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Attachment of an Electron-Withdrawing Fluorophore to a Cryptand for Modulation of Fluorescence Signaling

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The laterally nonsymmetric aza cryptand synthesized by condensing tris(2-aminoethyl)amine (tren) with tris{2-[(3-(oxomethyl)phenyl)oxy]ethyl}amine readily forms mononuclear inclusion complexes with both transition- and main-group-metal ions. The fluorophore 7-nitrobenz-2-oxa-1,3-diazole is attached to one of the secondary amines, to give an integrated fluorophore–receptor configuration. The fluorophoric system does not show any appreciable emission when excited due to an efficient photoinduced intramolecular electron transfer (PET) from the nitrogen lone pair. When a metal ion enters the cavity, the PET is blocked, causing recovery of fluorescence; Cd(II) gives the highest quantum yield. The fluorophore, with π-accepting ability, drastically alters the binding property of the cryptand. With perchlorate or tetrafluoroborate salts of Cd(II), the metal ion enters the cavity, causing recovery of fluorescence. However, in the presence of coordinating ions such as Cl^-, N_3^-, and SCN^-, the metal ion comes out of the cavity, causing PET to take place once again, and the fluorescence is lost. Thus, translocation of Cd(II) between the inside and outside of the cryptand cavity can lead to a reversible fluorescence on/off situation.

Introduction

A large number of fluorescent signaling systems exploiting the photoinduced intramolecular electron transfer (PET) mechanism and metal ions as input are known.[1−8] These systems are designed to covalently link fluorophores to nitrogen atoms present in acyclic or macrocyclic receptors. In the metal-free state, the nitrogen lone pair is donated to the excited fluorophore via PET, and the excited fluorophore comes to the ground state through a nonradiative pathway, causing quenching of fluorescence.[9] When a metal ion engages this lone pair through bonding, the PET is blocked, leading to recovery of fluorescence. The desired architecture of a molecular fluorescent signaling system demands that the PET causing fluorescence quenching should be (i) very fast and efficient in the metal-free molecule, (ii) more or less completely prevented when the receptor accepts a metal ion as input, and (iii) the orientation of the fluorophore with respect to the metal ion in the cavity should lead to minimum spin−orbit coupling that facilitates the S−T intersystem crossing. A system with fluorescent on/off capability can potentially act as a molecular photonic switch, which is the most important component of any true photonic device. Many problems remain with crafting and operating such a device. The immediately realizable objective is, however, to build molecular systems exhibiting useful photonic properties that can be modulated. We have previously shown[10] that trianthryl derivatives of laterally nonsymmetric aza cryptands exhibit

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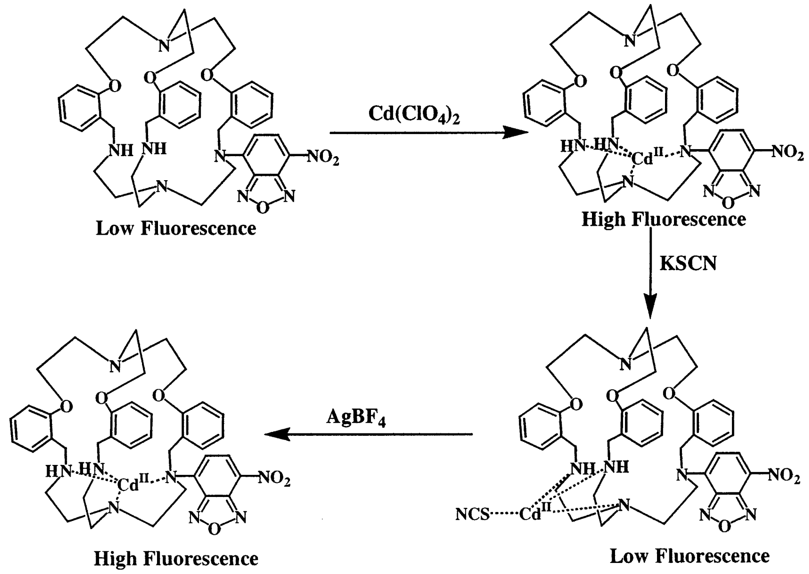
Scheme 1. Schematic Diagram of the Fluorophoric System **L** Showing Fluorescence Modulation upon Metal In and Metal Out



fluorescence enhancement in the presence of transition-metal ions with at least 1 order of magnitude higher quantum efficiency compared to known systems in the literature. We have also shown[11] that when a cryptand is attached to an electron-withdrawing group, a metal ion can translocate from inside to outside the cavity depending upon the nature of the counteranion. Putting these two ideas together, we have attached the fluorophore 7-nitrobenz-2-oxa-1,3-diazole with electron-withdrawing ability[12] to our cryptand. In this system, the secondary N atom acting as a donor is directly attached to the electron-withdrawing fluorophore acting as an electron acceptor. This is an example[13] of a "PET reagent" with a fluorescent on/off capability. It works well for Cd(II) ion, which acts as a reversible signal transducer (Scheme 1) due to translocation of the metal ion inside and outside the cryptand cavity depending upon the nature of the counteranion.

Experimental Section

Materials. All reagent grade chemicals were used without purification unless otherwise specified. The metal salts and tris(2-aminoethyl)amine were obtained from Aldrich. 4-Chloro-7-nitrobenz-2-oxa-1,3-diazole (4-chloro-7-nitrobenzofurazan) was obtained from Lancaster. Triethanolamine, salicylaldehyde, sodium borohydride, sodium hydroxide, anhydrous sodium sulfate, potassium carbonate, perchloric acid, and thionyl chloride were received from S. D. Fine Chemicals (India). Thionyl chloride and all the solvents were freshly distilled prior to use, and all the reactions were carried out under a N_2 atmosphere.

Synthesis. Cryptand $\mathbf{L_o}$ was synthesized as a colorless crystalline solid as reported[14] previously.

Cryptand L. To a suspension of $\mathbf{L_o}$ (1.12 g, 2 mmol) in dry toluene (100 mL) was added dropwise over a period of 3 h with constant stirring at 70 °C a solution of 4-chloro-7-nitrobenz-2-oxa-1,3-diazole (0.040 g, 0.2 mmol) in toluene (40 mL). After the addition was complete, the mixture was refluxed for 6 h, allowed to cool to room temperature, and finally kept overnight at ice temperature. Solids were removed by filtration, and the filtrate was evaporated using a rotary evaporator under reduced pressure to remove toluene. The red solid left behind was dried under vacuum. The desired product was purified further by being passed through a column (silica gel, 100−200 mesh) with a chloroform and methanol mixture (3:97 v/v) as eluent. Mp: 108 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS, ppm): (aliphatic) 2.66 (br, 6H), 2.83 (br, 6H), 3.78 (s, 6H), 4.19 (br, 12H), (aromatic) 6.93 (t, 4H), 7.10 (d, 6H) 7.3 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS, ppm): 157.0, 156.4, 145.5, 144.8, 144.4, 137.8, 136.3, 131.6, 130.0, 129.1, 123.3, 120.8, 120.5, 112.2, 111.1, 103.3, 79.245, 67.8, 66.9, 53.5, 52.9, 51.3, 46.0. FAB-MS (*m*/*z*): 723 (54%) [**L**]$^+$. Anal. Calcd for $C_{39}H_{46}N_8O_6$: C, 64.80; H, 6.41; N, 15.50. Found: C, 64.65; H, 6.49; N 15.44.

$[Cd(L_o)]\cdot(ClO_4)_2\cdot H_2O$, 1. To a stirring solution of $\mathbf{L_o}$ (0.56 g; 1 mmol) in 5 mL of acetone was added all at once $Cd(ClO_4)_2\cdot xH_2O$ (0.320 g, 1 mmol) dissolved in acetone (5 mL), and the resulting solution was stirred for 15 min at room temperature and filtered. The filtrate upon slow evaporation afforded colorless prismatic crystals suitable for X-ray crystallography. Yield: ~75%. Anal. Calcd for $C_{33}H_{47}N_5O_{12}Cl_2Cd$: C, 44.58; H, 5.33; N, 7.88. Found: C, 44.41; H, 5.44; N, 7.73.

Caution! Care should be taken while treating organic compounds with metal perchlorates as potentially explosive mixtures may be formed.

Measurements. The compounds were characterized by elemental analyses, ^{1}H NMR, ^{13}C NMR, and mass (positive ion) spectroscopy. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 FT (400 and 100 MHz, respectively) instrument in DMSO-d_6 with Me_4Si as the internal standard. 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 with an accelerating voltage of 10 kV, and the spectra were recorded at 298 K. Melting points were determined with an electrical melting point apparatus by PERFIT, India, and were uncorrected. FT-IR and elemental

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analyses were done at the microanalysis lab at Indian Institute of Technology, Kanpur. UV−vis spectra were recorded on a JASCO V-570 spectrophotometer in dry THF as well as other dried solvents at 298 K. Fluorescence spectra were obtained with a Perkin-Elmer LS 50B luminescence spectrometer at 298 K. The fluorescence quantum yield was determined[15] using quinine sulfate ($\phi_F = 0.54$) in 1 M H_2SO_4 as reference at a λ_{ex} of 350 nm. The standard quantum yield value thus obtained was used for the calculation of the quantum yield in each case by comparing the corrected spectrum with that of quinine sulfate by taking the area under the total emission. The error in ϕ_F is 15% for the free ligand, otherwise 10% in each case.

X-ray Structural Studies. Single-crystal X-ray data on **1** were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography*. The data integration and reduction were processed with SAINT[16] software. An empirical absorption correction was applied to the collected reflections with SADABS[17] using XPREP.[18] The structure was solved by the direct method using SHELXTL[19] and was refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[20] program package. All non-hydrogen atoms were refined anisotropically. The H atom positions or thermal parameters were not refined but were included in the structure factor calculations.

Results and Discussion

Compound **1** shows strong and broad absorption centered at 1100 cm^{-1} in the infrared spectra attributable[21] to the presence of perchlorate anion. To confirm that Cd(II) gets bonded inside the cavity, single-crystal X-ray analysis of **1** was carried out.[22] The structure of **1** consists of the cation $[Cd(\mathbf{L_o})]^{2+}$, two perchlorate anions, and a water molecule in the asymmetric unit. The metal ion enters the cavity and gets bonded to all of the eight donor atoms present (Figure 1). The bond distances and bond angles involving the metal ion are collected in Table 1. The conformation of the metal-bound cryptand is significantly distorted compared to that of the metal-free state although the bond distances and angles in the molecule lie within the normal range.

The two bridgehead N atoms show a distance of 4.978(4) Å, which is much closer compared to the distance of 6.249(5) Å in the free cryptand. The Cd−N distances span the range 2.382−2.518 Å, which is similar to the values found in other complexes[11,23] of Cd(II). However, the Cd−O distances (Table 1) are much longer compared[24] to those of other complexes of Cd(II) with oxygen donor ligands. This indicates that the metal ion preferentially goes to the N_4 end of the cavity.

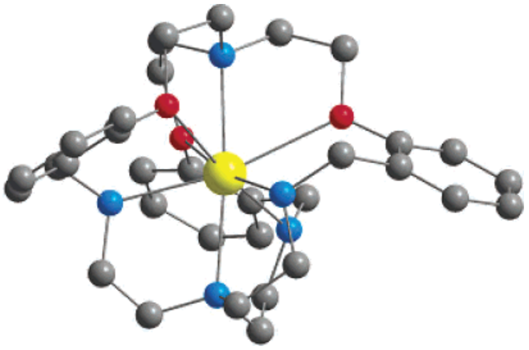

Figure 1. Structure of the Cd(II) cryptate of $\mathbf{L_o}$. Color code: Cd, yellow; O, red; N, blue; C, gray.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for the Complex $[Cd(\mathbf{L_o})](ClO_4)_2{\cdot}H_2O$, **1**

Cd1−N5	2.382(2)	N5−Cd1−N3	103.52(9)	N5−Cd1−N4	113.43(9)
Cd1−N3	2.400(2)	N3−Cd1−N4	116.92(10)	N5−Cd1−N1	110.65(9)
Cd1−N4	2.422(3)	N3−Cd1−N1	110.20(8)	N4−Cd1−N1	102.26(8)
Cd1−N1	2.465(2)	N5−Cd1−N2	71.65(10)	N3−Cd1−N2	73.29(9)
Cd1−N2	2.518(3)	N4−Cd1−N2	72.52(9)	N1−Cd1−N2	174.75(8)
Cd1−O1	2.635(2)	N5−Cd1−O1	173.35(8)	N3−Cd1−O1	72.17(7)
Cd1−O2	2.662(3)	N4−Cd1−O1	73.21(7)	N1−Cd1−O1	67.11(7)
Cd1−O3	2.757(5)	N2−Cd1−O1	111.15(9)		

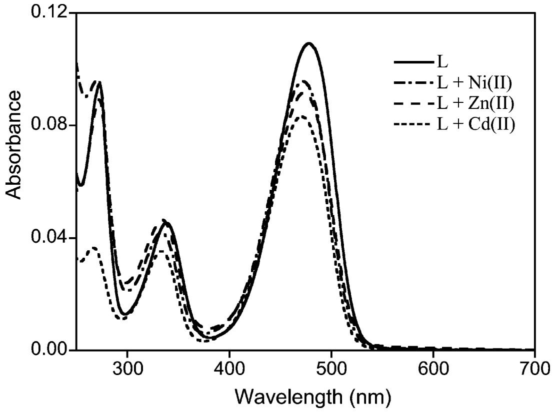

Figure 2. Absorption spectra of **L** alone and in the presence of Ni(II), Zn(II), and Cd(II) ions in dry THF at 1 × 10^{-5} M concentration.

UV−Vis Absorption Spectroscopy. The cryptand **L** exhibits absorption bands at 338 and 479 nm (Figure 2), where the unsubstituted cryptand $\mathbf{L_o}$ does not absorb. The lower energy absorption band ($\epsilon_{479} = 13034$ dm^3 mol^{-1} cm^{-1}) is assignable[25] to the intramolecular charge transfer (ICT) transition from the donor N atom of **L** to the acceptor nitro group of the 7-nitrobenzo-2-oxa-1,3-diazole moiety, which can accept the electron density in its available π symmetry orbitals. This ICT transition is found to be solvatochromic in nature ($\lambda_{max} = 460$ nm in hexane, which

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(22) Crystal data of **1**: $M_w = 889.06$ g mol^{-1}, monoclinic, space group $P2(1)/c$, $a = 9.7241(5)$ Å, $b = 21.0393(6)$ Å, $c = 17.8354(9)$ Å, $\alpha = 90.00°$, $\beta = 97.3540(10)°$, $\gamma = 90.00°$, $U = 3618.9(2)$ $Å^3$, $T = 100(2)$ K, $Z = 4$, $D_c = 1.632$ g cm^{-3}, $\mu = 0.822$ mm^{-1}, $F(000) = 1831.7$, crystal size 0.18 × 0.16 × 0.13 mm^3, total of 8469 reflections, 7466 unique, R1 = 0.0474, wR2 = 0.0986, with $I > 2\sigma(I)$, $S = 1.002$.

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Table 2. Emission Behavior of **L** in Various Solvents

solvent	λ_{abs}, nm (ϵ, dm^3 mol^{-1} cm^{-1})	λ_{em}, nm	ϕ_F
hexane	460 (nd)	503	nd
cyclohexane	461 (nd)	507	nd
toluene	474 (8909)	522	0.0343
1,4-dioxane	475 (6875)	524	0.0220
chloroform	481 (10561)	527	0.0168
dichloromethane	483 (12253)	528	0.0327
tetrahydrofuran	479 (13034)	523	0.0019
ethyl acetate	475 (12903)	524	0.0074
ethanol	479 (23234)	530	0.0067
methanol	481 (20185)	535	0.0083
acetone	483 (17558)	529	0.0031
acetonitrile	485 (12464)	530	0.0048
dimethylformamide	490 (25503)	534	0.0007
dimethyl sulfoxide	494 (26632)	540	0.0004

is 34 nm red-shifted in DMSO). The alkali and alkaline-earth metals do not show any change in the absorption as they occupy the upper deck of the cryptand. Complexation with transition- and heavy-metal ions, which occupy the lower deck (N_4 end), results in a small blue shift (6−12 nm) of the ICT transition, due to tying-up of the lone pair on the donor N atom. This small shift is because the cryptand is mostly preorganized and the conformational change is minimal when a metal ion enters the cavity as found[26] from our earlier X-ray crystallographic studies.

Fluorescence Studies. The ligand **L** shows a weak fluorescence although 4-chloro-7-nitrobenz-2-oxa-1,3-diazole is nonfluorescent in nature. This fluorescent behavior is due to inhibition of the intersystem crossing (ISC) that is operative in chloro-substituted compounds.[27] In dry THF, the emission band centered at 523 nm is due to the radiative decay of the charge transfer excited state and is solvatochromic in nature. The fluorescence intensity maximum is observed at 503 nm in hexane, whereas it is found at 540 nm in DMSO. However, this emission is low due to PET being operative from the HOMO of the donor tertiary N atom to the excited fluorophoric moiety. The fluorescence quantum yield (ϕ_F) is found to be higher in nonpolar than in polar solvents. This is because the PET process is considerably enhanced[28] in a polar medium due to charge−dipole and H-bonding interactions causing lower fluorescence quantum yield. The absorption and emission maxima and the fluorescence quantum yield (ϕ_F) of **L** in different solvents are given in Table 2.

Fluorescence in the Presence of Metal Ions. An enhancement of fluorescence occurs when a perchlorate/tetrafluoroborate salt of a transition/heavy-metal ion is added to **L** in dry THF medium due to disruption of the PET process. The emission band is slightly red-shifted with respect to that of the metal-free **L** as a result of a metal ion induced change in polarity around the fluorophore. Fluorescence enhancement is found to be rather small with a transition-metal ion. However, among the 3d-transition-metal ions studied, Zn(II) shows the highest enhancement because of its nonquenching nature. Heavy-metal ions such as Ag(I), Cd(II), and Pb(II) exhibit appreciable enhancement. Among all metal ions studied, Cd(II) shows maximum enhancement with respect to the metal-free **L** (~240-fold). Solution complexation studies with $\mathbf{L_0}$ and Cd(II) indicate[29] that the metal ion forms a very stable inclusion complex. On titration with Cd(II), the intensity of the emission band gradually increases and attains the maximum on the addition of 1 equiv of metal ion. The ϕ_F vs stoichiometry plot with Cd(II) indicates 1:1 complex formation (Figure 3).

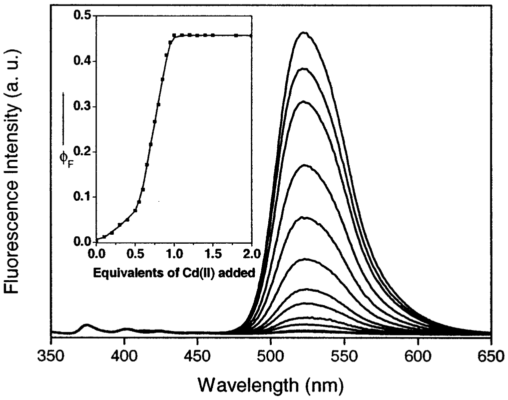

Figure 3. Corrected fluorescence spectra (λ_{ex} = 338 nm) of the ligand **L** (concentration 3.2 × 10^{-6} M) in the presence of a stoichiometric amount of Cd(II) ion in dry THF. Inset: ϕ_F vs the number of equivalents of Cd(II) added to **L**.

The fluorescence quantum yields and extent of enhancements are collected in Table 3. When coordinating anions such as Cl$^-$, SCN$^-$, or N$_3^-$ are added to the solution containing Cd(II) and ligand **L**, the fluorescence is completely quenched. This is due to the fact that in the presence of any of these anions, the metal comes out of the cavity and prefers to bind the receptor from the outside,[11] away from the electron-withdrawing fluorophore. So, the lone pair on the donor nitrogen atom is no longer engaged to the metal, causing restoration of the PET and quenching of the fluorescence (Table 3). The extent of quenching depends on the coordinating ability of the counteranion toward Cd(II). Among all the counteranions used, SCN$^-$ exhibits the lowest fluorescence quantum yield (ϕ_F = 0.0058), lowering the emission almost to the level of **L** alone (Figure 4). When AgBF$_4$ is added to the solution of **L** containing Cd(II) and SCN$^-$ (ϕ_F = 0.0058), the fluorescence is mostly recovered. This is because the Ag(I) binds SCN$^-$ preferably over Cd(II) and the Cd(II) is left with BF$_4^-$ anion, enabling it to enter the cavity, engage the lone pair on the N atom, and snap the PET process. The excess Ag(I) present in the solution was removed by adding NaCl in aqueous THF. Fluorescence recovery (ϕ_F = 0.3326) in this process is much higher compared to the situation when AgBF$_4$ is added to **L** (ϕ_F = 0.1503). This confirms that the enhancement is due to Cd(II) entering the cavity. However, the enhancement is still lower

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Table 3. Fluorescence Quantum Yield of **L** in the Presence of Different Ionic Inputs[a]

ionic input	solvent	ϕ_F	fluorescence enhancement
	THF	0.00189	1 (standard)
	THF:H_2O = 9.5:0.5	0.00192	~1
Mn(II)	THF	0.1387	74
Fe(II)	THF	0.1200	64
Co(II)	THF	0.0842	45
Ni(II)	THF	0.04538	24
Cu(II)	THF	0.05791	31
Zn(II)	THF	0.18008	95
Ag(I)	THF	0.1503	80
Pb(II)	THF	0.2088	111
Cd(II)	THF	0.4567	242
H^+	THF	0.02784	14
2,6-di-*tert*-butylpyridine (DBP)	THF	0.0019	~1
Cd(II) + KSCN	THF	0.00576	3
Cd(II) + KSCN	THF:H_2O = 9.5:0.5	0.00559	3
Cd(II) + NaN_3	THF:H_2O = 9.5:0.5	0.01751	9
Cd(II) + NH_4PF_6	THF	0.32459	172
Cd(II) + NaCl	THF:H_2O = 9.5:0.5	0.0536	28
Cd(II) + KSCN + Ag(I)	THF	0.3326	175
Cd(II) + KSCN + Ag(I) + NaCl	THF:H_2O = 9.5:0.5	0.3497	185
Cd(II) + KSCN + Ag(I) + DBP	THF	0.38178	202
Cd(II) + KSCN + Ag(I) + DBP + NaCl	THF:H_2O = 9.5:0.5	0.442	234

[a] Experimental conditions: medium, dry THF; concentration of free ligand, 3.2×10^{-6} M; concentration of ionic input, 3×10^{-5} M; $\lambda_{ex} = 338$ nm; excitation band-pass, 5 nm; emission band-pass, 5 nm; temperature, 298 K. ϕ_F is calculated by comparison of the corrected fluorescence spectrum with that of quinine sulfate in 1 N H_2SO_4 ($\phi = 0.54$) by taking the area under the total emission.

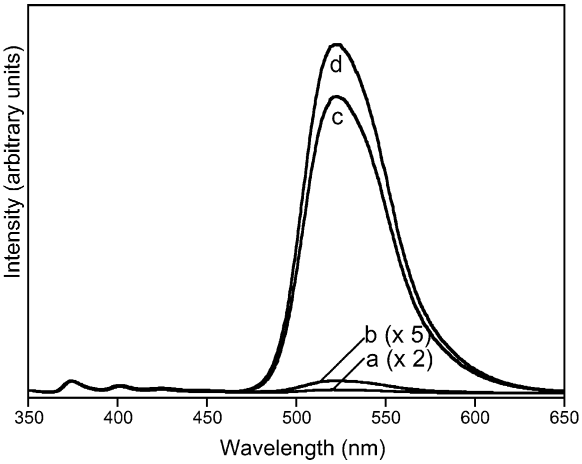

Figure 4. Fluorescence spectra of **L** (a) alone and (d) in the presence of Cd(II) in dry THF at 3.2×10^{-6} M concentration. When KSCN is added, the emission comes back to (b), and on further addition of Ag(I) fluorescence enhancement results (c).

compared to the situation when $Cd(ClO_4)_2$ is added to **L**, which could be due to protons generated in the system. Interestingly, when we add $AgBF_4$ to the solution of **L** containing Cd(II) and SCN^- ($\phi_F = 0.0058$) followed by NaCl in aqueous THF in the presence of a noncoordinating base such as di-*tert*-butylpyridine, the fluorescence recovery is almost the same ($\phi_F = 0.442$) as was initially obtained upon Cd(II) inclusion.

Controlled Experiments. The metal perchlorate salts are hydrated and can generate protons in organic solvents. The generated protons can engage the lone pair on N through protonation, causing fluorescence enhancement. To verify that the fluorescence enhancement is due to the metal ion and not because of protonation, certain controlled experiments were carried out. In the metal-free state, the ϕ_{FT} does not change or increases by a negligible amount on changing the solvent from dry THF to aqueous THF (THF:H_2O = 9:1 v/v). In the presence of $HClO_4$ (1×10^{-3} M), the fluorescence is enhanced by a factor of 14 in dry or aqueous THF medium. Moreover, different metal ions give different extents of enhancement. If the proton generation in the medium by the metal salts were responsible, then the extent of enhancement should have been almost the same in all the cases.

Conclusion

In conclusion, we find that when the cryptand is functionalized with an electron-withdrawing fluorophore, it behaves as a fluorescence on/off signaling system by translocating Cd(II) inside and outside the cryptand cavity. This translocation is engineered by varying coordinating tendencies of the counteranions. We are presently probing some other fluorescence on/off signaling systems based on acyclic receptors. This system can also be made potentially useful as an anion sensor. We are presently working in this direction.

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Supporting Information Available: Crystallographic data of **1** (CIF) and characterization of the ligand **L** including FABMS, ^{13}C NMR, ^{1}H NMR, and UV−vis spectral data and fluorescence spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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