Mechanism for the Sensitized Luminescence of a Lanthanide Ion Macrocycle Appended to a Cyclodextrin†

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Received: January 12, 1998; In Final Form: July 6, 1998

Aromatic hydrocarbons trigger a green luminescence on their association to a β-cyclodextrin (CD) modified with a Tb^{3+} diethylenetriaminepentaacetic acid (DTPA) macrocycle strapped across the bottom of the CD cup, [β-CD$\cup^2$(Tb$\subset$DTPA)]. The mechanism of this enhanced luminescence response is investigated with biphenyl as the aromatic hydrocarbon. Time-resolved emission spectroscopy reveals that excitation energy at the Tb^{3+} ion appears 12 μs after light is absorbed by biphenyl included within the CD cup. Excitation spectra are consistent with a photophysical mechanism comprising absorption-energy transfer-emission (AETE) from the aromatic hydrocarbon bound to the cavity of CD to the DTPA-encapsulated Tb^{3+} ion. A comparison of the luminescence decay kinetics for biphenyl associated to [β-CD$\cup^2$(Tb$\subset$DTPA)] and [β-CD$\cup^2$(Gd$\subset$DTPA)] complexes indicates that the pathway for the AETE process is absorption to the singlet excited state followed by intersystem crossing to the triplet, from which energy is transferred to the lanthanide ion.

Introduction

Supramolecules provide frameworks in which to organize subunits of complementary function. When the subunits are light-absorbing and light-emitting centers, the fundamental photophysical processes governing a variety of energy transduction mechanisms may be revealed.[1−13] We have been interested in designing supramolecules featuring a photoactive center, capable of emitting visible light, juxtaposed to a docking site for a target analyte. By manipulating the fundamental parameters governing energy flow within the supramolecule (i.e., the radiative, nonradiative, and quenching rate constants), bright luminescence may be triggered from the photoactive center upon the molecular recognition of the target analyte.[14] This approach to optical sensing is superior to those predicated on luminescence quenching because signal is measured against a dark background.

Of the diverse supramolecule archetypes considered in our chemosensor design strategy,[15] cyclodextrins (CD) provide an ideal architecture for the detection of many hydrocarbon analytes. The CD comprises D-glucose subunits catentated in a head-to-tail arrangement to form a miniature, water-soluble bucket with a hydrophobic interior that serves as the docking site for analytes.[16−18] The hydroxyl groups at the rim of the CD provide points of attachment for a photoluminescent center such as a lanthanide ion (Ln^{3+}) macrocycle,[14f] the electronic properties of which conform well to a triggered luminescent signal transduction scheme. Direct irradiation of the Ln^{3+} ion gives rise to little or no luminescence owing to the low absorbance (<1 M^{-1} cm^{-1}) of the ^5D_J emitting state manifold.[19] Yet, the emitting state can be indirectly excited with energy from a sensitizer by an absorption-energy transfer-emission (AETE) process.[20] Luminescence may be intense as long as energy transfer from sensitizer to the Ln^{3+} ion is efficient. We realized that this AETE process could be useful for sensing analytes such as aromatic hydrocarbons[21] because they possess large absorption cross sections with respect to Ln^{3+}. We suspected that, under the proper conditions, the aromatic hydrocarbon could absorb the incident light and pass it on to the Ln^{3+} ion to indirectly excite the latent emitting center. Hence, docking of analyte in the CD cup would effectively cause a dramatic increase in the population of the Ln^{3+} ion ^5D_J emitting state thus leading to a bright luminescence.

To this end, we appended the primary hydroxyl rim of the CD cup with a europium aza crown (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane) macrocycle. Tethered at only one nitrogen, the aza crown assumes a conformation that is swung away from the hydrophobic cup.[22] In this case, the red luminescence triggered from an Eu^{3+} ion by binding of the aromatic hydrocarbon to the interior of the CD cup may be weak owing to a long energy-transfer distance. Accordingly, an aza macrocycle was strapped across the bottom of the CD (primary hydroxyl side) via both of its nitrogens with the anticipation that the shorter distance imposed by the cradle geometry would result in a more efficient AETE process.[23] Surprisingly, the triggered luminescence response from this supramolecule is actually very weak as compared to the swing CD. Although the intrinsic AETE process is indeed efficient, the association of the aromatic hydrocarbon to the CD cup limits the overall optical response. The 3+ charge of the appended Eu^{3+} cradle makes the bottom of the cup less hydrophobic and hence decreases the association of the aromatic to the cup. Synthesizing a CD supramolecule strapped with the trianionic-binding site derived from diethylenetriaminepentaacetic acid (DTPA) (shown in Chart 1) solves this association problem.[24] We chose the nonreducible, green-emitting, Tb^{3+} as the lanthanide ion for this supramolecule in order to avoid interference from low-lying carboxylate ligand-to-metal charge-transfer excited states, which are prevalent for the reducible Eu^{3+} ion.[25] In aqueous solutions, the molecular recognition of the aromatic hydrocarbon in the CD cup is heralded by the appearance of a green luminescence.

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† In celebration of the 60th birthday year for R. S. H. Liu, D. C. Neckers, J. Saltiel, N. J. Turro, D. G. Whitten, and my colleague for 14 years, P. J. Wagner.

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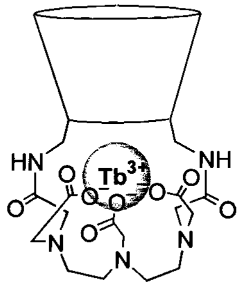
S1089-5639(98)00756-7 CCC: $15.00

CHART 1



The mechanism of the triggered luminescence response from [β-CD$\cup^2$(Tb$\subset$DTPA)] is reported herein, and the model for energy transfer that is at the underpinning of the signal response is derived from kinetics measurements.

Experimental Section

The DTPA cradle CD system was synthesized by functionalization of the primary hydroxyl rim of β-CD by using methods of Tabushi[26] to direct the A,D regiochemistry. The synthesis follows cleanly from A,D-diamino-β-CD and DTPA dianhydride as previously described.[24] Tb^{3+} or Gd^{3+} ion was introduced into the DTPA binding site from the corresponding chloride salt to yield the supramolecule complex [β-CD$\cup^2$(Ln$\subset$DTPA)] ($Ln^{3+} = Tb^{3+}$ or Gd^{3+}). Doubly deionized water was used for syntheses and all spectroscopic experiments.

The association of biphenyl to [β-CD$\cup^2$(Tb$\subset$DTPA)] was determined on a Cary 17 spectrometer retrofitted by On-Line Instruments Systems. The absorbance of biphenyl at 246 nm was monitored as 30-μL aliquots of a 0.01 M solution of [β-CD$\cup^2$(Tb$\subset$DTPA)] were added to an aqueous solution saturated in biphenyl (5×10^{-5} M). The [β-CD$\cup^2$(Tb$\subset$DTPA)] titration concentration was varied over a range of $3-18 \times 10^{-4}$ M. The reference cell contained saturated biphenyl solution; therefore the increase in absorbance was a direct measure of the association of biphenyl to [β-CD$\cup^2$(Tb$\subset$DTPA)], which was calculated by the solubility method.[27] The change in absorbance was plotted versus the concentration of [β-CD$\cup^2$(Tb$\subset$DTPA)] to give a straight line with slope equal to K_a (M^{-1}). To authenticate the appropriateness of our experimental method, the association of naphthalene to β-CD in aqueous solution was measured by our technique; the measured value of 770(50) M^{-1} compared well with the previously reported value[28] of 850(80) M^{-1}.

Emission spectra were recorded on a high-resolution instrument.[29] The luminescence produced upon excitation with the 266-nm wavelength light from a Hg−Xe lamp was captured with a R943-02 Hamamatsu photomultiplier tube as the detector. All measurements were performed at room temperature, and solutions comprising 3×10^{-5} M biphenyl and 2×10^{-3} M [β-CD$\cup^2$(Tb$\subset$DTPA)] were freeze/pump/thawed three times to remove oxygen.

The Tb^{3+} luminescence rise time and decay kinetics were determined with a previously described nanosecond time-resolved laser instrument and associated electronics.[30] Sample was excited with the 266-nm harmonic of a Quanta Ray DCR2 Nd:YAG pulsed laser, and emission was monitored at 546 nm. The faster time decays of biphenyl fluorescence were captured by time-correlated single-photon counting methods on a recently modified picosecond laser system.[31] The 285-nm excitation frequency was achieved by doubling the Rhodamine 6G dye laser output of a Coherent model 702 dye laser pumped by a mode-locked Nd:YAG (Coherent model 76S) laser.

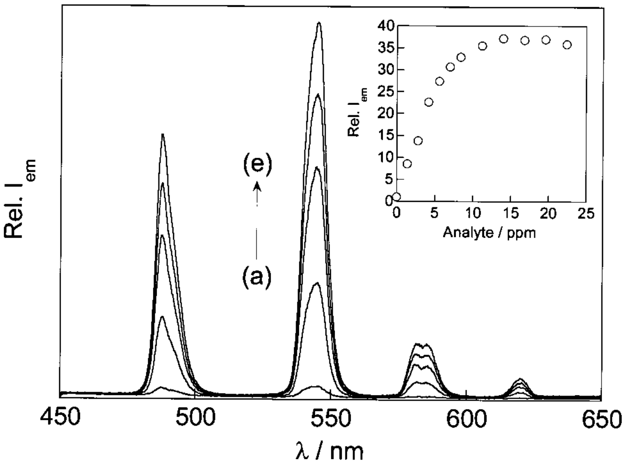


Figure 1. Growth of the luminescence intensity upon the addition of (a) 0, (b) 1, (c) 2, (d) 3, and (e) 4 μM biphenyl to aqueous solutions of [β-CD$\cup^2$(Tb$\subset$DTPA)] (2×10^{-3} M). The inset shows the relative Tb^{3+} emission intensity ($\lambda_{det} = 544$ nm) from aqueous solutions of [β-CD$\cup^2$(Tb$\subset$DTPA)] in the presence of biphenyl.

Results and Discussion

When aqueous solutions of [β-CD$\cup^2$(Tb$\subset$DTPA)] are directly excited, the weak Tb^{3+} luminescence originating from the $^5D_4 \rightarrow {}^7F_j$ state manifold is observed. The intensity of these transitions increases monotonically with the concentration of mono- and bicyclic aromatic hydrocarbons, reaching an asymptotic limit that is specific to the hydrocarbon. In the studies reported here, biphenyl was employed as the analyte. Binding studies show that biphenyl associates to [β-CD$\cup^2$(Tb$\subset$DTPA)] with an affinity similar to that observed for unsubstituted β-CD ($K_a = 428(14)$ and 654(46) M^{-1}, respectively). The similarity of these values demonstrates that the appended cyclodextrin does not largely affect the binding of biphenyl, which is most likely due to the neutralization of the lanthanide 3+ charge by the trianionic-binding site. Because this aromatic hydrocarbon engenders a bright luminescence response from the DTPA cradle complex, the overall luminescence process may be conveniently monitored. As shown in Figure 1, a factor of 40 increase in intensity of the $^5D_4 \rightarrow {}^7F_j$ luminescence bands, which are energetically invariant to the concentration of analyte, is observed for biphenyl present in 10 ppm. The titration profile of the luminescence intensity of the $^5D_4 \rightarrow {}^7F_5$ transition at 544 nm is shown in the inset.

The increase in emission intensity with added substrate is accompanied by the appearance of new bands in the excitation spectra. Figure 2 plots this result for the change in the intensity of the $^5D_4 \rightarrow {}^7F_5$ transition as the excitation wavelength is scanned from 240 to 320 nm. The new bands are energetically coincident with the $^1\pi\pi \rightarrow {}^1\pi\pi^*$ absorption profile of biphenyl. This result is a signature of the indirect excitation of the $^5D_4$ excited state via an absorption-energy transfer-emission (AETE) process where the incident light absorbed by the aromatic in turn is transferred to DTPA-encapsulated Tb^{3+} ion at the bottom of the CD cup. The spectroscopy of the native [Tb$\subset$DTPA] complex in the presence of biphenyl is accordant with this contention. In the absence of a CD cup, the luminescence intensity of the native [Tb$\subset$DTPA] complex is weak and insensitive to the concentration of biphenyl, and the $\pi\pi^*$ transitions of the biphenyl do not appear in the excitation spectrum of the [Tb$\subset$DTPA] complex as it is titrated with substrate.

We have studied the mechanism of the AETE process of the [β-CD$\cup^2$(Tb$\subset$DTPA)]·biphenyl complex by time-resolved lu-

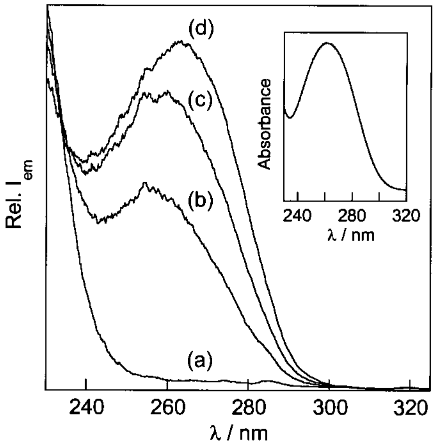


Figure 2. Excitation spectra (λ_{det} = 544 nm) of an aqueous solution of [β-CD$\cup^2$(Tb$\subset$DTPA)], with increasing concentrations of biphenyl (0, 2, 4, and 8 μM). The absorption spectrum of biphenyl, complexed to [β-CD$\cup^2$(Tb$\subset$DTPA)], is depicted in the inset.

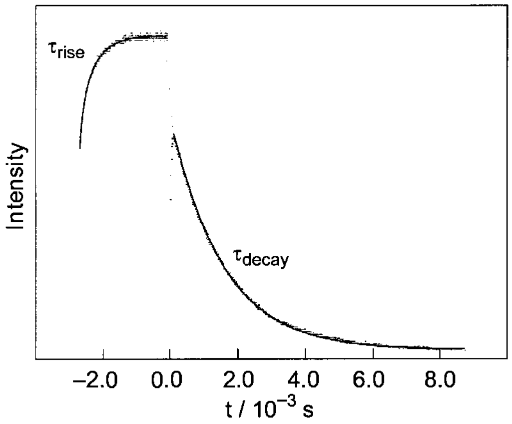


Figure 3. Growth and subsequent decay of Tb^{3+} luminescence (λ_{det} = 544 nm) from [β-CD$\cup^2$(Tb$\subset$DTPA)], upon the excitation of biphenyl with the fourth harmonic of a Nd:YAG nanosecond laser (λ_{exc} = 266 nm). The time axis for the inset is from 0 to 3×10^{-4} s. The exponential fits of the data, from which the rise time and decay rate constants were derived, are displayed by the solid lines.

minescence spectroscopy. Figure 3 shows the rise time for the appearance and subsequent decay of the Tb^{3+} luminescence after laser irradiation of an aqueous solution of [β-CD$\cup^2$(Tb$\subset$DTPA)] and biphenyl. Both components of the trace are described by monoexponential kinetics. The green luminescence from the ^{5}D$_4$ state of Tb^{3+} appears 12 μs after excitation of biphenyl, and it subsequently decays with its natural lifetime of 1.6 ms. The lifetime of the $^1\pi\pi^*$ excited state of biphenyl (τ = 16 ns[32]) is too short-lived to directly participate in energy transfer to the ^{5}D$_4$ emitting state. However, energy may flow from analyte to the emitting excited state via two indirect pathways. One pathway involves prompt energy transfer from the $^1\pi\pi^*$ excited state of the biphenyl into a high-energy state of the ^{5}D$_J$ manifold of the Tb^{3+} ion, followed by a rate-limiting internal conversion to the emitting ^{5}D$_4$ state. Here, the 12-μs rise time reflects the internal conversion process. Alternatively, energy transfer could be staged from the long-lived $^3\pi\pi^*$ excited state of biphenyl, populated by intersystem crossing from the $^1\pi\pi^*$ excited state.

In an effort to more clearly define the precise route of energy flow in the supramolecule, the time-resolved luminescence of biphenyl was measured in the presence of the [β-CD$\cup^2$(Ln$\subset$DTPA)] (Ln = Tb^{3+} or Gd^{3+}). As depicted in Figure 4 for the Tb^{3+} compound, luminescence decay curves are biexponential; the lifetimes are insensitive as to whether Tb^{3+} or Gd^{3+} resides in the DTPA binding site. Specifically, the respective short and long components of the lifetime decays are 1.64 and 11.3 ns for biphenyl in the presence of [β-CD$\cup^2$(Gd$\subset$DTPA)] and 1.63 and 10.6 ns in the presence of [β-CD$\cup^2$(Tb$\subset$DTPA)]. The decay rate constants of the long component are similar to those of biphenyl in water (τ = 9 ns) and thus attributed to biphenyl external to the CD cup. We attribute the shorter lifetime component to biphenyl residing in the CD cup proximate to the Ln^{3+} metal ion. In the case of [β-CD$\cup^2$(Gd$\subset$DTPA)]•biphenyl, the "quenched" lifetime is unlikely to arise from an AETE process because no emission is observed from the Gd^{3+} excited state ($E(^6\text{P}_{7/2}) = 32\,000$ cm^{-1}); energy transfer from the singlet is therefore negligible. However, the proximate Gd^{3+} can affect biphenyl decay in a [β-CD$\cup^2$(Gd$\subset$DTPA)]•biphenyl complex by enhancing intersystem crossing to the $^3\pi\pi^*$ excited state via an external heavy atom effect. We calculate an intersystem crossing rate of $k_{isc} = 5.7 \times 10^8$ s^{-1} for [β-CD$\cup^2$(Gd$\subset$DTPA)].[33] The observation of a similar rate constant for the decay process of electronically excited biphenyl included within [β-CD$\cup^2$(Tb$\subset$DTPA)] ($k = 5.8 \times 10^8$ s^{-1}) suggests that the primary decay of the $^1\pi\pi^*$ excited state is not AETE but rather intersystem crossing to the $^3\pi\pi^*$ excited state.

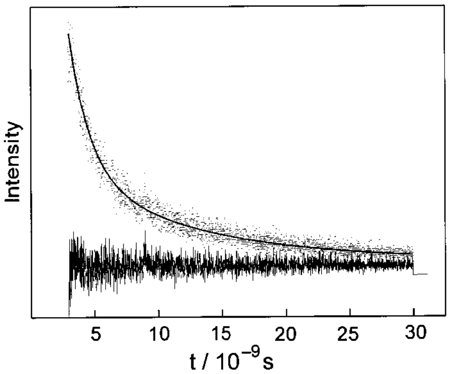
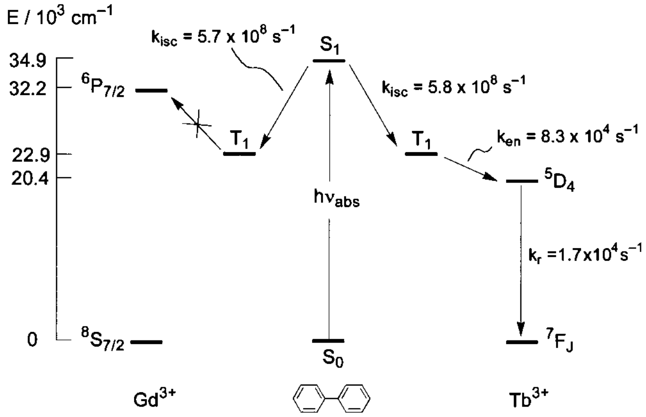


Figure 4. Time-resolved luminescence of biphenyl (5×10^{-5} M) dissolved in an aqueous solution of [β-CD$\cup^2$(Tb$\subset$DTPA)] (2×10^{-3} M). The solid line is a biexponential fit to the data. The lifetimes from this fit correspond to biphenyl included in the cup and free in solution. The residuals are shown by the lower trace.

SCHEME 1: Measured Rate Constants for AETE Process of the Binary Complex Formed between [β-CD$\cup^2$(Tb$\subset$DTPA)] and Biphenyl



The steady-state and time-resolved spectroscopic results for the [β-CD$\cup^2$(Ln$\subset$DTPA)]•biphenyl (Ln = Tb^{3+} or Gd^{3+}) complexes lead to the model shown in Scheme 1. The AETE process is initiated upon absorption of an incident photon to produce the $^1\pi\pi^*$ excited state of biphenyl. The lanthanide ion facilitates intersystem crossing to the triplet whereupon energy transfer occurs to produce the $^5D_4$ state of the Tb^{3+} ion. Consistent with this model, simple energy-transfer treatments appear to exclude participation of the singlet. The rate constant for a Coulombic energy transfer is given by[34]

$$k_{en} = 1/\tau_D(R_o/R) \qquad (1)$$

where τ_D is the natural lifetime of the donor (in the absence of the energy transfer), R is the energy-transfer distance, and R_o is the critical Förster radii (where the energy-transfer efficiency is 50%, i.e., $\Phi_{en} = 1/1 + (R_o/R)^6$). The spectral overlap of the biphenyl singlet emission spectrum with the absorption spectrum of Tb^{3+} yields a critical Förster radius of 4.3 Å (for a rigid donor−acceptor orientation). For the experimentally measured energy-transfer rate of 8.3×10^4 s^{-1} and fluorescence lifetime of 16 ns, an energy-transfer distance of 13.0 Å is calculated for energy transfer from the singlet. This distance is well beyond the calculated critical Förster radius, and consequently energy transfer from the biphenyl singlet should be inefficient by this mechanism. Owing to the Laporte and spin forbiddance of the lanthanide ion electronic transitions, coupling via an exchange mechanism should also be operative. But even here, the singlet should not have a predominant role in energy transfer. It has long been established[35] that the radially contracted f orbitals lead to a small electronic matrix element for electronic exchange, engendering slow energy-transfer rates with regard to the lifetime of the singlet excited state. Finally, it should be noted that the energy-transfer properties of $[\beta\text{-CD}\cup^2(\text{Tb}\subset\text{DTPA})]$ closely parallel a previous study of energy transfer from biphenyl to Tb^{3+} in a micellar microenvironment.[36] Molecular modeling calculations of an energy-minimized $[\beta\text{-CD}\cup^2(\text{Tb}\subset\text{DTPA})]$ places the biphenyl ~5 Å from the Tb^{3+} ion, similar to the 4-Å distance between micelle-occluded biphenyl and surface-bound Tb^{3+} ion. The energy-transfer rate of 5×10^4 s^{-1} for this system is concordant with the results of Figure 3.

The process depicted in Scheme 1 is not unique to $[\beta\text{-CD}\cup^2(\text{Tb}\subset\text{DTPA})]$. That the triplet excited state represents a staging area for energy transfer is an emerging trend in the photophysics of many other lanthanide ion supramolecules. For instance, the Tb^{3+} and Eu^{3+} complexes of modified calix[4]arenes also undergo AETE via the triplet excited state of donors.[37] These results, taken together with the systems described here, serve to emphasize the role of the Ln^{3+} ion to not only function as the emitting center in the AETE process but to also give rise to a long-lived donor excited state from which energy transfer may occur. In the absence of the heavy atom, the singlet excited state of the aromatic would return to its ground state before energy transfer could be enacted. By channeling the singlet to a long-lived triplet, ample time is provided for the slower energy-transfer process to effectively compete with the fast natural radiative and nonradiative processes of the analyte. Thus, the lanthanide ion plays a critical role of opening a conduit for energy flow in the supramolecule.

Acknowledgment. Effort was sponsored by the Air Force of Scientific Research, Air Force Material Command, USAF, under Grant No. F49620-98-1-0203. Partial financial support for this work was also provided by a Materials Research Science and Engineering Center sponsored by the National Science Foundation (DMR-9400417). The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the Air Force Office of Scientific Research or the U.S. Government.

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