

A Fluorescent 18-Crown-6 Based Luminescence Sensor for Lanthanide Ions

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Abstract—The synthesis and photophysical behavior of a luminescent chemosensor for the early lanthanide elements is described. The sensor is a 1,4-diphenylethynyl-benzene chromophore having 18-crown-6 moieties bound to the outer phenyl rings. The chromophore is luminescent and the emission is quenched by lanthanide (Ln^{3+}) ions with larger ionic radii and existing f–f transitions (Ce^{3+} , Pr^{3+} and Nd^{3+}). Alkali, alkaline earth ions and lanthanides with smaller radii (Ge^{3+} , Tb^{3+} , Dy^{3+} , and Yb^{3+}) do not affect the emission. © 2000 Elsevier Science Ltd. All rights reserved.

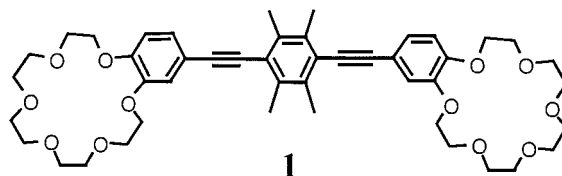
Introduction

The use of organic chromophores to sensitize the luminescence of particular lanthanides (Ln^{3+} ions) has drawn considerable attention in recent years.¹ This is in part due to the potential for generating systems that exhibit narrow band, lanthanide localized, luminescence from organic electroluminescent polymers. Sensitization of lanthanide excited states is known to occur via the triplet state of the organic chromophore.² In addition, the fluorescence yield of the sensitizer is also diminished in some systems because of either direct energy transfer to the lanthanide or, in covalently linked sensitizer/lanthanide systems, enhanced intersystem crossing in the sensitizer induced by a heavy atom effect of the bound lanthanide. Intramolecular fluorescence quenching has been shown to occur in supramolecular sensitizer/chelate systems capable of coordinating lanthanides.^{1,3,4} Among the systems investigated are various benzo-crown ether derivatives. Costa and coworkers found that, for benzo-15-crown-5 in alcohol solvents, Tb^{3+} effectively quenched the benzene fluorescence while only a small amount of quenching was observed with Eu^{3+} .³ Others have found that 15-crown-5 lanthanide complexes of Tb^{3+} , Eu^{3+} and Dy^{3+} all exhibit luminescence enhancement when an organic sensitizer is used as a counterion for the crown/lanthanide complex in nonaqueous solvents.⁴

Supramolecular chromophore/receptor systems can potentially be used for the selective detection of particular lanthanides. Selectivity can be achieved via: (a) control of the

particular receptor; (b) tuning the excited state characteristics of the chromophore; and (c) exploiting adventitious differences in quenching rate constants for different lanthanides. While the ionic radii of the lanthanide ions systematically decrease across the lanthanide series, the difference is relatively small (18 pm) as compared to, for instance, the alkali ions (>70 pm). However, Umetani and coworkers found that binding constants of different benzo-crown ethers with lanthanides vary by a factor of 10 or more across the series.⁵ For instance, a sulfonated benzo-18-crown-6 derivative studied by the group has a binding constant of 75 M^{-1} for coordination of La^{3+} and only 2 M^{-1} for Yb^{3+} . Some degree of selectivity can also be achieved by tuning the energetics of the organic sensitizer used. Nocera and coworkers showed that Gd^{3+} and Tb^{3+} , ions of nearly identical radius, can be distinguished by a system having biphenyl bound in the cavity of a cyclodextrin with the lanthanide coordinated on the periphery of the cyclodextrin.⁶ In this case the emitting excited state of Gd^{3+} is higher in energy than the biphenyl triplet excited state and is not sensitized while Tb^{3+} sensitization is energetically favorable.

In this paper we show that complex **1**, below, having a benzo-18-crown-6 receptor and a di(phenylethynyl)benzene chromophore discriminates between the early and late lanthanides through quenching of the chromophore fluorescence.



Keywords: chemosensor; lanthanide; luminescence; sensitization; crown ether.

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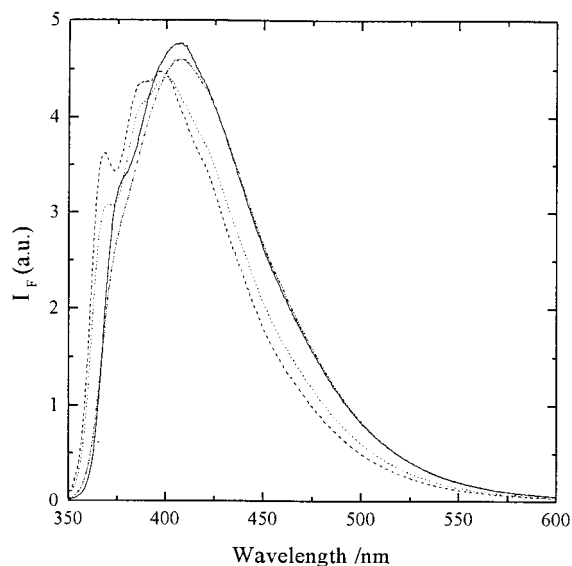


Figure 1. Emission spectra of compound **1** in acetonitrile following addition of different quantities of La^{3+} . $[\mathbf{1}]/[\text{La}^{3+}]$ ratio 1:0 (solid line), 1:1 (---), 1:2 (···), 1:3 (— · —). $[\mathbf{1}] = 2 \times 10^{-5}$ M.

The synthesis, spectroscopic properties and luminescence behavior of acetonitrile solutions of compound **1** in the absence and presence of various lanthanides is presented.

Results and Discussion

Ligand **1** was prepared by palladium catalyzed cross coupling methods similar to those used by others in making unsymmetric diaryl acetylene derivatives.^{7,8} Characterization by ^1H and ^{13}C NMR confirmed the structure of the bis-crown ligand. The absorption maximum for the ligand $\pi-\pi^*$ transition is at 340 nm ($\log \epsilon = 4.8$) with two shoulders, one at 370 nm and the other at approximately

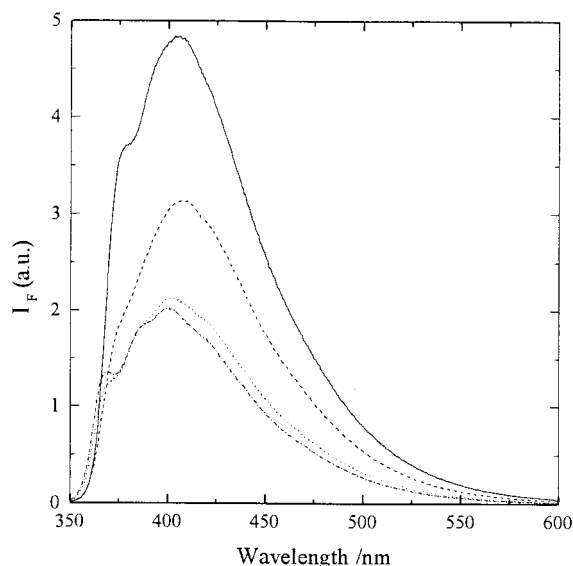


Figure 2. Emission spectra of **1** in acetonitrile following the addition of different amounts of Nd^{3+} . $[\mathbf{1}]/[\text{Nd}^{3+}]$ ratio 1:0 (solid line), 1:1 (---), 1:2 (···), 1:3 (— · —). $[\mathbf{1}] = 2 \times 10^{-5}$ M.

Table 1. Ionic radii of lanthanide ions and relative efficiencies for quenching **1** luminescence in CH_3CN

Lanthanide	Ionic radius, pm ^a	Quenched (%) ^b
La^{3+}	118	<10
Ce^{3+}	114	70
Pr^{3+}	114	65
Nd^{3+}	112	61
Tb^{3+}	104	<5
Dy^{3+}	103	15
Yb^{3+}	98	10

^a Radii for 8 coordinate Ln^{3+} ions from Handbook of Chemistry and Physics, 71st ed., Lide D. R., Ed.; CRC: Boca Raton, 1991; pp 4–126.

^b Percent quenched based upon decrease in luminescence intensity in solutions containing a large excess of the lanthanide ion.

390 nm. The absorption is similar to that of a related alkoxy 1,4-di(phenylethynyl)benzene derivative.⁹

Luminescence from **1** appears as the mirror image of the absorption with a maximum of 406 nm in CH_3CN . The quantum yield for emission in acetonitrile is high, 0.67 (relative to carbazole reference) and is more like the emission yield of poly(phenylene ethynylene) than that of the weakly emitting diphenylacetylene.¹⁰

The luminescence of **1** in the presence of increasing amounts of La^{3+} is shown in Fig. 1. The integrated luminescence intensity decreases slightly, the emission maximum shifts to the blue (395 nm) and the spectrum becomes more structured with a new band appearing at 368 nm. The luminescence is not significantly quenched, in part because La^{3+} has no f–f transitions and may also lack a ligand (phenoxy)-to-metal charge transfer transition at energies lower than the ligand localized $\pi-\pi^*$ state. The distinct emission spectral change without appreciable quenching of the luminescence intensity is unique to La^{3+} .

Addition of Ce^{3+} , Nd^{3+} and Pr^{3+} all induce similar emission spectral changes and, in addition, the luminescence is significantly quenched. Fig. 2 shows changes in the emission spectrum that occur upon addition of near stoichiometric quantities of Nd^{3+} to an acetonitrile solution of **1**. As with the La^{3+} complex, a new emission band is observed at 368 nm, but the emission intensity drops to approximately 40% that of the unquenched ligand. Very similar results are observed following addition of Ce^{3+} and Pr^{3+} to **1** in acetonitrile. The limiting degree of quenching is given in Table 1 and the fraction of **1** luminescence quenched as a function of the lanthanide concentration is shown in Fig. 3. Given the fact that the luminescence lifetime of the sensitizer **1** is <10 ns¹¹ and the concentration of the lanthanide is less than 10^{-4} M in these experiments, the emission spectral changes cannot be due to diffusional bimolecular reactions of excited **1** and the lanthanide and must be the result of formation of some sort of complex between the lanthanide and **1**.

Complexation of the lanthanide ions to **1** is further indicated by changes in the absorption spectra, shown in Fig. 4 for Nd^{3+} . While the observed spectral perturbation is much smaller than that observed in the emission spectra, a small blue shift in the absorption maximum is observed. It is clear

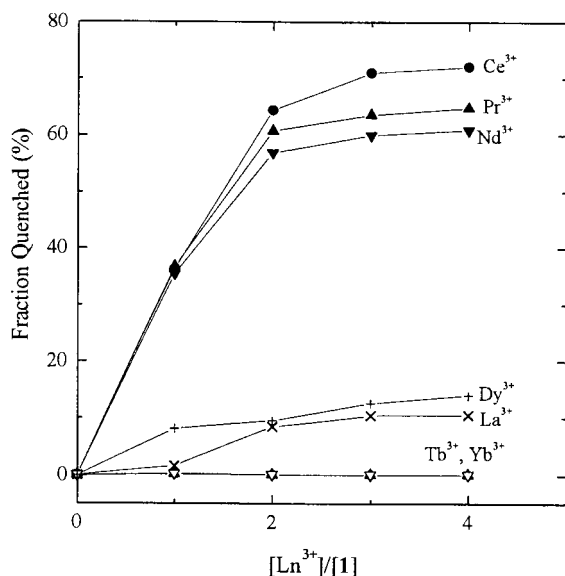


Figure 3. The percentage of **1** emission quenched as a function of the ratio of added lanthanide ions to compound **1** in acetonitrile. La^{3+} (\times), Ce^{3+} (\circ), Pr^{3+} (\blacktriangle), Nd^{3+} (\blacktriangledown), Dy^{3+} ($+$), Tb^{3+} (Δ), Yb^{3+} (∇). $[\mathbf{1}] = 2 \times 10^{-5}$ M.

from Fig. 4 that no isobestic point is observed.¹² This is expected since **1** has two crowns for coordination of the lanthanide and three absorbing species (**1**, $\text{Ln}\mathbf{1}^{3+}$ and $\text{Ln}_2\mathbf{1}^{3+}$) can exist in solution as shown in Eqs. (1a) and (1b) below.



The data indicate that the spectral changes appear complete when the added lanthanide is in approximately four-fold excess over the $20 \mu\text{M}$ **1** in acetonitrile. Fig. 3 also shows that the degree of quenching reaches a plateau and that the fraction of **1** emission quenched is between 60 and 75% for the three lanthanides exhibiting significant quenching. Since

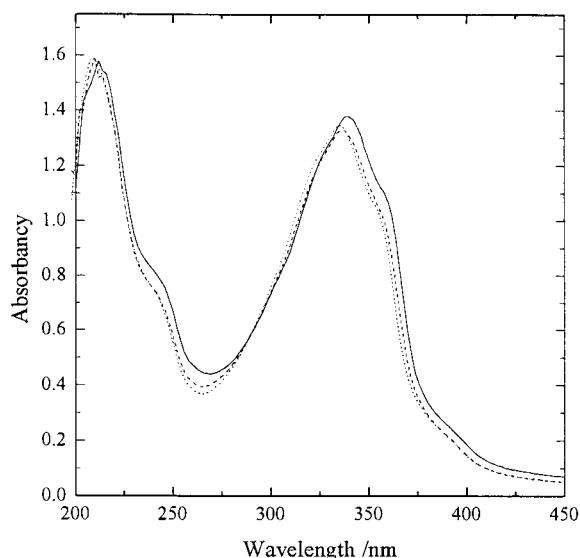


Figure 4. Absorption spectral changes of **1** in acetonitrile with the addition of different amounts of Nd^{3+} . $[\mathbf{1}]/[\text{Nd}^{3+}]$: 1:0 (solid line), 1:1 (—), 1:2 (⋯). $[\mathbf{1}] = 2 \times 10^{-5}$ M.

the luminescence lifetime of **1** is less than 10 ns,¹¹ a lower limit on the luminescence quenching rate constant can be estimated. For Nd^{3+} , the degree of quenching of the fully complexed **1** is approximately 65%; if the lifetime of **1** is assumed to be the upper limit of 10 ns, the quenching rate constant is approximately $3 \times 10^8 \text{ s}^{-1}$. Similar values are obtained for Ce^{3+} and Pr^{3+} . The data of Fig. 3 were fit using only equilibrium **1a**, estimating the plateau fractions quenched to be 80, 70 and 68% for Ce^{3+} , Pr^{3+} and Nd^{3+} , respectively, and using an equilibrium constant for association of $2 \times 10^5 \text{ M}^{-1}$. With an equilibrium constant of this magnitude and concentrations of **1** and lanthanide ion in the $20\text{--}80 \mu\text{M}$ range, approximately 90% of the fluorophore is coordinated to a lanthanide at the highest lanthanide concentrations.

The luminescence spectral bandshape and intensity are not changed significantly upon addition of a ten fold molar excess of lanthanides with smaller ionic radii including Dy^{3+} , Tb^{3+} and Yb^{3+} . For Dy^{3+} , the luminescence of **1** is partially quenched, but the spectral bandshape is unchanged. Neither Tb^{3+} or Yb^{3+} quench the fluorescence of **1** to any significant extent at near stoichiometric concentrations and no absorption spectral changes are observed in solutions containing low concentrations of the ions and **1** (approx. 10^{-5} M). The results suggest the binding constant for association of **1** with Tb^{3+} and Yb^{3+} may be significantly smaller than the binding constants for the other lanthanide ions.

The trend that emerges is illustrated in Table 1. All of the ions with radii greater than 110 pm associate with the 18-crown-6 moieties of **1** with large enough binding constants to leave relatively little uncomplexed **1** in solution even in the $40\text{--}80 \mu\text{M}$ range. The results of Umetani indicate that, for a benzo-18-crown-6, the binding constant difference between the ions with larger radii (La^{3+} , Ce^{3+} , Pr^{3+} and Nd^{3+}) and the ions with smaller radii (Dy^{3+} , Tb^{3+} and Yb^{3+}) is at least a factor of 6.⁴ The values measured by Umetani were obtained in aqueous solution and may not directly relate to acetonitrile solutions where the binding constants are much larger, however, the trend of decreasing binding constant with decreasing lanthanide radius is likely to be observed regardless of solvent. In dilute solutions of **1** and the lanthanide, a factor of 10 difference in binding constant is enough to result in order of magnitude differences in the fraction of free chromophore in solution. Thus for these lanthanides, examined in dilute solutions at near stoichiometric ratios of the lanthanide to sensitizer, relatively small binding constant differences can lead to large differences in the fraction of lanthanide bound to the sensitizer and the degree of quenching observed.

The mechanism of fluorescence quenching is not entirely clear in these systems. One mechanism involves energy transfer to create excited states of the lanthanide by either coulomb or exchange processes. The rate constant for energy transfer by coulombic interactions is determined by the radiative decay rate constant of the energy donor and the magnitude of overlap of the normalized donor emission and the acceptor absorption (weighted by the oscillator strength of the acceptor). Because the molar absorptivities of all the lanthanides are very small ($<10 \text{ M}^{-1}$

cm^{-1}), the overlap integral will be small even if the donor emission and acceptor absorption spectra overlap completely. As a result, calculated rate constants for coulombic energy transfer are several orders of magnitude lower than the radiative decay rate constant of **1**. Energy transfer from the singlet state of **1** to the lanthanides could also occur via an electron exchange process. The crown is covalently attached directly to the chromophore of **1** and, provided electronic coupling between the lanthanide and the chromophore is adequate, the energy transfer could occur by this mechanism. However, it is known that the contraction of the lanthanide *f* orbitals tends to result in very weak electronic coupling in energy transfer reactions.¹³ An alternate mechanism for fluorescence quenching involves increasing the efficiency for intersystem crossing in **1** as a result of spin-orbit coupling interactions of **1** with the lanthanide following complexation. This heavy atom effect depends strongly on the separation of chromophore and the lanthanide. Given the fact that La^{3+} , an ion having no low energy *f*–*f* states available for energy transfer, does not significantly alter the intensity of the luminescence of **1**, quenching by intersystem crossing enhancement seems less likely than quenching by energy transfer. We plan to examine this in greater detail using transient absorption spectroscopy to look at formation and decay of triplet **1** in the presence and absence of various lanthanide ions.

An additional point relating to these systems is that no lanthanide luminescence is observed. In the experiments involving addition of lanthanide ions to acetonitrile solutions of **1**, the lanthanide was dissolved in an aqueous solution and the solutions were aerated. Others have noted that lanthanide ion quenching of aromatic hydrocarbon chromophores yields no lanthanide luminescence and have attributed the observation to the existence of low lying charge transfer states.¹⁴ Given this, the lack of lanthanide luminescence in these systems is not unexpected.

Conclusion

This work illustrates that, through a combination of ion selectivity and differences in energy transfer efficiencies, some degree of selectivity is obtained in discriminating lanthanides in solution. The chromophore **1**, having two 10-crown-6 moieties, coordinates the early lanthanides more effectively than those at the end of the series. The association of the lanthanide can be detected spectrophotometrically, but much larger changes are observed in the chromophore fluorescence upon lanthanide coordination to **1**. The fluorescence of **1** is quenched upon complexation of particular lanthanides and preliminary results suggest quenching is via an intramolecular energy transfer process. The results also suggest that tuning of the crown ring size may allow some degree of selectivity in sensing lanthanides with very similar ionic radii from those with either larger or smaller radii.

Experimental

All solvents used were reagent grade and were used without further purification unless specified otherwise. The lantha-

nide salts were obtained from Fischer Chemical as nitrates and were used without additional purification.

Synthesis of 1,4-bis(3'-ethynylbenzo-18-crown-6)-2,3,5,6-tetramethylbenzene, 1. In a 25 ml rb flask $\text{Pd}(\text{OAc})_2$ (44 mg, 0.05 equiv.), CuI (37 mg, 0.05 equiv.) and triphenylphosphine (102 mg, 0.1 equiv.) were suspended in 6:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (3 ml) solution under an N_2 blanket. The mixture was stirred for 20 min. In a separate 250 ml rb flask 1,4-diiodo-2,3,5,6-tetramethylbenzene (1.5 g, 1 equiv.), trimethylsilylacetylene (1.5 g, 4 equiv.) and triethylamine (2.7 ml) were dissolved in 6:1: THF/ H_2O and purged with N_2 . The Pd containing solution was then transferred to the tetramethylbenzene solution by cannulation and the mixture was stirred under N_2 for 2 h. Following removal of the THF under reduced pressure, methanol (100 ml) was added and a brown precipitate formed. The precipitate was collected by filtration and purified by flash column chromatography on silica using hexane as eluent. The principal chromatographic band was evaporated to a small volume, precipitated by addition of methanol (50 ml) and filtered to yield 1,4-di(trimethylsilylethynyl)-2,3,5,6-tetramethylbenzene (0.5 g, 46%). This was dissolved in THF (50 ml) and tetrabutylammonium fluoride (1.8 ml, 1 M THF solution) was added. The mixture was stirred at room temperature overnight. To this 0.1N HCl (100 ml) was added and the resulting mixture was extracted twice with CH_2Cl_2 (100 ml). The organic layers were mixed, dried with MgSO_4 , purified by flash chromatography on silica using hexane eluent and the second fraction was collected to yield a yellow solid on evaporation. The solid was reprecipitated from CH_2Cl_2 /ethanol to yield 1,4-diethynyl-2,3,5,6-tetramethylbenzene (0.3 g, 92%).

Compound **1** was prepared by mixing the diethynylbenzene derivative (58 mg, 0.32 mmol) and 3'-bromobenzo-18-crown-6 (250 mg, 0.64 mmol) in piperidine (dried by P_2O_5 , 50 ml) and adding a N_2 purged piperidine solution of $\text{Pd}(\text{OAc})_2$ (7 mg), CuI (6 mg) and triphenylphosphine (17 mg). The resulting solution was heated to 80°C under an N_2 blanket for 2 h. The solution was cooled to room temperature and poured into 0.1N HCl (100 ml) and then extracted with CH_2Cl_2 (50 ml) twice. The organic layers were collected, dried with MgSO_4 , concentrated by evaporation and the product was precipitated by addition of methanol. The product was reprecipitated from CH_2Cl_2 /methanol twice and the resulting pale yellow solid of **1** was obtained by filtration. Yield 70 mg (71%). $^1\text{H NMR}$ (CDCl_3 , δ ppm): 7.14 (1H, d, $J=8$ Hz), 7.04 (1H, d, $J=3$ Hz), 6.84 (1H, d, $J=12$ Hz), 4.19 (4H, s), 3.94 (4H, s), 3.73 (12H, m), 2.49 (6H, s). $^{13}\text{C NMR}$ (CDCl_3 , δ ppm) 150, 149, 136, 120.6, 124.3, 117, 114, 98.6, 87.8, 71.3, 71.2 (m), 71.1(m), 69.9 (d), 69.5 and 69.4. IR (KBr, cm^{-1}): 2914, 2858, 1506, 1456, 1400, 1250, 1123, 1056. Elemental analysis for $\text{C}_{46}\text{H}_{58}\text{O}_{12}$ (%), C: 68.83; H: 7.23. Found: C: 69.32; H: 7.28.

Spectral analysis

NMR spectra were obtained on a GE-400 spectrometer (400 MHz). Absorption spectra were obtained on an HP 8452 diode array spectrophotometer. All luminescence measurements were made using a SPEX Fluorolog spectrofluorimeter equipped with a 450 W Xe arc lamp for excitation,

single grating monochromators and both CCD and thermoelectrically cooled PMT detectors. Spectra were not corrected for detector response.

UV–Vis spectra, fluorescence spectra ^1H NMR measurements were obtained by adding the concentrated solution of metal ions to a solution of ligands in a 1 cm path length cuvette by aliquot. No more than 10 μl of metal ion solution was added in 3 ml of the measuring solution for fluorescence and UV–Vis measurements. All absorption and luminescence measurements were made using aerated solutions.

Acknowledgements

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