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ARTICLE TYPE

Cucurbit[8]uril templated *H* and *J*-dimers of bichromophoric coumarin dyes: Origin of contrasting emission

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We report supramolecular control and mechanism for the contrasting dimer emission from selected bichromophoric coumarin dyes, caught in the cucurbit[8]uril cavity; a facile approach for photo-responsive molecular assemblies through structural tuning.

Supramolecular association of fluorophores with preorganized medium often lead to discrete assemblies with interesting properties which are valuable for several technological applications.¹ For such molecular assemblies, while the processes of assembly or disassembly at molecular level is governed by non-covalent interactions such as hydrogen bonding, π -stacking, van der Waals or solvophobic forces, the ensuing photophysical attributes are dictated by spatial arrangement, rigidity etc originating from the structural aspects of the constituents.^{2, 3} Therefore, gaining control over these noncovalent interactions and the molecular orientation/stacking parameters are crucial for management of optical properties of the fluorophores or its aggregates⁴ and can be accomplished by introducing, more specifically, macrocyclic hosts.⁵ Among various synthetic cavitand receptors, the cyclic oligomers obtained in the acid catalysed condensation of glycoluril with formaldehyde, known as Cucurbit[*n*]uril (CB*n*, *n* = 5-8, 10, 14) family of macrocyclic hosts, attracted a great deal of attention due to their hydrophobic cavity with carbonyl laced portals at either ends, which offer strong ion dipole interaction for cationic guests, such as organic or organometallic cationic moieties, metal ions/complexes, etc.⁶⁻⁸ Among the CB*n* homologues, by virtue of its larger cavity, the cucurbit[8]uril (CB8) often accommodates more than one small guest molecules in its cavity, which by and large, leads to dramatic makeover in the guest properties. Such ternary host-guest assemblies have been aptly used in microcapsules for on-demand release,⁹ controlled polymer folding,¹⁰ supramolecular polymerization,^{11, 12} photocatalysis,^{13, 14} protein dimerization and enzymatic activity.¹⁵

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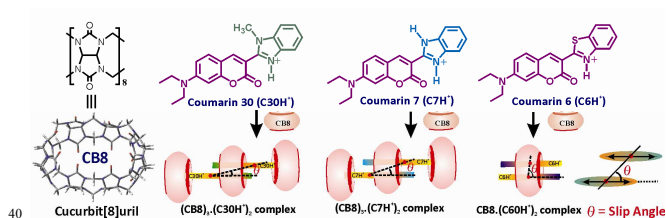


Chart-1 Structures of CB8 host; the protonated forms of C30, C7 and C6 guests and the proposed geometries of their Host-Guest complexes

Especially, in recognizing the contrasting optical properties of the fluorophore assemblies within the CB8 nanocavity,¹⁶⁻¹⁹ depending on the guest characteristics, CB8 supported both the contrasting phenomena of emission quenching as well as strong excimer emission.¹⁶⁻¹⁹ The photophysical modulations and its implications due to such non-covalent interaction is enormous and to best of our knowledge, there is no proper explanation for this intriguing spectroscopic changes, which we believe, need to be understood by the spatial arrangement of the chromophores in their dimeric/aggregate form within the host cavity, like the cases of *H* and *J*-type configurations.

In this study, we focus on the optical outcome of CB8 based ternary host-guest complexes with few selected coumarin laser dyes, coumarin 6 (C6), coumarin 7 (C7) and coumarin 30 (C30) (Chart-1), that display unusual photophysical properties in aqueous medium.^{20, 21} Apart from being well known laser dyes,²² these bichromophoric dyes, which differ only slightly with respect to the substitution/heteroatom on the benzimidazole unit, are also established as environment sensitive fluorescent probes for cellular imaging,²³ as well as dopants for organic light emitting diodes (OLEDs) and behaves as intramolecular push-pull (Donor-Acceptor) systems.²⁴⁻²⁶ Due to the finite structural variations at the benzimidazole ends of these dyes, dimeric/multiple uptake by CB8 would lead to subtle difference in their spatial arrangement within the cavity, akin to the case of *H* and *J*-type aggregation pattern. We anticipated that this would reflect in the optical response of the fluorophore. In this communication, we report, for the first time, spatial arrangement and the intrinsic mechanism of the novel emission from the CB8 templated *H* and *J*-dimers of the coumarin dyes.

With primary emphasis on the optical response of the supramolecular assembly of C30, C7 and C6 with CB8 host, their

interaction was studied in aqueous medium at pH 3, maintaining the dyes in their protonated forms. As shown in the Fig.1A, in the presence of CB8 the absorbance of C30 at 448 nm (absorption maximum) reduced considerably with a concurrent development of a new band, bathochromically shifted to 480 nm, with a clear isosbestic point at 463nm. Contrastingly, addition of CB8 to the C7 solution shifted the spectral maximum (475 nm) hypsochromically to 465 nm (Fig.1B), with isosbestic points at 455nm and 500nm. For the C6 dye too, hypsochromic shift from 517 nm to 492 nm was observed with neat isosbestic points as shown in Fig.1C. All these discrete spectral changes in the presence of CB8 clearly indicate a strong ground state interaction of the coumarin dyes with CB8.

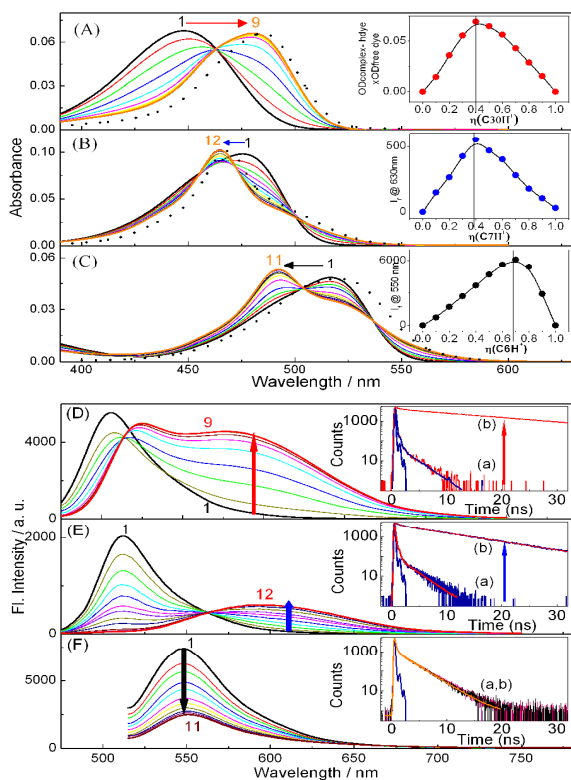


Figure 1 Absorption (A) and emission spectra (D, λ_{ex} 463nm) of C30 (1.2 μ M at pH 3) with [CB8]/ μ M: 0 (1); 0.4 (2); 0.9 (3); 1.3 (4); 1.8 (5); 2.2 (6); 2.7 (7); 3.6 (8); 4.5 (9), Absorption (B) and emission spectra (E, λ_{ex} 455nm) of C7 (1.3 μ M at pH 3) with [CB8]/ μ M: 0 (1); 0.2 (2); 0.4 (3); 0.7 (4); 0.9 (5); 1.1 (6); 1.3 (7); 1.6 (8); 1.8 (9); 2.2 (10); 2.7 (11); 3.6 (12), Absorption (C) and emission spectra (F, λ_{ex} 503nm) of C6 (1.3 μ M at pH <1) with [CB8]/ μ M: 0 (1); 0.2 (2); 0.4 (3); 0.9 (4); 1.3 (5); 2.3 (6); 3.2 (7); 4.5 (8); 5.8 (9); 7.2 (10); 9.0 (11). Insets: Job plots for CB8-C30H⁺ (in A); CB8-C7H⁺ (in B) and CB8-C6H⁺ (in C) systems. Comparative lifetime traces for C30 dye with [CB8]/ μ M: 0 (a); 4.5 (b) (in D); for C7 dye with [CB8]/ μ M: 0 (a); 3.6 (b) (in E) and for C6 dye with [CB8]/ μ M: 0 (a); 9 (b) (in F). (λ_{ex} 451nm)

Correspondingly in the emission front, the C30 and C7 dyes displayed remarkable spectral changes in the presence of CB8. With CB8, initially C30 displayed a decrease in emission intensity at 505 nm (λ_{em}^{max}), however, quite intriguingly, a new emission band developed in the long wavelength region. This eventually evolved into a broad spectral profile covering the wavelength region from 475-750 nm, having overlapping emissions centered at \sim 524 nm and \sim 580 nm. C7 under similar

experimental conditions, also displayed severe quenching of its normal fluorescence at 512 nm, on the other hand, evolved a broad but, a weak emission profile centered at 595 nm with an apparent isoemissive point at 562 nm. However, in contrast to the C30/C7 cases, the benzothiazole containing analogue, C6, displayed a steady quenching in the emission profile with increasing CB8 without any additional band (Fig.1F). Verification of their excitation spectrum corresponding to these novel emission bands (say for C30 and C7 at 600 nm and 630 nm, respectively) matched well with the absorption spectra of the complexes formed with CB8 (dotted line, Fig.1 A and B), whereas in the case of C6, the excitation spectrum (emission at 550 nm) more or less represented the absorption spectrum of free C6 dye (dotted line, Fig.1C). On introducing adamantylamine, a competitive binding agent for the CB8 cavity, the red emission band seen in case of CB8-C30/C7 systems and the quenched emission band of CB8-C6 regained their initial emission intensity and reversed to the spectral position of the free dye (Fig.S1, ESI), indicating the dissociation of the CB8-coumarin complexes. All these are found to be in tandem with the absorption spectral changes (Fig.S1, ESI), reiterating the origin of the new emission feature as that from the respective CB8-C30/C7/C6 complexes.

The above spectroscopic changes confirm the complexation of C30, C7 and C6 dyes with CB8 and the spectrally distinct novel emissions observed, may represent different stoichiometric and geometric arrangements feasible in the complexes. Such an indication is readily seen as two overlapping emission bands in the case of CB8-C30 (Fig.1D), whereas the CB8-C6 complex is found to be relatively non-emissive. Moreover, CB8-C30/C7 displayed much longer excited state lifetime as compared to that of free dyes in solution. In the presence of CB8 (\sim 6 μ M), the excited state lifetime of C30 increased remarkably ($>$ 150 times) from 0.13 ns (96%) to 19.8 ns (98%) (inset of Fig.1D), whereas that for C7 dye increased from \sim 0.17 ns (89%) to 10 ns (98%) (inset of Fig.1E) (see Note S1, Fig.S2, Table S1, ESI). For C6 dye, the excited state decay in presence of CB8 remained unaffected (Fig.1F), which, in other words, manifests the static quenching of C6 emission inside the CB8 cavity due to ground-state complex.

From the above results, the new emission bands having long excited state lifetimes are highly suggestive of a pre-associated dimer as per Winnik terminology,²⁷ which is sensitive to the spatial interaction among the coumarins within the CB8 cavity. A testimony of their state of overlap inside the cavity is seen from the contrasting bathochromic and hypsochromic shifts observed in the absorptions of CB8-C30/C7/C6 complexes (Fig.1A/B/C), which draw parallel to that expected from an end to end overlap as in *J* type aggregates and a face to face overlap as in *H* type aggregates.²⁸ To substantiate such emissive/non-emissive dimers in the CB8 cavity, we evaluated the stoichiometry of the CB8-C30/C7/C6 complexes by Jobs continuous variation method (Note S2, ESI) from the absorption/emission intensity changes at 480/630/550 nm, which exclusively corresponds to the absorption/emission of the complex. As shown in the inset of Fig.1A and B, the inflection point at 0.4 mole fraction of C30/C7 is suggestive of a dimeric association of the dye in a 3:2

(CB8:C30/C7) stoichiometry. However, the CB8-C6 system displayed the inflection point at ~ 0.66 (inset, Fig.1C), corresponding to a 1:2 stoichiometry.

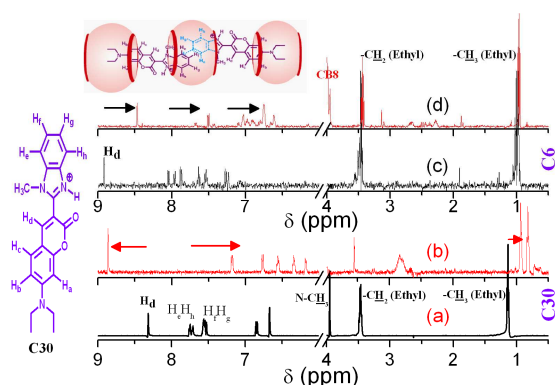


Figure 2 ^1H NMR spectra for C30 and C6 dyes in the absence (a, c) and in the presence (b, d) of CB8 host in D_2O at pH 3 (see Fig.S3-S4, ESI). The dye and the CB8 concentrations were $\sim 50\mu\text{M}$.

To comprehend the above observations mechanistically, we looked into the plausible structural distinction in these three dyes in penetrating the CB8 cavity, by ^1H NMR measurements. Considering the larger cavity dimension of CB8, one would normally expect a 1:2 (CB8:Dye) complexation, where the cationic benzimidazole ends are rather included from either side of the CB8 and the relatively bulky diethylamino substituted coumarin ends stay outward. This configuration renders magnetic equivalence of the aromatic protons of N-methylbenzimidazole units leading to only two sets of non-equivalent aromatic protons, namely H_a/H_h and H_i/H_g with impressive upfield shifts (1.00 and 1.21ppm, respectively) compared to that of free dye (Fig.2(a/b), Note S3, Fig.S3, ESI). Strikingly, the NMR spectrum also shows clear shifts in the ethyl protons of 7-N,N'-diethylamino group as well as the coumarin protons (see Fig.2(a/b)), which is likely when both the coumarin ends of the 1:2 complex are further encapsulated by another two CB8 moieties as shown in the inset of Fig.2. This 3:2 stoichiometry, where the H_d protons of C30 are placed in the deshielding region of the carbonyl portals of the CB8s, appears with ~ 0.54 ppm downfield shift (Fig.2). Similar changes found with C7 dye are discussed in Note S3, Fig.S4, ESI. Note that the data obtained from mass spectrometric measurements designated the formation of the 1:2 (CB8:(C30) $_2$ /(C7) $_2$) complexes, which is considered as the precursor for the 3:2 complex (Note S4, Fig.S5 A&B, ESI). The failure to observe the higher order complex could be a practical issue, such as the instability of the 3:2 host guest arrangements in the gas phase, during the ionization process in the mass spectrometer, compared to the solution phase.²⁹

To further consolidate the difference in overlap of the coumarin dyes within the CB8 cavity, semi-empirical geometry optimization and energy minimization calculations were performed for the 3:2 or 1:2 (CB8:Dye) stoichiometries using PM7 Hamiltonian with the continuum solvation model (Note S5, Fig.S6, ESI).³⁰ As shown in Fig.3, the complexes displayed distinct differences in the degrees of overlap within the CB8 cavity, a strong support for the assignment of *J*-type (in case of

C30) and *H*-type (in case of C6) orientations, elucidated from other spectroscopic measurements.

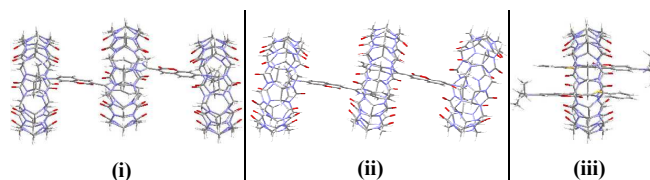


Figure 3 Geometry optimized structures for the CB8:Dye, in 3:2 stoichiometry for C30H^+ (i), C7H^+ (ii) and 1:2 stoichiometry for C6H^+ (iii).

It is now evident that the coumarin dyes primarily form a dimer with CB8 host and the extent of overlap or slip among the dyes inside the cavity leads to a *J*-type or *H*-type dimeric complexes, having varying slip angles, ' θ '. The slip angle is defined as the angle between the monomer transition moment and the axis joining the two chromophoric centers as represented in Chart-1. For *J*-dimers ' θ ' is always smaller than 54.7° and for *H*-dimers it is close to 90° . The former situation facilitates a strong exciton coupling between the two CB8 included dye molecules leading to strongly emissive dimer. It is well known that the *H*-aggregates are usually poor emitters, whereas *J*-aggregates typically show efficient luminescence.²⁸ In the presence of a monomer/dimer equilibrium, the slip angle among the dye molecules in a dimer can be deduced based on McRae and Kasha's theory (See Note S6, ESI).³¹⁻³⁴ With the estimated absolute fluorescence quantum yield ($\Phi_{f(\text{abs})}$) value for the C30.CB8 complex ($\Phi_{f(\text{abs})}=0.29$) (Table S2, ESI) and the corresponding fluorescence lifetime value (τ_f , Table S1A), the slip angles was estimated as 12° (16° calculated from Fig.3(i)). We believe that the presence of $-\text{NCH}_3$ group on the benzimidazole ring in C30 imposes a steric barrier and also provides hydrogen bonding at the CB8 portal so that the benzimidazole ring is not deeply engrossed into the CB8 cavity. Such an inclusion of C30 from either portals result in partial overlap of the benzimidazole ends within the CB8 cavity, mimicking a strongly emissive *J*-type dimer. This arrangement allows the $-\text{N}(\text{C}_2\text{H}_5)_2$ groups at the coumarin to bind another two CB8 moieties at these ends. This satisfies the contended 3:2 (CB8:C30) stoichiometry concluded from the Jobs plot, ^1H NMR as well as from the semi-empirical calculations. On the other extreme, the C6 dyes, bearing a benzothiazole group, are easily pressed deep inside the CB8 cavity facilitating complete structural overlap among the dyes with large slip-angle, $\sim 87^\circ$ as calculated from the optimized geometry in Fig.3(iii). This accounts to a *H*-dimer inside CB8 cavity, having no emission at all.²⁸ The blue shifted absorption during complexation and the excitation spectrum (Fig.1C) are in good support to this. Moreover, in the ^1H -NMR spectrum recorded for the CB8-C6 system (Fig.2,c/d), the $-\text{N}(\text{C}_2\text{H}_5)_2$ protons remained unaffected, which is very much expected from the structure shown in Fig.3 (iii). Between these two extreme cases of C30 (*J*-dimer) and C6 (*H*-dimer), there lies the changes observed in the CB8-C7 system. The protonated benzimidazole part of the C7 dye, gets further immersed into the CB8 cavity than C30 and provides better overlap. For the C7.CB8 complex, the slip angle estimated from

the $\Phi_{f(\text{abs})}$ (Table S2, ESI) and τ_f value (Table S1B, ESI) is found to be $\sim 18^\circ$ (22° from Fig.3(ii)). Virtually, this arrangement, which is more like a *J*-dimer, however, displayed much diminished red emission and narrower absorption band with a slight blue shift (Fig.1E/B). This intermediate configuration still allows the $-\text{N}(\text{C}_2\text{H}_5)_2$ groups to have 3:2 composition as documented in the NMR and the geometry optimized structure (Fig.3(ii)). In a control experiment, similar measurements on C30 and C7 dyes were carried out with γ -cyclodextrin, the classical host having comparable cavity dimension as that of CB8. Evidently (Note S7, Fig. S7, ESI), the system did not reveal any signature of dimer emission, upholding the unique capability of CB8 to host dimeric fluorescent assemblies of C30 and C7.

The isothermal titration calorimetric (ITC) measurements have been performed to evaluate the thermodynamic parameters for the complex formation and the titration curves are presented in Figs.S8/9 (Note S8, ESI). A 1:2 sequential binding model gave a satisfactory fit from which the overall binding constant of K ($= K_1 \times K_2$) $= (1.46 \pm 0.8) \times 10^{11} \text{ M}^{-2}$ for CB8-C30 complex, $(6.5 \pm 1.8) \times 10^9 \text{ M}^{-2}$ for CB8-C7 complex. However, due to the lack of convincing ITC titration data, the association constant for CB8-C6 system was evaluated as $K = (8.3 \pm 1.0) \times 10^{11} \text{ M}^{-2}$, based on fluorescence measurements (Note S8,C, ESI). Note that the thermodynamic parameters shown with Figs.S8/9 could be associated with a larger error due to the higher order complexation pattern and low absolute heats, limited by the solubility of CB8.¹⁷

In this study, we exclusively established hitherto unknown dimer emission from CB8-templated bichromophoric coumarin fluorophores, presenting > 150 fold increase in the excited state lifetime. We report, for the first time, the intrinsic mechanism of the dimer emission as due to the *slipped* spatial arrangement among the dimers within the CB8 cavity, like the cases of *H* and *J*-type aggregates. The slip angles, ' θ ', were found to be in right correlation with the emissive behaviour expected from the *H* and *J*-type configurations. Besides their intriguing photophysical perspectives, the contrasting and strong modulations observed in the optical response of these dyes, having very subtle change in the guest chemical structure, is promising towards the design of spatially restricted, CB8 based optically responsive novel self-assembled systems.

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Notes and references

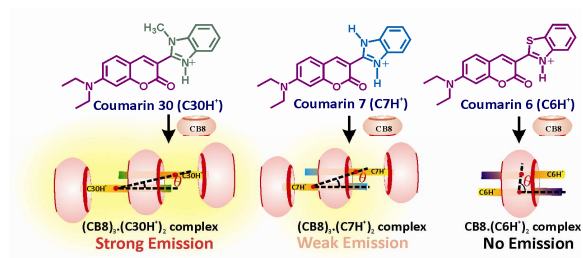
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TOC

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*N. Barooah, * J. Mohanty and A. C. Bhasikuttan**



Supramolecular control on the novel dimer emission from bichromophoric coumarin dyes caught in the cucurbit[8]uril cavity; a facile approach for photo-responsive molecular assemblies.