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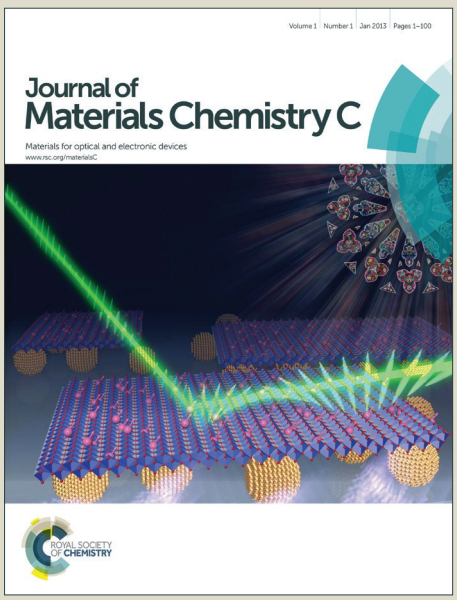

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REVIEW ARTICLE (for the Themed Issue on "Shape-Responsive Fluorophores")

Supramolecularly Assisted Modulations in Chromophoric Properties and their Possible Applications: An Overview

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In this article our efforts have been to review the supramolecularly assisted modulations in the properties of the organic chromophoric dyes, on their interactions with the macrocyclic host molecules, focusing on the possible uses of such modulated dye properties in different applications. We restrict ourselves on the modulations of two important properties of the chromophoric dyes, namely the fluorescence characteristics and the prototropic behavior, the properties that usually undergo large changes through host-guest inclusion complex formation of the dyes with the macrocyclic host molecules and show great prospects for their applications in diverse areas like sensors, catalysis, functional materials, electronic devices, pharmaceuticals, drug formulations, drug delivery, nanomedicines, and many others. To restrain the length of the article, our discussion has also been restricted to only two types of macrocyclic molecules, namely cyclodextrin (CD) and cucurbit[n]uril (CBn) hosts, that are realized to be most promising cavitand molecules in regard to their influences in modulating the dye properties leading to their applications in the aforementioned areas. We have considered suitable examples from the dye-CD and dye-CBn systems as reported in the literature by different research groups including ours to substantiate the discussions on different aspects of the macrocyclic hosts and those on the modulations of the fluorescence and acid-base properties of the organic chromophoric dyes, bringing out their possible applications in different areas, as have been the main objectives of the present review. We strongly feel that this review aricle will showcase the tittled theme, i.e. the supramolecularly assisted modulations in the properties of the chromophoric dyes, which can lead to different useful applications of the supramolecular host-guest systems, highlighting the immense prospects of such studies to explore the versatility of the supramolecular host-guest assemblies for their applications in the benefit of the mankind.

Introduction

Supramolecular chemistry deals with the structural assemblies that are formed through noncovalent interactions among the constituent molecular units, binding them together in a well organized manner.[1-18] Different noncovalent interactions like hydrophobic, van der Waals, hydrogen-bonding, π-π, electrostatic (e.g. ion-dipole or dipole-dipole interactions), etc. can be involved in combinations for the formation of the organized supramolecular assemblies. Exploring the supramolecular systems, from simple to complicated ones, formed through noncovalent interactions, aiming their uses in various applied areas have been the main impetus behind the long sustaining research activities in the supramolecular chemistry, spanning for not only more than one century, but also have been maintaining its intensity as one of the very active and frontier research areas in the chemical sciences even in the current times. The concept of supramolecular chemistry has attracted tremendous attention in all branches of science including chemistry, biology, medical science, pharmaceutical science, material science and so on, to explore the intricate details of various supramolecular systems keeping in view of their widespread applications in diverse areas like catalysis, functional materials, electronic devices, sensors, medical diagnostics, nanomedicine, and many others.[19-37]

Generally speaking, supramolecular materials include all kind of chemical systems that involve simple noncovalent interactions among the constituent components, leading either to the formation of well-defined organized supramolecular structures, disassembling of such assemblies to their constituent components, and also the transformation of one supramolecular structure to a new structure under the influence of a suitable stimulus, all happening in a spontaneous manner. Because noncovalent interactions are relatively weak, formation of the supramolecular assemblies is dynamic in nature and these assemblies are capable of displaying complete reversibility in their behaviour. Thus, their construction, dissociation and reconstruction are achievable quite easily by suitable adjustment of either the composition of the constituting components or by just using suitable external stumuli.[19-40] Further, the external stimuli can also often lead to the major structural or morphological changes in the supramolecular materials and such adaptive capability can be utilized in the design and fabrication of stimuli-responsive supramolecular functional materials, which can have applications in various fields, especially in fluorescent sensing, responsive polymer gels, biological sciences, pharmaceutical applications etc.[19-40] Fabrication of supramolecular nanomaterials having uniform sizes, good biocompatibility and low or negligible toxicity has been the topic of intense research in supramolecular sciences as these materials have many potential biomedical applications in particular, either as the diagnostic and therapeutic tools or as the nanomedicines.[11,16,29-32]

Taking advantages of the formation of the organized supramolecular assemblies from their building blocks, enormous efforts have been made by many research groups, especially for last about two decades, toward the fabrication of various nanoscale structures, aiming their applications in diverge areas ranging from targeted drug delivery to the development of functional

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materials.[11,16,19-45] In all these strides, molecular recognition-guided noncovalent interactions, which allow rational controls over the formation of the desired structural assemblies and bring out advantageous modulations in the properties of the active components of such assemblies, have been utilized very efficiently in developing various novel supramolecular systems that display unprecedented chemical, physical and biological responses.[19-45] Exotic molecular structures formed through supramolecular interactions have many advantages over those formed by covalent bonding. Thus, fabrication of the supramolecularly organized striking assemblies, which apparently look very complex in their arrangements and are also unique in their structures or constitutions, can quite easily be achieved through the participation of the noncovalent interactions, simply by mixing the correct building blocks in appropriate proportions in the solution and that too at the ambient conditions of the reaction environments usually, whereby the desired supramolecular structures are spontaneously formed through the recognition guided organization of the constituent units. Thus, the supramolecular approach provides a great opportunity to circumvent the complex multistep synthesis procedures and their associated product separation and purification complicacies for the construction of the complex functional materials involving covalent bondings.[19,47] Needless to say that the formation of the supramolecular assemblies through noncovalent interactions are also quite cost-effective in most of the cases and the fascinating systems thus obtained are generally benign to the environments.[19,47]

Amongst different supramolecular assemblies, the ones formed by the noncovalent interactions of the macrocyclic host molecules with suitable chromophoric organic guest dyes have occupied a large space in the realm of the supramolecular chemistry and have obviously been the topic of intense academic and applied research for at least last two to three decades.[38-73] Such host-guest interactions provide enormous opportunities for the construction of novel supramolecular structures that can have applications in diverse areas in chemistry and biology. Important macrocyclic host molecules that have attracted extensive studies in the host-guest chemistry are the cyclodextrins, calix[n]arenes, crown ethers, cyclophanes, cucurbit[n]urils, pillar[n]arenes, etc. All these host molecules possess macrocyclic cavities where suitable guest molecules can be encapsulated partially or fully, leading to the facile formation of the host-guest complexes that can often response to various physical and chemical stimulii.[38-46,64-72] The stability of such host-guest complexes (*expressed in terms of binding or formation constants; K_b or K_f*) depends on the extent of various noncovalent interactions that participate in a cooperative manner in the formation of these assemblies.[38-46,64-77] The stability of the host-guest complexes also depends largely on the compatibility of the size and shape of the concerned guest molecule and the dimension of the macrocyclic host cavity.[41-44] The K_f values for many of the cyclodextrin (CD) based host-guest systems can be of the order of 10^3-10^4 M^{-1}, which are considered to be reasonably high values and such systems can support the formation of reasonably stable host-guest complexes, serving the desired purposes of such supramolecular systems. The K_f values for cucurbit[n]uril (CBn) based host-guest systems are in general very high, often in the range of 10^5-10^7 M^{-1}, and are obviously best suited for the construction of very stable supramolecular host-guest assemblies. Such systems can truly lead to the formation of extremely robust supramolecular host-guest assemblies.

Among different macrocyclic host molecules, the CD and CBn homologues have attracted the most research interests in supramolecular chemistry, especially in regard to the applications of the host-guest systems in different biomedical applications, as these macrocyclic molecules are significantly bio-friendly and biocompatible. In our research group extensive supramolecular host-guest studies have been carried out involving especially different CD and CBn homologues as the macrocyclic hosts and various organic chromophoric dyes as the guest molecules. In this review article thus we restrict ourselves mostly to the interactions of the chromophoric and fluorogenic organic dyes with different CD and CBn hosts, with an emphasis to the supramolecularly assisted modulations in the photophysical and other properties of the guest dyes, looking for the prospective utilization of such supramolecularly modulated guest properties in different applications in chemical, biological and pharmaceutical sciences.

Macrocyclic Host Molecules

In the host-guest chemistry, the macrocyclic host molecules provide the suitable hydrophobic cavities for the effective incorporation and binding of the guest molecules resulting in the formation of stable host-guest complexes. As different types of the macrocyclic host molecules have their characteristic chemical constitutions, cavity shapes and cavity dimensions, their physical and chemical properties as well as their interaction characteristics with various guest molecules vary quite significantly. It is therefore essential to assimilate at the beginning the important structural and constitutional characteristics of the macrocyclic hosts, namely those of the CD and CBn homologues, as they are the focus of our present review, before moving to the other discussions on the host-guest assisted modulations in the properties of the organic chromophoric dyes and their prospective applications. Accordingly, important characteristics of the CD and CBn homologues in regard to their host properties are discussed in the following sub-sections.

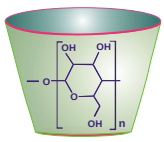
Cyclodextrins as the macrocyclic hosts

Among different macrocyclic molecules studied in the supramolecular host-guest chemistry the most widely investigated ones are undoubtedly the CD homologues.[29-31,48-60,78-83] These macrocyclic cavitand molecules are composed of d-glucopyranose monomer units which joined to each other by ether linkages in a cyclic manner.[78-83] Depending upon the number of monomer units involved, different CD homologues with varying cavity sizes are possible, of which αCD, βCD and γCD, containing 6, 7, and 8 d-glucopyranose units, respectively, are the most important CD molecules in regard to their supramolecular host-guest chemistry.

In biological systems the CDs are formed via the enzymatic degradation of starch.[29-31,48-60,78-83] Commercially also, most of the CD homologues are prepared through enzymatic reactions of starch precursors like potato, rice, corn, etc. The low costs of such preparations have made the vast utilizations of the CD homologues in different areas, from applied ones to the extensive academic researches. Ever since the discovery of CDs by Villiers in 1891,[84] these macrocyclic molecules have undergone very extensive studies in a variety of areas in the chemical, biological and pharmaceutical sciences, bringing out many of their widespread applications in all these areas.[29-31,48-60,78-90]

Structurally the CD hosts are the truncated cone-shaped hollow container molecules having a hydrophobic interior within the cavity and two significantly polar portals, the wider one composed of the secondary hydroxyl groups (*these groups are oriented outward at the cavity rim*) and the narrower one composed of the primary methinic hydroxyl groups (*these groups are oriented inward at the cavity rim*).

As expected, the cavity depths are very similar for all the αCD, βCD and γCD homologues. The dimensions of both the wider and the narrower rims of the CD homologues are, however, largely different for the three CD homologues, as these parameters are dependent on the number of glucopyranose units present in the macrocyclic molecule. The typical shape of the CD cavities is schematically shown in Chart 1. Important cavity parameters of the αCD, βCD and γCD hosts are also listed in Chart 1 for their quick comparision.[29-31,48-60,78-83]



Typical shape of a CD cage

Typical cavity dimensions of αCD, βCD and γCD hosts

	αCD (n=6)	βCD (n=7)	γCD (n=8)
Cavity depth:	7.9 Å	7.9 Å	7.9 Å
Wider rim diameter:	5.7 Å	7.8 Å	9.5 Å
Narrower rim diameter:	5.3 Å	6.0 Å	7.5 Å

Chart 1: Schematic representation of the typical shapes of the CD cavities. Important cavity dimensions of αCD, βCD and γCD hosts are also tabulated for a quick comparison.

The presence of the hydroxyl groups at the portals makes the external surface of the CD molecules fairly polar in nature and accordingly these macrocyclics show reasonable solubility in water, as are listed in Table 1 for the common CD hosts like αCD, βCD and γCD. The cavity interiors of the CD molecules are however nonpolar in nature and this property enables them to encapsulate and bind a variety of the guest molecules, especially the organic chromophoric dyes, through noncovalent interactions, resulting in the formation of well-defined host-guest complexes.[29-31,48-60,78-90] In many of the dye-CD systems, however, other specific noncovalent interactions like hydrogen bonding, dipole-dipole interaction, etc. can also contribute substantially in addition to the aforementioned hydrophobic interaction, rendering an extra stability to the host-guest inclusion complexes formed.

Table 1: Solubility in water (s_{water}) for the common cyclodextrin hosts, namely, αCD, βCD and γCD under normal conditions.[41,78]

Cyclodextrin	M.W.	S_{water} (mM)
αCD	972.84	149
βCD	1134.98	16.3
γCD	1297.12	179

Obviously the compatibility between the size and shape of the host cavity and molecular structure of the guest plays a vital role in the formation of the host-guest complexes Like many other host-guest systems, formation and dissociation of the dye-CD inclusion complexes are reversible in nature and dependent significantly on the environmental conditions like pH, temperature, presence of competitive guests, etc. Also Important to mention here that this latter responsive property that provides many of the dye-CD systems the useful features to react towards different kind of external stimuli that can consequently lead to many potential applications of such systems in diverge applied areas in chemistry and biology.[29-31,48-60,78-90]

As the macrocyclic hosts, CD homologues are having a number of beneficial properties, namely, they are easily prepared from natural sources and hence are of low cost, have reasonable water solubility (*cf*. Table 1), display extremely good biocompatibility, and are nontoxic towards biological systems.[29,78-83] Accordingly these macrocyclic hosts have been utilized very extensively in both academic research and also in many biomedical and other applications involving host-guest approach. Though in many of the host-guest studies the basic CD molecules or their simple derivatives have been used, but considering that the CD derivatives are good enzyme models, extensive efforts have also been made to introduce various active functional groups in the basic CD skeletons with aim to develop biomimetic artificial enzymes, targeting their uses in various bio-catalytic reactions.[24,29-32,35-37] As the CD derivatives have reasonable water solubility (*cf*. Table 1), many of the hydrophobic drugs that are otherwise insoluble or not adequately soluble in water, have been made sufficiently soluble in water through the formation of the host-guest complexes with the CD hosts and thereby increasing their availability and effectiveness in different applications.[29-31,48-60,78-83,85-95] In this regard, various chemically modified CD derivatives have also been developed that display improved aqueous solubility, better drug encapsulation/release ability, minimized toxicity, etc. for the better utilization in the pharmaceutical formulations, drug/gene delivery, bioimaging and many other important applications.[29-31,82,94-100] In fact, number of excellent research and review articles have been published in the literature assimilating the synthesis protocols of various functionalized CD derivatives and the uses of these macrocyclic hosts in the construction and utilization of various supramolecular assemblies and nanostructures for biomedical and other applations.[29-31,82,94-109]

Cucurbit[n]urils as the macrocyclic hosts

Among different macrocyclic hosts, the CBn homologues are understood to be an important category of the receptor molecules which have emerged as the versatile hosts in the supramolecular chemistry during last about one and half decades, in spite of their relatively late entry in the subject area compared to other cavitand molecules.[110-124] In general the CBn hosts form very strong inclusion complexes with a variety of the organic dyes, almost always much stronger than those formed by the other classes of the macrocyclic hosts.[14,15,49-53,66-77,125-145] The typical ranges of the K_f (or K_b) values for different chromophoric dyes with the CD and CBn macrocycles have been elegantly compared in graphical manner by Scherman and co-workers,[146] as has been extracted and shown in Figure 1 for a quick comprehension.

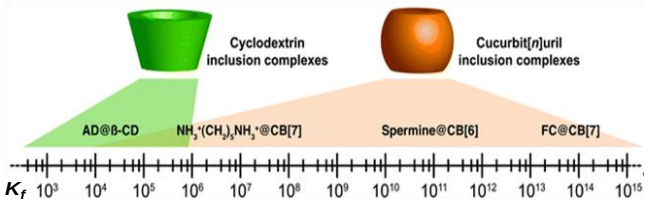


Figure 1. Typical ranges of the binding constant values (K_f) for different organic chromophoric dyes with different CD and CBn macrocyclic hosts. (*The schematic has been extracted from reference 146 with permission from the Royal Society of Chemistry*).

Chemically, CBn macrocycles are formed by joining glycoluril monomer units in a cyclic manner through a pair of methylene bridges. Based on the number of glycoluril units present, different CBn homologues are possible, e.g. CB5, CB6, CB7 and CB8, composed of 5, 6, 7 and 8 monomer units, respectively. Unlike the CDs, there is no natural source available for the commercial preparation of the CBn homologues.[29,46,69,110-117] Thus, the CBn macrocycles are always prepared synthetically following the acidic condensation of glycoluril

with formaldehyde at 75-90 °C for ~72 hrs.[29,46,69,110-117] The product thus formed is a mixture of the CBn homologues from which the individual components are isolated following tedious separation methods, mainly fractional crystallization, using various mixed solvent systems in sequences and involving multiple separation cycles.[110-117] Kim and co-workers were the first[110] and followed by many other research groups have successfully isolated different CBn homologues from the mixture of the products of the glycoluril-formaldehyde condensation reaction.[110-117] Day and co-workers isolated CB5 successfully that normally gets entrapped into the cavity of CB10 during the synthesis process.[111,114] An unique and green method to isolate CB7 by using an ionic liquid as a competitive and preferential guest has been used by Scherman et al.[117] to selectively isolate CB7 from the mixture of the other CBn homologues and the latter ones were subsequently separated using a solid state ion metathesis method.

Like other conventional macrocyclic hosts, CBn homologues also contain nonpolar cavities which encapsulate suitable organic guest molecules partially or fully, providing noncovalent hydrophobic interaction.[110-124] In addition to this usual hydrophobic interaction, which is always rendered by the nonpolar interior of the host cavities, the CBn macrocycles also offer other strong specific interactions like ion-dipole and/or charge-dipole interactions in suitable cases, especially when the guest dyes possess cationic charges or have intramolecular charge transfer (ICT) characters, enhancing the binding strengths of the dye-CBn complexes very largely, often much stronger than those involving conventional cyclodextrin hosts.[14,15,49-53,66-77,112-146] The beneficial Coulombic interactions for the CBn hosts arises specifically due to the presence of the highly polarizable carbonyl groups at the portals of these macrocyclic molecules. It is to be emphasised here that in spite of the quite late entry in the supramolecular chemistry, the favourable Coulombic interactions that the CBn hosts can render for unusually strong binding of many organic dyes has made these molecules as important category of the hosts for extensive studies in the supramolecular host-guest chemistry for last about one and half decade, as has been witnessed by large number of intriguing research and review articles.[REF]

For many cationic guest molecules, the CBn host provide unusually strong binding interaction. Extremely high K_f values, ranging from 10^{12} to 10^{15} M^{-1}, have been reported by Isaacs and co-workers for the inclusion complexes involving CB7 as the host and adamantane derivatives as the guests in NaO_2CCD_3 (50 mM) buffer solutions.[74,75] The K_f values in the range of ~10^{15} M^{-1} have also been reported involving either dicationic ferrocene derivatives or bicyclo[2.2.2]octane based cationic dyes as the guests and CB7 as the host.[76,77,128] Interesting to be noted here that so far the highest K_f value of $7.2x10^{17}$ M^{-1} has been reported by Isaacs and co-workers for a diamantane diammonium ion as the guest and CB7 as the host in pure D_2O solution using NMR studies.[75] Though these K_f values are amazingly high and are observed only with the special types of the guest dyes, yet in most of the host-guest complexes involving dye-CBn systems the k_f values are often found to be in the range of 10^5-10^7 M^{-1}, which are also remarkably high values and are large enough for the elaborate investigations of such host-guest systems following conventional photophysical studies and also to find their utilization in many practical applications.[19-46,64-72,125-127,129-139]

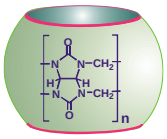
The solubility of most of the CBn homologues in water is significantly low, as listed in Table 2 for the common CBn hosts.[29,69,110-124] It is also interestingly found that in general the even numbered CBn homologues display significantly lower solubility in water in comparison to that of their odd numbered homologues.[69,115,116] Thus, while CB5 and CB7 have their solubility in the range of 3-4 mM, the CB6 and CB8 homologues show unusually lower solubility in water, only in the range of 10-20 μM, under normal conditions.[69,115,116] The low solubility of the CBn homologues in water is, however, often compensated by the exceptionally strong binding of many organic dyes by these hosts such that just tens of μM CBn concentrations can effectively lead to almost quantitative binding of the few μM dye concentrations in the solution, normally used in various photochemical studies.

Table 2: Solubility in water (s_{water}) for the common cucurbit[n]uril hosts, namely, CB5, CB6, CB7 and CB8, under normal conditions.

cucurbit[n]uril	M.W.	s_{water} (mM)	References
CB5	830.69	3-4	115,116
CB6	996.82	0.018	115,116
CB7	1162.96	3-4	69,115,116
CB8	1329.1	<0.01	115,116

An important aspect in relation to the water solubility of CBn homologues is that their solubility increases significantly both in acidic solutions and also in the presence of metal ions.[140-143] This happens because CBn macrocycles are strong cation receptors. Accordingly, host-guest studies in acidic aqueous solutions and also in the presence of metal cations (*especially the alkali and alkaline earth metal ions*) have been investigated quite extensively for number of dye-CBn systems, exploiting the competitive bindings of the metal ions or H_3O^+ to CBn hosts as an advantage in modulating the binding interactions of various dye-CBn systems, aiming their possible stimuli responsive applications in different areas and also to construct different exotic supramolecular assemblies for advanced applications.[14,34,38-40,64,115,123,140-145]

Structurally, CBn macrocycles are highly symmetrical pumpkin shaped molecules having two exactly identical and strongly polarizable and hydrophilic portal rims latched with carbonyl groups and a hydrophobic cavity suitable for encapsulation of suitable organic guest molecules. Like other host molecules, the recognition properties of the CBn homologues towards the organic dyes also vary largely depending on their cavity sizes. Thus, while the smaller CB6 cavity encapsulates and binds only the relatively smaller guest molecules like alkyl ammonium ions very strongly, the comparatively larger CB7 cavity easily encapsulates (*partially or fully*) and binds a large variety of organic dyes, rendering many possibility of such systems for multifaceted host-guest studies following photochemical means. Similarly, unlike CB7 host, which mostly participates in the formation of the dye-host inclusion complexes with 1:1 stoichiometric ratio, the significantly larger CB8 cavity can easily lead to the formation of the higher order dye-host inclusion complexes, especially those with 2:1 dye to host stoichiometric ratio, through simultaneous incorporation of two guest molecules into a host cavity.[29,69,72,115] The typical shapes of the CBn cavities is schematically shown in Chart 2. Important cavity parameters of CB5, CB6, CB7 and CB8 hosts are also listed in Chart 2 for their quick comparision.[29,69,115-124]



Typical shape of a CB cage

Typical cavity dimensions of CB5, CB6, CB7 and CB8 hosts				
	CB5 (n = 5)	CB6 (n = 6)	CB7 (n = 7)	CB8 (n = 8)
Cavity depth:	9.1 Å	9.1 Å	9.1 Å	9.1 Å
Rim diameter:	2.4 Å	3.9 Å	5.4 Å	6.9 Å
Inner diameter:	4.4 Å	5.8 Å	7.3 Å	8.8 Å

Chart 2: Schematic presentation of the typical shape of the CBn cavity. Important dimensions of CB5, CB6, CB7 and CB8 cavities are also tabulated for a quick comparison.

Modulations in the properties of chromophoric dyes through interactions with macrocyclic hosts

Inclusion complex formation of the chromophoric dyes with the macrocyclic hosts can lead to large modulations in their photophysical and other properties, as are reported and reviewed quite extensively in the literature.[14,24,29,45,46,49,68,69,73,92,130,131] Such modulations arise because the microenvironment for the guest dyes changes very significantly as they are encapsulated into the host cavities in comparison to the microenvironment of the free dye in aqueous solution. Moreover, confinement of the dyes by the host cavities introduces a large restriction towards the rotational and vibrational motions of the guest dyes and this in turn causes a large reduction in the nonradiative deexcitation pathways for the excited dye molecules inside the host cavities. In many cases the encapsulated dyes can also participate in some specific interactions with the host molecules which are otherwise absent or insignificant for the free dye in the solution. Consequently, incorporation of chromophoric dyes into host cavities causes a large modulation in the fluorescence properties of the dyes which can have many implications in regard to the applications of the dye-host systems in various photochemical, photobiological and other relevant applications.[125-139] In this respect the comprehensive review written by Nau and co-workers is of worth mentioning where authors have assimilated a huge quantity of information on fluorescence modulations and various applications for large number of dye-CD, dye-CBn and dye-calix[n]arene systems.[69]

Apart from the photochemical properties, other chemical and physiochemical properties of the organic dyes can also be largely modulated on their encapsulation into the host cavities. Accordingly, host-guest systems involving organic dyes and cavitand macrocyclic molecules can provide immense opportunities for the supramolecular host-guest studies both from the viewpoints of the academic interests and also for the prospective uses of such changes in different applications. In fact, dye-host inclusion complexes have been investigated very extensively for many years and several of such systems have indeed found applications in different areas of chemistry and biology. In the forthcoming sub-sections our efforts will be to overview some of the aspects of modulations in the guest properties of the organic chromophoric dyes on their interactions with the CD and CBn hosts, as have been reported in the literature mainly through photochemical studies, looking forward for the prospective applications of such systems in different applied areas.

Modulations in the fluorescence properties of the organic chromophoric dyes

Inclusion complex formation in general affects the excited state properties of the dyes very significantly, as the deexcitation pathways for their excited states are very sensitive to the microenvironments.[69,147-150] Internal conversion (IC) is one of the most important excited state deexcitation process that is largely affected by the formation of the host-guest complexes.[56-60,65-73,87-90,151-169] One of the reason for this effect is that the encapsulated dye experiences a significantly less polar microenvironment than that of the free dye in bulk water. For excited dyes the IC rate generally decreases on decreasing the solvent polarity.[147-150] Accordingly a significant reduction in the IC rate is expected as the dye is encapsulated into the host cavity. Apart from this, the geometrical confinement of the dye into the host cavity imposes a large steric restriction towards the rotational and vibrational motions of the dye and accordingly its IC and many other nonradiative deexcitation pathways would undergo a large retardition.[56-60,65-73,87-90,125-169] Further, due to inclusion complex formation, the dyes are compelled to be physically isolated and consequently being protected from the external reactive species present in the bulk water phase, which can either be the dissolved oxygen, a naturally present and very reactive species towards most excited dyes,[65-69,125-131,147-150] an added solute/quencher that diminishes the population of excited dyes either by a chemical reaction or just by a physical quenching,[65-69,125-131,147-150] or the solvent molecules themselves which often act as the strong quenchers for the excited states of the dyes involving them into the chemical processes like hydrogen bonding, proton transfer, electron transfer, etc.[69,125-131,147-150,153-155,170,171]

We know that fluorescence yield (Φ_f) of a dye is related to its different deexcitation pathways by the following relation.[147-150]

$$\Phi_f = \frac{k_f}{\sum k_{nr} + k_f} \quad (1)$$

where k_f is the radiative (fluorescence) rate constant and $\sum k_{nr}$ is the sum of all the nonradiative rate constants for the excited dyes. Since k_f is a chromophoric property of the dye, this parameter does not change much by the solvent environments. On the other hand, $\sum k_{nr}$ is strongly dependent on the characteristics of the solvent environments like polarity, viscosity, temperature, specific solute-solvent interactions, etc.[69,147-150] One can thus expect from eq. 1 that the deceleration of the nonradiative deexcitation processes for the encapsulated dyes would effectively lead to enhanced fluorescence yields and extended fluorescence lifetimes, as have been observed in many of the inclusion complexes involving CD and CBn hosts.[54,56-58,64,69,71,129,138,152-169] There are, however, examples where reduction in the fluorescence yields and shortening of the fluorescence lifetimes (*fluorescence quenching*) of the guest dyes are also observed on their inclusion into the CD and CBn cavities.[60,69,153,172-181] While in the cases of the dye-CD systems the quenching is mostly due to some specific interaction, e.g. hydrogen bonding of the encapsulated dye with the closely placed multiple hydroxyl groups at the CD portals,[60,69,172-176] for the dye-CBn systems the fluorescence quenching of the dyes generally takes place due to the incorporation of two dye molecules (dimers) into a single host cavity, as mostly happens with the larger CBn hosts like CB8, because the dimeric dyes are usually nonfluorescent or very weakly fluorescent in nature.[69,153,178-181]

That a chromophoric dye experiences a much lower micropolarity on its encapsulation into the host cavity and also that the confinement of the dye causes a significant reduction in the nonradiative deexcitation channels for its excited state causing an enhancement in the fluorescence yield is nicely demonstrated by the polarity sensitive dye 6-Propionyl-2-dimethylamino-naphthalene (PRODAN) in aqueous solution in the presence of the γCD host.[69,157,182] Typical steady-state fluorescence results reported by Baker et al.[182] for the PRODAN-γCD system in aqueous solution are shown in Figure 2, clearly

displaying the distinctly different emission bands for the free dye in bulk water and the dye bound to the γCD cavity, along with a large fluorescence enhancement for the γCD bound dye.

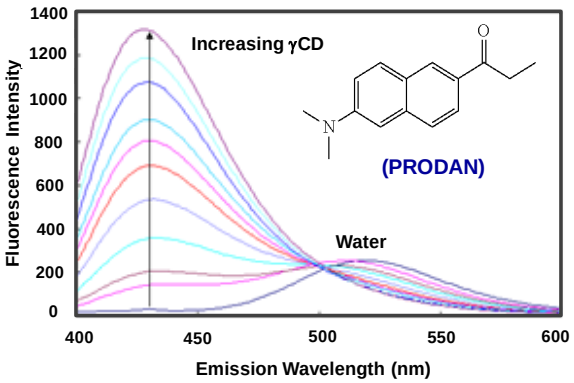


Figure 2. Changes in the emission spectra of PRODAN with gradually increasing concentration of γCD in aqueous solution. The free dye in bulk water and the dye-γCD complex show distinctly different emission bands. *The figure has been extracted from reference 182 with permission from the American Chemical Society*.

Significant blue shift along with a large fluorescence enhancement have also been reported for the polarity sensitive dyes like 1-Anilinonaphthalene-8-sulfonic acid (1,8-ANS) and 2-Anilinonaphthalene-6-sulfonic acid (2,6-ANS) dyes on their interactions with both CD and CBn hosts.[69,151,152,162,176] The dye neutral red (NR) also shows a considerable blue shift and significant fluorescence enhancement on its binding with both βCD and CB7 cavities, the effect being more prominent with the CB7 host, which is in accordance with the fact that NR binds more strongly with CB7 host (K_f = 6.5x10^3 M^{-1}) compared to that with βCD host (K_f = 4.1x10^2 M^{-1}),[38,69,129,165] even though both βCD and CB7 have comparable cavity dimensions.[29,69,110-124] Figure 3A and B exemplifies the kind of fluorescence enhancements accompanied by significant blue shifts in the emission spectra for the 2,6-ANS and NR dyes in the presence of the CB7 macrocyclic host. All these results clearly indicate that the dyes experience a relatively nonpolar microenvironment as well as a strong confinement effect as the dyes are encapsulated into the macrocyclic host cavities.[54,56-58,64,69,71,129,138,152-169]

There are number of chromophoric dyes that show exceptionally low or negligible fluorescence yield in their free state in bulk water but display unusually large fluorescence enhancement on their binding to the macrocyclic hosts.[69] These dyes are very important probes in various sensor applications where fluorescence "turn ON" and "turn OFF" mechanisms can be suitably applied for the recognition of the targeted analytes, manipulating the binding and release of the probe dye to the macrocyclic host cavity in the presence of the analyte and/or applying suitable external stimulus. To name few of such dyes that have important sensor applications in chemical, biological and other research areas are: PRODAN, 1,8-ANS, 2,6-ANS, thioflavin T (ThT), berberine (BE), coptisine (CP), 1-(4-aminophenyl)imidazole (API), 1-(4-hydroxyphenyl)imidazole (HPI), 2-[4-(Dimethylamino)-styryl]-1-methylpyridinium iodide (2ASP), 4-[4-(Dimethylamino)-styryl]-1-methylpyridinium iodide (4ASP), dapoxyl sulfonic acid (DSA), methylene blue (MB), etc. The kind of fluorescence modulations that these dyes undergo on their interactions with different macrocyclic hosts, especially those belonging to the cyclodextrin, cucurbituril and calixarene families are elaborately discussed by Dsouza, Pischel and Nau in one of their comprehensive review article.[69]

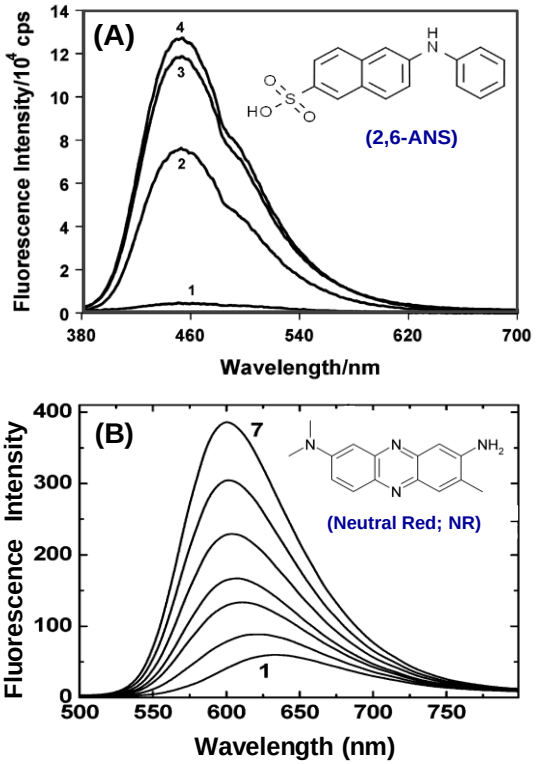


Figure 3. Changes in the emission spectra of (A) 2,6-ANS/CB7 and (B) NR/CB7 in aqueous solution with increasing host concentrations. *The figures in panel (A) and (B) have been extracted from references 162 and 129, respectively, with permission from The American Chemical Society*.

Large enhancement in the fluorescence intensity of methylene blue (MB) dye, as it is released from the CB8 cavity due to the competitive binding of an analyte, i.e. the chromophoric dye paraquat (PQ), to the macrocyclic host cavity, can be suitably utilized to detect the analyte in the geological environments and other biosystems, which is nicely demonstrated by Sun and co-workers.[183] PQ is one of the most widely used herbicides in the world and its migration to the geological environments and/or biosystems is a serious issue.[184-187] In the absence of PQ, the dye MB binds strongly to the larger CB8 cavity in the dimeric form giving rise to the 2:1 MB_2•CB7 inclusion complexes. Since the dimeric MB is non-fluorescent in nature,[183,188] there is a large fluorescence quenching for the dye on its binding to the CB8 host in the absence of PQ and this is the "OFF state" of the studied system. As PQ is a strong competitive binder for the CB8 host, in the presence of PQ the probe dye MB is replaced from the CB8 cavity and the monomeric MB thus released in the aqueous solution shows large enhancement in its fluorescence intensity, which is the "ON state" for the studied system. Typical changes in the absorption and fluorescence characteristics for the MB-CB8-PQ system with the gradually added concentration of the analyte PQ are shown in Figure 4. The fluorescence "OFF" to "ON" switching mechanism as it happens in the MB-CB8-PQ system with changing constitution of the supramolecular host-guest systems is also conceptually shown in Scheme 1.[183]

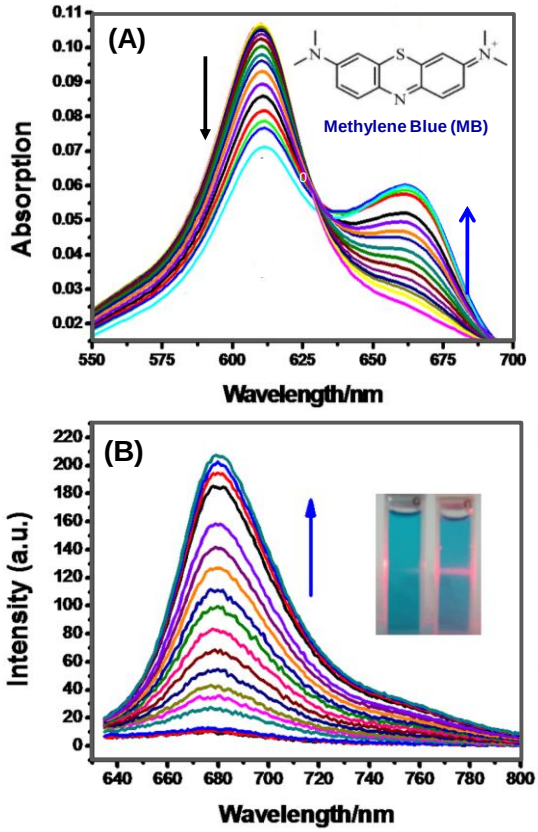
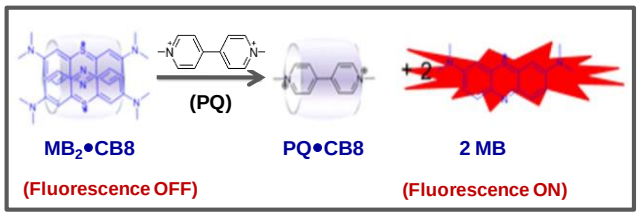


Figure 4. (A) Absorption and (B) fluorescence spectral changes of MB-CB8 system upon addition of PQ in tris-HCl buffer solution (pH = 7.14). Inset of (B) is the pictures taken under 625 nm laser irradiation, Left: MB-CB8 only and Right: MB-CB8-PQ system; the fluorescence recovery ("ON state") for the MB-CB8-PQ case is clearly indicated by the clear observation of fluorescence along the light path of the laser beam. *The figures have been extracted from reference 183 with permission from the journal Scientific Reports, ISSN 2045-2322.*



Scheme 1. Conceptual presentation of the fluorescence "OFF" to "ON" mechanism as it happens in the MB-CB8-PQ system with changing constitution of the host-guest systems. *The scheme has been extracted from reference 183 with permission from the journal Scientific Reports, ISSN 2045-2322.*

As mentioned earlier, the size of the chromophoric dye molecule and the dimension of the macrocyclic host cavity play an important role in deciding the extent of incorporation of the dye into the host cavity and thus to determine the extent of the binding strength for the concerned host-guest system. This aspect is nicely demonstrated by the different extent of enhancements in the fluorescence intensities of the dye, 1,4-dyhydroxy-9,10-anthraquinone (quinizarin; QZ), on its binding to αCD, βCD and γCD hosts, as are shown in Figure 5.[58]

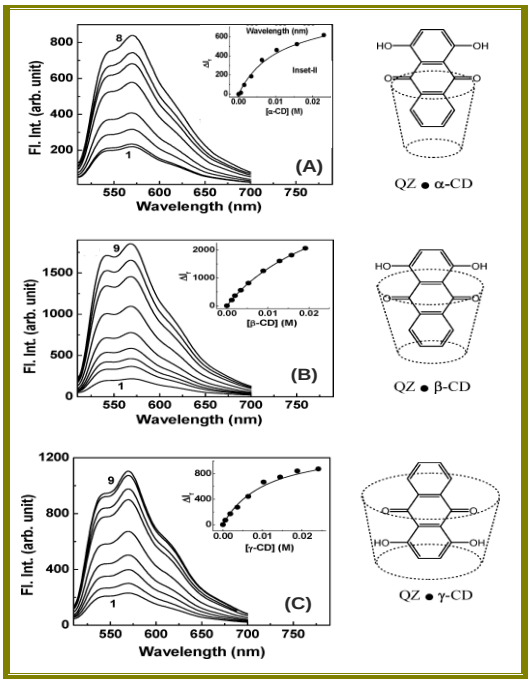


Figure 5. Observed fluorescence enhancements for the dye QZ on its interaction with αCD, βCD and γCD hosts. Different extent of penetrations of the dye into the αCD, βCD and γCD hosts, as it happens due to the relative sizes of the dye and host cavities are also schematically shown. *The figures in panel (A) to (C) have been extracted from reference 58 with permission from The Royal Society of Chemistry.*

Observed results for QZ-CD systems clearly showcase the different extent of incorporation of the dye into these host cavities, depending upon the relative size and shape of the guest and the macrocyclic host cavities, as could be convincingly revealed from the observed photochemical results.[58] Since QZ molecule has lone pairs both at its hydroxyl and quinonoid groups which are available for coordination with the metal ions, the dye can form strong coordination complexes with various metal cations.[189,190] Utilizing this property of the dye and following the reactions of different QZ-CD inclusion complexes with Al(III) ions, the binding motifs of the dye with the αCD, βCD and γCD cavities were convincingly established, as are shown alongside the panels A, B and C in Figure 5 for different QZ•CD complexes.[58] Observed results from this study clearly demonstrate how the hydrophobic and the steric control of the inclusion processes drastically influence the mode of binding and hence the reactivity of the CD bound guest dyes, resembling much to the ways in which enzymes bind substrates and carry out specific bio-catalytic processes.

A steep increase in the fluorescence intensity for palmatine (P) and dehydrocorydaline (DHC) alkaloid guest molecules have been reported by Jia and co-workers[191] in the presence of CB7 host in aqueous solution. In these cases the fluorescence enhancements are so large that one can readily recognize the changes simply by naked eye. Figure 6 shows the observed fluorescence enhancements for the two dyes with the increasing concentration of CB7 in aqueous phosphate buffer solution at pH 7.2. Visual emissions observed in these cases are also shown in panel (C) of Figure 6 for a comparison.

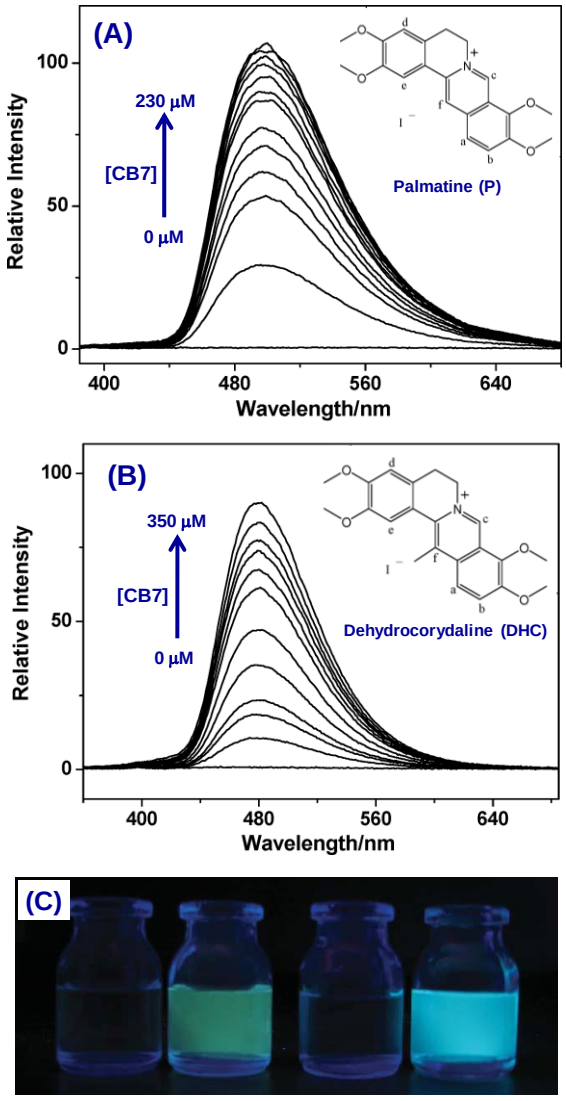


Figure 6. Changes in the fluorescence spectra of **(A)** palmatine (P; $1.25x10^{-5}$ M) and **(B)** dehydrocorydaline (DHC; $1.42x10^{-5}$ M) in aqueous phosphate buffer solution (pH 7.2) with increasing CB7 concentration. From left to right in panel **(C)** shows the visible emission observed from P, P + CB7, DHC, and DHC + CB7 cases, respectively. *The figures in panel (A) to (C) have been extracted from reference 191 with permission from The Royal Society of Chemistry.*

Between the P-CB7 and DHC-CB7 systems, the dye in the former case undergoes a relatively deep encapsulation into the CB7 cavity compared to the latter dye which undergoes a relatively shallow encapsulation into the host cavity. These differences in the extent of inclusion of the dye for the studied systems have been recognized as the cause for the large differences in the fluorescence enhancements in the two host-guest systems. This is unambiguously supported by the larger formation constant for the P-CB7 system (K_f = $4.26x10^4$ M^{-1}) compared to that of the DHC-CB7 system (K_f = $7.86x10^3$ M^{-1}). The solvent and salt effects towards the propensities of complexations in these systems have also been investigated and in both cases the binding ability as well as selectivity of the CB7 host is found to be influenced significantly for the two alkaloid guests studied. Since alkaloid compounds have various biochemical and pharmacological applications,[192-194] present study is projected to have a direct consequence to the bioorganic and the medical chemistry including determination, purification and separation of alkaloids and their uses in the drug delivery.[191]

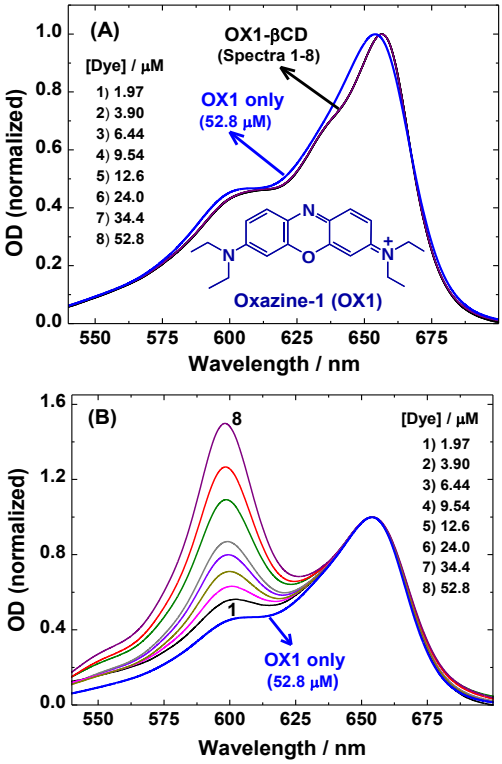


Figure 7. Changes in the absorption spectra for OX1 dye with the changing dye concentration in the presence of a fixed concentration of (A) βCD (18 mM) and (B) γCD (30 mM) hosts. All the spectra were normalized at 654 nm. Dimeric OX1 absorption band at 598 nm for dye readily develops in the presence of γCD. *The figures in panel (A) and (B) have been extracted from references 60 with permission from The American Chemical Society.*

Many organic dyes show strong affinity to undergo aggregation in aqueous solution.[60,69,138,153-155,179,183,195-197] Since the dye aggregates are usually nonfluorescent or very weakly fluorescent in nature, their uses as the fluorescence probes in different applications, especially in aqueous solutions, become very limited. In many host-guest interactions, especially those involving macrocycle host molecules that are having cavity sizes comparable to that of the chromophoric dyes or a part of their hydrophobic residues, the inclusion complexes are mainly formed with 1:1 dye to host stoichiometry whereby monomeric dye molecules are only incorporated into the host cavities. For such systems, thus, the inclusion complex formation turns out to be an important approach to resist the unwanted aggregation of the dyes and thus to make it beneficial in improving the fluorescence properties of the dyes in aqueous solution, leading to their widespread applications in diverse areas.[60,69,138,153-155,179,183,195-197] On the other hand, more than one chromophoric dye molecules, in most cases the dimeric dyes, can simultaneous get incorporated into the host cavities, when the cavity sizes of the macrocyclic molecules are much larger than the sizes of the dye molecules.[60,64,69,153,178-183] Figure 7 shows the typical such cases for the interaction of oxazine-1 (OX1) dye with βCD and γCD hosts, respectively. While OX1 dye

participates almost exclusively in the 1:1 dye to host inclusion complex formation with the relatively smaller βCD host and thus avoids aggregation of the dye in aqueous solution, the dye on the contrary undergoes a preferential 2:1 dye to host inclusion complex formation with the larger γCD host, assisting an efficient dimerization/aggregation of the dye in the solution in the presence of the γCD host.[60]

In the context of the supramolecularly assisted dimerization of OX1 dye by the γCD host, it is interesting to mention here that though CB7 and CB8 are considered to have similar cavity sizes as those of the βCD and γCD hosts, respectively, unlike the OX1-γCD system, the dye OX1 almost exclusively forms the 1:1 inclusion complexes not only with the smaller CB7 host but also with the larger CB8 host.[138] It is suggested that as the portal rims of the CBn hosts are much narrower than especially the wider rims of the corresponding CD hosts (*cf*. Charts 1 and 2), two OX1 molecules cannot find enough space at the rims even for the larger CB8 host to enter simultaneously into the host cavity.[138] However, many other chromophoric dyes with smaller side braches/substituents are known to form 2:1 dye to host inclusion complexes with the larger CB8 host.[64,69,153,178-183] To be mentioned that chromophoric dyes with suitable sizes and shape are also known to form 2:1 dye to host inclusion complexes even with the relatively smaller CB7 cavity, albeit such examples are not very common.[198]

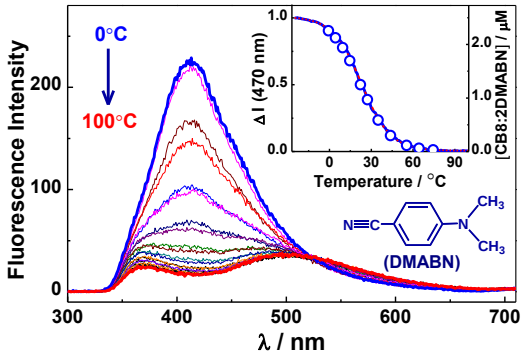


Figure 8. The excimer emission band of DMABN (5 μM) as assisted by CB8 (51 μM) and the disintegration of the DMABN excimer with the increasing temperature, eventually leading to the LE and ICT bands of the dye. *The figure has been extracted from reference 72 with permission from The Wiley-VCH Verlag GmbH.*

Though in many cases the higher order stoichiometric complexes, say 2:1 dye to host complexes, may be considered to be undesirable, especially when one looks for the fluorescence enhancement of the dyes in aqueous solution by the assistance of the supramolecular host-guest complex formation, in many of the cases, however, such higher order complex formation can become beneficial, either in some specific applications or in the exploration of newer chromophoric features that are otherwise not observed in the absence of the hosts.[64,69,72,178-183] In this respect, the example shown earlier in Figure 4 is one such case where CB8 assisted dimerization of MB dye becomes useful in the detection of PQ as the analyte.[183] Another important example in the present context is the dimerization of *p*-dimethylaminobenzonitrile (DMABN) dye into the CB8 cavity which leads to the identification of the hitherto unknown excimer emission of the dye as its third emission band in addition to its intriguing locally excited (LE) state and intramolecular charge transfer (ICT) state emission bands, adding a new dimension to the photophysics of the most controversially discussed dye DMABN.[72] The strong excimer emission band of DMABN, that develops only in the presence of CB8 host and which is found to be very sensitive to the solution temperature, is recently reported by us and the intriguing results are shown in Figure 8. Such tunable multiemissive behavior of the dye on their complexation with macrocyclic hosts can find applications as sensitive optical supramolecular thermometer, in the construction of the logic gates and in differential and ratiometric sensing processes.[72]

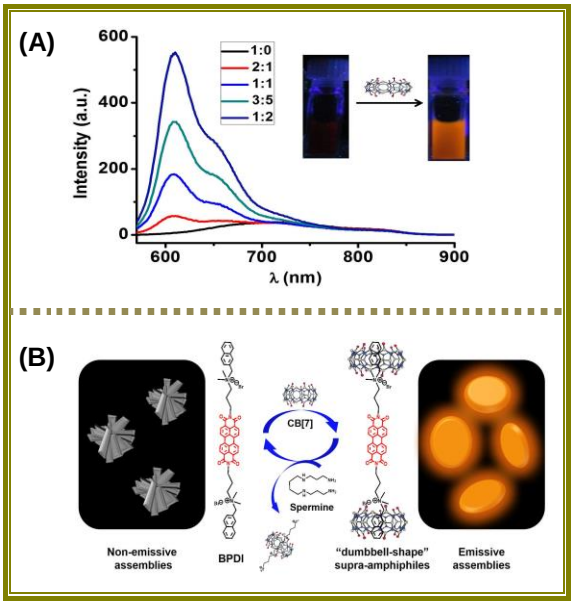


Figure 9. (A) The fluorescence of BPDI•$(CB7)_2$ complexes at different dye to CB7 molar ratios. **Inset:** Shows the photographs of the only BPDI (left) and BPDI•$(CB7)_2$ (right)systems in aqueous solution upon irradiation with a 354 nm light. BPDI concentration was $5.0x10^{-4}$ M. **(B)** Schematic presentation of the nanostructure formations of BPDI (left; nonfluorescent) and BPDI•$(CB7)_2$ (right; strongly fluorescent) systems. Furthermore, the reversibility of the host-guest interaction allows the present BPDI•$(CB7)_2$ nanostructure to be used as a smart supramolecular sensor for spermine, an important tumor biomarker. *The figures in panel (A) and (B) have been extracted from reference 199 with permission from the journal Scientific Reports, ISSN 2045-2322.*

A macrocyclic host with relatively smaller cavity size can encapsulate only a monomeric dye or only a part of it if the dye is having an extended molecular structure. In the latter cases thus it is possible that a second host molecule can easily bind to the other end of the dye resulting in the formation of the 1:2 dye to host inclusion complexes and thus bringing out newer chromophoric properties for the guest molecules. Formation of highly fluorescent supramolecular assemblies through the formation of 1:2 inclusion complexes between a perylene diimide (PDI) based bola-amphiphilic dye, BPDI, having two naphthalene-methanaminium moieties connected to the PDI moieties through long alkyl chains, and CB7 host, has been demonstrated by Zhang and coworkers.[199] In aqueous solution the PDI dyes including BPDI undergo severe aggregation through the stacking of their planar perylene moieties. In the presence of CB7 host, the dye BPDI undergoes efficient 1:2 dye to host inclusion complex formation which in turn brings out a dramatic increase in the fluorescence intensity of the dye, as clearly indicated in Figure 9A.

Interestingly, due to the amphiphilic nature of the BPDI•$(CB7)_2$ complexes they also undergo spontaneous self-association resulting in the formation of well-defined disc-shaped nanostructures in which the bulky CB7 bound heads of the BPDI•$(CB7)_2$ complexes prevents the π-π interaction between the adjacent perylene diimide groups and thus the assemblies show unusually strong fluorescence behavior. Furthermore, the reversibility of the host-guest interaction allows the present supramolecular material to be used as a smart supramolecular sensor for the analyte spermine, an important tumor biomarker. Schematics of the formation of reversible fluorescent BPDI•$(CB7)_2$ nanostructure and its response to the analyte spermine are conceptually shown in Figure 9B. Facile supramolecular approach has also been utilized by Nau and co-workers to encapsulate various PDI dyes into CB8 cavity forming the stimuli responsive highly fluorescent supramolecular assemblies and thereby eliminating the self-aggregation mediated fluorescence quenching of the PID dyes.[200]

As one can understand the preferential formation of the 1:1 inclusion complexes of the chromophoric dyes with the macrocyclic hosts, especially with those of the relatively smaller cavity sizes, can largely suppress the aggregation of the dyes in aqueous solution.[60,69,138,153-155,179,183,195-197] Effect of CB7 on the deaggregation of rhodamine and other chromophoric dyes have been extensively studied by Nau and coworkers.[69,153-155] The macrocyclic host assisted de-aggregation of the dyes in aqueous solution can have many beneficial effects, manly, the enhancement in the fluorescence intensity and brightness, increased photostability, protection of the dyes from the reacting species/quenchers present in the bulk aqueous phase, increased dye solubility, reduced non-specific dye adsorption on the container surfaces, and so on.[69,153-155] These improvements in the properties of the chromophoric dyes can lead to many practical applications of such systems in different areas like, sensors, indicators, fluorescence-based assays, drugs, bio-labeling, imaging, confocal microscopy, dye lasers, etc. using benign water as the convenient solvent.[60,69,138,153-155,179,183,195-197] Taking advantage of the CB7 assisted de-aggregation of the dyes and their enhanced photostability, our research group in collaboration with professor Nau and co-workers has in fact successfully demonstrated the operation of very stable supramolecularly assisted aqueous dye laser systems under both broad band and narrow band operating conditions for a number of rhodamine series of the chromophoric dyes using CB7 as the macrocyclic host for the dye encapsulation through 1:1 stoichiometric complexation.[201,202]

Figure 10 shows the typical lasing efficiency plots for rhodamine 6G (Rh6G) and sulforhodamine B (Kiton red S; KRS) dyes in aqueous solution in the presence of the increasing CB7 concentrations, measured under broad band and narrow band operating conditions, respectively, using 532 nm pumping light from a Q-Switched Nd–YAG laser for the excitation of the dyes in the solutions. The plots show almost comparable efficiencies at the saturation limits as that of the dyes in ethanol solutions.[201,202] That the lasing efficiencies in the present cases are slightly lower than those of the dyes in ethanol solutions are understandably due to the reduced radiative decay rates (k_f) of the dyes on their incorporation into the CB7 cavities as compared to those of the dyes in ethanol solutions, because the stimulated emission rate of a dye is directly proportional to its radiative decay rate.[203] To be mentioned here that the reduction in the k_f values for the encapsulated dyes in the present cases are mainly due to the lower polarizability inside the CB7 cavity.[69,153-155,204] Following Strickler and Berg relation,[69,147-150,153-155] the radiative rate of a dye is directly related to the square of the refractive index of the solvent medium and the polarizability is such a function of the refractive index that with a decrease in the refractive index of the solvent environment the polarizability also decreases, as it happens inside the CB7 cavity.[69,153-155,204]

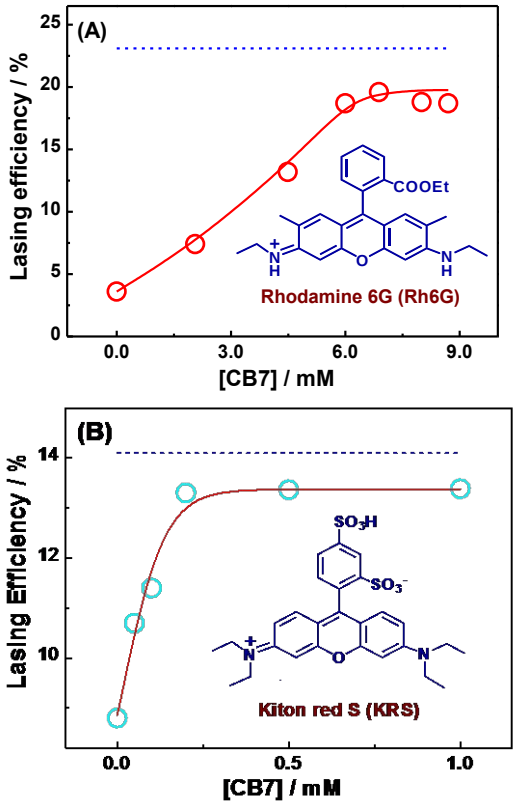


Figure 10. Lasing efficiency of **(A)** Rh6G (120 μM) under broad band operating condition and that of **(B)** KRS (200 μM) under narrow band operating conditions, measured in aqueous solution as a function of CB7 concentration. The 532 nm light from a Q-Switched Nd-YAG laser was used for the pumping of the dye laser systems. Dashed lines present the lasing efficiencies of the dyes in ethanol solution, shown for a comparison. *The figures in panel (A) and (B) have been redrawn based on the results reported in references 201 and 202 with permission from Wiley-VCH Verlag GmbH.*

For the studied dye-CB7 systems in aqueous solutions, the laser beam profiles were also found to be more symmetric compared to those obtained for the dye ethanol solutions. Typical comparison of the shapes of the laser beam profiles for the dye KRS in the cases of dye-CB7-water and dye-ethanol systems are shown in Figure 11. The perfect spherical shape of the laser beam for the dye-CB7-water system in comparison to the dye-ethanol system is understandably due to the better thermo-optic properties of water as the solvent medium than those of ethanol. The photo-thermal deflection measurements,[205,206] as carried out involving KRS-CB7-water and KRS-ethanol systems, clearly showed a much less localized heating and faster heat dissipation from the pumping zone of

the dye lasers in the case of the former system than the latter, as are indicated in Figure 12.

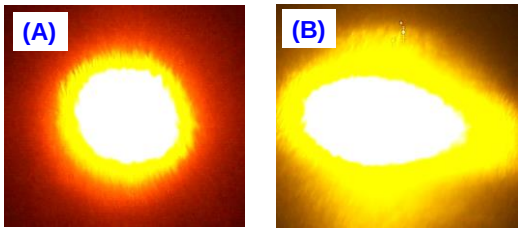


Figure 11. Laser beam profiles for the KRS dye (200 μM) in **(A)** water with 200 μm CB7 and in **(B)** ethanol, obtained using CCD camera. *These profiles have been extracted from reference 202 with permission from Wiley-VCH Verlag GmbH.*

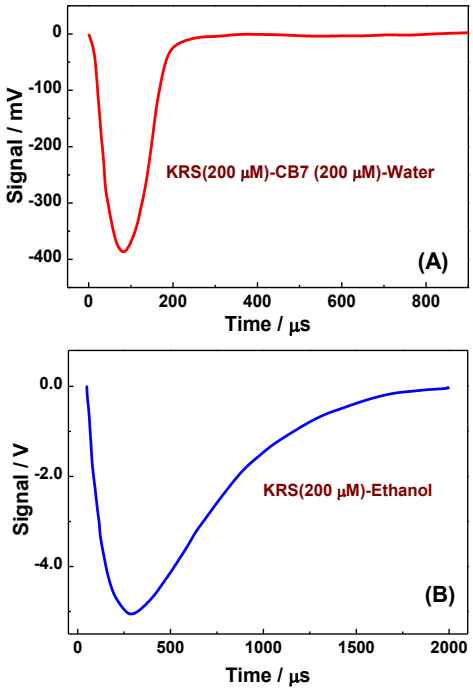
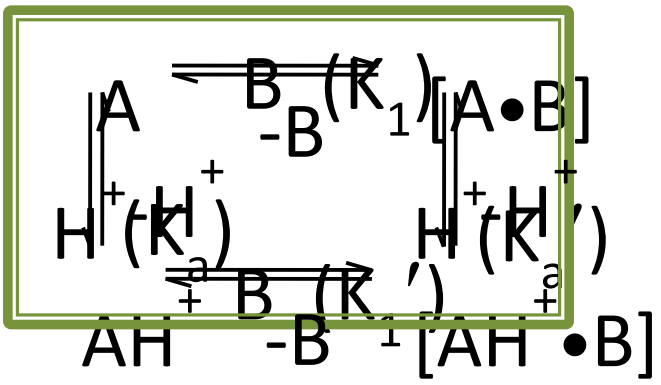


Figure 12. Photothermal deflection signals for KRS (200 μM) dye as measured (A) in water in the presence of 200 μM CB7 and (B) in EtOH solution. *The figures in panel (A) and (B) have been extracted from reference 202 with permission from Wiley-VCH Verlag GmbH.*

For the dye-CB7-water systems, the photostability of the dyes is also found to be at least three times better than that of the dye-ethanol systems. This effectively leads to improved laser operation for much longer operation times with better lasing efficiency and thereby reducing the maintenance intervals for replacement of the dye solutions, which is a major concern especially for the industrial or field applications of the concerned dye lasers. In brief, thus, the presently discussed work has been demonstrated that the addition of the macrocyclic host like CB7 to aqueous solutions of the chromophoric laser dyes can allow the development of the "supramolecular dye lasers" with number of environmental and safety benefits and having high lasing efficiency, better laser stability with longer operational times and with an impressive beam quality. Such systems can definitely find applications in areas where dye lasers are already being used presently and also in areas where dye lasers have not yet been employed yet broadly as a consequence of some limitations.

Modulations in the prototropic properties of the organic chromophoric dyes

Along with the modulations in the photophysical properties, the inclusion complex formation of the prototropic organic dyes with the macrocyclic host molecules also often modulates the acid-base properties of the dyes as their different prototropic forms can have largely different binding affinities towards the host molecules. For a prototropic dye, its acid-base or prototropic equilibria and the inclusion complex formation equilibria with the host molecule in the solution are always thermodynamically connected. Thus, for a simple prototropic dye having only one prototropic equilibrium and hence a single pK_a value, its free acid (AH^+) and base (A) forms and their respective inclusion complexes ([A•B]) and ([AH^+•B]), respectively) with the host (B) molecule will maintain a coupled equilibrium condition that can be represented by a four-state thermodynamic cycle as shown in Scheme 2,[24,39,127,129,173-175,207-213] where K_1 and K_1' are the binding constants of the A and AH^+ forms of the dye with the host molecule and K_a and K_a' are the acid dissociation constants of the free and the bound acid forms of the dye, respectively.



Scheme 2. Four-state thermodynamic equilibrium cycle is shown for a prototropic dye A in the presence of a host molecule B in the solution, considering all possible stages of the host-guest interactions and the acid dissociation processes involved in such systems.

Following the above thermodynamic cycle, the binding constants K_1 and K_1' and the acid dissociation constants K_a and K_a' can be shown to relate with each other by the following relation.

$$\frac{K_1}{K_1'} = \frac{10^{-pK_a'}}{10^{-pK_a}} \qquad (2)$$

It is evident from scheme 2 and eq. 2 that the acid dissociation constant of the AH^+ form and hence its pK_a value (-log K_a) can be modulated quite appreciably through the differential binding of the two prototropic forms of the dyes to the macrocyclic host cavity or through the largely different protonation-depeotonation rates of the free and host-bound dyes in the solution.

In the literature large number of host-guest systems have been reported that display substantial extent of pK_a shifts for the dyes on their binding with the macrocyclic host molecules.[14,24,34,39,123,129,131,165,173-175,207-225] Though there are some short reviews published in the literature on the host assisted modulations in the prototropic properties of the chromophoric dyes,[14,24,123,131,218] a comprehensive review on this aspect is still awaited. Based on the thermodynamic cycle in Scheme 2 and

following eq. 2 it is evident that if the base form A of the dye binds stronger with the macrocyclic host than the acid form AH^+, the dye would necessarily undergo a downward pK_a shift on its intraction with the host molecule. Similarly, an upward pK_a shift would be observed if the acid form AH^+ of the dye binds stronger with the host molecule than the base form A. Interestingly, however, it is also possible that the protonation and deprotonation rates of the free and the host-bound A and AH^+ forms of the dyes can be inherently quite different, leading either to an upward or a downward pK_a shift of the encapsulated dyes.

Though the aspect of the differential bindings of the AH^+ and A forms of the prototropic dyes with the host molecules to correlate the observed pK_a shifts have been well discussed in the literature,[24,34,39,127,129,165,173-175,207-225] the latter aspect of the differential protonation and deprotonation rates of the free and the host-bound dyes are only recently estimated and discussed quite elaborately by Thomas and Bohne.[225] Following stopped-flow measurements for 2-aminoanthracene-CB7 system at different pH conditions the authors have arrived at the conclusion that the observed upward pK_a shift of ~3.1 as observed for this system is mainly due to the lower deprotonation rate of AH^+•CB7 complex compared to the free AH^+ in the solution.

From the analysis of the observed results, it has also been proposed by Thomas and Bohne.[225] that two association modes, i.e. the direct guest inclusion and the formation of exclusion complex, depending on the directionality of approach of the guest and the host molecule, actually prevails at the initial stage of the host-guest interaction in the studied systems, though the exclusion complex thus formed eventually converts to the stable inclusion complex in a subsequent step. According to this two step interaction it is evident that the overall inclusion complex formation dynamics would be retarded significantly if the exclusion complex to inclusion complex conversion is not substantially fast. As indicated by these authors, for neutral form of the dyes the exclusion complexes convert very quickly to the inclusion complexes as the former species are quite unstable. For the cationic form of the dyes, however, exclusion complexes can last for longer times, especially in the cases where the host molecules are strong cation receptors, e.g. CBn hosts, due to the strong electrostatic interaction. In fact from the observed results it has been unambiguously inferred by Thomas and Bohne[225] that involving CBn host the observed binding dynamics for inclusion complex formation is always much faster for the neutral form of the dyes than their corresponding cationic forms, even though the binding constant values (K_f) for the inclusion complexes are invariably much higher for the cationic form of the dyes than the neutral forms, due to the additional stabilization arising from strong ion-dipole interaction.

As discussed by Thomas and Bohne,[225] the position of the cationic center in the AH^+ form of the dyes and the overall size of the dye molecules jointly determine if the observed inclusion complex formation dynamics would be effectively influenced by the exclusion complex formation at the initial step. It is suggested that for the dyes where cationic charge is centrally located in the dye molecule, e.g. in berberine cation (*cf*. Chart 3), the exclusion complex formation is mostly excluded and the inclusion complex formation is quite faster. On the other hand, if the cationic charge is located at one end of the dye molecule, e.g. in 2-aminoanthracenium cation (*cf*. Chart 3), the inclusion complex formation kinetics is largely influenced by the exclusion complex formation. However, if the size of the dye cation is reasonably small, e.g. 2-naphthyl-1-ethylammonium cation (*cf*. Chart 3), the dye molecule can easily slip into the host cavity lead the inclusion complex formation directly without involving the exclusion complexes. To be mentioned here that although the mechanism and kinetic detail of the AH^+•CB7 inclusion complex formation could be largely dependent on the nature of the host-guest system, yet the thermodynamic cycle shown in Scheme 2 always remains applicable.[225] Accordingly, this thermodynamic cycle and eq. 2 have been widely used in correlating the observed pK_a shifts for the host-guest systems, considering the differential binding strengths of the A and AH^+ forms of the dyes with the host molecules involved.[24,34,39,127,129,165,173-175,207-225]

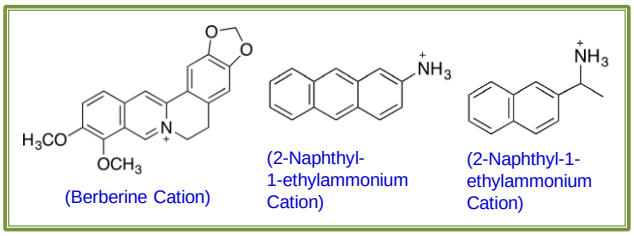


Chart 3. Chemical structures of berberine, 2-aminoanthracenium and 2-naphthyl-1-ethylammonium cations, indicating the locations of the cationic charges in these dyes and their relative sizes in regard to the dynamics of their inclusion versus exclusion compolex formations as discussed by Thomas and Bohne.[225]

As reported in the literature, downward pK_a shift is very common with CD hosts, especially when the acid form of the dye is positively charged (AH^+) and consequently the base form (A) is the neutral species, as are normally the cases with the organic dyes having amino and alkylamino substitunents in the chromophoric moieties or for the chromophoric dyes with heteroaromatic rings having basic nitrogen atoms in their chromophoric structures.[129,165,173-175,207,212] For such dyes thus, even at a pH of the solution somewhat lower than the pK_a value of the free dye, where the acid form AH^+ of the dye would otherwise be expected to exist in predominance in the solution in the absence of the host, the base form A of the dye can be induced to be formed preferentially in lieu of its acid form AH^+ just by the presence of a suitable macrocyclic host in the solution. Such a situation happens because in these systems the [A•B] inclusion complexes are formed more favorably than the [AH^+•B] complexes and thereby the host molecules assists to drift the equilibrium cycle in Scheme 2 gradually towards the [A•B] complex with an increase in the host concentration in the solution, causing more and more protolytic dissociation of the acid form (both AH^+ and [AH^+•B]) of the dye.

The macrocyclic host assisted acid dissociation of a prototropic dye is nicely demonstrated by Koner and co-workers for the dapoxyl sodium sulfonate (DSS) dye on its interaction with βCD host in aqueous solution, as shown in Figure 13.[212] The free protonated form of the dye, $DSSH^+$, has its pK_a value of 4.1 and accordingly at a pH ~4 the dye exists more towards the $DSSH^+$ form in the solution in the absence of the βCD host. On complexation with the host, there is about 0.8 unit of downward pK_a shift ($pK_a' = 3.3$), as neutral DSS form binds more strongly ($K_1 = 2910\ M^{-1}$) with the βCD host than its protonated $DSSH^+$ form ($K_1' = 400\ M^{-1}$). Accordingly, on addition of βCD host in the dye solution at pH ~4, there is a host induced deprotonation of the dye due to the preferential formation of the [DSS•βCD] complex as compared to the [$DSSH^+$•βCD] complex and this is clearly indicated by the gradual decrease in the fluorescence intensity for the shorter wavelength emission band (380 nm), arising from the locally excited state of the $DSSH^+$ form of the dye, with the concomitant and dramatic

increase in the fluorescence intensity for the longer wavelength emission band (540 nm), arising from the charge transfer state of the DSS form of the dye, even at the acidic pH of the solution, as considered in the present measurements. Such macrocyclic host assisted changes in the prototropic forms of the dyes without changing the pH of the solution can have potential applications in pharmaceutical formulations for drug stabilization and controlled drug delivery (*through suitable switching between pro-drug to drug and vice versa*), as supramolecular fluorescence probes and fluorescence sensors, in acid/base catalysed hydrolysis of included guests, etc.[207-225]

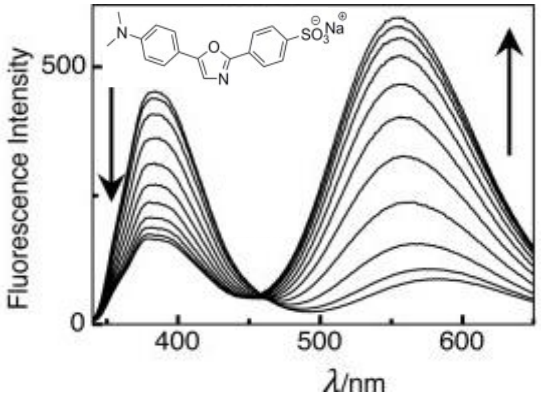


Figure 13. Changes in the fluorescence spectra of the dye dapoxyl sodium sulfonate (DSS; 5 μM) at pH 4.0 with the changing βCD concentration (0 to 5 mM), displaying the conversion of protonated $DSSH^+$ to neutral DSS at an acidic pH due to the βCD assisted downward pK_a shift of the dye. *The figure has been extracted from reference 212 with permission from Elsevier.*

The βCD assisted downward pK_a shifts in the range of about 1 unit have been reported by Nau and coworkers for a number of bridgehead-substituted azoalkane derivatives.[207] From our group, a downward pK_a shift of about 0.7 unit has been reported for the biologically important dye acridine orange (AO), on its binding with βCD host cavity.[173] Similarly for the dye acridine (Ac), a model antitumor agent and a fluorescence probe for studying various drug-protein and drug-DNA interactions in biological systems, we have observed a downward pK_a shift of about 0.4 unit on its complexation with βCD host,[174] and a much larger downward pK_a shift of about 1.0 unit on its interaction with hydroxypropyl-β-cyclodextrin (HPβCD) host.[175] A comparison of the pH titration curves for the free dye, dye-βCD and dye-HPβCD systems as obtained following the absorbance changes of the Ac dye at a suitable wavelength are shown in Figure 14, indicated the supramolecularly induced pK_a shift for the dye. For these dye-host systems, it is realized that the extended cage structure of the HPβCD host, as it happens due to the presence of the hydroxypropyl substituents at one of the rims of the basic βCD structure, provides a much stronger hydrophobic interaction for the encapsulated neutral Ac form of the dye compared to that offered by the simple βCD host (K_1 = 1000 M^{-1} and 303 M^{-1}, respectively, for Ac-HPβCD and Ac-βCD systems).[174,175] Importantly also, for both the βCD and HPβCD hosts, their binding affinity for the acidic AcH^+ form of the dye is virtually negligible. It is thus quite evident following Scheme 2 and eq. 2 that the Acridine-HPβCD system would undergo a much larger downward pK_a shift as compared to that observed for the Acridine-βCD system.[174,175]

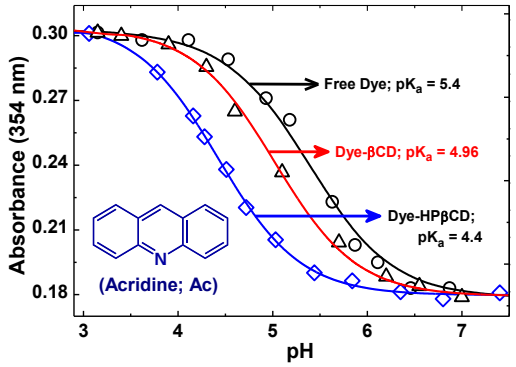
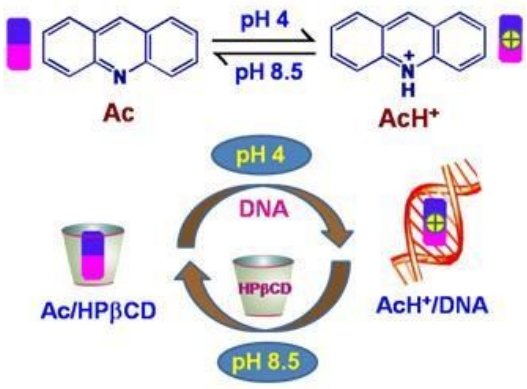


Figure 14. Comparison of the pH titration curves for the free dye, dye-βCD and dye-HPβCD systems as obtained following the absorbance changes of the dye at 354 nm. The pK_a values in each of these cases were estimated from the inflection points and are indicated in the plots. *The figure has been redrawn based on the results reported in references 174 and 175 with permission from Elsevier and The Royal Society of Chemistry, respectively.*



Scheme 3: A conceptual presentation of the pH triggered relocation of acridine dye from HPβCD cavity to DNA binding sites at acidic pH and reverse transfer at moderately alkaline pH are shown in this scheme. *The scheme has been extracted from reference 175 with permission from The Royal Society of Chemistry.*

Following the significantly larger pK_a shift for the acridine dye on its binding with the HPβCD host, the acridine-HPβCD-DNA ternary system was subsequently explored in our study to reveal a pH responsive dye/drug relocation from the HPβCD cavity, a model drug nanocarrier, to the targeted DNA sites, aiming a possible application of such strategy in drug delivery.[175] From pH dependent changes in the absorption and fluorescence characteristics of the dye in the dye/HPβCD/DNA ternary system it has been revealed that in moderately alkaline solution (pH ~8.5), the dye is predominantly bound to the HPβCD cavity. However, when the pH of the solution is lowered to a moderately acidic region (pH ~4), the dye is proficiently detached from the HPβCD cavity and gets almost exclusively bound to the target DNA. It was thus possible in this study to demonstrate a smart supramolecular assembly that responses to pH as a simple stimulus for the controlled uptake and targeted release of the dye/drug. A conceptual presentation of the pH triggered relocation of acridine dye from HPβCD cavity to DNA binding sites at acidic pH and reverse transfer at moderately alkaline pH is shown in Scheme 3. As pH is an essential and sensitive factor in various biological processes, such simple pH responsive supramolecular systems can hopefully find applications in host-assisted delivery of prodrugs at the intended binding sites, especially in cancer or tumour

environments, with an improved drug stability, enhanced bioavailability and superior reactivity of the drugs. Such stimuli responsive supramolecular systems can also find applications in the design of new fluorescent probes, sensors and smart materials for various applications in nanosciences.

Contrary to the CD hosts, which preferentially bind neutral forms of the prototropic dyes and show almost negligible interaction for the protonated acid forms, the CBn host molecules bind the positively charged acid forms much more strongly than the corresponding uncharged base forms. This preferential binding affinity for the AH^+ forms of the dyes by the CBn hosts arises due to the presence of the highly polarizable carbonyl groups at the portals of these hosts.[14,15,49-53,66-77,112-145] It is thus expected that interaction of the prototropic dyes with the CBn hosts would cause an upward pK_a shift of the dyes, a supramolecular pK_a modulation that is just opposite to that usually observed on using CD homologues as the macrocyclic hosts.

A large number of host-guest systems have been reported in the literature that display dramatic upward pK_a shifts for the dyes on their host-guest inclusion complex formation with the CBn hosts.[24,34,39,127,129,167,173,208-225] Nau and coworkers[214] synthesized a derivative of 3-amino-9-ethylcarbazole dye with a diamino-alkyl anchoring group, designated as Dye-I in Figure 15, that undergoes a large upward pK_a shift of about 4.5 units, particularly on complexation with CB8 host. Figure 15A shows the large changes in the fluorescence spectra of Dye-I in aqueous solution as a function of pH, indicating the characteristic emission bands around 458 nm and 375 nm for the neutral and the protonated forms of Dye-I, having a pK_a value of 5.3. Upon inclusion of the diamino-alkyl anchoring group of the dye into the CB6 cavity the pK_a of the dye dramatically increases to 9.8. Accordingly, even in a 10 mM NH_4OAc buffer solution at pH = 7, the Dye-I undergoes an efficient protonation, as indicated in Figure 15B, clearly showing the conversion of the emission band for the neutral form of the dye to that of the protonated form of the dye on increasing the CB6 concentration in the solution.[214] This system has also been shown to act as an efficient fluorescence sensor for the direct monitoring of the enzymatic activity of lysine decarboxylase through the indicator displacement mechanism.

That the prototropic dye *trans*-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (DSMI) undergoes a significant upward pK_a shift (pK_a = 3.1 and pK_a' = 5.6) and thus experiences a CB7 assisted protonation, even at a neutral pH condition, is also nicely demonstrated by Peng and co-workers,[221] following the changes in the absorption spectra of the dye in the presence of the CB7 host, as shown in Figure 16. As indicated from this figure, the absorption maximum for DSMI changes from 450 nm to 469 nm through the interaction of the dye with the CB7 host and these changes are in accordance with the fact that the dye experiences a lower polarity on its inclusion into the host cavity. That the absorbance for the 450 nm absorption band of the dye decreases very significantly on addition of the CB7 host in the solution with the concomitant appearance of another new absorption band with peak at around 330 nm clearly demonstrate that the base form DSMI of the dye undergoes a CB7 assisted protonation to preferentially form the $DSMIH^+$•CB7 complex even at pH = 7.4, a pH condition where the free dye would otherwise exclusively exist in its deprotonated DSMI form in the solution.

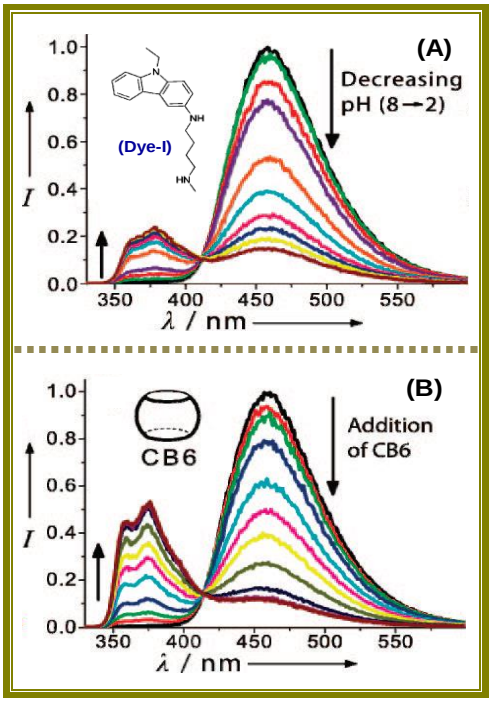


Figure 15. Changes in the fluorescence spectra of Dye-I (47 μM, λ_{exc} = 311 nm); **(A)** Upon changing the pH in aqueous solution and **(B)** Upon addition of CB6 (up to 50 μM) in 10 mM NH4OAc buffer, pH 7. *The figures in panel (A) and (B) have been extracted from reference 214 with permission from The American Chemical Society*.

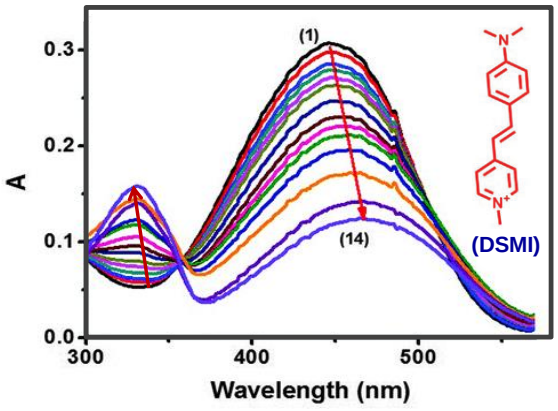


Figure 16. Changes in the absorption spectra of DSMI with the increasing CB7 concentration in the solution at pH 7.4. [CB7] : (1) to (14), 0, 0.2, 0.6, 1.0, 1.4, 1.8, 2.2, 2.6, 3.0, 4.0, 5.0, 6.0, 8.0, 10.0 $x10^{-5}$ M and [DSMI] = $1x10^{-5}$ M. *The figure has been extracted from reference 221 with permission from The Royal Society of Chemistry*.

Macrocyclic host assisted pK_a shift can have a beneficial effect in stabilizing the sensitive prototropic forms from the thermal or the photochemical degradations. This has been nicely demonstrated by Macartney and co-workers[215] to stabilize the base-off forms of vitamin B_{12} and coenzyme B_{12} by the encapsulation of their α-axial 5,6-dimethylbenzimidazole (α-DMB) groups (*in the "base-off" forms the α-DMB nucleotide base is detached from the respective Co(III) centers*) with the CB7 host cavities with an extremely strong binding affinity, with a binding constant in the range of 10^6-10^7 M^{-1} and resulting an upward pK_a shift of about 3.7 units. Similarly large pK_a shifts, as large as about 4 units, of different benzimidazole derivatives on their interaction with CB7 host have been reported by

Nau and coworker.[217] A pK_a shift as large as about 5.2 units has been reported by us for the coumarin-6 dye on its inclusion complex formation with the CB7 host.[39] It is interesting to mention here that with the CBn hosts, in particular with CB7, based on the consideration of their strong binding affinity for the cationic aromatic guests, metallocenes, anti-tumour platinum complexes, etc., their effects to lead a pK_a shift and the consequent prototropic conversion and the subsequent stabilization of the sensitive organic dyes/drugs are increasingly drawing attentions of many researchers for the utilization of such supramolecular methodologies for different pharmaceutical and biological applications.[29,69,125-139,167,191-194,215]

The supramolecular host-guest interactions of two biologically important prototropic dyes, namely, neutral red (NR) and acridine orange (AO), have been investigated by us using both CB7 and βCD hosts, to compare the effects of the two kind of hosts in modulating the acid base behavior of the studied dyes.[34,129,165,173] While NR has been extensively used as a fluorescent probe, as a intracellular pH indicator and as a stain for biological systems,[226-230] the AO is used as an important fluorescence probe along with its extensive use in biological systems, especially to detect and distinguish DNA and RNA.[231-234] For both NR and AO dyes, the CB7 and βCD hosts induce contrasting pK_a shifts by the host-guest complex formation with these dyes. Thus, while the pK_a values of the NR and AO dyes undergo downward shifts of about 0.74 and 0.7 units, respectively, on interaction with the βCD host, the pK_a values of the dyes interestingly undergo large upward shifts of about 2.0 and 2.6 units, respectively, on their interaction with the CB7 host.[34,129,165,173]

The CB7 assisted pK_a shift for NR dye was further explored in our study to understand the effect of external stimulus like added salts to fine-tune the pK_a shift for the NR-CB7 system and thus to explore the possibility of the dye binding/stabilization and the controlled relocation/delivery of the dye to biolomacromolecular pockets, using transport protein BSA as the model biosystem.[34] In the absence of any host, the free NRH^+ shows its pK_a of 6.8 and this value is upward shifted to 8.8 ($\Delta pK_a = 2$) on its independent interaction with CB7 and downward shifted to 6.3 ($\Delta pK_a = 0.5$) on its independent interaction with BSA . These contrasting pK_a shifts for NRH^+ by CB7 and BSA hosts are in accordance with the observations that NRH^+ from of the dye binds much more strongly with CB7 host ($K_1' = 3.1x10^6\ M^{-1}$) than its NR form ($K_1 = 6.5x10^3\ M^{-1}$) while the neutral NR form of the dye is seen to bind much more strongly with the biolomacromolecular host BSA ($K_a = 1.0x10^4\ M^{-1}$) than its cationic NRH^+ form ($K_a' = 6.1x10^3\ M^{-1}$).[34]

For the NR-CB7 system it is interestingly found that the pK_a shift for the dye can be fine tuned by the addition of a salt (e.g. NaCl) in the solution as a stimulus, causing a gradual reduction in the pK_a value for the NR-CB7 system with an increase in the salt concentration, as clearly indicated from the pH titration curves shown in Figure 17A. The results undoubtedly suggest that the CB7 bound dyes are triggered to be released gradually as the salt concentration is increased in the solution. As the results indicate, the pK_a for the NR-CB7 system can be easily fine-tuned between 8.8 to 6.8, that is between the pK_a values of the dye-CB7 system and the free dye, respectively, in the absence of the salt, just by adjusting the salt concentration in the solution.[34] Understandably, such a pK_a tuning for the NR-CB7 system by the added salt arises because the CB7 host is a cation receptor[14,15,49-53,66-77,112-139] such that the metal cations compete with NR and NRH^+ for binding to the CB7 hosts present in the solution.

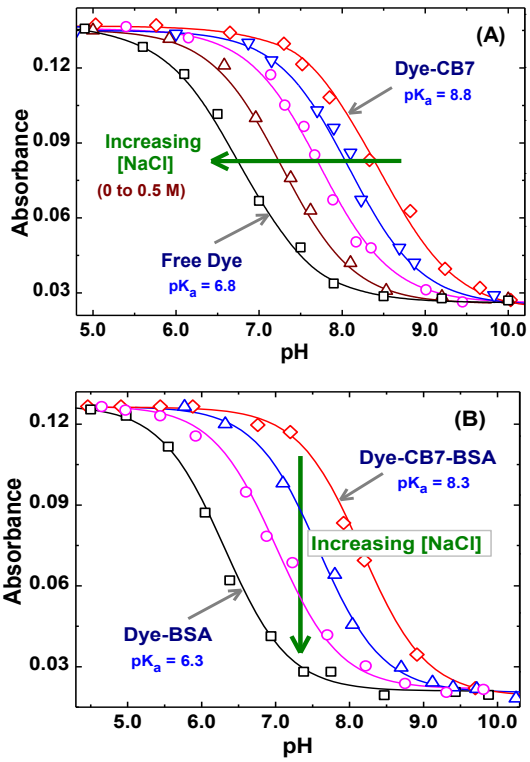
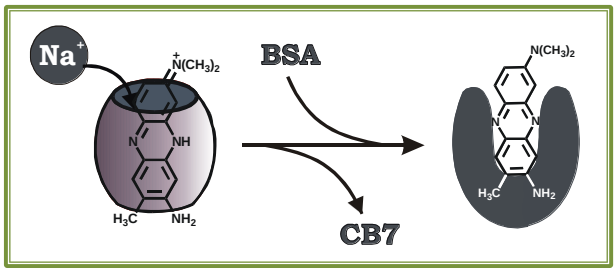


Figure 17. Tuning of the pH titration curves for (A) NR-CB7 and (B) NR-CB7-BSA systems with added NaCl concentration in aqueous solution. *The plots are reproduced from reference 34 with permission from The Royal Society of Chemistry.*



Scheme 4. Simplistic schematic representation of the salt-induced transfer of neutral red dye from the CB7 cavity to the BSA pocket near a neutral pH condition (pH ~7). *The scheme has been extracted from reference 34 with permission from The Royal Society of Chemistry.*

Interestingly, for the NR-CB7-BSA ternary system also, the pK_a of the dye is seen to undergo a similar fine tuning by the addition of the salt, namely between the pK_a values estimated independently for the dye-CB7-BSA system ($pK_a' = 8.3$) and for the dye-BSA system ($pK_a' = 6.3$), as shown in Figure 17B.[34] The salt induced pK_a tuning for the NR-CB7-BSA ternary system necessarily corresponds to the release of the dye from the CB7 cavity as the salt cations gradually binds to the CB7 portals and consequently assists the relocation and preferential binding of the dye to the BSA pocket. The net effect of the added salt to the NR-CB7-BSA ternary system at around neutral pH condition, say at around pH ~7.3, favouring the disintegration of the NRH^+•CB7 complex and assisting the formation of the NR•BSA complex can be easily realized following the downward arrow in Figure 17B and conceptually be shown as depicted in Scheme 4. Such a relocation and simultaneous conversion of the prototropic form of a dye assisted by an external stimulus can considered as similar to the

delivery of a prodrug into the biological system and consequent conversion of the prodrug into the active from of the drug for the required biological activity with higher efficiency. Such a strategy of binding, stabilization and relocation of prodrug into the active form of the drug from a macrocyclic host cavity to a biological system possibly can find applications in drug formulations and controlled drug delivery systems.[34]

Summary

In summary, we have attempted in this article to review within a reasonable length how the fluorescence and acid-base properties of the organic chromophoric dyes are modulated on their host-guest complex formation with the two types of macrocyclic hosts, namely cyclodextrins and cucurbit[n]urils. We have cited examples of the dye-CD and dye-CBn systems discussing some of the applications of the modulated fluorescence and acid-base properties of the chromophoric dyes in different applied areas. Efforts have been made to showcase that quite large number of host-guest systems have been reported in the literature demonstrating the potentials of the supramolecularly assisted modulations in the guest properties in many chemical and biological applications. Numerous prospects naturally exist for the supramolecular host-guest systems to explore more on the supramolecularly assisted modulations in the photochemical, chemical and other physiochemical properties of the chromophoric dyes to find their diverse applications in the areas like sensors, catalysis, functional materials, electronic devices, pharmaceuticals, drug formulations, drug delivery, nanomedicines, and many others. In short, prospects of the supramolecular host-guest systems are really very plentiful and such systems indeed deserve further extensive studies in very comprehensive manners to bring out their potential uses in the benefit of the mankind.

Acknowledgement

Authors are thankful to all the researchers in our group, our collaborators and others, whose results and findings have been used in this review article, to substantiate the discussion on the supramolecularly assisted modulations in the properties of the organic chromophoric dyes and in exploring their possible applications in different applied areas. Authors are also thankful to Bhabha Atomic Research Centre, Government of India, for the generous financial and academic supports in perusing authors' scientific endeavours.

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Table of Contents Entry

Supramolecularly Assisted Modulations in Chromophoric Properties and their Possible Applications: An Overview

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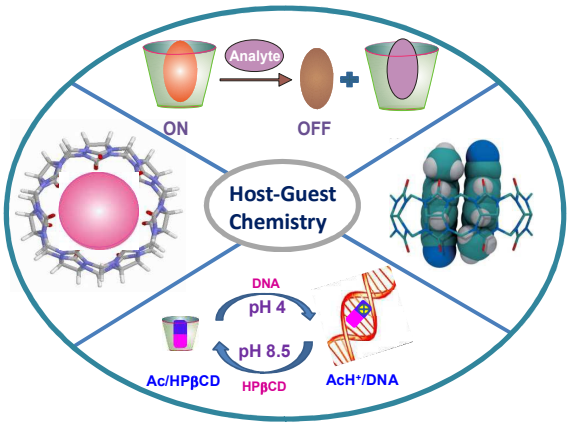

Highlight:

Macrocyclic host assisted modulations in the fluorescence and acid-base properties of organic chromophoric dyes and their possible applications are reviewed comprehensively.