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# **Electronic Supplementary Information**

# Light-induced piston nanoengine: ultrafast shuttling of a styryl dye inside cucurbit[7]uril

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# 1. Synthesis and characterization

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

Dyes **1** and **2** were firstly synthesized and fully characterized by our group earlier.<sup>[3-6]</sup>

(*E*)-1-methyl-4-(2-(2,3,5,6,8,9,11,12-octahydrobenzo[b][1,4,7,10,13]pentaoxacyclopentadecin-15-yl)vinyl)pyridin-1-ium perchlorate (dye **1**) synthesized according to the reported methods from methyl 4-methylbenzenesulfonate and 4-[2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13benzopentaoxacyclopentadecin-15-yl)vinyl]pyridine in 48% yield.<sup>[3,4]</sup>

(E)-4-(4-(1,4-dioxa-7,13-dithia-10-azacyclopentadecan-10-yl)styryl)-1-methylpyridinium perchlorate (dye **2**) was synthesized according to the reported methods from 1,4-dimethylpyridinium perchlorate and 4-(1,4-dioxa-7,13-dithia-10-azacyclopentadecan-10-yl)benzaldehyde in 71% yield.<sup>[5,6]</sup>

# 2. Materials and equipment

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

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

Steady-state fluorescence spectra measurements were performed using a FluoroLog-3 (Jobin Yvon) spectrofluorimeter. All measured fluorescence spectra were corrected for the nonuniformity of detector spectral sensitivity.

Temperature dependence studies of fluorescence quantum yields were performed using a diode array fiber-optic spectrometer AvaSpec-2048.

# 3. Time-resolved fluorescence spectroscopy

This experiment was based on a femtosecond 1 kHz Ti:Sapphire system producing 30 fs, 0.8 mJ laser pulses centered at 800 nm (Femtopower Compact Pro) coupled with optical parametric generator (Light Conversion Topas C) and frequency mixers to excite samples at the maximum of the steady-state absorption band. All excited state lifetimes were obtained using depolarized excitation light. The highest pulse energies used to excite fluorescence did not exceed 100 nJ and the average power of excitation beam was 0.1 mW at a pulse repetition rate of 1 kHz focused into a spot with a diameter of 0.1 mm in the 10 mm long fused silica cell. The fluorescence emitted in the forward direction was collected by reflective optics and focused with spherical mirrors onto the input slit of a spectrograph (Chromex 250) coupled to a streak camera (Hamamatsu 5680 equipped with a fast single sweep unit M5676, temporal resolution 2 ps). The convolution of a rectangular streak camera slit in the sweep range of 250 ps with an electronic jitter of the streak camera trigger pulse provided a Gaussian (over 4 decades) temporal apparatus function with a FWHM of 20 ps. The fluorescence kinetics were later fitted by using the Levenberg-Marquardt least-squares curve-fitting method using a solution of the differential equation describing the evolution in time of a single excited state and neglecting depopulation of the ground state:

$$\frac{dI(t)}{dt} = Gauss(t0, \Delta t, A) - \frac{I(t)}{\tau}$$

where I(t) is the fluorescence intensity, *Gauss* is the Gaussian profile of the excitation pulse, where t0 stands for the excitation pulse arrival delay,  $\Delta t$  is the excitation pulse width, and A is the amplitude. The parameter  $\tau$  represents the lifetime of the excited state. The initial condition for the equation is  $I(-\infty) = 0$ . In the case of more complicated excited state behaviour, a system of interdependent differential equations was used. Typically, the fit shows a  $\chi^2$  value better than  $10^{-4}$  and a correlation coefficient R > 0.999. The uncertainty of the lifetime was better than 1%. Routinely, the fluorescence accumulation time in our 35 measurements did not exceed 90 s.



**Figure S1.** Fluorescence decay profiles of dye **1** (solid line) and its complex CB[7]–**1** (dashed line), in all cases c=20  $\mu$ M, H<sub>2</sub>O, 20°C. Excitation was at 400 nm, and emission was collected at the maximum of emission band.



**Figure S2.** Fluorescence decay profiles of dye **2** (solid line) and its complex CB[7]–**2** (dashed line), in all cases c=20  $\mu$ M, H<sub>2</sub>O, 20°C. Excitation was at 470 nm, and emission was collected at the maximum of emission band.

### 4. DFT calculations

#### Free dyes 1 and 2

The calculated maximum absorption band is in good agreement with experiment for dye 1  $(\lambda_{max}(calc) = 374 \text{ nm}, \lambda_{max}(exp) = 382 \text{ nm})$  and the deviation between theory and experiment is within the expected accuracy of TD-DFT. Surprisingly, the deviation from the experimental value is larger for 2 than the calculations underestimated the energy of the transition ( $\lambda_{max}(calc) = 405 \text{ nm}, \lambda_{max}(exp) = 456 \text{ nm}$ ). However, the calculations qualitatively reproduce the red shift of the maximum absorption from 1 to 2.

**Table S1.** Calculated absorption and emission wavelengths ( $\lambda_{abs}$ , nm), oscillator strengths (*f*) and orbital composition for the first vertical transitions of **1** and **2**.

	$\lambda_{abs}$	f	Orbital		$\lambda_{emission}$
			composition		
	1				
$S_0 \rightarrow S_1$	374	1.16	HOMO → LUMO	$S_1 \rightarrow S_0$	434
$S_0 \rightarrow S_2$	288	0.16	HOMO-1 →		
			LUMO		
$S_0 \rightarrow S_3$	250	0.01	HOMO →		
			LUMO+1		
	2				
$S_0 \rightarrow S_1$	405	1.54	HOMO → LUMO	$S_1 \rightarrow S_0$	502
$S_0 \rightarrow S_2$	270	0.01	HOMO-1 →		
			LUMO+3		
$S_0 \rightarrow S_3$	263	0.00	HOMO →		
			LUMO+1		

The  $\lambda_{max}$  is ascribed to a HOMO->LUMO single electronic excitation. The frontier orbitals are sketched in Figure S3 and show a strong different localization as expected for a push-pull molecule: the HOMO is localized on the dimethoxyphenyl or dimethylaminophenyl moiety while the LUMO orbital is mainly localized on the pyridinium moiety of the molecule. The computed vertical  $S_1$ -> $S_0$  transition wavelengths for 1 and 2 are reported in Table S1. The analysis of the orbitals involved in the transition shows that the emission corresponds to a LUMO  $\rightarrow$  HOMO mono-electronic transition.



**Figure S3**. HOMO (bottom) and LUMO (top) frontier orbitals implied in the  $S_0 \rightarrow S_1$  transition for **1** and **2** (contour threshold: 0.03 a.u.).

To obtain additional information on the nature of the excited states, we analyzed the charge distribution and the evolution of such distribution when going from ground to the first excited state. The variation of the charge distribution is displayed in Figure S4. It can be clearly seen that the positive charge is mainly localized on the pyridinium moiety on the ground state and such distribution is in accordance with the chemical sense. For the excited state responsible for the maximum absorption ( $S_0 \rightarrow S_1$  transition) we calculated an electronic charge transfer of 0.33 |e| in 1 and 2 from the benzene to the pyridinium group while the ethylene bridge remains a constant value. Consequently, the electronic excitation to the first excited state leads to a decreasing positive charge on the piridinium groups and an increasing positive charge on the dimethoxyphenyl or dimethylaminophenyl moieties.



**Figure S4**. Schematic representation of charge distribution of the ground state ( $S_0$ ) and the first excited singlet state ( $S_1$ ) for dyes 1 and 2 in water.

**Table S2.** Calculated main bonds lengths in the optimized geometries of 1 and 2 in the ground  $(S_0)$  and first excited singlet  $(S_1)$  states.

	Na ⊕	d f			Na ⊕	e d	h g j	s v s		
	dye <b>1</b>					dye <b>2</b>				
	а	b	c	d	e	f	g	h	i	
1										
$S_0$	1.350	1.370	1.407	1.450	1.347	1.457	1.394	1.390	1.390	
$S_1$	1.365	1.360	1.435	1.406	1.403	1.410	1.425	1.372	1.440	
2										
$S_0$	1.353	1.368	1.411	1.445	1.351	1.447	1.402	1.380	1.413	
<b>S</b> <sub>1</sub>	1.366	1.360	1.435	1.408	1.401	1.410	1.431	1.363	1.432	

#### 1:1 host-guest complexation

The formation of CB[7]–1 and CB[7]–2 inclusion complexes were also studied using DFT calculations. The interaction energy  $\Delta E_{int}$  between host and guest in the complex was calculated using the following equation (1):

$$\Delta E_{int} = E_{complex} - (E_{CB[7]} + E_{guest}) \tag{1}$$

where  $E_{complex}$ ,  $E_{CB[7]}$  and  $E_{guest}$  are the energies of the inclusion complex, the host CB[7] and the guest; *i.e.* **1** or **2**, respectively.  $\Delta E_{int}$  can provide a description of the intermolecular interaction strength in the complex. It should be noted that the calculation of the interaction energy was performed in solvent and the Basis Set Superposition Error (BSSE) are only available in gas phase. Therefore we estimated the BSSE with the counterpoise method in gas phase on the A and B optimized structures of CB[7]–2 complexes. Calculations lead to BSSE correction of 9 kcal/mol in both complexes, a value somewhat smaller than the interaction energy (The energies interaction for A and B CB[7]–2 complexes in gas phase are calculated to be -46.2 kcal/mol and -40.8 kcal/mol respectively, after BSSE correction).

To study the inclusion complex formation and locate the possible minimum energy structures, we performed an energy scan calculation with both isolated host and guest kept frozen at the optimized structure corresponding to the isolated molecule. Therefore, we calculated the evolution of the energy with respect to a scan coordinate d chosen as the distance between the carbon atom of the methyl group of 1 or 2 and a dummy atom located in the center of mass of the CB[7] cavity. The approach of the guest into the cavity has followed a straight line

corresponding to the symmetry axis of the cavity as shown on the Figure S5 and Figure 1 in the main text. The first point of the curve was chosen so that the guest is almost outside the cavity (d=0 Å). This distance was then elongated until a value of d=6.8 Å corresponding to a structure of the complex showing a significant inclusion of the guest into the cavity. The relative energies  $(E_{rel} \text{ in kcal/mol})$  were evaluated from the most stable structure obtained on the energy profile. The large size of the cucurbit host–guest complexes makes the quantum chemical investigation of the excited state computationally demanding. Therefore, energy scan calculation in the first excited state was performed using the Slater transition state approach [STS] consisting of fractional occupations of orbital. The S<sub>1</sub> state was then approximated by promotion of half an electron from HOMO to the LUMO.



**Figure S5**. CAM-B3LYP/6-31G(d) potential energy curves for interaction of dye 1 with CB[7] as function of the distance d in S<sub>0</sub> (solid line and  $\blacksquare$ ) and S<sub>1</sub> (dotted line and  $\bullet$ ) states. The red arrow shows the direction of approach of the guest in the cavity. The structures displayed on the curve shows the minimum energy structures.



**Figure S6**. CAM-B3LYP/6-31G(d) potential energy curves for interaction of dye 2 with CB[7] as function of the distance d in S<sub>0</sub> (solid line and  $\blacksquare$ ) and S<sub>1</sub> (dotted line and  $\bullet$ ) states. The arrow shows the direction of approach of the guest in the cavity. The structures displayed on the curve shows the minimum energy structures.

The potential energy curves presented in Figures S5 and S6 allow identifying one minimum energy structure for the complexation of **1** with CB[7] and two minima energy structures with the dye **2**. It is worth noting that the inclusion of **1** or **2** in the cavity occurs without or very low energy barrier for the formation of an encapsulated complex. The inclusion process of **1** with CB[7] is associated with a strong decrease of energy from the initial structure (d=0 Å) to the minimum structure (d=4.2 Å). In the minimum energy structure, the interaction energy  $\Delta E_{int}$  calculated using the equation (1) is found to be -13.3 kcal/mol and suggest that there is an energy gain during the complex formation and that **1** and CB[7] are strongly bound through intermolecular forces. The structure of the complex in the minimum shows that the pyridinium moiety of **1** is completely inside the cavity and the electrostatic interaction between the pyridinium and the portal oxygen of CB[7] can take place.

The inclusion process of **2** with CB[7] shows two minima, namely A and B (Figure S6) located at distances d= 3.4 Å and 6.2 Å. The minimum A is more stable than B by about 10 kcal/mol. The interaction energy calculated in the lowest minimum A is -9.8 kcal/mol a value somewhat greater than the interaction energy obtained in the **1**-CB[7] complex indicating that **2** is more weakly bound to CB[7]. In addition, it can be seen that the energy decrease from the initial position of **2** (d=0 Å) to the minimum A (d= 3.4 Å) is calculated to 5.5 kcal/mol while the gain in energy calculated for the encapsulation of **1** is 8.5 kcal/mol. This result suggests that the guest **2** can move in the cavity by translation more easily than **1**. Surprisingly the ground state potential

energy curve in Figure S6 shows another minimum for d= 6.2 Å (minimum B). The minimum B is found less stable than A by 10.9 and 8.6 kcal/mol in the ground state and first excited state S<sub>1</sub>, respectively. It should be recall that the energy scan curves were obtained using a frozen geometry of host and guest.

To describe more accurately the intermolecular forces, we also used the range-separated hybrid functionals [ $\omega$ B97X-D]. Indeed, this functionals includes an empirical term describing dispersion effects. The obtained potential energy scans for inclusion of **1** and **2** in CB[7] at the ground states S<sub>0</sub> are displayed in Figure S7 and show similar behaviors as found with CAM-B3LYP functional. The inclusion of **1** in CB7 shows only one minimum while the inclusion of **2** reveals two minima A and B. A is calculated more stable than B by 7.4 kcal/mol.



**Figure S7**.  $\omega$ B97X-D/6-31G(d) potential energy curves for interaction of dye **1** (solid line and **■**) and **2** (solid line and **●**) with CB[7] as function of the distance *d* in ground state S<sub>0</sub>. The red arrow shows the direction of approach of the guest in the cavity. The structures displayed on the curve shows the minimum energy structures.

Figure S8 shows the structures of A and B obtained after complete optimization in ground and  $S_1$  excited states.



**Figure S8.** Top views (left panel) and side (right panel) of the optimized geometries of the complex of **2** embedded in the CB[7] macrocycle (a) A complex in  $S_0$  state (b) B complex in  $S_0$  state (c) A complex in  $S_1$  state (d) B complex in  $S_1$ . Geometries were obtained at the CAM-B3LYP/6-31G(d) level in water as solvent.

Selected structural parameters of optimized molecular complex are collected in Table S3. The CB[7] can be characterized by several relevant geometric parameters:  $d_{portal}$  is the distance between the O atoms at the portals,  $d_{belt}$  is the distance between C atoms at its belt and *h* is the

height of the macrocycle (Figure S8). It can be shown that the macrocycle is only a little affected by the guest molecule inclusion.

	Icolated CP[7]		DC		DC
	Isolated CD[7]	A-30	D-30	A-31	<b>D-3</b> 1
d <sub>portal</sub> average	8.26	8.19	8.27	8.16	8.24
range		7.99-8.49	8.02-8.48	7.76-8.59	7.94-8.58
$d_{\text{belt}}$					
average	11.66	11.30	11.36	11.31	11.31
range		10.86-11.69	10.83-11.76	10.91-11.72	10.76-11.94
h	6.11	6.08	6.12	6.06	6.10

**Table S3.** Calculated selected structural parameters for CB[7] either isolated or in complex with **2** in A and B minima.

The isolated CB[7] has almost a  $D_{7h}$  point group symmetry with similar distances between O atoms at the portal. Upon complexation the cavity accommodates the guest molecule and shows some deformations of the ideal  $D_{7h}$  geometry. However it can be seen that the geometric changes of the macrocycle are small and no significant structural deformation is observed (for instance, the minimal  $d_{portal}$  values are 7.99, 8.02, 7.76 and 7.94 for A-S<sub>0</sub>, B-S<sub>0</sub>, A-S<sub>1</sub>, and B-S<sub>1</sub>, respectively, while the maximal  $d_{portal}$  values are 8.49, 8.48, 8.59 and 8.58 for A-S<sub>0</sub>, B-S<sub>0</sub>, A-S<sub>1</sub>, and B-S<sub>1</sub>, respectively).

The electrostatic potential of CB[7] shows a negative potential (in blue) in the vicinity of the oxygen atoms portal and a positive potential (in red) in the area of the carbon belt (Figure S9). Compound 2 in the ground state exhibits a positive potential on the pyridinium aromatic ring and a more negative potential on aminophenyl moiety. Therefore the overlap of the positive potential of pyridinium with the negative potential of CB[7] is responsible for electrostatic stabilization when the pyridinium moiety is deeply embedded in the CB[7] cavity and is close to the oxygen atoms of CB[7] as in the minimum A. In the ground state minimum B, the aminophenyl moiety is in the close contact with the oxygen atoms of CB[7] and electrostatic stabilization is expected to be less. By contrast, the electrostatic potential of 2 in the first excited state shows a remarkable difference with that of ground state. The positive potential is less pronounced on the pyridinium moiety while it increases on the aminophenyl unit. This electrostatic potential reflects the intramolecular electronic charge transfer from aminophenyl to the pyridinium residue as showed from the charge analysis. As a consequence, the sliding of the guest in the cavity from the minimum A to B and the increase in the stability can therefore be explained by changing the electrostatic potential stabilization upon electronic excitation that promotes a positive charge to the aminophenyl group that interacts with oxygen atoms of CB[7].



**Figure S9.** Electrostatic potential surface of: (a) CB[7] (top and side views), (b) **2** in the ground state and (c) **2** in the excited  $S_1$  state.

We used a non-covalent index (NCI) [NCI] method for identifying the regions in 3D space where weak intermolecular interactions occur between 2 and CB[7] in A and B optimized ground state geometries (Figure S9). This method is based on the analysis of the evolution of electron densities  $\rho(r)$  and their reduced gradients, s(r). Regions with low electron density  $\rho(r)$ and reduced density gradient s(r) correspond to the occurrence of noncovalent interactions. Using NCI index, different regions of weak interactions can be identified by color. Blue regions correspond to a stronger attractive interaction such as established in hydrogen bond. The interaction marked by green color can be identified as Van der Waals interaction region. Finally, the regions showing strong steric effect are colored in red. Color filled isosurfaces graphs were calculated using the Multiwfn [Multiwfn] and have been plotted using VMD programs [VMD]. For the complexes colour filled isosurfaces have been plotted and green region show weak and attractive interactions. Numerous small regions of weak interaction (green area in the Figure S10) appear between the oxygens atoms of the portals of CB[7] and hydrogens atoms (aromatic and aliphatic hydrogens) of **2** either in A or in B minima.



**Figure S10.** NCI isosurfaces (strong attractive interactions are represented in blue, weak interactions in green, and repulsive interactions in red).

#### Absorption spectra

The TD-DFT method is able to detect accurate absorption wavelengths at a relatively small computing time, which correspond to vertical electronic transitions computed on the ground state geometry. To investigate the nature of electronic transitions, the electronic spectra of the studied complex of **2** with CB[7] were calculated using the time-dependent density functional theory (TD-DFT) approach at the CAM-B3LYP/6-31G(d) level on the basis of fully optimized ground-state structure. Calculations are performed in water.



Figure S11. Calculated absorption spectra of 2 and 2-CB[7] in A minimum.

The TD-DFT absorption spectrum of A complex shows a band centered at 411 nm assigned to the HOMO  $\rightarrow$  LUMO electronic excitation (Figure S11). Both HOMO and LUMO orbitals are

localized on compound **2**. The complexation of **2** by CB[7] induces a redshift of the maximum absorption ( $\lambda$ =456 nm for **2** and  $\lambda$ =482 nm for **2**-CB[7]) and calculation is in qualitative agreement with this result ( $\lambda$ =405 nm for **2** and  $\lambda$ =411 nm for **2**-CB[7]).

#### **Computational details**

All the calculations have been performed with Gaussian09 [G09] using Density Functional Theory (DFT) and the 6-31G(d) Pople basis sets. We have selected the CAM-B3LYP functional [CAM-B3LYP] which belongs to the range-separated hybrid (RSH) family and includes a growing fraction of Hartree-Fock-like exchange when the inter-electronic distance increases. This functional is designed to overcome the DFT failures like the description of weak interactions or charge transfer and it has been shown that accurate estimate of charge transfer excitation energies can be obtained [TDDFT-CT]. To obtain the convoluted absorption spectra, a broadening Gaussian with FWHM = 0.3 eV has been systematically applied. The first low-lying electronic singlet excited states have been calculated using the Time-Dependent DFT method [TD-DFT] to obtain theoretical absorption spectra. All the calculations (geometry optimizations, TD-DFT calculations) have been performed in water as in the experiment and solvent have been included in the calculations by means of the polarizable continuum model by the integral equation formalism (IEFPCM) in single point calculations as well as for the fully optimized minimum energy structures. All the geometry optimizations were led without symmetry constraints and followed by a vibrational frequency computation to ensure that they correspond to true energetic minima. The calculations of the vertical emission transitions of 1 and 2 were performed following the TD-DFT analytical gradients available in Gaussian 09 and using the linear response (LR) solvatation scheme [LR]. The emission wavelength was obtained from the energy difference between the energy of optimized  $S_1$  state and the energy of the ground state computed with non-equilibrium solvatation, at the excited state geometry and with the static solvatation reaction field from the excited state.

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## 5. Temperature dependence of fluorescence quantum yields

Temperature dependent studies of fluorescence quantum yields were performed to provide deeper insight into the de-excitation process of dye **2** and complex CB[7]–**2** excited states. Radiative relaxation rate constants  $k_r$  for dye **2** and complex CB[7]–**2** are found to be  $k_r = \frac{\varphi}{\tau} = (1.43\pm0.13)\cdot10^8 \text{ s}^{-1}$  and  $k_r = (1.35\pm0.06)\cdot10^8 \text{ s}^{-1}$ , where  $\varphi$  is the fluorescence quantum yield and  $\tau$  is the excited state lifetime. These values are practically the same so the decrease of non-radiative rate constant of dye **2** on complex formation should be the main reason of the observed fluorescence enhancement. The temperature dependence of fluorescence quantum yield,  $\varphi$ , considering  $k_r$  to be temperature independent, can be expressed using the modified Arrhenius equation:<sup>7</sup>

$$\frac{1}{\varphi} = 1 + \frac{k_{nr}}{k_r} = 1 + \left(\frac{1}{k_r}\right) k_{nr}^0 exp\left(-\frac{\Delta E_a}{RT}\right),$$

where  $k_{nr}^0$  is the pre-exponential factor and  $\Delta E_a$  is the observed activation energy for the nonradiative deactivation process in the excited S<sub>1</sub> state. According to this equation, linear  $\ln\{(1/\phi) - 1\}$  vs. 1/T plots were obtained for both **2** and CB[7]–**2** (Figures S7, S8).



**Figure S11.** Dependence of  $\ln(1/\phi - 1)$  vs 1/T for dye **2** in water.  $\phi$  - fluorescence quantum yield.



**Figure S12.** Dependence of  $\ln(1/\phi - 1)$  *vs* 1/T for complex CB[7]–2 in water.  $\phi$  - fluorescence quantum yield.

The  $\Delta E_a$  values for 2 and CB[7]–2 have been estimated from the slopes of  $\ln\{(1/\phi) - 1)\}$  vs. 1/T plots as  $\Delta E_a = 3.9\pm0.3$  kcal/mol (16.2±1.1 kJ/mol) and  $\Delta E_a = 3.8\pm0.15$  kcal/mol (15.9±0.6 kJ/mol), respectively. From y-intercept of the same plots the Arrhenius pre-exponential factors  $k_{nr}^0$  for 2 and CB[7]–2 are found to be  $1.1\cdot10^{13}$  and  $2.2\cdot10^{11}$ . It can be seen that the activation barriers for the nonradiative deactivation process in the excited state of dye 2 and complex CB[7]–2 are close to each other and also to activation energy of viscous flow for pure water, 15.9 kJ/mol,<sup>8</sup> while the Arrhenius pre-exponential factors differ by approximately two orders of magnitude.

Thus temperature dependent studies indicate that the differences in fluorescence quantum yields for **2** and CB[7]–**2** are not connected with different activation barriers of de-excitation process but with decreasing in the Arrhenius pre-exponential factor on complex formation. The importance of changes of the pre-exponential factor on reaction kinetics has previously been found for various compounds.<sup>9</sup> If the TICT state formation is the main pathway for the non-radiative deactivation process, one may conclude that the formation of TICT state is less probable for CB[7]–**2** than for dye **2** and radiative relaxation becomes more dominant for CB[7]–**2** complex. The theory of the activated complex for unimolecular reactions<sup>10</sup> can be used to qualitatively understand the difference of the pre-exponential factors for dye **2** and complex CB[7]–**2** as it has been shown earlier by Rettig et al for dimethylaminobenzonitrile derivatives.<sup>24</sup>

Following to<sup>10,11</sup> the preexponential factor A can be expressed as being a function of the activation entropy  $\Delta S$ :

# $A=B exp(\Delta S/R)$

For unimolecular reactions with a tight transition state,  $\Delta S$  is negative and A < B. To justify the observed differences in non-radiative deactivation process for dye and it complex, the activation entropy  $\Delta S$  must be more negative for CB[7]–2 than for 2. Taking into account that  $\Delta S$  can be described by the fraction of thermal energy of the molecule which is necessary to be concentrated along the reaction coordinate within the activated complex, one can conclude that this process is more difficult in the complex than in the free dye molecule.

# 6. Femtosecond transient absorption spectroscopy

This experiment was based on a femtosecond 1 kHz Ti:Sapphire system producing 30 fs, 0.8 mJ laser pulses centered at 800 nm (Femtopower Compact Pro) coupled with optical parametric generator (Light Conversion Topas C) and frequency mixers to excite samples at the maximum of the steady-state absorption band. White light continuum (360 nm – 1000 nm) pulses generated in a 2 mm  $D_2O$  cell were used as the probe. The variable delay time between excitation and probe pulses was obtained using a delay line with 0.66 fs resolution. The solutions were placed in 2 mm circulating cell. White light signal and reference spectra were recorded using a two-channel fiber spectrometer (Avantes Avaspec-2048-2). A home written acquisition and experiment control program in LabVIEW made it possible to record transient spectra with an average error less than  $10^{-3}$  of optical density for all wavelengths. The temporal resolution of the set-up was better than 50 fs. A temporal chirp of probe pulse was corrected by a computer program with respect to a Lawrencian fit of a Kerr signal generated in a 0.2 mm glass plate used in a place of sample.



**Figure S13.** The kinetic trace of the dynamics of solvation fitted with a a) biexponential function with constant  $\tau_1=0.34$  ps and  $\tau_2=0.97$  ps for free dye **2**, b) monoexponential function with constant  $\tau=0.57$  ps for complex CB[7]–**2**, measured by femtosecond pump-probe technique.



**Figure S14.** TRABS map of complex CB[7]-2 in H<sub>2</sub>O measured upon 470 nm laser excitation in the 500–700 nm spectral range by femtosecond time-resolved pump-probe technique.



**Figure S15.** The kinetic trace of the dynamics of solvation fitted with a biexponential function with constant  $\tau_1=0.35$  ps and  $\tau_2=1.90$  ps for free dye **1** (a); monoexponential function with constant  $\tau=1.75$  ps for complex CB[7]–**1** (b), measured by femtosecond pump-probe technique.



**Figure S16.** The kinetic trace of the stimulated emission displacement during first several picoseconds for dye **1** (circles) and its complex CB[7]–**1** (squares), measured by femtosecond time-resolved pump-probe technique.



Figure S17. The map of dye 1 (a) and complex CB[7]-1 (b) in H<sub>2</sub>O measured upon 400 nm laser excitation in the 420–700 nm spectral range measured by femtosecond time-resolved pump-probe technique.

### 7. Excited state study of dye molecules

Molecule **1** shows the following relaxation processes of the exited state in the solutions with high polarity: i) fluorescence (minor contribution), ii) *trans-cis* isomerisation (rotation around a double bond) and iii) formation of TICT (Twisted Intramolecular Charge Transfer) states (rotation around a single bond located close to the phenyl residue) (Scheme S1).<sup>[12]</sup> Upon excitation, firstly the fast equilibration between syn and anti conformers appears. In parallel, the isomerisation starts the non-radiative relaxation through relatively low barrier to the *trans* and *cis* ground states. These two processes (equilibration and isomerisation) produce a biexponential fluorescence kinetics.<sup>[12c]</sup>



Scheme S1. Schematic representation of the potential energy surfaces of molecule 1 for relaxation pathways of the exited states: *trans-cis* isomerization, fluorescence and TICT state.

Molecule 2 shows the following relaxation processes of the exited state in the solutions with high polarity: i) fluorescence (minor contribution) and ii) formation of TICT (Twisted Intramolecular Charge Transfer) states (rotation around a single bond located close to the phenyl residue) (Scheme S1). In the sharp contrast to molecule 1, the high-energy barrier to rotation around the central double bond in  $S_1$  state prevents photoisomerization of molecule 2 in most of the solvents with high dielectric constant. For molecule 2 TICT process is the only possible non-radiative

relaxation pathway in the solutions with high polarity. Radiative channel via fluorescence also makes a minor contribution in relaxation pathway.<sup>[5,12]</sup>



**Scheme S2.** A schematic representation of the potential energy surfaces of molecule **2** for relaxation pathways of the exited states: *trans-cis* isomerization, fluorescence and TICT state.

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