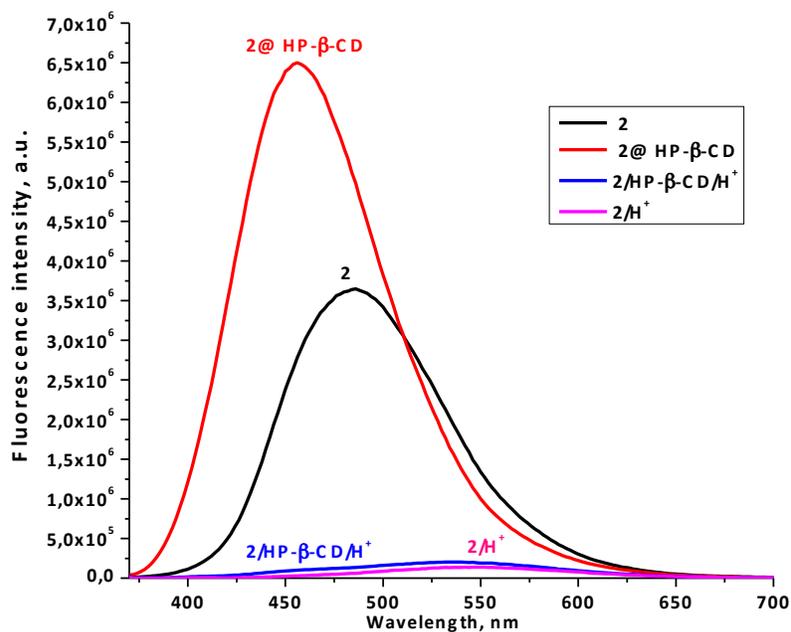
**Figure S17.** UV-Vis spectra of **1** ( $C_1 = 1 \cdot 10^{-5}$  M); **1**·HP- $\beta$ -CD ( $C_1 = 1 \cdot 10^{-5}$  M,  $C_{\text{HP-}\beta\text{-CD}} = 1 \cdot 10^{-2}$  M); of **1** ( $C_1 = 1 \cdot 10^{-5}$  M) in the presence of HClO<sub>4</sub> ( $C_{\text{HClO}_4} = 1 \cdot 10^{-1}$  M) and  $C_{\text{HP-}\beta\text{-CD}} = 1 \cdot 10^{-2}$  M); of **1** ( $C_1 = 1 \cdot 10^{-5}$  M) in the presence of HClO<sub>4</sub> ( $C_{\text{HClO}_4} = 1 \cdot 10^{-1}$  M).



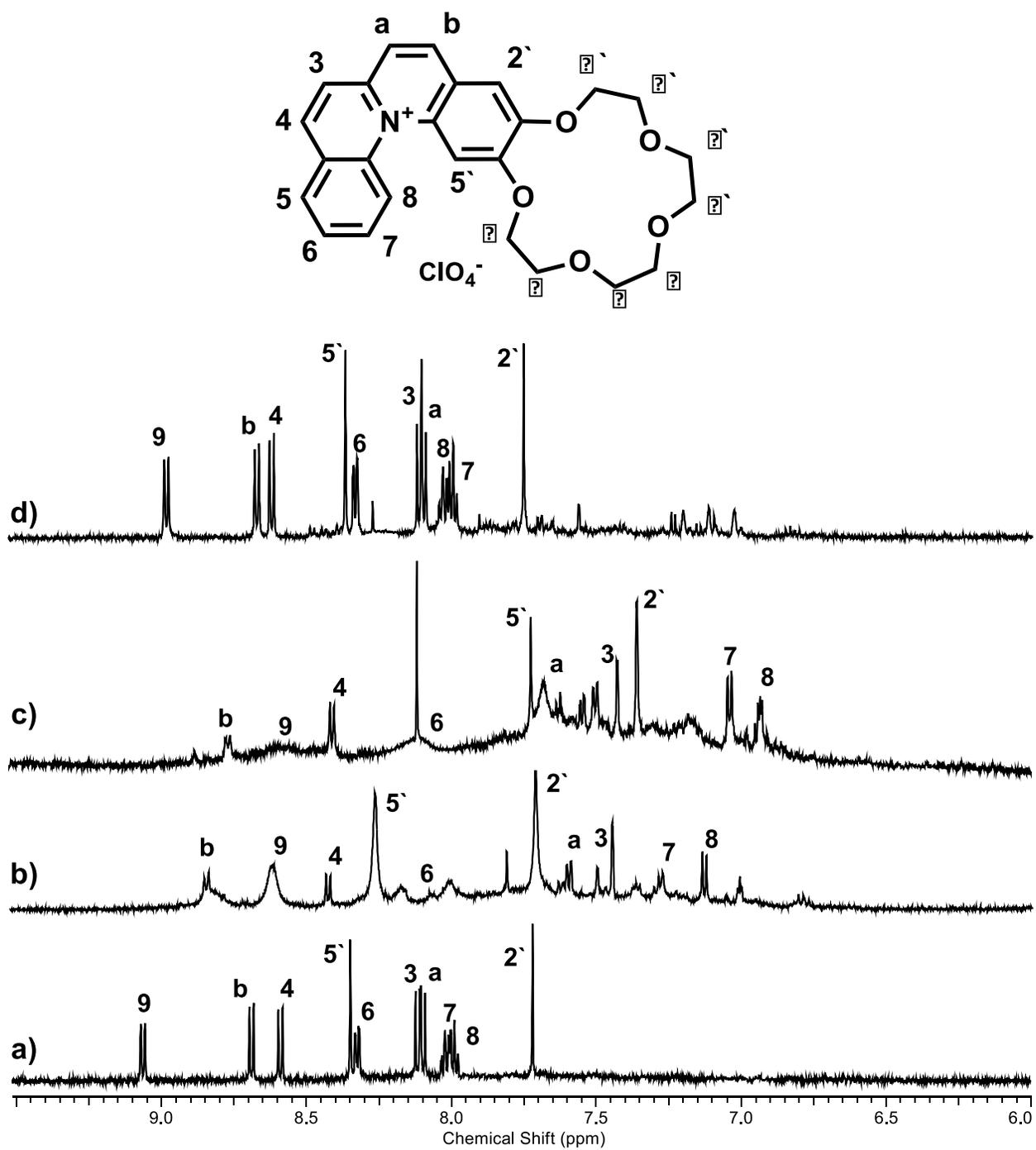
**Figure S18.** Fluorescence spectra of **1** ( $C_1 = 1 \cdot 10^{-5}$  M); **1**·HP- $\beta$ -CD ( $C_1 = 1 \cdot 10^{-5}$  M,  $C_{\text{HP-}\beta\text{-CD}} = 1 \cdot 10^{-2}$  M); of **1** ( $C_1 = 1 \cdot 10^{-5}$  M) in the presence of HClO<sub>4</sub> ( $C_{\text{HClO}_4} = 1 \cdot 10^{-1}$  M) and  $C_{\text{HP-}\beta\text{-CD}} = 1 \cdot 10^{-2}$  M); of **1** ( $C_1 = 1 \cdot 10^{-5}$  M) in the presence of HClO<sub>4</sub> ( $C_{\text{HClO}_4} = 1 \cdot 10^{-1}$  M),  $\lambda_{\text{exc}} = 358$  nm.



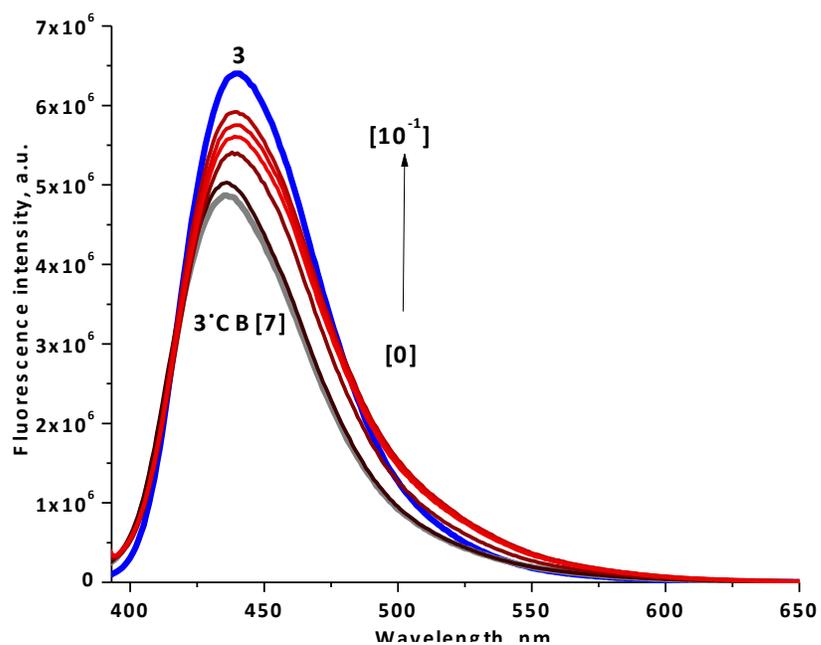
**Figure S19.** UV-Vis spectra of **2** ( $C_2 = 1 \cdot 10^{-5}$  M); **2**·HP-β-CD ( $C_2 = 1 \cdot 10^{-5}$  M,  $C_{\text{HP-}\beta\text{-CD}} = 1 \cdot 10^{-2}$  M); of **2** ( $C_2 = 1 \cdot 10^{-5}$  M) in the presence of HClO<sub>4</sub> ( $C_{\text{HClO}_4} = 1 \cdot 10^{-1}$  M) and  $C_{\text{HP-}\beta\text{-CD}} = 1 \cdot 10^{-2}$  M); of **2** ( $C_2 = 1 \cdot 10^{-5}$  M) in the presence of HClO<sub>4</sub> ( $C_{\text{HClO}_4} = 1 \cdot 10^{-1}$  M).



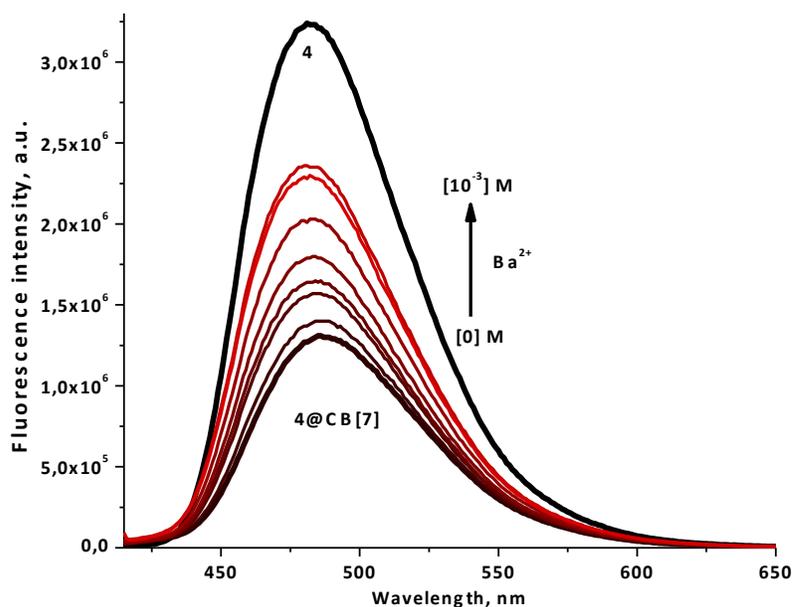
**Figure S20.** Fluorescence spectra of **2** ( $C_2 = 1 \cdot 10^{-5}$  M); **2**·HP-β-CD ( $C_2 = 1 \cdot 10^{-5}$  M,  $C_{\text{HP-}\beta\text{-CD}} = 1 \cdot 10^{-2}$  M); of **2** ( $C_2 = 1 \cdot 10^{-5}$  M) in the presence of HClO<sub>4</sub> ( $C_{\text{HClO}_4} = 1 \cdot 10^{-1}$  M) and  $C_{\text{HP-}\beta\text{-CD}} = 1 \cdot 10^{-2}$  M); of **2** ( $C_2 = 1 \cdot 10^{-5}$  M) in the presence of HClO<sub>4</sub> ( $C_{\text{HClO}_4} = 1 \cdot 10^{-1}$  M),  $\lambda_{\text{exc}} = 357$  nm.



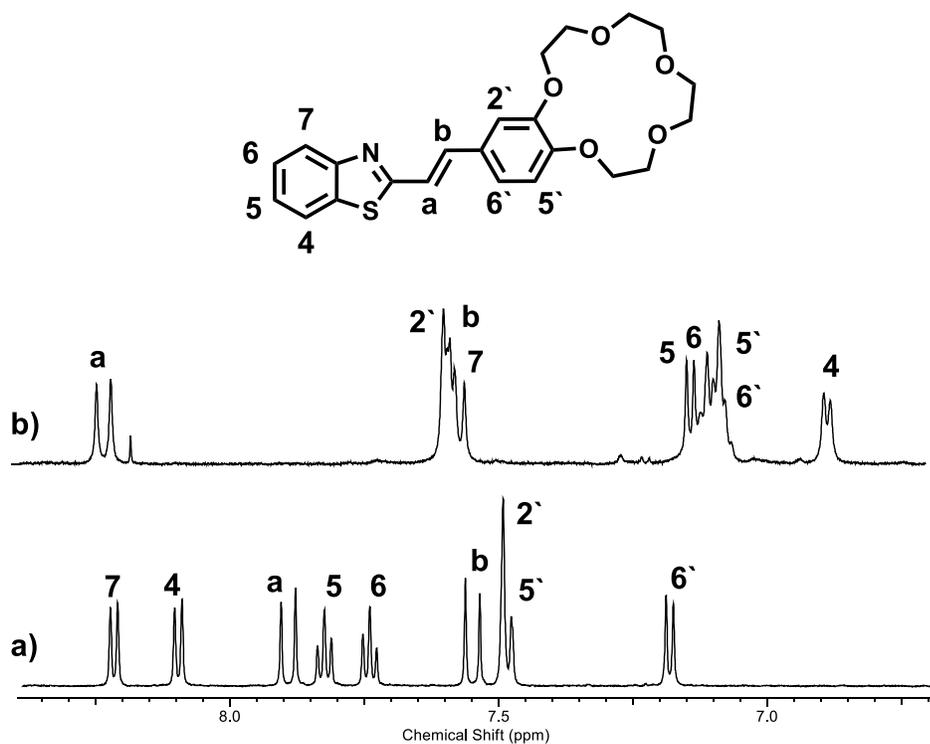
**Figure S21.** <sup>1</sup>H NMR spectra recorded (600 MHz, D<sub>2</sub>O) for **4**: a) free (1·10<sup>-3</sup> M); b) in presence of CB[7] (1·10<sup>-3</sup> M); c) in presence of CB[7] (5·10<sup>-3</sup> M); d) in the presence of 5·10<sup>-3</sup> M CB[7] and 1·10<sup>-1</sup> M Ba(ClO<sub>4</sub>)<sub>2</sub>.



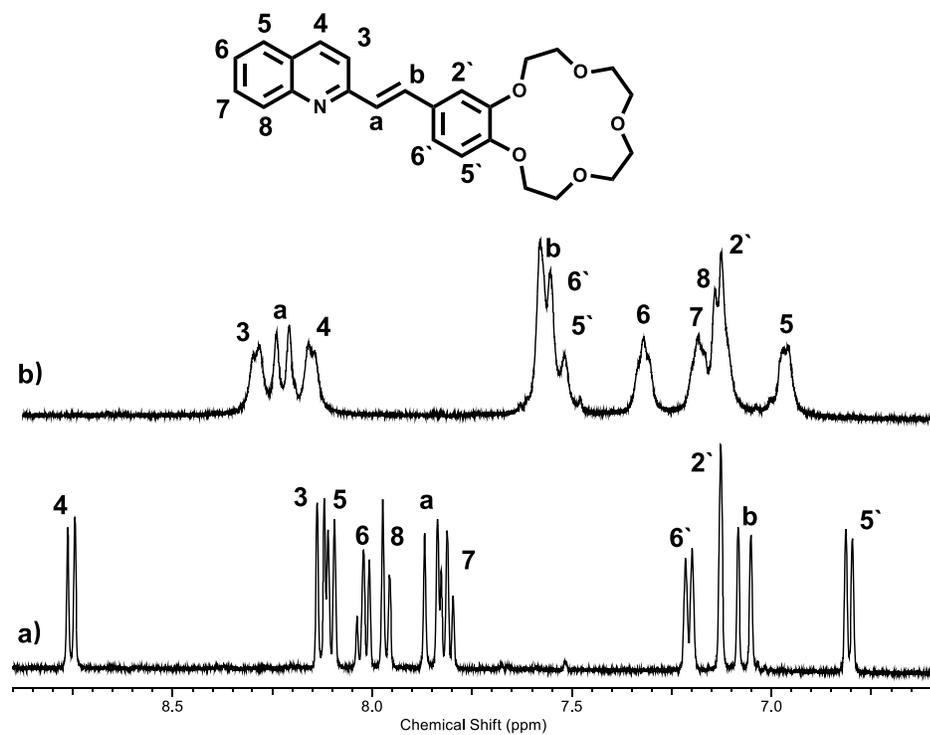
**Figure S22.** Changes in fluorescence spectra of 3-CB[7] upon the addition of  $\text{Ba}(\text{ClO}_4)_2$ ,  $C_3 = 1 \cdot 10^{-5}$  M,  $C_{\text{CB}[7]} = 1 \cdot 10^{-3}$  M,  $C_{\text{Ba}(\text{ClO}_4)_2} = 0, 20, 50, 100, 200, 500$  and  $1000 \times 10^{-4}$  M in  $\text{H}_2\text{O}$ ,  $\lambda_{\text{exc}} = 378$  nm.



**Figure S23.** Changes in fluorescence spectra of 4-CB[7] upon the addition of  $\text{Ba}(\text{ClO}_4)_2$ ,  $C_4 = 4 \cdot 10^{-5}$  M,  $C_{\text{CB}[7]} = 1 \cdot 10^{-3}$  M,  $C_{\text{Ba}(\text{ClO}_4)_2} = 0, 1, 5, 10, 20, 50, 100$  and  $200 \times 10^{-4}$  M in  $\text{D}_2\text{O}$ ,  $\lambda_{\text{exc}} = 406$  nm.



**Figure S24.**  $^1\text{H}$  NMR spectra recorded (600 MHz,  $\text{D}_2\text{O}$ ) for **1**: a) **1** ( $2 \cdot 10^{-3}$  M) in the presence of  $2 \cdot 10^{-2}$  M  $\text{HClO}_4$ ; b) **1** ( $2 \cdot 10^{-3}$  M) in the presence of CB[7] ( $1 \cdot 10^{-2}$  M) and  $2 \cdot 10^{-2}$  M  $\text{HClO}_4$ .



**Figure S25.**  $^1\text{H}$  NMR spectra recorded (600 MHz,  $\text{D}_2\text{O}$ ) for **2**: a) **2** ( $2 \cdot 10^{-3}$  M) in the presence of  $2 \cdot 10^{-2}$  M  $\text{HClO}_4$ ; b) **2** ( $2 \cdot 10^{-3}$  M) in the presence of CB[7] ( $1 \cdot 10^{-2}$  M) and  $2 \cdot 10^{-2}$  M  $\text{HClO}_4$ .

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