

Photophysical and Transition-Metal Ion Signaling Behavior of a Three-Component System Comprising a Cryptand Moiety as the Receptor

Sandip Banthia and Anunay Samanta*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

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The synthesis, photophysical behavior, and transition-metal ion signaling ability of a three-component system (**I**) comprising a 4-aminophthalimide moiety as the fluorophore, a cryptand moiety as the metal ion receptor, and a dimethylene group as the spacer have been described. A lower fluorescence efficiency and a shorter fluorescence lifetime of the system compared to the corresponding properties of the bare fluorophore (4-aminophthalimide) are attributed to photoinduced intramolecular electron transfer between the fluorophore and the receptor moiety of the molecule. In the presence of transition-metal ions, **I** exhibits significant changes in its absorption and fluorescence properties, which have been used to estimate the strength of the binding interaction between the system and the metal ions. Even though **I** exhibits fluorescence enhancement in the presence of the transition-metal ions, which are notorious for their fluorescence quenching abilities, the magnitude of the enhancement is found to be significantly lower than that exhibited by a structurally similar system (**II**) containing a much simpler amino group as the metal ion binding site. This observation has been interpreted by taking into consideration the efficiency of the photoinduced intramolecular electron-transfer process in the two systems, and the implication of this result in the design of fluorosensors for transition-metal ions has been highlighted.

1. Introduction

The design and development of molecular systems capable of signaling various guest molecules or ions have been active areas of contemporary research.^{1,2} The keen interest in this field can be rationalized by considering the ever-increasing air and water pollution and the consequential need to monitor polluting species such as Pb^{2+} , As^{3+} , and CO , etc. Even though a wealth of information describing the design strategies for various guests is available in the literature,² appropriate molecular devices for the signaling of several important guests are still elusive. One of the most commonly utilized design strategies for fluorescence signaling systems² is the development of three-component systems with a fluorophore–spacer–receptor architecture containing components that are chosen such that the communication³ between the fluorophore and receptor leads to quenching of the fluorescence of the system. In the presence of a guest, the communication between the terminal moieties, which is responsible for fluorescence quenching, gets cut off, thus leading to the recovery of the fluorescence of the system. This is commonly referred to as “off–on” fluorescence signaling of a guest. Interestingly, the off–on fluorescence signaling systems for the transition-metal ions, which are well-known for their fluorescence quenching abilities,⁴ have been developed only very recently.⁵ Ghosh et al. succeeded in suppressing the quenching influence of the transition-metal ions by using a cryptand moiety as the receptor in their fluorophore–spacer–receptor systems and by demonstrating for the first time that fluorescence enhancement (FE) is indeed possible in the presence of the transition-metal ions.⁵ We, on the other hand, avoided the quenching influence of the transition-metal ions by using an electron-deficient fluorophore component while retaining a

simple amino group as the receptor.⁶ We have shown that when the photoinduced intramolecular electron transfer (PIET) process, the most commonly utilized mechanism for communication between the two terminal moieties, is made highly efficient by employing an electron-deficient fluorophore component in the fluorophore–spacer–receptor system, the quenching influence of the transition-metal ions becomes unimportant, and it is then possible for structurally simpler systems to exhibit fluorescence enhancement in the presence of the quenching transition-metal ions.⁶ This rationale led to the development of simple molecules such as **II** (Chart 1), which display fluorescence enhancement in the presence of quenching metal ions.

In view of the fact that a cryptand-based fluorophore–spacer–receptor system such as **I** is expected to bind the metal ions much more strongly than **II** (a structurally similar system containing a simpler amino moiety as the metal ion binding site (receptor)) does, the signaling efficiency of the former system is expected to be superior to that of the latter system. With this in mind, we have synthesized the three-component system, **I**, consisting of an electronically deficient 4-aminophthalimide moiety as the fluorophore and a macrobicyclic cryptand moiety (**III**) as the receptor. In this paper, we report the synthesis and the photophysical and metal ion-sensing behavior of **I**.

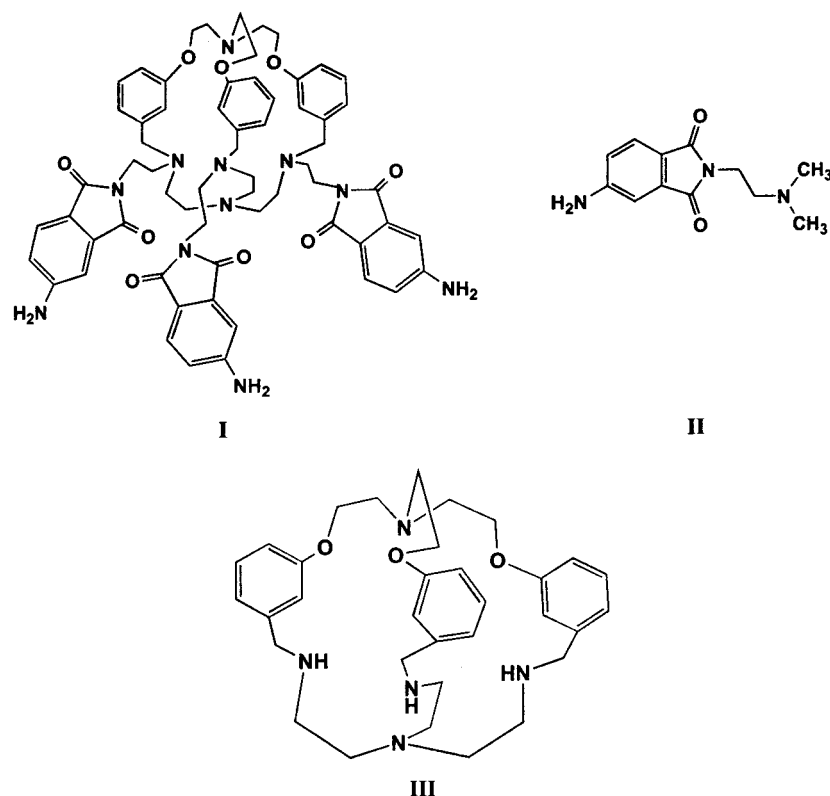
2. Experimental Section

2.1. Synthesis of I. **I** was synthesized in three steps: the first step consisted of the preparation of 2-bromo-1-(4-aminophthalimido)ethane, the second step involved the preparation of **III**, and the third step involved the reaction between 2-bromo-1-(4-aminophthalimido)ethane and **III** to obtain the desired product, **I**.

Step 1: 4-Aminophthalimide (5 mM) was treated with previously washed NaH (25 mM) in dry *N,N*-dimethylforma-

* Corresponding author. E-mail: assc@uohyd.ernet.in. Fax: +91-40-301 2460.

CHART 1



amide (10 mL) at room temperature with constant stirring for 1 h. Subsequently, 1,2-dibromoethane (10 mM) was added to the reaction mixture and stirred for 24 h at room temperature. The excess NaH present in the reaction mixture was destroyed with water (5 mL), and the product was extracted with chloroform (3×20 mL). The chloroform extract was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The resulting solid was purified by column chromatography (neutral alumina and 1:1 hexane/ethyl acetate). The purified compound gave satisfactory spectral data. Yield 60%.

Step 2: **III** was prepared according to the procedure suggested by Chand and Bharadwaj.⁷

Step 3: **III** (1 mM) was added to 40 mL of dry acetonitrile in a 100-mL three-necked round-bottom flask and was heated to 335 K for 30 min to dissolve it completely. To this solution were added 2-bromo-1-(4-aminophthalimido)ethane (5 mM), potassium carbonate (5 mM), and a catalytic amount of KI. The mixture was allowed to reflux under a nitrogen atmosphere for 36 h with constant stirring. Subsequently, the solvent was evaporated, and the solid residue was extracted with chloroform (3×40 mL). The chloroform extract was dried over anhydrous Na_2SO_4 and evaporated to obtain a pale yellow solid that was purified by column chromatography (neutral alumina, 98:2 CHCl_3 /methanol). Yield 30%. The desired product was characterized by the following analytical results.

CHN analysis calculated for $\text{C}_{63}\text{H}_{69}\text{N}_{11}\text{O}_9$: C, 67.31; H, 6.14; N, 13.71. Found: C, 66.12; H, 6.26; N, 12.79. FAB-MS m/z (%): 1125 (100) $[\text{M} + 1]^+$. ^1H NMR (CDCl_3): δ 2.3 (s, 12H), 2.5 (t, 6H), 2.9 (t, 6H), 3.4 (s, 6H), 3.6 (t, 6H), 3.8 (t, 6H), 4.4 (s, 6H), 6.5–7.5 (m, 21H). ^{13}C NMR (CDCl_3): δ 35.9, 51.3, 52.2, 53.3, 56.8, 58.8, 68.5, 108.5, 114.1, 114.2, 117.7, 120.6, 121.1, 124.8, 128.7, 135.0, 141.2, 152.4, 158.9, 168.4, 168.5.

2.2. Instrumentation and Methods. The absorption and fluorescence spectra were recorded on a Shimadzu spectrophotometer (UV-3101PC) and a Spex spectrofluorimeter (Fluoro-

max-3), respectively. All fluorescence spectra were corrected for instrumental response. The fluorescence decay profiles were recorded on a single photon-counting spectrofluorimeter (IBH, model 5000). The instrument was operated with a thyatron-gated flash lamp filled with hydrogen at a pressure of 0.5 atm. The lamp was operated at a frequency of 40 kHz, and the pulse width of the lamp under operating conditions was ~ 1.2 ns. The lifetimes were estimated from the measured fluorescence decay curves and the lamp profile using a nonlinear least-squares iterative fitting procedure.⁸ The details concerning the instrument can be found elsewhere.^{9–11} The goodness of the fit was evaluated from the χ^2 values and the plot of the residuals. Microanalysis (C, H, N) was performed on a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded on a Bruker ACF-200 spectrometer. The quantum yields of the samples were measured relative to that of 4-aminophthalimide ($\phi_f = 0.7$ in tetrahydrofuran).¹² The solvents used in this study, tetrahydrofuran (THF) and acetonitrile (AN), were rigorously purified following standard procedures.¹³

3. Results

The electronic absorption and fluorescence spectra of **I** are shown in Figure 1. Broad bands typical of the transition to the intramolecular charge-transfer state of the fluorophore moiety¹² characterize the low-energy absorption as well as the fluorescence spectra. Although the absorption spectrum is rather insensitive to the solvent, the location of the fluorescence maximum is determined by the polarity of the media (Table 1). This behavior is consistent with a higher dipole moment of the excited state of the fluorophore. Apart from a shift of the wavelength of the absorption and fluorescence maxima, the spectral features of **I** and 4-aminophthalimide are remarkably similar (spectral data for the two compounds are listed in Table 1). However, although 4-aminophthalimide is highly fluorescent (ϕ_f of 0.7 in THF and 0.63 in AN),¹² we measured the

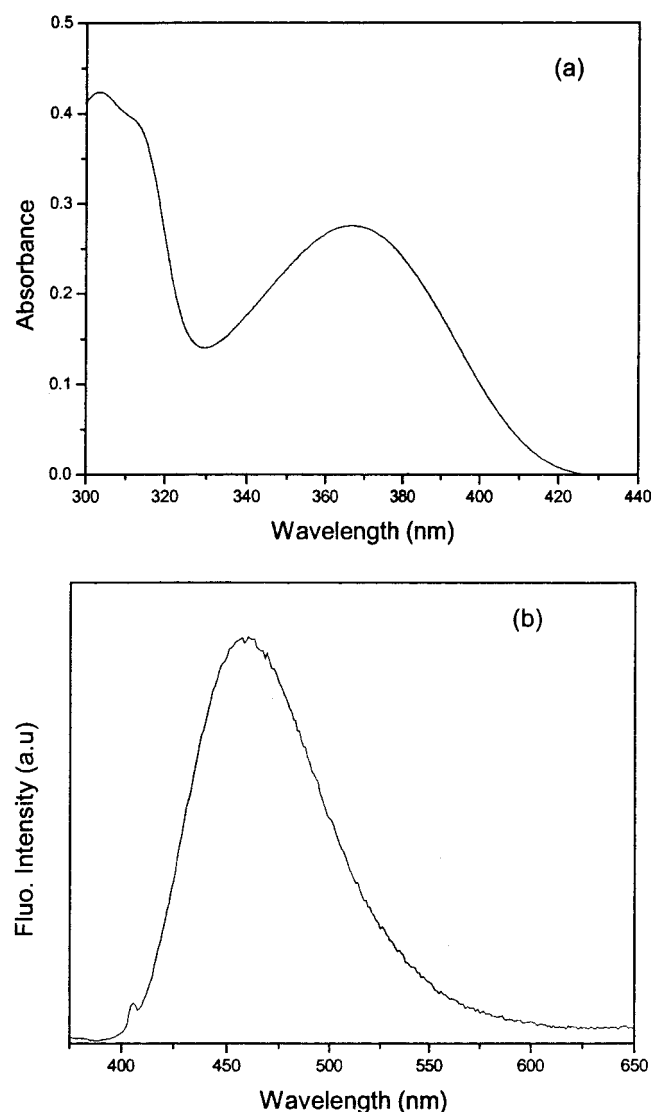


Figure 1. Absorption (a) and fluorescence (b) spectra of **I** (4×10^{-5} M) in THF. The fluorescence spectrum was obtained by exciting the sample at 363 nm.

fluorescence quantum yield of **I** (Table 1) to be only 0.028 in THF and 0.025 in AN. Moreover, although the fluorescence lifetime of 4-aminophthalimide is reported to be 14.0 ns in THF and 12.4 ns in AN,¹² **I** exhibits multiexponential decay behavior (Figure 2), with the lifetime of the major component of the decay measured to be approximately 0.2 ns (92%) in THF and 0.9 ns (65%) in AN (Table 1). Taking into consideration the through-space nature of PIET,⁶ the molecular flexibility afforded by the dimethylene spacer group, and the presence of several tertiary nitrogen atoms (which can involve in PIET), it is not surprising that **I** exhibits multiexponential decay behavior. Essentially, the components of the decay are representative of the various

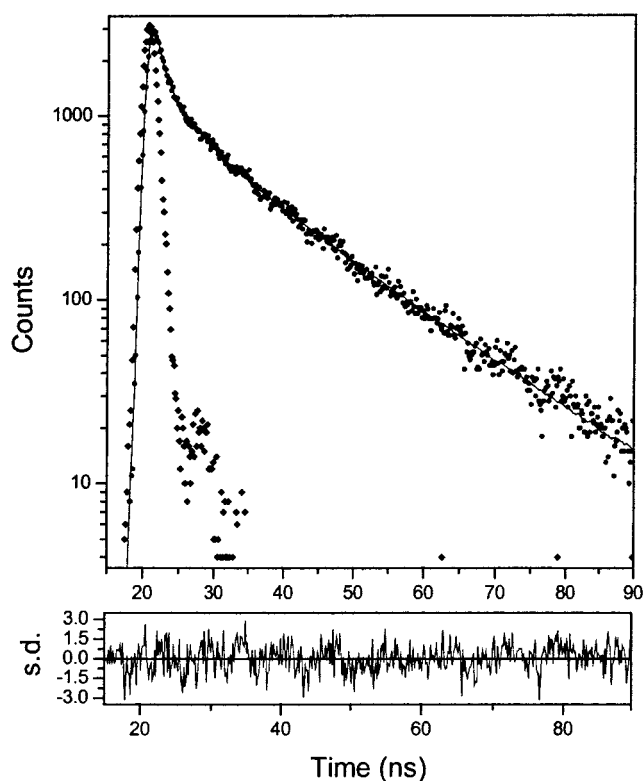


Figure 2. Fluorescence decay behavior of **I** in THF. The solution was excited at 366 nm, and the fluorescence was monitored at 460 nm. The solid line represents the best fit to the decay profile. The fitting parameters obtained for this particular decay profile are as follows: $\tau_1 = 0.2$ ns, $a_1 = 0.92$; $\tau_2 = 3.0$ ns, $a_2 = 0.04$; $\tau_3 = 15.5$ ns, $a_3 = 0.04$.

dominant conformations of the molecule. The shortest lifetime (the major component) clearly originates from a conformation in which PIET is most feasible.

Typical changes in the absorption spectrum of **I** in the presence of the transition-metal ions are depicted in Figure 3. Addition of the metal salts leads to a bathochromic shift of the absorption maximum, with the shift ranging between 4 and 10 nm depending on the metal ion. An isosbestic point (at around 358 nm in AN and 363 nm in THF) could be observed with most of the metal salts over a certain concentration range, suggesting 1:1 complexation between **I** and the metal ions.¹⁴ However, as seen from Figure 3b, in the case of Cr^{3+} (and Fe^{3+}), a continuous shift of the spectral maximum could be observed in the concentration range ($0\text{--}24 \times 10^{-5}$ M) employed in the measurement.

Addition of the metal salts leads to a Stokes shift (vide Table 2) of the fluorescence maximum (22–24 nm in THF and 3–7 nm in AN) and is associated with an enhancement of the fluorescence intensity of the system (Figure 4). The fluorescence parameters of the system in the presence of the metal ions are collected in Table 2. The magnitude of the fluorescence

TABLE 1: Absorption and Fluorescence^a Properties of **I and 4-Aminophthalimide in Tetrahydrofuran (THF) and Acetonitrile (AN)**

system	THF				AN			
	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}^b$	$\lambda_{\text{max}}^{\text{flu}}/\text{nm}^b$	ϕ_f^c	$\tau_f/\text{ns}^{c,d}$	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}^b$	$\lambda_{\text{max}}^{\text{flu}}/\text{nm}^b$	ϕ_f^c	$\tau_f/\text{ns}^{c,d}$
I	366	460	0.028	0.2(92%) 3.0(4%) 15.5(4%)	366	480	0.025	0.9(65%) 6.3(27.5%) 19.6(7.5%)
AP ^e	357	445	0.70	12.4	357	458	0.63	14.0

^a $\lambda_{\text{exc}} = 366$ nm. All fluorescence spectra were corrected for instrumental response. ^b ± 2 nm. ^c $\pm 10\%$. ^d Quantities in parentheses indicate the relative amplitude of each component. ^e These data have been collected from ref 12.

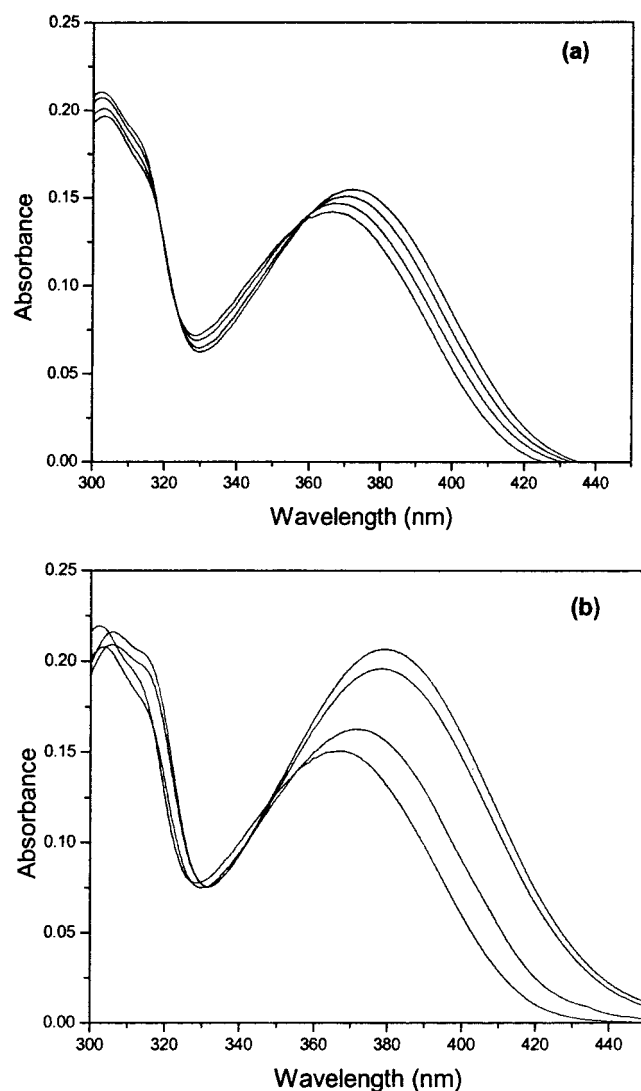


Figure 3. Effect of the metal ions on the absorption spectrum of **I** in AN: (a) Ni^{2+} (b) Cr^{3+} . The various concentrations of Ni^{2+} in increasing order of the absorbance at 380 nm are 0, 4.5×10^{-5} , 10.5×10^{-5} , and 24.0×10^{-5} M. The concentrations of Cr^{3+} are 0, 6×10^{-5} , 12×10^{-5} , and 24×10^{-5} M.

enhancement (FE), which is a measure of the signaling efficiency of the present system, is found to vary between 6 and 14. The highest enhancement is observed in the presence of Zn^{2+} , a metal ion that has a d^{10} electronic configuration and is well-known for its nonquenching ability. Interestingly, FE in the presence of Fe^{3+} , a metal ion that has a d^5 electronic configuration and is known to be one of the most efficient

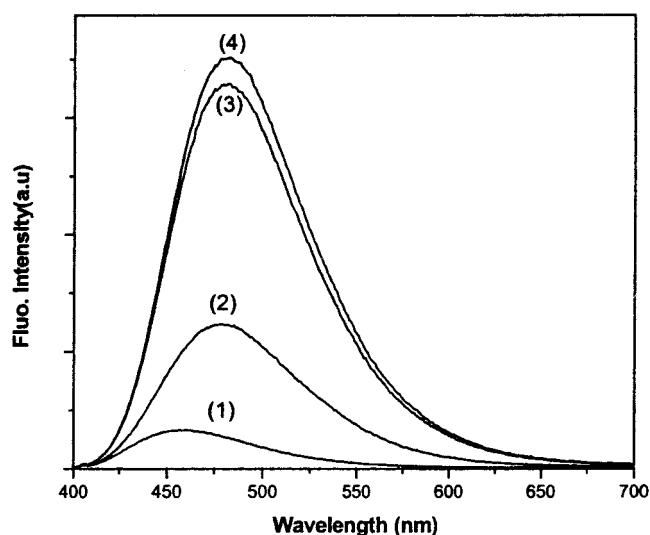


Figure 4. Fluorescence spectra of **I** in THF in the presence of Ni^{2+} . The concentrations of the metal ion in increasing order of the fluorescence intensity are (1) 0, (2) 2.8×10^{-6} , (3) 1.4×10^{-5} , and (4) 2.8×10^{-5} M. The excitation wavelength was 363 nm.

fluorescence quenchers among the transition-metal ions, is considerably high. Mn^{2+} , another metal ion with d^5 configuration, also exhibits a fairly high value of FE.

We studied the effect of the transition-metal salts on the fluorescence decay behavior of the system. The subnanosecond component of the decay disappeared completely in the presence of the metal ions, and we observed instead a significant increase in the amplitude of the long component. The decay parameters observed in the presence of Zn^{2+} ($2.6\text{--}4.0 \times 10^{-5}$ M) are as follows: 4.4 (0.77) and 13.4 ns (0.23) in AN and 4.5 (0.47) and 15.3 ns (0.53) in THF. An increase in the lifetime of the system in the presence of the metal ions is in accordance with metal ion-induced suppression of PIET in **I**. The lifetime of the long component ($\tau_f = 13.4\text{--}15.3$ ns) of **I** that is observed in the presence of the metal ions is, as expected, very similar to that of the bare fluorophore, 4-aminophthalimide ($\tau_f = 12.4\text{--}14.0$ ns).¹²

4. Discussion

A lower fluorescence efficiency and a shorter fluorescence lifetime of **I** compared to those of the bare fluorophore (4-aminophthalimide) suggest that there is photoinduced intramolecular electron transfer (PIET) between the tertiary nitrogen atoms of the cryptand moiety and the fluorophore. Because the fluorescence yield of **I** is lower than that of the bare fluorophore by a factor of 25 in THF and a factor of 25.2

TABLE 2: Maximum Fluorescence Enhancement (FE)^a Observed for **I and **II**^b in the Presence of Different Metal Salts**

metal ion ^c	I			II			II	
	in THF			in AN			in AN	
	$[\text{M}^{n+}]/10^{-5}$ M	$\lambda_{\text{max}}^{\text{flu}}/\text{nm}$	FE	$[\text{M}^{n+}]/10^{-5}$ M	$\lambda_{\text{max}}^{\text{flu}}/\text{nm}$	FE	$[\text{M}^{n+}]/10^{-4}$ M	FE
none		460	1		480	1		1
Mn^{2+}	2.7	483	12	5.7	487	6	1.7	32 ^d
Fe^{3+}	3.0	482	13	3.8	485	6	1.0	34
Ni^{2+}	2.8	483	13	5.9	485	7	3.0	37
Cr^{3+}	3.2	484	13	6.2	486	6	1.2	39
Cu^{2+}	2.1	484	12	2.5	486	6	1.9	38 ^d
Zn^{2+}	2.6	482	14	4.0	483	8	3.9	55

^a Concentration of **I** was maintained around 2×10^{-5} M, and the samples were excited at the isosbestic point $\pm 10\%$. ^b Unless otherwise indicated, from ref 6. ^c Hydrated perchlorate salts of the metals were used. ^d From Ramachandram, B. Ph.D Thesis, University of Hyderabad, Hyderabad, India, 2000.

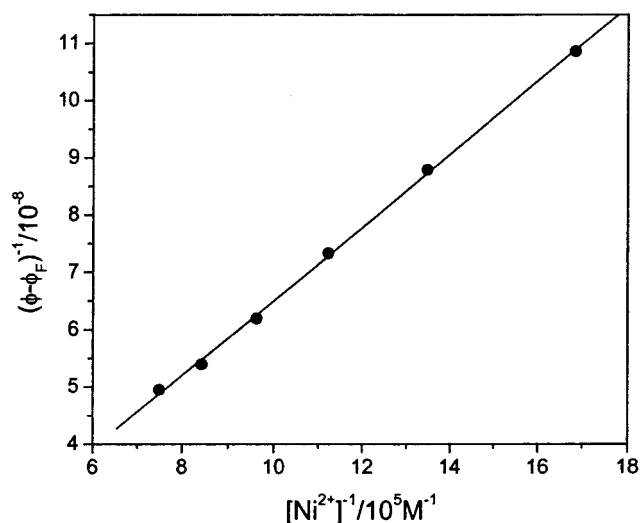
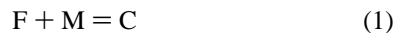


Figure 5. Typical plot from which the binding constant was estimated. The data shown in the plot are for Ni^{2+} in AN.

in AN, the maximum FE values expected for **I** in the presence of the metal ions, assuming complete recovery of fluorescence, are 25 and 25.2 in THF and AN, respectively. The observed FE values (shown in Table 2), particularly those in THF, are not very different from the expected values of the maximum FEs. Comparatively lower FE values in acetonitrile can be accounted for when taking into consideration the strength of the interaction between the metal ions and **I** in THF and AN. The cryptand receptor, which consists of two different tripodal binding sites separated by the aromatic rings, is believed to form transition-metal complexes through the tripodal N_4 moiety.⁷ Because 1:1 complexation between **I** and the metal ions is evident in many cases from the absorption spectral data, the complexation constants (K) can be evaluated from the absorption and fluorescence spectral data. However, because metal ion-induced changes of the fluorescence spectra are more pronounced than those of the absorption spectra, we preferred to evaluate the K values from the fluorescence data. In a few cases, we have measured the K values from absorption data as well and have found that these values are in agreement with those measured from fluorescence. The method based on that from which the K values have been estimated is given below.

Complexation (1:1) between the fluorosensor (F) and the metal ions (M) can be represented as



where C stands for the complex.

At equilibrium, the equilibrium constant

$$K = \frac{[\text{C}]_e}{[\text{F}]_e [\text{M}]_e} \quad (2)$$

$$= \frac{[\text{C}]_e}{\{[\text{F}]_0 - [\text{C}]_e\} \{[\text{M}]_0 - [\text{C}]_e\}}$$

where $[\text{C}]_e$, $[\text{F}]_e$, and $[\text{M}]_e$ are the equilibrium concentrations of the species and $[\text{F}]_0$ and $[\text{M}]_0$ are the initial concentrations.

Because the measurements were performed with an $[\text{F}]_0 \gg [\text{M}]_0$, $\{[\text{F}]_0 - [\text{C}]_e\} \approx [\text{F}]_0$.

Hence,

$$K = \frac{[\text{C}]_e}{[\text{F}]_0 \{[\text{M}]_0 - [\text{C}]_e\}} \quad (3)$$

By rearranging, we obtain

$$[\text{C}]_e/[\text{F}]_0 = K[\text{M}]_0/\{1 + K[\text{F}]_0\} \quad (4)$$

TABLE 3: Binding Constant (K)^a of Some Metal Ions with **I in THF and Acetonitrile Estimated from Fluorescence Spectral Data**

metal ion	K/M^{-1}	
	in THF	in acetonitrile
Mn^{2+}	2.5×10^5	6.7×10^3
Ni^{2+}	6.4×10^5	1.0×10^4
Zn^{2+}	2.5×10^5	6.7×10^3
Cu^{2+}	1.0×10^5	6.0×10^3

^a K values have been estimated only in those cases where 1:1 complexation was clearly evident from the absorption spectra.

The total fluorescence yield, ϕ , is

$$\phi = (\phi_F I_F + \phi_C I_C)/(I_F + I_C)$$

where ϕ_F and ϕ_C represent the fluorescence yield of the fluorophore and the complex, respectively and I_F and I_C stand for the number of photons absorbed per unit volume per unit time by the fluorophore and the complex, respectively.

Therefore, we can write

$$\phi = (\phi_F + \phi_C I_C/I_F)/(1 + I_C/I_F) \quad (5)$$

Also, $I_F/I_C = \epsilon_F[\text{F}]_0/\epsilon_C[\text{C}]_e$ where ϵ_F and ϵ_C are the molar extinction coefficients of the fluorophore and the complex, respectively, at the exciting wavelength.

Hence,

$$[\text{C}]_e/[\text{F}]_0 = \epsilon_F I_C/\epsilon_C I_F \quad (6)$$

By combining eqs 4 and 6 and using $\epsilon_C = \epsilon_F$, we get

$$I_C/I_F = K[\text{M}]_0/\{1 + K[\text{F}]_0\} \quad (7)$$

By substituting eq 7 into eq 5, we obtain

$$\phi = \frac{(\phi_F + \phi_C K[\text{M}]_0/\{1 + K[\text{F}]_0\})}{(1 + K[\text{M}]_0/\{1 + K[\text{F}]_0\})}$$

After rearranging, we get

$$1/(\phi - \phi_F) = \frac{\{(1 + K[\text{F}]_0)/K(\phi_C - \phi_F)\}/[\text{M}]_0 + 1/(\phi_C - \phi_F)}{\quad} \quad (8)$$

Hence, a plot of $(\phi - \phi_F)^{-1}$ against $[\text{M}]_0^{-1}$ should be a straight line whose slope (m) and intercept (c) are given by $m = \{(1 + K[\text{F}]_0)/K(\phi_C - \phi_F)\}$ and $c = 1/(\phi_C - \phi_F)$.

Therefore, the complexation constant $K = \{m/c - [\text{F}]_0\}^{-1}$.

A typical plot from which the binding constants have been evaluated is shown in Figure 5. The binding constants (K) of the metal ions with **I**, which were estimated from the fluorescence data by assuming the formation of 1:1 complex, lie between 1×10^5 and $7 \times 10^5 \text{ M}^{-1}$ in THF and between 6×10^3 and $1 \times 10^4 \text{ M}^{-1}$ in AN for the various metal ions studied in this work (see Table 3). These data suggest that **I** does indeed form tight complexes, though these are not as strong in AN as in THF. A comparatively lower magnitude of the K values in AN accounts for the lower FE values observed in this medium. The K values for the various complexes involving the present cryptand moiety, as estimated from the potentiometric titration in aqueous solution, lie between $10^{3.25}$ and $10^{15.22} \text{ M}^{-1}$.¹⁵ A comparison of these values with the ones we have estimated may not be relevant because the media of the complexation and hence the actual complexes in the two cases are quite different.

Moreover, although the K values reported in aqueous media are for the cryptand that is not attached to any fluorophore, the K values estimated by us are for the cryptand moiety that is covalently linked to three 4-aminophthalimide moieties.

It should be noted here that even though the observed FE values are sufficiently high, thus pointing to the potential utility of the present system in sensing applications, it is interesting that the FE values for **I** in the presence of the metal ions are significantly lower than those observed for **II** (vide last column of Table 2), which is a simpler system containing the same fluorophore and spacer but with a much simpler receptor moiety. Quite obviously, a tighter binding of the metal ions by the cryptand receptor alone cannot ensure a higher degree of fluorescence enhancement, even though a tighter binding does allow for the detection of a smaller quantity of the metal ions, as is evident from the data provided in Table 2.

The fluorescence yields of **I** and **II** are 0.025 and 0.013,⁶ respectively. These values suggest that PIET between the receptor and the fluorophore is more efficient in **II** than in **I**. Thus, even though **II** contains a receptor that is not as good from the viewpoint of the binding of the metal ions, a more efficient PIET in **II** gives rise to a higher FE value of this system in the presence of transition-metal ions. Therefore, as far as the design strategy of a fluorosensor for the metal ions is concerned, one really needs to select the various components for the fluorophore–spacer–receptor system such that PIET in the system and the binding of the guests are optimized. In the present case, a $-\text{CH}_2-\text{CH}_2-$ group separates the fluorophore and the receptor. It is quite possible that PIET could be relatively more efficient in similar systems in which a single $-\text{CH}_2-$ group separates the receptor and the fluorophore. Studies in this direction are in progress.

In summary, the results of the present investigation suggest that even though a fluorophore–spacer–receptor system containing a cryptand moiety binds the metal ions tightly, thereby enabling their detection in trace quantities, the limiting value of the fluorescence enhancement of such a system in the presence of the metal ions need not be higher than that of a similar system containing a much simpler amino moiety as the receptor. The lesson that we learn from this study is that the molecular components of a sensor system have to be chosen such that optimized conditions for PIET and guest-binding are attained.

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