Development of Efficient Fluorosensors for the Transition Metal Ions by Tuning of Photoinduced Intramolecular Electron Transfer (PIET) Communication between the Components

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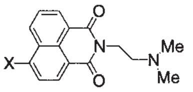
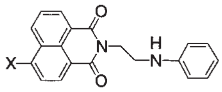
4-Methoxy-1,8-naphthalimide derivatives, **1** and **2**, with improved PIET interaction, show significant fluorescence enhancement in the presence of transition metal ions.

Systems capable of performing light induced logic operations such as sensing of a guest are considered to be quite useful in a variety of applications and there is a great deal of current interest in the development of fluorosensors for various guest species such as protons, metal ions, anions, neutral molecules, etc.[1,2] Photoinduced intramolecular electron transfer (PIET) is the most commonly exploited mechanism for the design of the fluorosensors that are essentially multi-component systems comprising a signaling unit (fluorophore) and a guest binding site (receptor); the two are often separated by a spacer unit.[2] In the present systems, the components are chosen such that in the absence of the metal ions PIET communication between the fluorophore and receptor quenches the fluorescence of the system (fluorescence off state). However, in the presence of a guest that binds to the receptor moiety, engaging the lone pair of electrons, the PIET communication between the fluorophore and receptor gets cut-off, leading to the fluorescence recovery of the sensor system (fluorescence on state). In general, the efficiency of the PIET interaction between the fluorophore and the receptor in the unbound state of a system plays a crucial role towards its signaling performance and the same can be modulated to achieve the maximum communication by changing the electronic nature of the substituents on the either side. Basically, we have considered herein, how and to what extent the modulation of the PIET communication between the components in the unbound state helps in the designing of an efficient sensor system for transition metal ions, notorious quenchers of common organic fluorophores.[3]

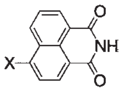
We have recently reported the sensing behavior of **3**, **4** and few other systems towards the transition metal ions and protons.[4] The fluorescence enhancement data (FE) of these systems, especially for **3**, is too low to be considered as fluorescence switches for the transition metal ions (Table 1). We ascribe this failure to be due to two major reasons; an inefficient PIET in the systems and high quenching interaction between the electron rich fluorophore, 4-amino-1,8-naphthlimide (**5**) and the metal ions.[4] The present situation can be overridden simply by choosing a structurally similar but electronically deficient fluorophore, 4-methoxy-1,8-naphthalimide (**6**) in which a strongly donating 4-amino group of **5** is replaced with a weakly donating methoxy group, in the construction of multi-component fluorosensors.[5] Further, it may be noted that the higher singlet energy of **6** is also expected to enhance the PIET communication and hence the overall performance.[6]



1; X = OMe
3; X = NH_2



2; X = OMe
4; X = NH_2



5; X = NH_2
6; X = OMe

The fluorescence spectra of **1** and **2** are broad and devoid of any vibronic structure, characteristic of intramolecular charge transfer (ICT) emitting state.[4,5] The attachment of the spacer and receptor moieties results in the reduction of the fluorescence quantum yield compared to that of **6** by a factor of ca. 26 in **1** and 680 in **2** in acetonitrile. The extent of PIET communication in these systems is fairly high when compared to that in **3** (1.3) and in

Table 1. Fluorescence response of **1**, **2**, **3**, and **4** as a function of different metal ion input in acetonitrile[a].

Metal Ion	**1**		**2**		**3**		**4**	
	$[M]^b$ (M)	$FE^{c,d}$	$[M]^b$ (M)	$FE^{c,d}$	$[M]^b$ (M)	$FE^{c,d}$	$[M]^b$ (M)	$FE^{c,d}$
Cr^{3+}	5.0×10^{-4}	25	4.3×10^{-3}	110	4.3×10^{-5}	1.1	3.0×10^{-3}	8.0
Mn^{2+}	6.0×10^{-4}	21	2.0×10^{-3}	60	8.5×10^{-5}	1.5	6.0×10^{-4}	14
Fe^{2+}	3.9×10^{-4}	15	3.9×10^{-4}	400	2.6×10^{-5}	1.1	2.2×10^{-4}	21
Co^{2+}	4.7×10^{-4}	26	4.7×10^{-3}	6.0	1.1×10^{-5}	1.1	3.1×10^{-4}	15
Ni^{2+}	7.1×10^{-4}	27	2.0×10^{-3}	5.5	1.7×10^{-5}	1.1	1.0×10^{-3}	5.0
Cu^{2+}	3.5×10^{-4}	23	2.3×10^{-4}	50	2.6×10^{-5}	1.2	8.8×10^{-4}	7.0
Zn^{2+}	3.3×10^{-4}	28	5.5×10^{-4}	500	2.2×10^{-4}	1.3	5.7×10^{-3}	2.0

[a]Experimental conditions: ~ 2.0×10^{-5} M solution of the compounds in acetonitrile was used at 298 K, λ_{ex} = 350 nm for **1** and **2** and 425 nm for **3** and **4**, excitation and emission bandwidths were 3 nm. [b]Represents the concentration of the metal ion for which the maximum FE was observed, any further increase in concentration led to fluorescence quenching. [c]With reference to the fluorescence intensity of the respective compounds in the absence of the metal ions. [d]±5%.

4 (32), respectively. The driving force (ΔG^*) for the PIET process that was estimated from the measured redox potentials of the couples using the Weller equation [$\Delta G^* = E_{ox}(R) - E_{red}(F) - E_{0,0}$] is more negative for **1** and **2**.[6] The measured fluorescence decay profiles could only fitted to a biexponential expression indicating the presence of two components; one with a short lifetime, in which the proximity of the fluorophore and receptor results in the quenching and the other, with long-lifetime, in which spatial distribution of the two is unfavorable for PIET and a through space fluorescence quenching mechanism is proposed.[4,5] The high percentages of short-lived components observed in the case of **1** and **2** also confirm the efficient PIET communication in the systems.[7]

The fluorescence spectra of **1** in the presence of various concentrations of Co^{2+} are illustrated in Figure 1 and FE data for **1**, **2**, **3** and **4** are depicted in Table 1. The metal ion induced FE is associated with a red shift of the fluorescence band maximum probably due to a redistribution of the charge densities in the fluorophore upon metal ion binding to the receptor.[2c,8] The insignificant effect of the metal ions on the fluorescence band maxima of the parent fluorophore reveals that the shift dose not originate from the metal ion induced change in the polarity of the medium but from an interaction of the metal ions involving both the receptor and the fluorophore.[2c,8]

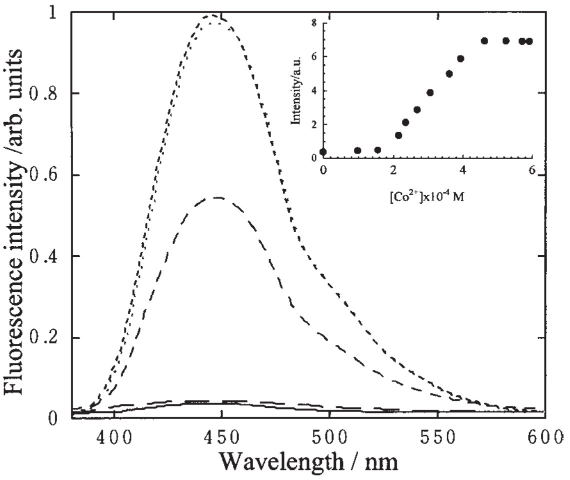


Figure 1. Fluorescence spectra of **1** ($\sim 2.0 \times 10^{-5}$ M) in acetonitrile in the presence of various concentrations of $Co(H_2O)_6(NO_3)_2$. Co^{2+} concentrations, in increasing order of the fluorescence intensity, are 0, 1.6×10^{-4}, 3.1×10^{-4}, 6.3×10^{-4}, and 4.7×10^{-4} M. $\lambda_{ex} = 350$ nm. The inset shows the correlation graph plotted for the metal ion concentration versus the fluorescence intensity.

The FE values of **1** and **2** presented in the Table 1 are very high when compared to **3** and **4** respectively, in the presence of any metal ion studied. This is due to an enhanced PIET in the unbound state of **1** and **2**. The maximum FE values, 28 and 500 (almost 100% recovery), are observed for **1** and **2**, respectively in the presence of non-quenching metal ion, Zn^{2+}. It is quite interesting to note here that other notable fluorescence quenching metal ions also display quite high FE values (Table 1). Further it can be seen that the quenching influence of the metal ions is more visible in the case of **3** and **4** with inefficient PIET interaction than in **1** and **2**.

In summary, we have shown herein, the fine-tuning of the PIET communication between the components of the simple multi-component systems provides an efficient signaling system for the transition metal ions. Further, for the first time, high fluorescence enhancement in the presence of metal ions such as Fe^{2+} and Cr^{3+}, known for their high quenching abilities,[3] has been observed.

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References and Notes

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6 The E_{ox} for triethylamine and *N*-methylaniline are 0.49 and 0.50 V respectively, Ref 9. The measured E_{red} values of **5** and **6** are -1.61 and -1.11 V respectively. $E_{0,0}$ values, estimated from the fluorescence band maxima of the fluorophore, **5** and **6** are 55.04 and 65.3 kcal mol^{-1} respectively. The estimated ΔG^* values are -28.4 kcal mol^{-1} for **1**, -28.2 kcal mol^{-1} for **2**, -6.6 kcal mol^{-1} for **3** and -6.4 kcal mol^{-1} for **4**, in acetonitrile.

7 The percentages of the short-lived components are 97, 90, 2 and 70 for **1**, **2**, **3** and **4** respectively.

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