Luminescence from Supramolecules Triggered by the Molecular Recognition of Substrates

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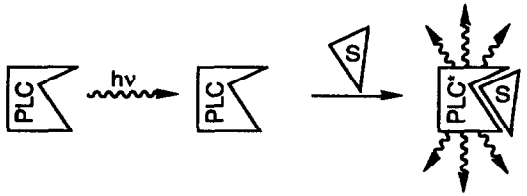
Abstract

Supramolecules containing a photoluminescent center (PLC) exhibit prompt and intense luminescence upon the molecular recognition of substrates. Luminescence from supramolecular assemblies is triggered by substrates that are light-harvesting and able to coordinate metal ion PLCs, light-harvesting and non-coordinating to PLCs, and non-absorbing and non-coordinating. Our efforts to elaborate the photophysical schemes for these three classes of substrates are described herein.

A. Introduction

Supramolecular chemistry is concerned with molecular architectures bearing multiple recognition sites for substrate binding [1-3]. When one or more of the guests residing in the binding sites of the supramolecular structure are photoactive, a variety of processes may take place that are modulated by the organization of the receptor and photoactive subunits. Such supramolecular architectures provide models for the study of fundamental photochemical processes such as photoinduced energy migration, charge separation by electron transfer, or selective photochemical reactions [4].

We have been interested in designing supramolecules that contain a photoluminescent center (PLC) whose response is triggered by the molecular recognition of substrate (S). The overall process, which is schematically represented in eq (1), is challenging owing to the propensity of substrates to typically attenuate luminescence from a PLC (eq (2)) [5-7] as opposed to enhancing it,



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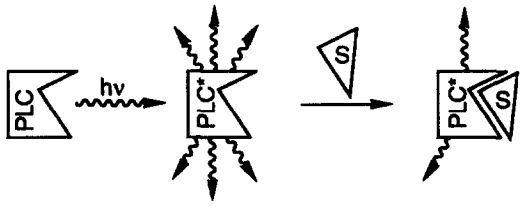

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Depending on the nature of substrate, we have focused on elaborating the three energy transduction processes depicted in Figure 1. Substrates that can absorb light in the ultraviolet or visible spectral region may induce luminescence by the absorption-energy transfer-emission (AETE) process popularized by Balzani and Lehn in recent years [1,2,4]. In this scheme, light absorbed by S to produce its excited state S*, is channeled to the PLC to produce electronically excited PLC*, which in turn relaxes with the emission of a photon. Because the rate constant for energy transfer exhibits a $1/r^6$ (Förster) or $e^{-\alpha r}$ (Dexter) distance dependence [8,9], efficient AETE processes demand that the light-harvesting substrate (S_{LHC}) be juxtaposed to the PLC. By virtue of the nature of S_{LHC} two AETE schemes are generated. For those S_{LHC} that are ligands, AETE is established upon coordination of the S_{LHC} to the PLC, which is typically a metal ion. For those S_{LHC} that are not ligands, the short distances needed for AETE may be imposed with the spatial constraints of a supramolecule. Of course the AETE scheme is circumvented by substrates tha are poor light-harvesters. In this case, we have elaborated the absorption-intersystem crossing-emission (AICE) process where fluorescence is replaced by phosphorescence when substrate is present. Regardless of the specific mechanism, the three schemes are characterized by the appearance of bright emission from the supramolecular assembly upon the molecular recognition of substrate. Described below is our progress in developing each of the schemes represented in Figure 1.

B. Lanthanide Cryptand Supramolecules – Triggered Luminescence by Coordinating, Light-Harvesting Substrates

We have studied triggered luminescence for this class of substrates by employing lanthanide-cage supramolecules. The scheme is predicated the weak luminescence of lanthanide ions (Ln^{3+}) under direct irradiation, owing to the low absorbencies of the emitting states [10]. However in the presence of S_{LHC}, AETE may be established to channel excitation energy to the Ln^{3+} PLC, which is an efficient emitter when indirectly excited.

A major obstacle to the design of lanthanide-based schemes is that the luminescence from the Ln^{3+} center is quenched efficiently by water. The high frequency O–H oscillators of coordinated water molecules result in efficient nonradiative decay of the Ln^{3+} excited state [11]. This deleterious effect of O–H oscillators on the excited state properties of Ln^{3+} ions can be minimized by encapsulating the ions in molecular cages of cryptand ligands [12,13] such as the one shown in Figure 2 (called 2.2.1). The two nitrogens and five oxygens comprising the three straps of the 2.2.1

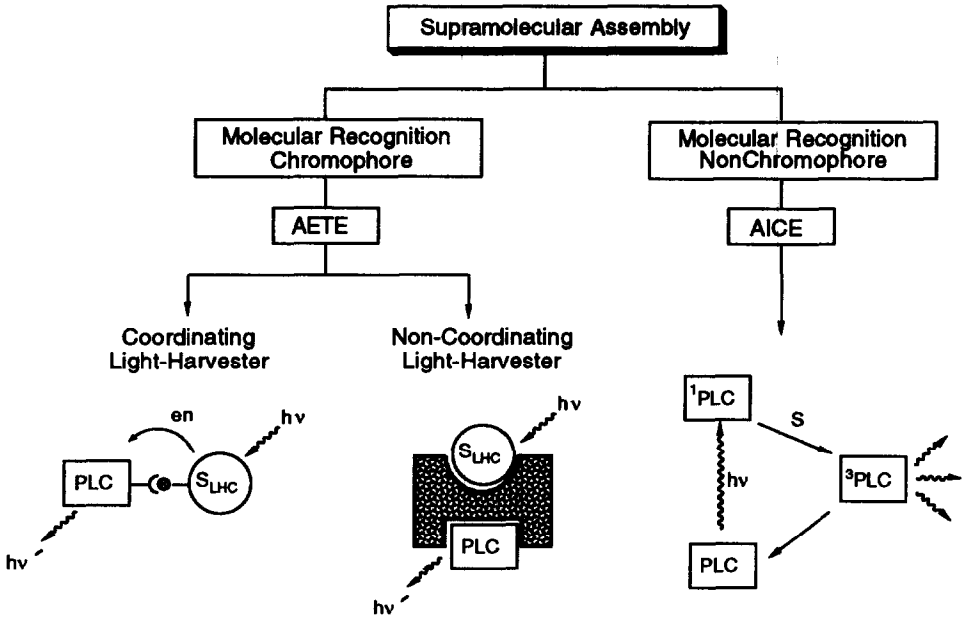


Figure 1. Three energy transduction schemes for supramolecular assemblies, depending of the nature of substrate (S). In each case bright luminescence from a photoluminescent center (PLC) is triggered by the presence of S.

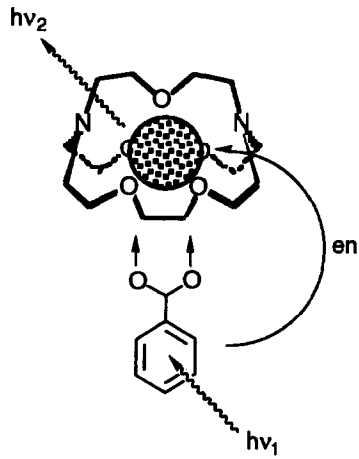


Figure 2. The 2.2.1 cryptand molecular cage encapsulates the photoluminescent Tb^{3+} ion (indicated by shaded ball). The two remaining coordination sites of the Tb^{3+} cryptand complex can be occupied by light-harvesting substrates such as benzoic acid.

cryptand ligand occupy seven of the nine coordination sites of the Ln^{3+} ion. The presence of the two remaining coordination sites of the Ln^{3+} cryptand complexes provides the opportunity for light-harvesting substrates (S_{LHC}) to enter the coordination sphere of the PLC and be detected by the AETE process. In this manner the optical excitation is efficiently pumped to the Ln^{3+} excited state via the S_{LHC}. Light-harvesting substrates possess much stronger absorption cross-sections than native $Ln^{3+}\subset$2.2.1 complexes ($\varepsilon(Ln^{3+}\subset 2.2.1) \leq 10\ M^{-1}\,cm^{-1}$ and $\varepsilon(Ln^{3+}\subset 2.2.1(S_{LHC})) > 10{,}000\ M^{-1}\,cm^{-1}$). Therefore, we have been able [14] to increase the emission efficiency of Tb^{3+} and $Eu^{3+}\subset$2.2.1 complexes by upwards of three orders of magnitude upon coordination of S_{LHC}'s such as β-diketonates and carboxylic acids. Compelling evidence that the increase in emission intensity is due to AETE comes from the excitation spectrum, which is not that of the native $Eu^{3+}\subset$2.2.1 as is the case when no S_{LHC} is present, but rather corresponds to the absorption spectrum of the S_{LHC}.

We have applied picosecond laser spectroscopic techniques to follow each of the energy transduction steps in the AETE process of the $Ln^{3+}\subset$2.2.1 system with acetylacetonate (acac) as the S_{LHC} [14]. In the absence of $Tb^{3+}\subset$2.2.1 , the luminescence decay of acac is monoexponential with a lifetime of 1.7 ± 0.4 ns, which is consistent with simple decay of the $^3\pi\pi^*$ state of acac. Conversely, in the presence of $Tb^{3+}\subset$2.2.1, biexponential behavior is indicative of more complicated decay kinetics from the acac triplet excited state; a lifetime of 103 ± 23 ps for a short component and a decay time of 1.73 ± 0.07 ns is determined for the long component. We have shown that the long component originates from the $^3\pi\pi^*$ decay of unbound acac, and that the short component arises from triplet decay of acac when bound to the encapsulated Tb^{3+} center. Concomitant with this disappearance of the luminescence from bound acac, is the appearance of Tb^{3+} luminescence. The rise time of Tb^{3+} emission at 546 nm ($^5D_4 \rightarrow {}^7F_5$), occurs on a time scale (85 ± 40 ps) that is commensurate with the decay of acac emission. The congruence of the acac decay and Tb^{3+} rise time kinetics strongly supports direct energy migration from the acac triplet to the excited state manifold of the luminescent Tb^{3+} center. The luminescence of the caged Tb^{3+} luminescence occurs subsequently at long times (1.7 ms), which is consistent for simple radiative decay from the $^5D_4$ excited state of Tb^{3+}.

The AETE process of the lanthanide supramolecules is very sensitive to distance of the light-harvesting center from the PLC and the shape of S_{LHC}. The results of the AETE process with carboxylates as the S_{LHC} are shown in Figure 3. The system shows the important result that the most efficient AETE and hence sensing occurs when the light-absorbing benzene ring is near the Ln^{3+} center. As the number of methylenes between the carboxylate anchoring moiety and the benzene ring is increased Ph–$(CH_2)_x$–COO^- (x = 0, 1, 2, 3, and 4), the intensity of the observed luminescence decreases exponentially, as predicted by Dexter theory [9]. The slightly jagged dependence between even and odd number of carbons is most likely a result of slightly different distance dependencies for the even and odd series. Consistent with this contention are molecular mechanics calculations. The trans gauche conformation of the methylene

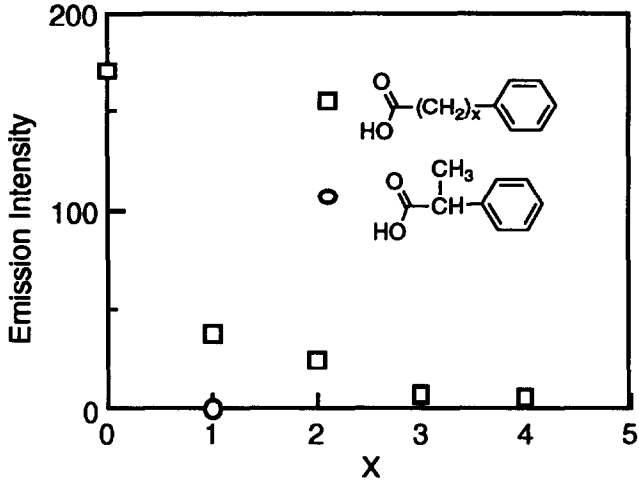


Figure 3. Distance dependence for luminescence intensity of phenyl carboxylates (□) and shape selectivity is demonstrated with the replacement of H by CH_3 on the methylene carbon for the x = 1 system (O).

chain causes the benzene ring on average to move away along a direction normal to the Ln^{3+} ion for the even series, while the benzene ring moves away from the Ln^{3+} ion at a canted angle for odd methylene chains. In regard to selectivity, steric constraints between the carboxylate and the straps of the cryptand cage can play a crucial role in the photophysics. For instance consider the case for x = 1. When a hydrogen is removed from the methylene spacer and replaced with a methyl group, luminescence from the PLC is lost. Molecular models reveal that the appended methyl on the methylene carbon will bump into the cryptand straps if the carboxylate were to bind to the Ln^{3+} ion, thereby precluding binding of this carboxylate to the caged Ln^{3+} ion. In this case, AETE can not be established and the carboxylate is incapable of triggering a luminescent response from the PLC. Thus a simple lock-and-key mechanism provides selectivity within a homologous carboxylate series.

C. Cyclodextrin Supramolecules – Triggered Luminescence by Non-Coordinating, Light-Harvesting Substrates

The close distances needed for efficient AETE, and correspondingly efficient detection of S_{LHC}, in the previous section are ensured by incorporating light-harvesting centers in the primary ligating sphere of the lanthanide ion. This approach can place severe restrictions on the design of the assembly inasmuch as only light-harvesting centers that coordinate the lanthanide ion can be considered. For those light-harvesting substrates that are not ligands, the short distances needed for

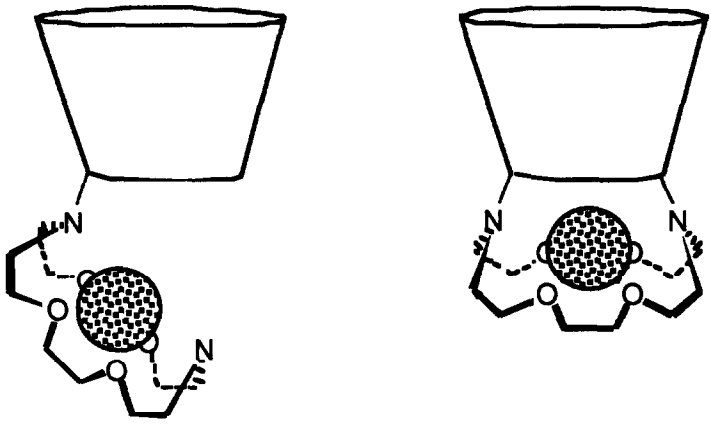


Figure 4. Two supramolecular active sites from which luminescence is triggered by non-coordinating, light-harvesting substrates. The appended aza ligand assumes a swing conformation when tethered to the CD at one nitrogen (β-CDU[1]aza-⊃Eu^{3+}), but is cradled underneath the CD cup when tethered at both nitrogens (β-CDU[2]aza⊃ Eu^{3+}).

efficient AETE must be imposed by the spatial constraints of a supramolecule.

Of the diverse molecular templates available for supramolecule design [1,4,15-18], a properly functionalized cyclodextrin (CD) can ideally play the role of the receptor in such a supramolecular approach. Cyclodextrins are cyclic oligosaccharide molecules consisting of 6, 7 or 8 α(1-4) linked D-glucose units (α-, β-, and γ-CD, respectively) arranged in a torus to give a rigid conical structure with a hydrophobic cavity [19-21]. Modification schemes of the CD [22-26] primarily rely on the differences in chemical reactivity between the primary and secondary hydroxyl groups on the glucose subunits, with the former exhibiting greater reactivity than the latter. This feature provides the foundation on which to build cyclodextrins functionalized with a juxtaposed recognition site external to the CD cup.

Figure 4 shows two supramolecular assemblies that we have constructed. The monosubstitution of a primary alcohol of β-CD with a tosyl group and its subsequent replacement by the macropolycyclic ligand 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (aza) affords an aza-modified CD [27], which we designate β-CDU[1]aza. Tethered at only one nitrogen, the aza crown can assume a conformation that is swung away from the hydrophobic cup; we call this supramolecule a swing CD [28]. We have also prepared, by employing synthetic strategies elaborated for carbohydrates [29-31], a double-strapped or cradle CD (designated β-CDU[2]aza) [32] where the aza crown ether is tethered to the primary side of

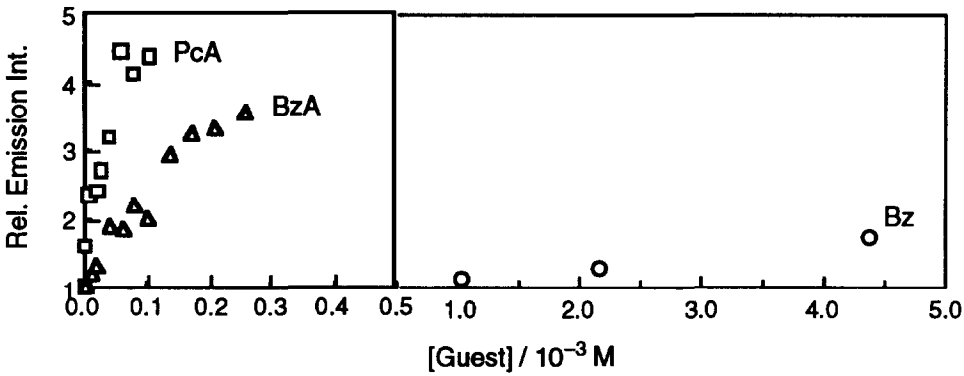


Figure 5. Relative emission intensity from aqueous solutions of β-CD∪^{1}aza⊃Eu^{3+} upon addition of light harvesting guests (PcA, picolinic acid; BzA, benzoic acid; Bz, benzene). Please note discontinuity in the abscissa.

the CD cup via its two nitrogens. In both of these structures there are two binding sites. One is for the Ln^{3+} ion, which resides in an aza ligand attached to carbon of the primary alcohol functionality of the β-CD (i.e. attachment at the bottom of the CD cup). The other is the conical and hydrophobic cavity of the β-CD, which is capable of including a variety of substrates.

We have triggered luminescence from these supramolecules with a variety of aromatic hydrocarbons [32,33]. Figure 5 displays the dependence of the integrated emission intensity from water solutions of the β-CD∪^{1}aza⊃Eu^{3+} supramolecule on the concentration of the aromatic substrate. Significant enhancement of Eu^{3+} luminescence is observed when benzene is added to solution. Even greater enhancements are observed for benzoic and picolinic acids. The bright emission from the Eu^{3+} center is triggered by the molecular recognition of the aromatic substrate in the CD cup. In this AETE process, the electronic energy from irradiated substrate residing in the cup of the CD is transferred to the aza-encapsulated Eu^{3+} PLC. The acids show increased enhancements relative to benzene for two reasons. (1) The most efficient AETE process results when hydrophobic recognition of the guest by the CD cup is cooperative with metal-guest recognition. This bifunctional recognition of anionic guests by the CD supramolecule serves to increase the association of the guest with the modified CD. (2) In addition, we believe that the unimolecular AETE process occurs from benzene to an aza⊃Eu^{3+} that is swung away from the base of the CD cup [32]. In the case of the acids, the binding of the carboxylate to the Eu^{3+} center pulls the swing under the cup and shortens the donor/acceptor distance for energy transfer. We would not expect a large difference between the AETE processes of these substrates with β-CD∪^{2}aza⊃Eu^{3+} because the ideal conformation of the aza⊃Eu^{3+} site nestled under the CD cup is already achieved by virtue of the cradle

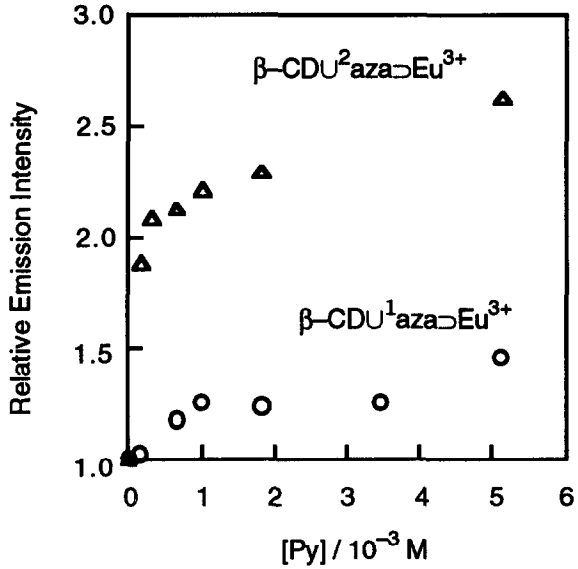


Figure 6. Relative emission intensity from aqueous solutions of β-CD∪^{1}aza⊃Eu^{3+} and β-CD∪^{2}aza⊃Eu^{3+} upon addition of pyridine as the light harvesting guest.

conformation. It was with this motivation that the synthesis of β-CD∪^{2}aza⊃Eu^{3+} in Figure 5 was undertaken.

Addition of benzene to solutions of β-CD∪^{2}aza⊃Eu^{3+} does not show any enhancement in Eu^{3+} luminescence. Binding studies reveal that the association constant of benzene to the cradle CD is $<10\ M^{-1}$. Apparently, the 3+ charge of the appended aza⊃Eu^{3+} cradle at the bottom of the CD cup decreases the hydrophobicity of the aromatic hydrocarbon binding site thereby attenuating the association of benzene. The AETE process with pyridine supports this contention. The polar pyridine is observed to enter the cup of the cradle CD, though at a smaller association constant than observed for swing CD (K_a(swing) = 1047 M^{-1} and K_a(cradle) = 348 M^{-1}). Nevertheless, the enhancement of Eu^{3+} emission is greater for the cradle CD (Figure 6). In view of the relative binding constants, this greater enhancement is attributed to a more efficient AETE process owing to the shorter distance imposed by the cradle geometry for energy transfer between Eu^{3+} and pyridine.

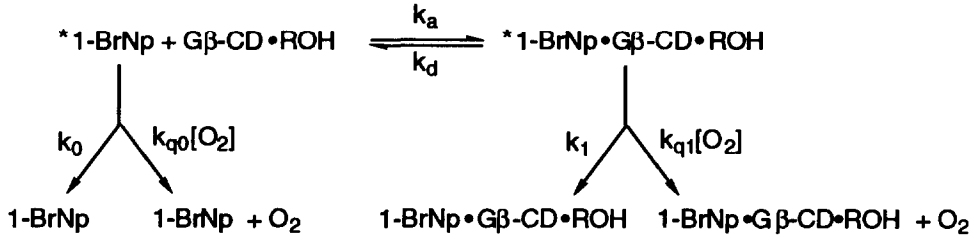
D. Ternary Complexes of Cyclodextrins – Triggered Luminescence by Non-Coordinating, Non-Light Harvesting Substrates

An obvious limitation of AETE schemes is their inability to incorporate substrates that are poor light harvesters. For instance, there is great interest in optically detecting long chain aliphatic hydrocarbons,

chlorocarbons, and alcohols. Yet the inability of these substrates to coordinate metal ions and absorb ultraviolet or visible light obviates an AETE approach. For these reasons the AICE scheme was elaborated, where the fluorescence from a lumophore is replaced by phosphorescence when substrate is present. Initial work has focused on demonstrating an AICE scheme with alcohols as substrates [34].

Our approach has been to integrate the concepts of room temperature phosphorescence of lumophores in CD cups [35-38] with that of ternary complex formation [39-42] to design a scheme in which the luminescence is triggered by alcohols. The long-lived and bright green phosphorescence from 1-bromonaphthalene (1-BrNp) is efficiently quenched by oxygen, as is the case for phosphorescence of all organic compounds. Even in β-CD cups, oxygen quenching of 1-BrNp is efficient. We have found, however, that quenching is perturbed in the presence of alcohols [34]. Enhancement in the intensity and lifetime of the green phosphorescence of 1-BrNp is observed when a variety of alcohols are added to solutions of a glucosyl-modified β-CD (Gβ-CD) and 1-BrNp. As indicated by the quantum yields in Table 1, the intensity of the observed phosphorescence exhibits a marked dependence on the nature and concentration of alcohol. In each case, the emission intensity (and quantum yield) increases monotonically with increasing alcohol concentration to an asymptotic limit, which differs from one alcohol to another. The enhancement in the intensity of phosphorescence may be significant as is the case for *t*-BuOH, which attains a limiting value that is 6,250 greater than that observed in its absence.

The photophysics responsible for alcohols triggering the bright green phosphorescence of CD-included 1-BrNp have been completely described with the following scheme [34],



where k_a and k_d are the second-order association and first-order dissociation rate constants of complex, respectively, k_0 and k_1 are the excited state decay rate constants of the phosphorescence of 1-BrNp in water and within Gβ-CD, and k_{q0} and k_{q1} are the bimolecular oxygen quenching rate constants of 1-BrNp in water and within the Gβ-CD, respectively. Every rate constant and equilibrium constant in the above scheme has been independently measured. From these data, we have shown that a ternary complex is formed among the alcohol, Gβ-CD and 1-BrNp with the equilibrium constants given in Table 1. The alcohol influences the

TABLE 1
Equilibrium Constants, Photophysical Data, and Oxygen Quenching Rates of 1-Bromonaphthalene/β-Cyclodextrin/Alcohol Complexes

1-BrNp•Gβ-CD•ROH	K/M^{-1} [a]	$\phi_e/10^{-4}$ [b]	τ/ms [c]	$k_q^{obs}(O_2)/10^5$ $M^{-1}s^{-1}$ [c]
1-BuOH	3205	1.9	0.14	231
1-PrOH	1950	4.1	0.17	228
2-PrOH	3370	80	0.59	45.9
2-BuOH	2320	47	0.67	39.2
t-BuOH	2990	340	4.6	8.87
CycOH	760	350	3.9	1.17

[a] Equilibrium constant $K = k_a/k_d$ in above Scheme. [b] Quantum yields for phosphorescence of 1-BrNp in the concentration independent range of alcohol for the ternary complex. [c] Phosphorescence lifetimes of 1-BrNp in the concentration independent range of alcohol for the ternary complex.

binding of 1-BrNp to the CD cup, but it is the affect of the alcohol on the bimolecular reactivity of 1-BrNp included in the CD cup that leads to the appearance of the bright green luminescence.

The phosphorescence intensity correlates closely with the bulkiness of the alcohol. With the exception of CycOH, the quantum yields of the different ternary complexes increase with the branching at the α-carbon (i.e. $1° < 2° < 3°$). The role of alcohol branching in determining the photophysical properties of the ternary complex becomes apparent when the oxygen quenching rate constants are considered. To a first approximation, the highest quantum yields for phosphorescence (Table 1) are observed for those ternary complexes with the smallest oxygen quenching rate constants. For equivalent branching, the quantum yield of phosphorescence simply reflects the formation constant of the ternary complex for a given alcohol. The only anomaly to the above analysis is CycOH, whose oxygen quenching rate constant is commensurate with that of *t*-BuOH. But similar behavior of these alcohols in CD ternary complexes has been observed for numerous other ternary complexes [39-41] where steric factors are dominating.

A schematic of the proposed mechanism for the triggered phosphorescence response by alcohols is shown in Figure 7. We propose the alcohols to hydrogen bond to the rim of the CD cup, and the aliphatic ends of the alcohol flip into or over the hydrophobic interior of the CD cup. To this end the alcohol acts as a lid of the CD cup thereby preventing the approach of oxygen to 1-BrNp. Thus *1-BrNp is shielded from oxygen, and its intense green phosphorescence is preserved.

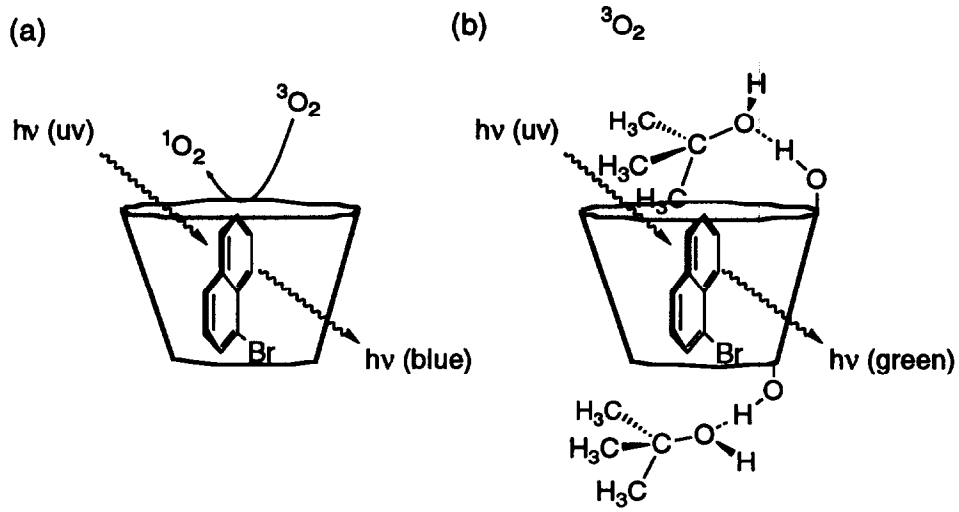


Figure 7. Proposed mechanism for triggered phosphorescence response from 1-BrNp included in a glucosyl-modified β-CD cup by alcohols. (a) In the absence of alcohols, the bright green phosphorescence of 1-BrNp is quenched by oxygen and blue fluorescence is only observed. (b) A ternary complex is formed upon alcohol addition; 1-BrNp is shielded from oxygen and hence bright green phosphorescence becomes apparent.

The approach described here complements the recent work of Ueno [43] et al., who has prepared CDs appended with molecules that fluoresce from a normal planar (NP) excited state within the CD cup. Upon molecular recognition of exogenous substrates, the fluorophore is displaced from the cup and the red-shifted emission from the twisted intramolecular charge transfer (TICT) excited state is observed.

E. Concluding Remarks

Photophysical schemes whose function is derived from a triggered optical response are not only fundamentally important but are practically interesting as well. The processes described herein may be exploited as active sites for the design of optical sensors. To date, most optical detection schemes are based on a quenching approach where luminescence is attenuated in the presence of a substrate. A luminescence response triggered by substrate has the obvious benefit that detection occurs relative to a dark background, and therefore is intrinsically more sensitive. Moreover from a supramolecular context, the approach is powerful because high selectivities can be achieved by manipulating both the excited state properties of the PLC and the molecular recognition properties of the remote site by controlling steric constraints of substrates within the recognition site, the number of sites to which substrate can bind, the chemical nature of the binding pocket (*e.g.* acidity, hydrophilicity), and electronic coupling

from the active site to the PLC (i.e. communication channels). All of these factors provide general guidelines for new detection schemes for a wide variety of substrates.

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