Electronic Supplementary Information

Non-Covalent Interactions of Coumarin Dyes with Cucurbit[7]uril Macrocycle: Modulation of ICT to TICT State Conversion

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Method M1:

In the present systems, the binding constants (K_{eq}) for the the dye with the host cavity were estimated by the fluorescence titration method assuming 1:1 complexation stoichiometry according to eq. 1, which afforded satisfactory fitting results.[1]

$$I_f = I^0_{Dye}\frac{[Dye]_{eq}}{[Dye]_0} + I^{\infty}_{Dye\bullet CB7}\frac{[CB7 \bullet Dye]_{eq}}{[Dye]_0} \qquad (1)$$

where I^0_{Dye} is the initial fluorescence intensity in the absence of CB7 and $I^{\infty}_{\mathrm{Dye\bullet CB}}$ corresponds to the fluorescence intensity if all the dye molecules in the solution were complexed by CB7. $[\mathrm{Dye}]_0$ and $[\mathrm{CB7}]_0$ are the respective total concentrations of dye and host, and $[\mathrm{Dye}]_{\mathrm{eq}}$ is the equilibrium concentration of uncomplexed dye in the solution. For fitting, the change in the fluorescence intensity ($\Delta I^{\lambda}_{\mathrm{f}}$) was plotted against the total host concentration and the obtained titration curve was fitted according to the rearranged eq. 2:

$$\Delta I^{\lambda}_{f} = \left(1 - \frac{[Dye]_{eq}}{[Dye]_0}\right)\left(I^{\infty}_{CB7\bullet Dye} - I^{0}_{Dye}\right) \qquad (2)$$

where, $[\mathrm{Dye}]_{\mathrm{eq}}$ is expressed as

$$[Dye]_{eq} = \{K_{eq}[Dye]_0 - K_{eq}[CB7]_0 - 1 + \sqrt{(K_{eq}[Dye]_0 + K_{eq}[CB7]_0 + 1)^2 - 4K^2_{eq}[Dye]_0[CB7]_0}\,\}/2K_{eq}\,.$$

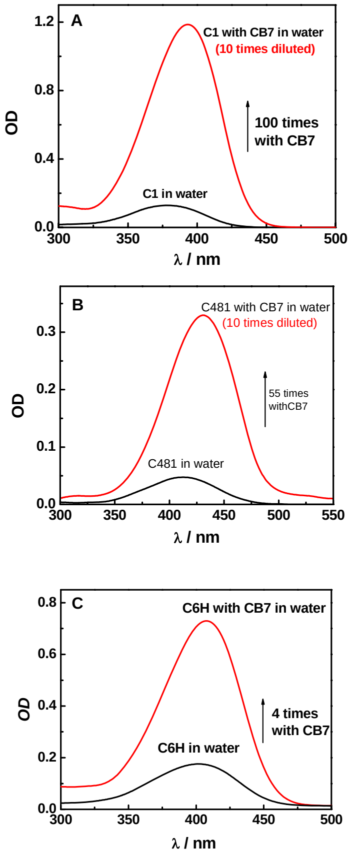

Figure S1. Absorption spectra recorded for C1 (**A**), C481 (**B**) and C6H (**C**) in the absence (solid black line) and presence of CB7 (0.5 mM, solid red line). The solubility enhancement factors are given along the arrows with CB7.

Table S1. Excited state decay time constants and photophysical parameters evaluated for CB7•C1, CB7•C481 and C6H complexes at varying CB7 concentrations. The decays were analyzed by biexponential kinetics.

	[CB7] (μM)	τ_1 (ns) a_1(%)	τ_2 (ns) a_2(%)	χ^2	Φ_f	$k_r \times 10^8$ s^{-1}	$k_{nr} \times 10^8$ s^{-1}
CB7-C1	0	0.028 (17)	0.32 (83)	1.04	0.051	1.9	35.1
	3.7	0.28 (26)	5.04 (74)	1.07	0.24	0.63	2.00
	8	0.28 (14)	5.07 (86)	1.12	0.42	0.96	1.31
	12.5	0.27 (9)	5.07 (91)	1.11	0.56	1.23	0.94
	17.5	0.26 (7)	5.08 (93)	1.06	0.66	1.41	0.72
	25.0	0.25 (6)	5.08 (94)	1.08	0.73	1.52	0.56
	35.0	0.26 (5)	5.09 (95)	1.07	0.78	1.61	0.45
	47.5	0.25 (4)	5.10 (96)	1.08	0.81	1.65	0.39
	62.5	0.25 (4)	5.10 (96)	1.03	0.83	1.69	0.35
	82.0	0.26 (3)	5.10 (97)	1.02	0.85	1.71	0.30
CB7-C481	0	0.053 (14)	0.21 (86)	1.04	0.012	0.64	52.5
	5.0	0.19 (22)	1.95 (78)	1.00	0.04	0.26	6.31
	12.5	0.21 (12)	1.95 (88)	1.11	0.07	0.40	5.40
	25.0	0.21 (8)	1.95 (92)	1.12	0.11	0.61	4.97
	50.0	0.19 (6)	1.96 (94)	1.20	0.13	0.71	4.72
	87.5	0.24 (6)	2.00 (94)	1.20	0.15	0.81	4.56
	138.0	0.21 (5)	1.99 (95)	1.18	0.16	0.84	4.44
CB7-C6H	0	5.32 (100)	---	1.06	0.58	0.11	0.78
	25	5.78 (100)	---	1.15	0.62	0.11	0.65
	50	6.29 (100)	---	1.15	0.67	0.11	0.53
	100	6.68 (100)	---	1.05	0.72	0.11	0.42
	150	6.73 (100)	---	1.07	0.73	0.11	0.41

Note 1

We have studied the complexation of C6H with CB7 (1.5 eq) by ^{1}H-NMR spectroscopy which indeed demonstrate the interaction of CB7 with CB7. The ^{1}H-NMR spectra is shown below. As seen from the spectra one coumarin aromatic proton Ha (δ 6.07, d, J= 10 Hz) does not show any complexation induced shift. However, Hb (δ 7.83, d, J= 10 Hz 0 and Hc (δ 7.12, s)shows an downfield shift of 0.13 ppm indicating its presence close to the carbonyl portal of CB7. On the other hand Hc (δ 7.12, s) display a large upfield shift of 0.56 ppm upon complexation to CB7.This large upfield shift indicates that Hc feels the effect of the highly shielded region of CB7 cavity. Unfortunately, in presence of CB7, the aliphatic protons appeared as broad signals restricting their detailed interpretation. It is therefore difficult to realize a clear structural picture of the C6H:CB7 complex from the ^{1}H-NMR data.

To gain a better overview of the structural aspects of C6H-CB7 complex, we have performed gas phase geometry optimization at semi empirical PM3 (MM) level with Gaussin package. Geometry optimization at this level shows that the CB7 cavity is not large enough to completely encapsulate the guest C6H. Moreover, the host-guest complex formation by encapsulation of the coumarin part by CB7 is destabilized by a positive heat of formation. Among various optimized geometries, the complex with partial encapsulation of tilted C6H molecule at the portal itself is stabilized by approx. -3 kcal/mol. Since, solvents play an important role on the dynamics of the coumarin dyes, a detailed study incorporating solvent molecule is very much essential, which is being pursued.

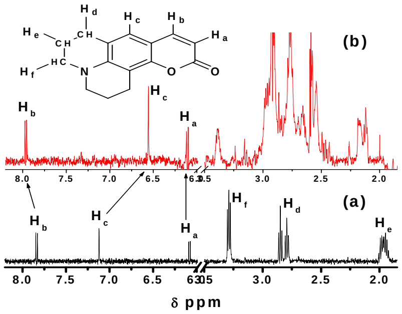

Figure S2. 1H NMR spectra of C6H in the absence of (a) and in the presence of CB7 (b).).

1 J. Mohanty, A. C. Bhasikuttan, W. M. Nau and H. Pal, *J. Phys. Chem. B* 2006, **110**, 5132-5138.