# Transition Metal (II)/(III), Eu(III), and Tb(III) Ions Induced Molecular Photonic OR Gates Using Trianthryl Cryptands of Varying Cavity Dimension

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Received April 28, 1997. Revised Manuscript Received August 4, 1997<sup>®</sup>

**Abstract:** Three heteroditopic cryptands with different cavity dimensions have been synthesized in high yields at 278 K without employing any templating metal ion. The three secondary amino nitrogens in each cryptand could be derivatized with anthryl groups to have a fluorophore–spacer–receptor configuration. The fluorophores in these systems do not show any fluorescence due to an efficient photoinduced intramolecular electron transfer (PET) from nitrogen lone pairs. However, the fluorescence can be recovered to different extents in the presence of different metal ions and protons as well. On complexation by a transition metal ion or on protonation in a solvent like dry THF, each exhibits large fluorescence enhancement as the nitrogen lone pairs responsible for PET are engaged in bonding. Inner-transition-metal ions like Eu(III) or Tb(III) show remarkable discrimination and give high fluorescence enhancement only in one case where the cavity size is smaller than that of other two. Each system exhibits large fluorescence enhancement with Pb(II) among the heavy metal ions studied. The present study shows that transition metal ions and Pb(II), which are known for quenching, can indeed cause fluorescence enhancement in cryptand-based systems. It is also reported for the first time that inner-transition-metal ions cause fluorescence. The enhancement in each case is interpreted in terms of a communication gap between the metal ion and fluorophore. Such cryptand-based fluorophores can be useful as potential molecular photonic devices and metal ion sensors as well.

### Introduction

The fluorescent sensing of ions is of considerable current interest as sensors<sup>1–3</sup> in biomedical research and as chemical logics<sup>4–6</sup> in molecular information processing. In chemical logics, the binding of a guest species to a host molecule (logic input) results in a change in fluorescence intensity (logic output). Depending upon the input/output functionality, chemical logics have been divided<sup>4a</sup> as YES, NO logic functions or as OR, AND logic gates. Whenever multiple chemical inputs independently produce one output they can be regarded as OR logic gates. To have an effective OR logic gate it is required that the receptor part of the molecule have poor chemoselectivity. Research

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groups of Czarnik,<sup>1,7</sup> de Silva,<sup>2,8</sup> and others<sup>9–11</sup> have reported several acyclic/macrocyclic hosts with nitrogen donors and covalently linked aromatic fluorophores. In such systems, alkali/ alkaline earth metal ions and metal ions with filled d orbitals have been used as inputs. Whenever a metal ion is bonded to the host, the lone pairs of the nitrogens are engaged, preventing the photoinduced electron transfer (PET) from nitrogens to the aromatic fluorophore, thereby allowing the fluorescence to

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<sup>&</sup>lt;sup>®</sup> Abstract published in Advance ACS Abstracts, November 1, 1997.

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Figure 1. (a) Plan of the higher generation molecular photonic OR logic gate. (b) Heteroditopic cryptands (1, 2, and 3) and their trianthryl derivatives ( $L_1$ ,  $L_2$ , and  $L_3$ ).

occur. Most of these studies have been carried out in nonaqueous media. In a significant contribution, Czarnik had shown that an aqueous medium<sup>1a</sup> can also be used in certain cases-a result which might lead to biomedical applications of such systems. Transition metal ions are known to quench fluorescence very effectively, and therefore, molecular fluorescent signaling systems with these metal ions were not available until recently. We have shown for the first time that Cu(II) and Ni-(II) ions can also cause fluorescence enhancement in a cryptandbased fluorophore.<sup>6</sup> Such systems might prove useful not only as sensors in biology but also as versatile chemical logic devices. We have designed heteroditopic macrobicyclic receptors for transition/inner-transition-metal ions where three anthryl groups are covalently attached to the receptor unit in order to have transition/inner-transition-metal mediated molecular photonic switches. Herein, we present that transition metal ions in general, can function as efficient logic inputs for molecular photonic OR gates. To date, no fluorescence enhancement with inner-transition-metal ions has been reported<sup>2b</sup> as these metal ions are mostly involved in energy transfer with the fluorophore resulting in luminescence. We present here the first example of fluorescence enhancement with Eu(III) and Tb(III) ions. Finally, the Pb(II) ion, which is a known quencher, is also shown to cause enhancement. Also, we report here that the extent of enhancement with the metal ions studied depends crucially upon the flexibility as well as the cavity size of the macrobicyclic receptor.

Fluorescence intensity enhancement rather than quenching is better understood in sensors and in chemical logics. Design of an efficient sensor/device based on the "fluorophore–spacer– receptor" configuration depends significantly upon the total architecture of the whole system (Figure 1a). The desired architecture of a molecular photonic device/sensor demands the following: (i) the PET causing quenching of the fluorescence should be very fast and efficient in the free molecule, (ii) the PET should be more or less completely prevented when the receptor unit accepts an ionic input, and (iii) the distance and orientation of the metal ion entering the receptor unit with respect to the  $\pi$ -system should be such that the spin–orbit coupling which facilitates the S–T intersystem crossing would be minimum. In other words, for efficient fluorescence sensing, the metal ion–fluorophore communication should be much less



**Figure 2.** UV spectra of free  $L_1$  (solid line) and that of the Cu(II) complex (broken line) in dry THF.

than the metal—receptor interaction.<sup>12</sup> A cryptand-based system thus becomes attractive as the host binds the metal ion strongly due to cryptate effect. And the cavity is somewhat shielded from outside interference.<sup>13</sup> Both of these factors weaken metal—fluorophore communication while at the same time increase metal—receptor interactions.

## **Results and Discussion**

The parent cryptands and their trianthryl derivatives are illustrated in Figure 1b.

(1) UV-Visible Absorption Spectroscopy. Freshly purified THF is used as the solvent. In the region of interest, the unsubstituted cryptands or their metal complexes have negligible absorption. In Figure 2, the UV spectra of free and Cu(II)complexed  $L_1$  are shown. The spectra of the uncomplexed trianthryl cryptands are characteristic<sup>14</sup> of 9-monoalkylsubstituted anthracene with well-resolved structures with the (0,0) band appearing at 388.0 nm and vibrational structures at 368.0, 350.0, and 333.0 nm. This indicates no interaction between the nitrogen lone pairs of the receptor part and the anthracene ring in the ground state. Both  $L_1$  and  $L_2$  present slight bathochromic shifts (2-5 nm) of the peak positions upon complexation with transition metal ions at room temperature. However, in case of  $L_3$ , detectable shifts in the peak positions can be observed only in the presence of Cu(II) and Fe(III). With Eu(III) and Tb(III) as well as with heavy metal ions such as Hg(II), Pb(II), and Tl(I), no shifts in the peak positions can be detected except in case of  $L_2$  with Pb(II) ion. Earlier, we showed from X-ray crystallographic studies<sup>15</sup> that cryptand receptors of both  $L_1$  and  $L_2$  (i.e., 1 and 2 in Figure 1) underwent conformational changes to different extents upon complexation with Cu(II), Ni(II), and Zn(II) ions. However, the receptor part of  $L_3$  (3) being preorganized via ligand synthesis did not undergo appreciable change in conformation upon complexation.

(2) Stoichiometry and Nature of Complexation. The unsubstituted cryptands 1, 2, and 3 (Figure 1) readily accept a single metal ion in the cavity forming 1:1 inclusion complexes. These are versatile ligands for first-row transition metal ions such as Cu(II), Ni(II), Co(II), Fe(III), and Mn(II). These



**Figure 3.** Corrected fluorescence emission of  $L_1$  in dry THF at different concentrations:  $5 \times 10^{-5}$  M (A),  $2 \times 10^{-5}$  M (B), and  $1 \times 10^{-5}$  M (C).

transition metal ions occupy the N<sub>4</sub> end of the cavity. This has been shown<sup>15</sup> by X-ray crystallography in cases of Co(II), Cu-(II), Ni(II), and Zn(II) ions. With other transition metal ions, however, this has been inferred on the basis of spectroscopic characteristics of the complexes formed. Inner-transition-metal ions Eu(III) and Tb(III) as well as heavy metal ions like Hg-(II), Pb(II), or Tl(I) usually prefer<sup>16</sup> higher than hexacoordination. Therefore, these metal ions may engage both N and O donors present in the cryptands.

(3) Fluorescence Emission Spectra of Free L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub>. Metal-free L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub> show a well-resolved anthracene monomer emission along with a red-shifted broad structureless emission centered at 550 nm in THF at 298 K (Figure 3). When studied as a function of concentration in THF, the intensity of

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<sup>(15) (</sup>a) The metal ion receptor units of  $L_1$ ,  $L_2$ , and  $L_3$  are the heteroditopic cryptands 1, 2, and 3, respectively, as illustrated in Figure 1. 1 crystallizes in the triclinic space group P1 with a = 10.133(2) Å, b =11.972(3) Å, c = 13.433(3) Å,  $\alpha = 106.69(2)^{\circ}$ ,  $\beta = 90.93(2)^{\circ}$ ,  $\gamma = 91.38$ - $(2)^{\circ}$ , Z = 2,  $R_f = 0.054$ , and  $R_{wf} = 0.061$ . It has an *endo-endo* conformation and a pseudo-3-fold symmetry axis passing through the two bridgehead nitrogens in the solid state. <sup>1</sup>H NMR data indicate that the 3-fold symmetry is maintained in CDCl<sub>3</sub> solution at 298 K. The distance of 6.249(5) Å between the two bridgehead nitrogens in 1 changes only slightly to 6.410-(5) Å when a Ni(II) ion is bonded at the  $N_4$  end of the cavity accepting in a H<sub>2</sub>O molecule as well, although the conformation of this end undergoes significant changes (Ghosh, P.; Sengupta, S; Bharadwaj, P. K. J. Chem. Soc., Dalton Trans. 1997, 935). (b) 2 crystallizes as a trihydrate in the monoclinic space group C2/c with a = 15.398(12) Å, b = 20.062(6) Å, c= 25.207(3) Å,  $\beta = 103.80(2)^\circ$ , Z = 8,  $R_f = 0.088$ , and  $R_{wf} = 0.123$ . It has a pronounced endo-endo conformation with a collapsible cavity. The distance of 5.291(14) Å between the two bridgehead nitrogens increases to 7.263(10) Å when a Zn(II) ion binds at the N4 end of the cavity still maintaining the endo-endo conformation. Conformational changes at the N4 end of the cavity are also substantial (Ghosh, P.; Bharadwaj, P. K. J. Chem. Soc., Dalton Trans. 1997, 2673). (c) 3 crystallizes in the monoclinic space group  $P2_1/c$  with a = 10.756(5) Å, b = 27.407(9) Å, c = 12.000(2)Å,  $\beta = 116.22(3)^\circ$ , Z = 4,  $R_f = 0.060$  and  $R_{wf} = 0.058$ . The cavity is the largest among the three cryptands with the distance between the two bridgehead nitrogens being  $\hat{9}.904(7)$  Å. The N<sub>4</sub> end of the cavity can accommodate a Cu(II) ion, which can accept an anion, forming cascade complexes. In this situation, the N4 end maintains its conformation although the upper part skews away to accommodate the anion (Chand, D. K.; Bharadwaj P. K. Inorg. Chem. 1996, 3380). (d) Similar changes in the ligand topology are observed when a Co(II) and a SCN- ion are bonded in a distorted trigonal bipyramidal fashion at the N4 end (Chand, D. K.; Bharadwaj, P. K. Inorg. Chem., in press).



**Figure 4.** Wavenumber of the exciplex emission maxium at 298 K of L<sub>1</sub> as a function of the solvent polarity parameter  $f - \frac{1}{2}f'$ ;  $f = (\epsilon - 1)/(2\epsilon + 1)$ ,  $f' = (n^2 - 1)/(2n^2 + 1)$ . Solvents  $(f - \frac{1}{2}f')$ : dichloromethane (0.319); THF (0.306); cyclohexane (0.100); *n*-hexane (0.092).

the monomer emission decreases while that of the structureless emission increases with concentration (Figure 3). To ascertain that the structureless broad emission is due to an intramolecular exciplex<sup>17</sup> and not due to excimer formation, the emission experiments are carried out in different solvents. In each case, the position of the emission maximum is found to be sensitive to the nature of the solvent showing the charge-transfer character of the emitting complex. Solvent studies show a red-shift of the band with increasing solvent polarity. The linear relationship found (Figure 4) between  $v_{ex}(max)$  and the solvent polarity parameter is consistent with the Weller equation.<sup>18</sup> Similar results were reported<sup>19</sup> earlier by other workers for intramolecular exciplex formation.

The quantum yields of monomer emission,  $\Phi_{FM}$ , and that of the exciplex emission,  $\Phi_{FE}$ , are presented in Table 1. In all cases,  $\Phi_{FT}$  (total quantum yield,  $\Phi_{FT} = \Phi_{FM} + \Phi_{FE}$ ) values are extremely low, indicating very efficient photoinduced electron transfer (PET) from the HOMO of tertiary N atoms to the anthracene  $\pi$ -system. Anthraceno cryptands and anthrylazamacrocycles reported<sup>11d,19</sup> earlier showed much higher quantum yields for both  $\Phi_{FM}$  and  $\Phi_{FE}$ .

(4) Fluorescence Emission Spectra in the Presence of **Transition Metal Cations.** The  $\Phi_{FM}$  increases highly when a transition metal ion is used as an input; the extent of enhancement depends upon the nature of the metal ion as well as the receptor (Table 1). Cavities of both  $L_1$  and  $L_2$  are flexible in nature,  $L_2$  being more so.<sup>15a,b</sup> In either case, the donor atoms at the N<sub>4</sub> end of the cavity in the receptor part can adjust for efficient binding of a metal ion. Therefore, with a metal ion like Co(II), Cu(II), or Zn(II) that prefers tetracoordination, the fluorescence recovery is maximum due to strong donation of the lone pairs of the N atoms which effectively lowers the communication between the lone pairs and the fluorophore. It is interesting to note here that ions like Mn(II), Ni(II), and Fe-(III) which prefer higher coordination also exhibit a high intensity of fluorescence. It is guite possible, however, for these metal ions to achieve higher than four coordination by binding solvent molecules inside as well as outside the cavity.15a,d With

**Table 1.** Fluorescence Output of  $L_1$ ,  $L_2$ , and  $L_3$  with Different Cation Inputs<sup>*a*</sup>

	ionic	(0,0) band	fluorescence output quantum yield <sup>14</sup> $\Phi_F$		
fluorophore	input	position (nm)	$\Phi_{\rm FM}$	$\Phi_{ ext{FE}}$	$\Phi_{\text{FT}}$
$\mathbf{L}_1$	nil	394.8	0.0005	0.0005	0.001
	Mn(II)	405.0	0.301	_	0.301
	Fe(III)	404.0	0.226	-	0.226
	Co(II)	405.6	0.215	_	0.215
	Ni(II)	403.2	0.210	—	0.210
	Cu(II)	405.0	0.280	_	0.280
	Zn(II)	405.8	0.310	—	0.310
	Pb(II)	405.0	0.180	—	0.180
	Eu(III)	394.8	0.077	—	0.077
	Tb(III)	395.0	0.100	—	0.100
$\mathbf{L}_2$	nil	394.6	0.001	0.001	0.002
	Mn(II)	403.6	0.370	—	0.370
	Fe(III)	404.2	0.289	—	0.289
	Co(II)	403.4	0.512	—	0.512
	Ni(II)	404.6	0.309	—	0.309
	Cu(II)	403.2	0.266	_	0.266
	Zn(II)	403.4	0.603	_	0.603
	Pb(II)	404.4	0.420	_	0.420
	Eu(III)	394.4	0.005	0.001	0.006
	Tb(III)	394.8	_	_	0.007
$\mathbf{L}_3$	nil	395.5	0.001	0.0005	0.0015
	Mn(II)	401.0	0.136	_	0.136
	Fe(III)	403.0	0.156	_	0.156
	Co(II)	397.0	0.131	_	0.131
	Ni(II)	395.5	0.080	_	0.080
	Cu(II)	403.0	0.110	_	0.110
	Zn(II)	396.0	0.150	_	0.150
	Pb(II)	395.6	0.148	_	0.148
	Eu(III)	395.8	0.024	_	0.024
	Tb(III)	395.8	0.036	_	0.036

<sup>*a*</sup> Experimental conditions: medium, dry THF; concentration of  $L_1$ and  $L_3$ ,  $10^{-5}$  M; concentration of ionic input,  $10^{-3}$  M; concentration of  $L_2$ ,  $5 \times 10^{-6}$  M; concentration of ionic input,  $5 \times 10^{-4}$  M. Excitation at isobestic point 370 nm with excitation band-pass of 5 nm; emission band-pass, 5 nm; temperature, 298 K;  $\Phi_F$  calculated by comparison of corrected spectrum with that of anthracene ( $\Phi_F = 0.297$ ) taking the area under the total emission. The error in  $\Phi_F$  is within 10% in each case, except free ligands, where the error in  $\Phi_F$  is within 15%.

 $L_3$ , however, the enhancement is considerably lower. The cavity of the receptor unit in  $L_3$  is more rigid<sup>15c</sup> and does not adjust upon metal coordination inside. Hence, the bonding interactions between the lone pairs of nitrogen and a metal ion will be less than those in the other two cases. The binding abilities of  $L_1$ ,  $L_2$ , and  $L_3$  toward a metal ion, e.g. Cu(II), are nicely reflected in the quantum yields of fluorescence in the three cases. Cu-(II) gives  $\Phi_{FM}$  of 0.280 with L<sub>1</sub>, 0.266 with L<sub>2</sub>, and only 0.110 with  $L_3$ . For the other transition metal ions studied,  $L_2$  exhibits the highest  $\Phi_{FM}$ . This common tendency of higher  $\Phi_{FM}$  with  $L_2$  is probably due to its cavity being the most flexible among the three which facilitates stronger binding interactions with a metal ion and nitrogen lone pairs. In all of the complexes of  $L_1$ ,  $L_2$ , and  $L_3$  with transition metal ions, the emission spectra show slight red-shifts (Table 1), concomitant broadening of both the (0,0) and other vibrational bands, and a different intensity ratio of the (0,0) and the first vibrational band compared to those of the free cryptands (Figure 5). Fluorophores are known to show emission bands which are solvatochromic in nature. Therefore, a possible mechanism for such a red-shift can be due to an metal ion induced change in polarity around the fluorophore. No exciplex emission can be observed in these complexes as the lone pairs of the N atoms are engaged to the metal ions. In all three ligand systems, Zn(II) shows the highest enhancement among the metal ion inputs due to its nonquenching nature.

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**Figure 5.** Corrected fluorescence spectra of free  $L_1$  (A), of  $L_1$  in the presence of Tb(III) (B), and of  $L_1$  in the presence of Cu(II) (C) in dry THF medium. The broad band in A represents intramolecular exciplex emission. The extra peaks in B are due to emission from the Tb(III) complex as shown. All spectra are drawn with arbitrary intensity scales for clarity.

(b) Inner-Transition-Metal Cations. We have used Eu-(III) and Tb(III) ions as metal inputs to the three systems. The results are collected in Table 1. The system  $L_1$  shows fluorescence enhancement with both Eu(III) and Tb(III) ions. However,  $L_2$  does not exhibit a similar enhancement with these ions, although with a transition metal ion, the enhancement is comparable with both  $L_1$  and  $L_2$  (vide supra). We attribute this to significantly lower metal-receptor interactions between  $L_2$ and Eu(III)/Tb(III) ions which cannot attenuate communication between the fluorophore and the lone pairs on nitrogens. It is known that inner-transition-metal ions prefer16 higher coordinations compared to transition metal ions. Therefore, Eu(III)/Tb-(III) ion would like to occupy the position in the middle of the cavity to achieve higher coordination by engaging all the donor atoms. The receptor unit in  $L_1$  is able to wrap around the Eu-(III)/Tb(III) ion to establish numerous binding interactions and to sense its size and shape. In contrast, the receptor in  $L_2$  having a larger cavity cannot effectively bind either metal ion. Interestingly, with  $L_2$ , the exciplex emission is observed (Figure 6) in the presence of Eu(III)/Tb(III) ion. This further shows that no significant donation occurs<sup>11d,19</sup> from the anthrylsubstituted N atoms toward the lanthanide ions. It is of significance to note here that, in cases of Eu(III) and Tb(III) complexes of  $L_1$ , the (0,0) band position remains uneffected and the spectral resolution is similar to that of the free  $L_1$  (Figure 5 and Table 1). The energy of the lowest triplet state of anthracene is lower than the emitting states of Eu(III) and Tb-(III) ions. The lower  $\Phi_{FT}$  observed for the lanthanide complexes of  $L_1$  compared to that of any of the transition metal complexes of the same ligand is presumably due to nonradiative decay of the fluorescent state of anthracene to the lowest triplet state through the rare-earth (III) ion states. In case of  $L_3$ , the fluorescence recovery is much less than that with  $L_1$  due to less metal-ligand interaction in the former. Although the emission intensity enhancement is much less here compared to that of the transition metal cryptates, the lanthanide systems can potentially function as an ideal OR gate since there is no shift of the emission band (Table 1).



**Figure 6.** Corrected fluorescence spectra of free  $L_1$  (A), of  $L_1$  in the presence of Eu(III) (B), of free  $L_2$  (C). and of  $L_2$  in the presence of Eu(III) (D) in dry THF medium. The broad bands in A, C, and D represent intramolecular exciplex emissions. The extra peaks in B and D are due to emission from the Eu(III) complex as shown. All spectra are drawn with arbitrary intensity scales for clarity.

(c) Heavy-Metal Cations. The emission signal undergoes drastic enhancement (Table 1) when any of the fluorophores is treated with Pb(II) ion in dry THF medium although other heavy metal ions such as Hg(II), Tl(I), and Ag(I) do not show any appreciable enhancement. The emission with Pb(II) is a structured red-shifted one without any exciplex like those found in the case of transition metal ions with  $L_1$  and  $L_2$ . With  $L_3$ , however, no red-shift is observed. With the other heavy metal ions, the spectra are similar to those of free  $L_1$ ,  $L_2$ , and  $L_3$ . This can be attributed to the fact that only Pb(II) ion enters the cavity of  $L_1$ ,  $L_2$ , and  $L_3$  and engages the nitrogen lone pairs. Like in the case of transition metal ions,  $L_2$  shows the highest  $\Phi_{\text{FT}}$ among the three systems (Table 1), probably due to best fit of the Pb(II) ion in the relatively larger and flexible cavity of  $L_2$ . While Pb(II) is a known quencher, an earlier report is available where it was found to enhance fluorescence.<sup>7e</sup>

**Control Experiments.** The metal perchlorate or nitrate salts are hydrated and can generate protons in organic solvents. The generated protons can engage the lone pairs of nitrogens through protonation causing fluorescence enhancement. To prove that the large fluorescence enhancement by transition, inner-transition, and Pb(II) ions are indeed due to the metal ions and not due to the protons generated, certain control experiments are carried out.

When no ion is added in THF:H<sub>2</sub>O (9:1) medium,  $\Phi_{FT}$  increases by a negligible factor of 1.2 compared to the case when dry THF is used. When the input is a hydrated metal salt (10<sup>-2</sup> M) in THF:H<sub>2</sub>O (9:1) medium,  $\Phi_{FT}$  with L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub> (10<sup>-5</sup> M) spans the range 0.025–0.035 and remains unchanged even after 40 h. When the concentration of the metal ion input is 10<sup>-3</sup> M,  $\Phi_{FT}$  values lie in the range 0.010–0.015. This could be due to partial protonation of the nitrogens in the receptor unit as a result of generation of protons upon addition of a metal ion in aqueous THF medium. However, when H<sup>+</sup> (as HCl/HClO<sub>4</sub>; 10<sup>-3</sup> M) is used as the input, the  $\Phi_{FT}$  value ranges between 0.21 and 0.225 in aqueous THF and between 0.23 and 0.250 in dry THF for these three systems and remains unchanged with time.



**Figure 7.** (a) Corrected fluorescence spectra of  $L_2$  in the presence of Pb(II) in THF:H<sub>2</sub>O, 10:0 (A), 9:1 (B), 8:2 (C), 6:4 (D), and 4:6 (E). Spectra B–E are multiplied by 10 for clarity. (b) Corrected fluorescence spectra in dry THF of  $L_2$  in the presence of Pb(II) (A), of  $L_2$  in the presence of Pb(II) and H<sup>+</sup> (HClO<sub>4</sub>) (B), and of  $L_2$  in the presence of H<sup>+</sup> (HClO<sub>4</sub>) (C). (c) Corrected fluorescence spectra in dry THF of  $L_1$  in the presence of Pb(II) and H<sup>+</sup> (HClO<sub>4</sub>) (C). (d) Corrected fluorescence spectra in dry THF of  $L_1$  in the presence of Pb(II) and H<sup>+</sup> (HClO<sub>4</sub>) (C). (d) Corrected fluorescence spectra in dry THF of  $L_1$  in the presence of Tb(III) (A) and of  $L_2$  in the presence of Tb(III) (B). All spectra are drawn with arbitrary intensity scales for clarity.

We have made further control experiments with  $L_2$  as it gives the highest  $\Phi_{FT}$  values among the three systems. When hydrated Pb(II) ion (10<sup>-3</sup> M) is used as an input for  $L_2$  (10<sup>-5</sup> M) in different THF:H<sub>2</sub>O (9:1, 8:2, 6:4, and 4:6) binary solvents, very small fluorescence enhancement is observed with respect to the case when dry THF is used under exactly similar experimental conditions (Figure 7a). Any combination of THF and H<sub>2</sub>O shows almost the same enhancement of fluorescence intensity. Thus, in aqueous THF medium, Pb(II) ion generates almost an equal amount of protons, which leads to partial protonation of the nitrogen atoms in the cryptand unit. On the other hand, in dry THF medium, the only source of water is the water of hydration associated with the Pb(II) salt which is negligibly small to generate any appreciable amount of protons. Hence, the enhancement on addition of hydrated Pb(II) salt to  $L_2$  in dry THF is attributable to Pb(II). Interestingly, when we add HClO<sub>4</sub> (10<sup>-3</sup> M) to the system containing hydrated Pb(II) salt and  $L_2$  in dry THF, the  $\Phi_{FT}$  value decreases (Figure 7b) from 0.420 to the value close to that obtained with  $L_2$  and an acid. In case of L<sub>1</sub>, hydrated Pb(II) salt in dry THF medium under the conditions as above shows  $\Phi_{FT}$  as 0.180, which increases (Figure 7c) to the acid value when  $HClO_4$  (10<sup>-3</sup> M) is added. All of the transition metal ions mentioned in Table 1 are found to behave like the Pb(II) ion.

Further evidence comes from the fact that when Tb(III) is used as the input to  $L_1$  in dry THF significant fluorescence enhancement ( $\Phi_{FT} = 0.100$ ) is observed, whereas with  $L_2$ negligible enhancement is seen ( $\Phi_{FT} = 0.006$ ) (Table 1 and Figure 7d). Keeping in mind that both  $L_1$  and  $L_2$  show almost equal enhancement on protonation, the enhancement in the case of  $L_1$  and Tb(III) is definitely due to the metal ion.

We have recorded the fluorescence emission spectra with a metal ion input in the presence of 2,6-di-*tert*-butylpyridine ( $10^{-2}$  M), which is a noncoordinating base. It shows that there is no difference in enhancement of fluorescence in the presence/absence of the base. However, we have found that the fluorescence enhancement obtained after protonation of  $L_1/L_2/L_3$  with trifluoroacetic/perchloric acid is not lost upon addition of excess of 2,6-di-*tert*-butylpyridine. This result shows that the pyridine added cannot deprotonate the protonated ligand. This is not surprising as it has been reported<sup>20</sup> that protonated cryptands cannot be deprotonated by adding any base under drastic conditions.

# Conclusion

It has been known for a long time that transition metal ions effectively quench<sup>21-27</sup> fluorescence, and a number of mechanisms have been forwarded to rationalize such behavior. These are conversions of electronic energy to kinetic via collisions, heavy atom effects, magnetic perturbations, formations of charge transfer complexes, electronic energy transfers from/to the metal ion, etc. In the present situation, the heavy atom effect is probably not operational as Pb(II) ion shows significant enhancement as well. Moreover, the 3d metal ions are not regarded as heavy. The giant macrocyclic system will also not take part in intermolecular collisional energy loss to any noticeable extent. No evidence for charge-transfer interaction of the anthryl groups with the metal ion has been found. Charge-transfer interactions between an excited-state fluorophore and a metal ion should produce an exciplex. We have not seen any exciplex formation when the metal ions is inside the cavity. Also, no alteration in the fluorescence band envelope is introduced by a metal ion. For the other two mechanisms to be operative, the fluorophore and the metal ion should have bonding interactions via the spacers or should be flexible enough for the metal orbital(s) and the orbitals with the proper symmetry on the fluorophore to come closer to make direct overlap. However, the host is designed in such a way that the inside and outside of the cavity are not in communication to a significant extent. Direct evidence for this comes from the fact that, when any of the host cryptands is derivatized with redox active<sup>28</sup> side groups such as a nitrobenzyl, the redox potential of the side group remains unchanged whether a metal ion enters the cavity or not. In the case of communication between outside and inside the cavity, there should have been a significant change

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## Fluorescence Enhancement by Transition Metal Ions

in the redox potential values. Thus we show here that fluorescence enhancement with transition metal ions is a general phenomenon with cryptand-based systems. We have shown for the first time that inner-transition-metal ions can act as logic inputs to give one output like an OR logic gate and a slight change of the cryptand cavity dimension significantly influences fluorescence output. It is also shown here that Pb(II) ion, which is a known quencher, can cause fluorescence enhancement. Syntheses of similar systems and detailed studies on them with transition/inner-transition-metal ions are in progress. Efforts are also on to have water-soluble systems to study possible fluorescence enhancement with transition metal ions.

### **Experimental Section**

**General Procedures.** <sup>1</sup>H NMR spectra were recorded on Bruker WP-80 FT (80 MHz) and Bruker WM-400 FT (400 MHz) spectrometers. The chemical shifts are reported in parts per million on the scale using tetramethylsilane as a reference. FAB mass (positive ion) data were recorded on a JEOL SX 102/DA-6000 mass spectrometer using argon as the FAB gas at 6 kV and 10 mA. The accelarating voltage was 10 kV and the spectra were recorded at 298 K. Melting points were obtained using an electrical melting point apparatus by Perfitt (India) and were uncorrected. UV and visible absorption spectra were recorded on a Hitachi model 3021 spectrophotometer at 298 K. Fluorescence spectra were obtained with a Hitachi model F-4010 spectrofluorimeter and corrected for emission. Fluorescence quantum yield was determined in each case by comparing the corrected spectrum with that of anthracene in ethanol, taking the area under the total emission.

**Materials.** All chemicals were of reagent grade which were used without further purification unless otherwise noted. Triethanolamine, salicylaldehyde, tris(2-aminoethyl)amine, sodium borohydride, 9-an-thracenemethanol, triphenylphosphine, and the metal salts were obtained from Aldrich (U.S.). Tris(3-aminopropyl)amine was purchased from Strem Chemicals (U.S.). Sodium hydroxide, anhydrous sodium sulfate, bromine, potassium iodide, potassium carbonate, perchloric acid, and thionyl chloride were received from S.D. Fine Chemicals (India). Thionyl chloride was purified prior to use. Chlorofrom, methanol, ethanol, acetonitrile, dichloromethane, tetrahydrofuran, cyclohexane, and *n*-hexane were received from Merck (India) and were purified prior to use following standard methods. Tetrahydrofuran (THF) was dried under a nitrogen atmosphere from potassium benzophenone ketyl.

**Trialdehyde.** Ortho- and meta-substituted trialdehydes were prepared according to our published<sup>15</sup> procedures.

Syntheses of the Cryptands 1–3. Syntheses of the cryptands were achieved by following our method.<sup>15</sup> Generally, a tripodal trialdehyde is allowed to react with a tripodal triamine at 5 °C in a suitable solvent under moderate dilution conditions. The Schiff base thus formed is reduced in situ with an excess of NaBH<sub>4</sub> first at room temperature followed by refluxing over a period of time. It is then shaken with cold water, and the entire solvent is removed in a rotary evaporator. The cryptand is then extracred with CHCl<sub>3</sub>, and after usual workup, the desired product is isolated as a colorless solid which are finally crystallized from acetonitrile.

**9-Bromomethylanthracene.** 9-Bromomethylanthracene was prepared from 9-hydroxymethylanthracene according to a literature<sup>29</sup> method.

General Synthesis of the Trianthryl Cryptands, L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub>. A general method of synthesis was adopted for all the trianthryl cryptands. The macrobicyclic cryptand (1-3) (1 mmol) was taken in 40 cm3 of dry MeCN in a 100 cm3 three-necked round-bottom flask. It was heated to 335 K for  $\sim$ 30 min to dissolve the cryptand completely. To this solution were added 9-bromomethylanthracene (5 mmol), potassium carbonate (5 mmol), and potasium iodide (20 mg). The mixture was allowed to reflux under nitrogen atmosphere for 12 h with constant stirring. In course of the reaction, a light yellow solid precipitated. At the end of the period, the reaction mixture was filtered in hot condition and the light yellow residue was first washed with hot MeCN and then stirred with cold water  $(3 \times 40 \text{ cm}^3)$  for 1 h; the watersoluble part was removed by filtration, and the remaining solid was washed with 2-propanol  $(2 \times 20 \text{ cm}^3)$  followed by ether. The pale yellow solid thus obtained was air-dried. Further purification of the compound was achieved by recrystallization from CH2Cl2:MeCN (1:5 ratio by volume) as a pale yellow microcrystalline solid. All attempts to obtain any of the products in single crystal form suitable for X-ray crystallography remained unsuccessful.

**Trianthryl Cryptand L1.** Yield: 73%. Decomposition above 210 °C. Anal. Calcd for C<sub>78</sub>H<sub>75</sub>N<sub>5</sub>O<sub>3</sub>: C, 82.90; H, 6.68; N, 6.20. Found: C, 82.76; H 6.73; N 6.03%. FAB-MS: m/z (%) 1131 (75) [**L**<sub>1</sub> + 1]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ 2.3 (m, 12 H), 3.3 (t, 6H), 3.5 (s, 6H), 4.1 (s, 6H), 4.3 (t, 6H), 6.6–8.4 (m, 39H).

**Trianthryl Cryptand L2.** Yield: 78%. Decomposition above 205° C. Anal. Calcd for  $C_{81}H_{81}N_5O_3$ : C, 83.01; H, 6.96; N, 5.97. Found: C, 83.11; H, 6.62; N, 6.01%. FAB-MS: m/z (%) 1172 (60)  $[L_2]^+$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  0.8 (m, 6H), 1.2 (t, 6H), 2.0 (t, 6H), 3.2 (t, 6H), 3.5 (s, 6H), 3.9 (s, 6H), 4.2 (s, 6H), 6.7–8.3 (m, 39H).

**Trianthryl Cryptand L<sub>3</sub>.** Yield: 75%. Decomposition above 210 °C. Anal. Calcd for C<sub>78</sub>H<sub>75</sub>N<sub>5</sub>O<sub>3</sub>: C, 82.90; H, 6.68; N, 6.20. Found: C, 82.76; H 6.73; N 6.03%. FAB-MS: m/z (%) 1130 (100) [**L**<sub>3</sub>]<sup>+</sup>. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ 2.2 (m, 12 H), 3.05 (sb, 12H), 3.9 (t, 6H), 4.2 (s, 6H), 6.3–8.5 (m, 39H).

Synthesis of Tri(2-nitrobenyl) Cryptand L<sub>4</sub>. Synthesis of L<sub>4</sub> was achieved by following the procedure adopted for trianthrylcryptands as a yellow crystalline solid. Yield: 75%. Mp: 201 °C. Anal. Calcd for C<sub>54</sub>H<sub>60</sub>N<sub>8</sub>O<sub>9</sub>: C, 67.26; H, 6.27; N, 11.62. Found: C, 67.12; H, 6.34; N, 11.52%. FAB-MS: m/z (%) 965 (100) [L<sub>4</sub> + 1]<sup>+</sup>. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  2.2 (sb, 12H), 3.2 (t, 6H), 3.6 (s, 12H), 4.2 (t, 6H), 6.9–7.8 (m, 24H).

Acknowledgment. Financial support for this work from the DAE (No. BARC/ApCD/BRNS/94/105 to P.K.B.), the DST (No. SP/S1/F-13/91 and IRHPA, No. 6P/S1/F-47/89 to P.K.B.), and CSIR, New Delhi, to S.G. is gratefully acknowledged. J.R. thanks CSIR for a fellowship. P.K.B. thanks the reviewers for excellent suggestions and constructive criticism of the work.

**Supporting Information Available:** Characterization of the  $L_1$ ,  $L_2$ ,  $L_3$ , and  $L_4$ , including <sup>1</sup>H NMR and FABMS, and UV spectral data (9 pages). See any current masthead page for ordering and Internet access instructions.

JA9713441