Ni(II), Cu(II), and Zn(II) Cryptate-Enhanced Fluorescence of a Trianthrylcryptand: A Potential Molecular Photonic OR Operator

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Received July 27, 1995

Molecular systems that combine binding ability and photochemical/photophysical properties are of great interest for designing chemosensors[1] and molecular devices.[2] A photonic molecular device is defined as an assembly of molecular components that, because of the specific arrangement of the components in the dimensions of space and energy, is able to perform light-induced functions. A number of crown ether-based systems have been studied as YES, NO logic functions or as AND, OR logic gates.[2−4] Recently, many investigations have been done on chelation-enhanced fluorescence[5−14] to make chemosensors. While most of these studies have been carried out in nonaqueous solvents, chemosensors that are functional in wholly aqueous media have been known[15] for some time and were recently reviewed by Czarnik.[14b] In all these systems, complexation by non-transition-metal ions or protonation of the amino groups present enhances the fluorescence quantum yield, as fluorescence quenching due to photoinduced intramolecular electron transfer (PIET) in the receptor molecule will no longer be operative. Transition-metal-based molecular fluorescent signaling systems are not available but are eagerly awaited.[2,16] These systems would be useful not only as real-time and real-space monitoring devices in biology but also as versatile molecular switching devices. Transition metal ions are known to effectively quench fluorescence.[17,18] We present here the first system where transition metal ions Cu(II) and Ni(II), along with H$^+$ and Zn(II) ions, cause enhancement of fluorescence.

To improve the fluorescence intensity enhancement of the receptor upon binding of cations, one needs to carefully design the receptor molecule containing a fluorophore (or, better still, more than one fluorophore[19]) so that the PIET responsible for fluorescence quenching is maximized in the receptor, whereas PIET is minimized in the cation-bound state of the receptor. In the present communication, we report a cryptand (Figure 2) containing[20] three anthryl moieties (**1**) that is capable of functioning as a very efficient multiinput OR logic gate (Figure 1b). The high efficiency of PIET in the cryptand from the tertiary N atoms to anthracene moieties should be ascribed to its special geometry, where overlap factor through space as well as through bonds is greatly enhanced, to reduce the ϕ_F to a value of 0.001 (reduction factor is about 300, when compared to free anthracene in THF under the same experimental conditions).

The input species are found to be Ni(II), Cu(II), and Zn(II) (as hydrated perchlorate salts) in THF medium and H$^+$ and NH$_4^+$ in THF/H$_2$O medium (9:1 v/v). The metal ions, Ni(II), Cu(II), and Zn(II), bind in the lower region of the molecule designated A and tie-up the lone pairs, thus stopping PIET. Alkali/alkaline earth metal ions are found to be totally ineffective to enhance the fluorescence intensity. This report shows for the first time that Cu(II) and Ni(II) can be used for large enhancement ($>$200-fold) of the fluorescence intensity (Table 1). When no ion is added in the THF/H$_2$O (9:1) medium, ϕ_F increases by a negligible factor of 1.2. When Cu(II) or Ni(II) or Zn(II) ion is added as the hydrated perchlorate salt in THF/H$_2$O (9:1) medium, ϕ_F increases only by a factor of 25−35 and remains unchanged even after 40 h. This could be due to partial protonation of the nitrogens in the cryptand unit as a result of generation of protons upon addition of a metal ion in the aqueous THF medium. However, addition of H$^+$ in the form of HCl increases the ϕ_F value by a factor of 187. The fluorescence spectrum of the cation-bound cryptand undergoes a slight red shift and a slight loss of vibrational features (Figure 3) compared to that of the free cryptand.

In all other previous studies, it has been reported that transition metal ions decrease the fluorescence quite effectively.[16−18]

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[20] The synthesis of the cryptand (N_5O_3) using Cs(I) ion as the template has been published (Ragunathan, K. G.; Bharadwaj, P. K. *Tetrahedron Lett.* **1993**, *34*, 7581−7584). The molecule crystallizes in the triclinic space group $P\bar{1}$, with $a = 10.133(2)$, $b = 11.972(3)$, and $c = 13.433(3)$ Å; $\alpha = 106.69(2)$, $\beta = 90.93(2)$, and $\gamma = 91.38(2)°$; $Z = 2$, $R_f = 0.054$, $R_{wf} = 0.061$, and GOF = 1.891. The trianthracenyl derivative has been prepared by refluxing the cryptand with 9-(bromomethyl)anthracene in the presence of K_2CO_3 and a catalytic amount of KI in dry acetonitrile medium, followed by the usual workup. Yield, 73%. The compound was recrystallized from 1:1 THF/*n*-propanol as a colorless crystalline solid. Anal. Calcd for $C_{78}H_{75}N_5O_3$: C, 82.90; H, 6.64; N, 6.20. Found: C, 82.76, H, 6.73; N, 6.03. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.25 (m, 12H); 3.25 (t, 6H); 3.45 (s, 6H); 4.10 (s, 6H); 4.30 (t, 6H); 6.6−8.4 (m, 39H). FABMS: *m/z* 1130 (M + 1). The Ni(II) cryptate crystallized with the formula $[(N_5O_3)Ni(MeCN)(H_2O)]\cdot 2ClO_4$ in moist MeCN gives $a = 13.937(3)$, $b = 14.547(3)$, and $c = 22.951(5)$ Å; space group $P2_12_12_1$; $Z = 4$; $R_f = 0.06$, $R_{wf} = 0.05$, and GOF = 2.87. The Ni(II) ion is hexacoordinated with bonding from four nitrogens inside the end of the cavity designated (A). The fifth and sixth coordination sites are occupied by the O of the H_2O inside the N atom of the MeCN molecule from outside the cavity. The Cu(II) ion (based on spectroscopic studies) is also found to occupy the same end of the cavity in both the N_5O_3 and 1 (Ghosh, P.; Bharadwaj, P. K., to be published).

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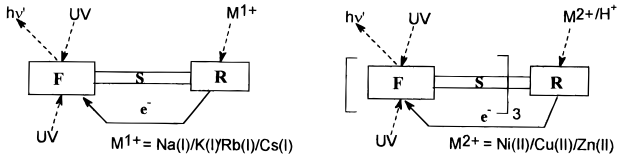

(1a) **(1b)**

Figure 1. Plan of molecular photonic OR gate. F, fluorophore; S, spacer; R, receptor. (a) An OR gate and (b) a higher generation OR gate. The upper portion of each figure indicates cation bound state, and the lower portion indicates cation free state.

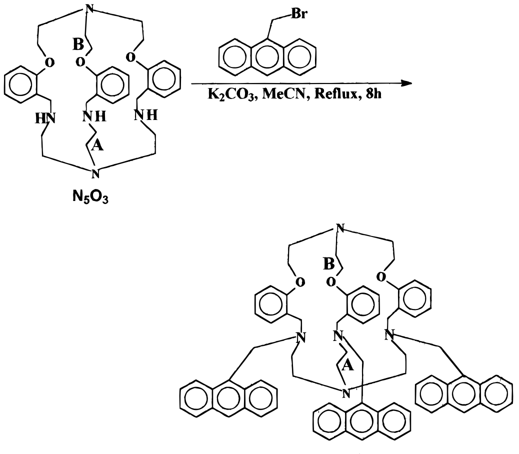

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Figure 2. Synthetic scheme for **1**.

Table 1. Fluorescence Output of the Cryptand with Different Cation Input[a]

medium	ionic input (concn, μ)	fluorescence output (quantum yield, ϕ_F)[24]	fluorescence enhancement factor
THF		0.001	1.0 (standard)
THF/H_2O (9:1)		0.0012	1.2
THF/H_2O (4:6)		0.009	9.0
THF	Zn(II) (0.5×10^{-5})	0.052	52
THF	Zn(II) (1×10^{-5})	0.088	88
THF	Zn(II) (5×10^{-5})	0.108	108
THF	Zn(II) (1×10^{-4})	0.117	117
THF	Zn(II) (1×10^{-3})	0.218	218
THF	Zn(II) (1×10^{-2})	0.329	329
THF	Ni(II) (1×10^{-2})	0.227	227
THF	Cu(II) (1×10^{-2})	0.283	283
THF/H_2O (9:1)	HCl (1×10^{-2})	0.187	187
THF/H_2O (9:1)	NH_4^+ (1×10^{-2})	0.021	21

[a] Experimental conditions: 10^{-5} M the cryptand dissolved in the medium, excited at 360 nm with excitation bandpass of 5 nm; emission bandpass, 5 nm; temperature, 298 K; ϕ_F calculated by comparison of corrected spectrum with that of anthracene ($\phi_F = 0.297$), taking the area under the total emission.

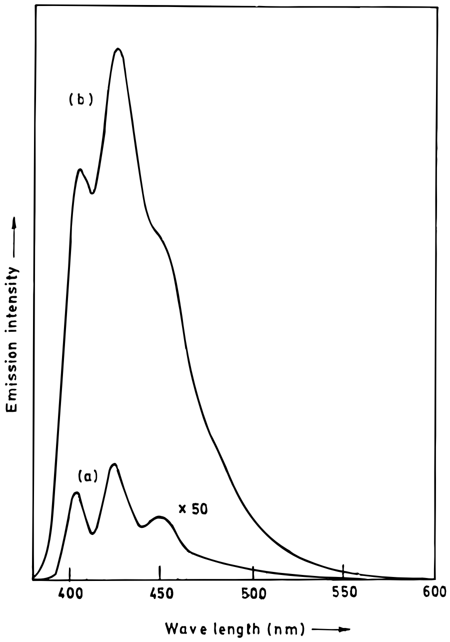

Figure 3. Emission spectra of free **1** (a) and its Zn(II) complex (b).

Several distinct processes, *viz.*, the magnetic perturbations, redox activity, electronic enegy transfer, etc., have been invoked[17] in the past to rationalize fluorescence quenching by transition metal ions. In the present case, obviously none of these processes are operational. We believe this is due to the special topology of the host cryptand molecule. The X-ray structures of the free cryptand and its Ni(II) complex[20] indicate that the cryptand is largely preorganized before complexation and imposes an unusual geometry on the metal ion. Due to the strong cryptate effect,[21] the redox activity of the metal ion is suppressed, as donor atoms' rearrangement upon oxidation/reduction is energetically quite unfavorable. We have not observed any significant oxidative or reductive waves in the cyclic voltammogram of either Cu(II) or Ni(II) cryptate in the range −1.0 to +1.0 V (*vs* SCE). The magnetic perturbations or electronic energy transfer mechanisms will be operative when there is a substantial amount of covalency[22] in the metal−ligand bonds. In the present case, the nitrogen donors behave as hard donors, resulting in less covalency of the metal−ligand bonds. This is also reflected in the cyclic voltammetric results of Cu(II) and Ni(II) cryptates. The EPR spectrum of the Cu(II) cryptate shows an axial signal with very small ($A_{\parallel} = 60 \times 10^{-4}$ cm^{-1}) hyperfine coupling; however, it can be attributed[23] to the hybridized state of the Cu(II) ion rather than covalency of the metal−ligand bond.

In summary, we have shown for the first time that transition metal ions like Cu(II) and Ni(II) do not quench fluorescence in a trianthrylcryptand system. The mechanism(s) responsible for the observed effect can be ascertained by detailed photophysical studies on this and related systems with a host of transition metal ions. We have synthesized a number of similar cryptand-based systems with varying cavity size and shape to probe them with a number of transition/non-transition-metal ions. These systems will be compared with tripodal-based systems to sort out whether the cryptate effect plays any role in enhancing fluorescence.

Acknowledgment. Financial support from the DSTRDAE (to P.K.B.) and CSIR (to S.G.) is gratefully acknowledged. X-ray work has been done at the National X-ray Diffraction Facility, Department of Chemistry, IIT Kanpur, funded by the DST. P.K.B. wishes to express his sincere thanks to the referees for excellent suggestions and constructive criticism of the work.

Supporting Information Available: Experimental details for the synthesis and characterization of **1**, including ^{1}H-NMR and FABMS; characterization of N_5O_3, including ^{1}H-NMR and ORTEP drawings of N_5O_3 and its Ni(II) complex (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA952520D

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