Modulation of metal–fluorophore communication to develop structurally simple fluorescent sensors for transition metal ions

B. Ramachandram and A. Samanta*

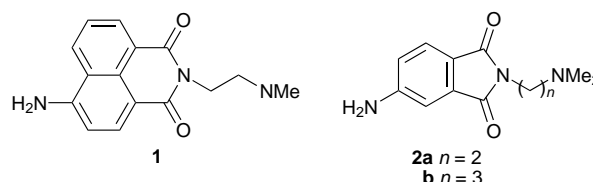*School of Chemistry, University of Hyderabad, Hyderabad 500 046, India*

Fluorophores 2a and 2b show significant fluorescence enhancement in the presence of transition metal ions.

Molecular systems that contain a guest binding site (receptor) and a photon interaction site (fluorophore) as components with a mechanism of communication between the two are considered useful as chemosensors or molecular switching devices.[1–6] A variety of photoinduced electron transfer (PET) chemosensors in 'Fluorophore–Spacer–Receptor' format have been developed in recent years[1–5] which perform light-induced simple YES or NO logic operations and hence may find application as photonic molecular devices in molecular information processing. While the majority of these chemosensors possess one input and one output functionality, logic systems with two input devices which act as AND gates are also reported.[3]

While molecular signalling systems for several ions have been available for some time, only very recently an anthracene derivative with a cryptand receptor has been developed by Ghosh *et al.* that is described as the first sensor for transition metal ions such as Ni^{II} and Cu^{II}.[4] In the PET sensing mechanism, the receptor–fluorophore interaction 'switches off' the fluorescence and the 'switching on' takes place in the presence of a guest (usually protons or metal ions) when the fluorophore is released as a result of guest binding with the receptor. Therefore, the fluorescence sensing mechanism requires the metal ion (M)–fluorophore (F) communication to be less than the M–receptor (R) interaction. Obviously, for transition metal ions, which are efficient quenchers for organic fluorophores, the M–F communication is too strong compared with the other interaction for commonly used receptors. The recent success of Ghosh *et al.* has been ascribed to the special topology of the cryptand receptor that binds M more strongly within the cavity making it unavailable for fluorescence quenching.[4] In other words, the M–R interaction has been increased to reduce indirectly the communication between M and F. We find that no attempt has been made to find out whether direct manipulation of the M–F communication can be made to develop fluorescent sensors or switches for the transition metal ions. Since redox interaction between F and M is one of the important quenching mechanisms,[7] it should be possible to reduce this communication simply by making the fluorophore more electron deficient either by suitable substitution or simple structural modifications. Such modification not only minimises the redox activity between M and F in the metal-bound state but also enhances PET in the unbound state, both favouring an increase in the efficiency of the system. Since no studies based on this approach have been reported, the following work was undertaken.

The proton sensory behaviour of some compounds related to **1** is reported in the literature with low fluorescence enhance-

ment (FE) values.[8] The fluorescence outputs of **1**† in the presence of some transition metal ions are collected in Table 1. These values are too low to consider this system as a possible fluorescent switch for d-block transition metal ions. We ascribe this failure partly to inefficient PET[9] and partly to the quenching interaction between M and F. Since, according to our rationale, both these drawbacks can be rectified by choosing a structurally similar but relatively electronically deficient fluorophore, 4-aminophthalimide (AP),‡ much improved switching functions are expected from **2a** and **2b**. Further, it may be noted that the higher singlet energy of these derivatives is also expected to enhance PET and hence their performance.

The fluorescence spectra of **2a** and **2b**† are characterised by broad bands typical of an intramolecular charge transfer transition within the fluorophore.[10] Attachment of the spacer and receptor results in a reduction of the fluorescence quantum yield of the original fluorophore, AP by a factor of *ca.* 50 in **2a** and 27 in **2b** in acetonitrile§ which is a clear indication of PET in both cases. The driving force (ΔG^*) for the PET process, estimated from the measured redox potentials of the couples

Table 1 Fluorescence output of **1**, **2a** and **2b** as a function of different metal ion input[a]

Input metal ion[b]	**1**		**2a**		**2b**	
	[M]/ mol dm^{-3}[c]	Output[d] FE	[M]/ mol dm^{-3}[c]	Output[d] FE	[M]/ mol dm^{-3}[c]	Output[d] FE
Cr^{III}	4.3×10^{-5}	1.1	1.2×10^{-4}	39	1.1×10^{-4}	25
Fe^{III}	2.6×10^{-5}	1.1	1.0×10^{-4}	34	1.0×10^{-4}	27
Co^{II}	1.1×10^{-5}	1.1	1.9×10^{-4}	38	9.2×10^{-4}	12
Ni^{II}	1.7×10^{-5}	1.1	3.0×10^{-4}	37	1.8×10^{-2}	22
Cu^{II}	2.6×10^{-5}	1.2	2.7×10^{-4}	41	4.0×10^{-4}	27
Zn^{II}	2.2×10^{-4}	1.3	3.9×10^{-4}	55	6.8×10^{-4}	30

[a] Experimental conditions: *ca.* 5×10^{-5} mol dm^{-3} acetonitrile solution of the compounds was used, at 298 K, λ_{exc} = 425 nm for **1** and 400 nm for **2a** and **2b**, excitation and emission band widths were 3 nm. [b] The salts used for the experiments were $CrCl_3 \cdot 6H_2O$, $FeCl_3$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(ClO_4)_2 \cdot 6H_2O$. [c] Represents the concentration of the metal ion for which FE was maximum, any further increase in concentration beyond this led to fluorescence quenching. [d] With reference to the fluorescence intensity of the respective compound in the absence of metal ion.

using the Weller equation [$\Delta G^* = E_{ox}$ (R) $- E_{red}$ (F) $- E_{0,0}$] is more negative for **2** [-6.6 kcal mol^{-1} for **1** and -12.7 kcal mol^{-1} for **2** in acetonitrile (1 cal = 4.184 J)].¶ Since the fluorescence decay curves of **2a** and **2b** are biexponential‖ with one short component representing the lifetime of the PET quenched state and a long-lived component whose lifetime is very similar in magnitude to that of the methylated AP, a through-space quenching mechanism with two dominant configurations of the fluorophore is suggested; one in which proximity of the fluorophore and receptor results in quenching and the other in which spatial distribution of the two is unfavourable for PET.

Fig. 1 illustrates the effect of the addition of metal ions on the fluorescence intensity of the compounds. As can be seen, beyond a certain concentration of the metal ion (values of which are indicated in Table 1 for each metal ion) the quenching influence starts becoming visible. The metal ion induced FE is associated with a shift of the fluorescence maximum. Similar shifts with these metal ions are also observed in the case of **1** and **2b**. Since metal ion addition to solutions of AP or 1,8-naphthalimide (ANP) did not produce any shift, the shift does not originate from a change in the polarity of the environment. Further, it also clearly indicates that the M–F interaction alone is not responsible for the shift. Therefore, we conclude that the shift arises from an interaction of the metal ion involving both the receptor and the fluorophore.

The FE values of **2a** and **2b** with the metal ions, collected in Table 1, are large enough to consider these simple systems as efficient fluorosensors for transition metal ions. A comparatively larger FE value for **2a** (for any given metal ion) is due to enhanced PET in the unbound state because of a favourable conformation. The maximum FE value is observed with Zn^{II} due to its non-quenching nature. The fluorescence recovery in this case is nearly 100%. It is gratifying to note a 35-fold enhancement even in the case of Fe^{III}, reported to be the most quenching transition metal ion[7] and for which no reported FE data has come to our notice. Further, it can be seen that the quenching influence of the metal ions is more visible at a lower concentration in the case of electron rich **1** than with electron deficient **2a** or **2b**. This is a reflection of the modification of redox activity between M and R.

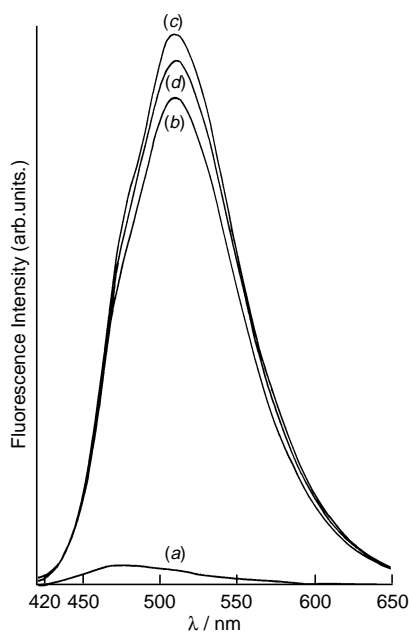In summary, we have shown for the first time that metal–fluorophore communication can be directly modulated to develop structurally much simpler PET fluorosensors (OR gate) for the d-block metal ions and as such there is no need to design a receptor with any special topology that involves more synthesis. Further, for the first time, fluorescence enhancement in the presence of metal ions such as Fe^{III} and Cr^{III}, known for their high quenching abilities, has been observed.

Footnotes

* E-mail: assc@uohyd.ernet.in
† **1** was prepared by reacting 4-amino-1,8-naphthalic anhydride with *N,N*-dimethylaminoethylamine. **2a** and **2b** were prepared by condensation of 4-aminophthalimide with corresponding dialkylaminoamines.
‡ The measured E_{ox} of AP and 4-amino-1,8-naphthalimide are 1.50 V and 1.27 V (Ag–AgCl reference electrode), respectively.
§ The fluorescence quantum yield of 4-aminophthalimide in acetonitrile, as reported in ref. 10(*a*), is 0.63.
¶ The E_{ox} for triethylamine used for calculation is 0.49 V, ref. 11. The SCE value was corrected for Ag–AgCl electrode by subtracting 0.27 V. The E_{red} values of AP and 4-amino-1,8-naphthalimide (ANP) used for the calculations are -1.66 and -1.61, respectively. $E_{0,0}$ values, estimated from the fluorescence maxima of AP and ANP, are 62.2 and 55.04 kcal mol^{-1}.
‖ The lifetimes of the PET quenched state of **2a** and **2b** in acetonitrile are *ca.* 0.5 and 0.8 ns, respectively, with 98 and 64% contribution to the total decay at time $t = 0$. The unquenched component has lifetime in the range 17–18 ns. The measured lifetime of methylated AP in acetonitrile is 18.5 ns.

References

1 M. E. Huston, K. W. Haider and A. W. Czarnik, *J. Am. Chem. Soc.*, 1988, **110**, 4460.
2 A. P. de Silva, H. Q. N. Gunaratne and G. E. M. Maguire, *J. Chem. Soc., Chem. Commun.*, 1994, 1213; A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson and M. Nieuwenhuizen, *Chem. Commun.*, 1996, 1967; A. P. de Silva, H. Q. N. Gunaratne, C. McVeigh, G. E. M. Maguire, P. R. S. Maxwell and E. Hanlon, *Chem. Commun.*, 1996, 2191.
3 A. P. de Silva, H. Q. N. Gunaratne and C. P. McCoy, *Nature*, 1993, **364**, 42; A. P. de Silva, H. Q. N. Gunaratne and C. P. McCoy, *Chem. Commun.*, 1996, 2399.
4 P. Ghosh, P. K. Bharadwaj, S. Mandal and S. Ghosh, *J. Am. Chem. Soc.*, 1996, **118**, 1553.
5 R. A. Bissel, A. P. de Silva, H. Q. N. Gunaratne, P. L. M. Lynch, G. E. M. Maguire and K. R. A. S. Sandanayake, *Chem. Soc. Rev.*, 1992, **21**, 187; *Fluorescent Chemosensors for Ion and Molecule Recognition*, ed. A. W. Czarnik, American Chemical Society, Washington, DC, 1993; R. A. Bissel, A. P. de Silva, H. Q. N. Gunaratne, P. L. M. Lynch, G. E. M. Maguire, C. P. McCoy and K. R. A. S. Sandanayake, *Top. Curr. Chem.*, 1993, **168**, 223; A. W. Czarnik, *Acc. Chem. Res.*, 1994, **27**, 302; A. W. Czarnik, in *Topics in Fluorescence Spectroscopy*, ed. J. R. Lakowicz, Plenum, New York, 1994, vol. IV, p. 49; B. Valeur, in *Topics in Fluorescence Spectroscopy*, ed. J. R. Lakowicz, Plenum, New York, 1994, vol. IV, p. 21; T. D. James, P. Linnane and S. Shinkai, *Chem. Commun.*, 1996, 281.
6 *Molecular Electronic Devices*, ed. F. L. Carter, R. E. Siatkowski and H. Wohltjen, Elsevier, Amsterdam, 1988; J. M. Lehn, *Angew Chem., Int. Ed. Engl.*, 1988, **27**, 89; J. M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304.
7 A. W. Varnes, R. B. Dodson and E. L. Wehry, *J. Am. Chem. Soc.*, 1972, **94**, 946; J. A. Kemlo and T. M. Shepherd, *Chem. Phys. Lett.*, 1977, **47**, 158.
8 A. Pardo, J. M. L. Poyato, E. Martin, J. J. Camacho and D. Reyman, *J. Lumin.*, 1990, **46**, 381; D. Yuan and R. G. Brown, *J. Chem. Res. (S)*, 1994, 418.
9 Inefficient PET in a structurally similar molecule is recently reported. A. P. de Silva, H. Q. N. Gunaratne, J. L. Habib-Jawan, C. P. McCoy, T. E. Rice and J. P. Soumillion, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1728.
10 (*a*) T. Soujanya, R. W. Fessenden and A. Samanta, *J. Phys. Chem.*, 1996, **100**, 3507; (*b*) T. Soujanya, T. S. R. Krishna and A. Samanta, *J. Phys. Chem.*, 1992, **96**, 8544.
11 H. Siegerman, in *Techniques of Chemistry*, ed. N. L. Weinberg, Wiley, New York, 1975, vol. V, part II, p. 803.

Fig. 1 Fluorescence spectra of **2a** in acetonitrile for different concentrations of Fe^{III}: (*a*) 0, (*b*) 5.3 $\times$ 10^{-5}, (*c*) 1.0 $\times$ 10^{-4} and (*d*) 1.6 $\times$ 10^{-4} mol dm^{-3}