Letter

Fluorescence signaling of transition metal ions: a new approach†

N. B. Sankaran,[a] S. Banthia,[a] A. Das[b] and A. Samanta*[a]

[a] *School of Chemistry, University of Hyderabad, Hyderabad 500 046, India.*
E-mail: assc@uohyd.ernet.in; Fax: +91 40 301 2460; Tel: +91 40 301 0715
[b] *Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, Gujarat, India*

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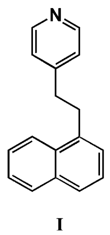
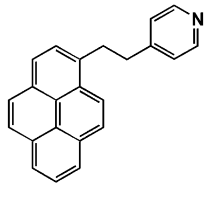
Fluorescence signaling of transition metal ions by the *fluorophore-spacer-receptor* systems I and II is based on an unconventional mechanism.

The current interest in molecular systems capable of performing logic operations is largely due to likely application of these systems as molecular devices in information processing and computation.[1] The simplest molecular fluorescent sensors are multi-component systems consisting of a signaling unit (fluorophore) and a guest binding site (receptor); the two are usually linked *via* a spacer.[2,3] These molecular components are chosen such that communication[4] between the two terminal moieties of the *fluorophore-spacer-receptor* system leads to quenching of the fluorescence. The fluorescence is recovered when the species to be signalled cuts off this communication. Essentially, 'off-on' fluorescence signaling by a fluorophore-spacer-receptor system depends on whether the guest can *cut off or disrupt* the communication between the fluorophore and the receptor.[2,5] Herein, we report signaling behaviour of **I** and **II**[6] towards various transition metal ions[7] that shows that 'off-on' fluorescence signaling by the present fluorophore-spacer-receptor systems is linked to guest-induced *enhancement* of the communication between the fluorophore and the receptor.



I



II

Even though the molecular architecture of **I** and **II** is typical of that of a photoinduced intramolecular electron transfer (PET) fluorosensor,[2] the photophysical behaviour of the two systems is mainly governed by *through-space* interaction of the π clouds of the fluorophore and the receptor; PET between the two is rather insignificant.[6,8] The systems exhibit a broad emission band on excitation of the intramolecular complex formed as a result of π-π interaction of the terminal moieties.[6] Essentially, the photophysical behaviour of **I** and **II** is consistent with the structure shown on the left-hand side in Fig. 1.

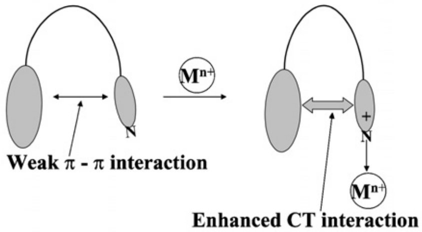


Fig. 1 Intramolecular interaction in the fluorophore-spacer-receptor systems in the absence and in the presence of metal ions.

Fig. 2 illustrates the typical influence of transition metal salts[9] on the UV-vis absorption spectrum of **I**. While an isosbestic point could be observed with some of the metal ions (over a certain concentration range), a number of metal ions do not show a clear isosbestic point and instead, show a gradual shift of the absorption maximum towards longer wavelengths.[10]

Addition of the metal salts leads to quenching of the original fluorescence of **I** (Fig. 3), as expected. Interestingly, it also gives rise to a new fluorescence band at a longer wavelength.[11,12] Unlike the original fluorescence, the new fluorescence band is quite sensitive to the polarity of the media. A bathochromic shift (*ca.* 20–40 nm) of the fluorescence maximum is observed on changing the solvent from tetrahydrofuran (THF) to acetonitrile (ACN) (Table 1).[13]

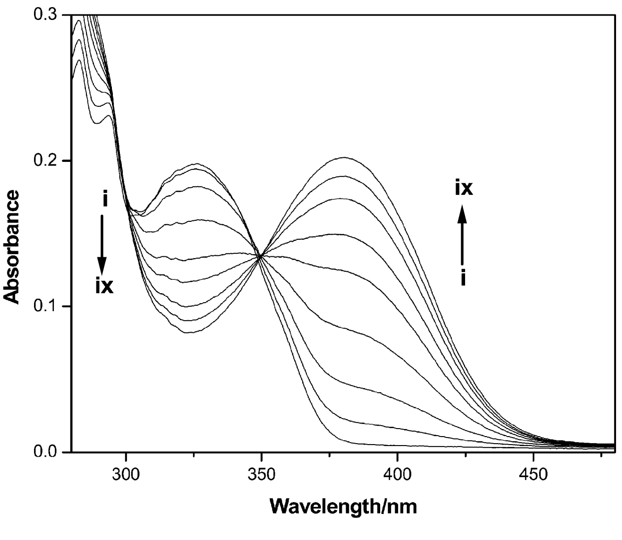


Fig. 2 Absorption spectra of **I** (4×10^{-5} M) in acetonitrile in the presence of varying quantities of Cr^{3+}. [Cr^{3+}] varied from 0 to 6.5×10^{-5} M in spectra i to ix.

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† Electronic supplementary information (ESI) available: Tabulated fluorescence output in THF, figures showing fluorescence excitation spectrum and the influence of the media and $NaClO_4 \cdot H_2O$ on the fluorescence behaviour of **I**. See http://www.rsc.org/suppdata/nj/b2/b206364f/

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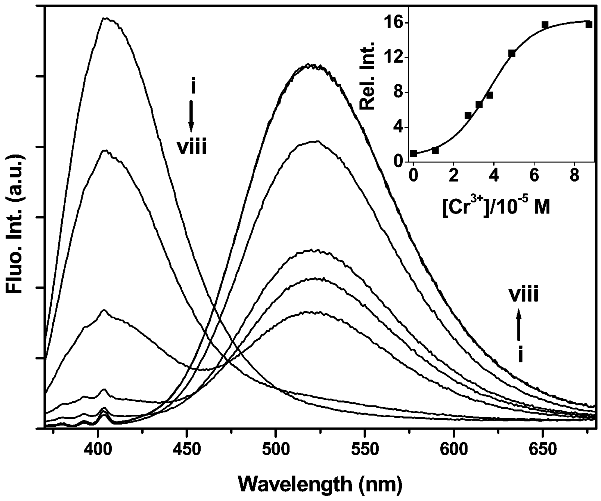

Fig. 3 Fluorescence spectra ($\lambda_{ex} = 360$ nm) of **I** (4×10^{-5} M) in the presence of Cr^{3+}. Spectra labelled i to viii correspond to [Cr^{3+}] (in 10^{-5} M) of: 0, 1.09, 2.18, 3.27, 3.82, 4.91, 6.54 and 8.72, respectively. The insert shows the fluorescence titration curve for Cr^{3+}.

Since the hydrated metal salts may contain acidic impurities and protons also show an effect (Table 1) similar to what is observed with the metal ions, it is possible that the observed spectral changes are due to the acidic impurities present in the hydrated perchlorate metal salts used here. That the species responsible for the effect are indeed the metal ions, is unambiguously established by observing that (*i*) $NaClO_4{\cdot}H_2O$ does not give rise to any new absorption or emission band, as observed with the transition metal salts and (*ii*) the metal salt induced fluorescence output of the systems is hardly affected by the presence of small amounts (3–4 mM) of Na_2CO_3.

Since the present systems contain a pyridyl moiety, which forms complexes with the metal ions under similar experimental conditions,[10] the metal ions are likely to attack this unit, making it an electronically deficient moiety analogous to the pyridinium ion. This event is not only expected to *enhance* its communication with the electron-rich fluorophore, but also expected to introduce significant charge transfer (CT) character to it. The dipolar nature of the complex, as evident from the solvent response of the fluorescence, is fully consistent with this interpretation. Moreover, this mechanism is also in agreement with the literature reports on the formation of CT complexes between pyridinium ion and various aromatic hydrocarbon moieties.[14,15] Based on the literature, the expected λ_{max} for the CT absorption band of the electron donor–acceptor complex of the pyridinium ion with 1-methylnaphthalene is ~365 nm and that with pyrene is ~404 nm.[16] Interestingly, these values are not very different from what we have observed. The intramolecular interaction in **I** and **II** in the presence of the metal ions is pictorially illustrated on the right-hand side of Fig. 1.

Table 1 Fluorescence parameters of **I** and **II** in the absence and in the presence of different metal salts

	λ_{max}/nm[a]				Fluorescence output[b]			
	I		**II**		**I**		**II**	
M^{n+}	THF	ACN	THF	ACN	400 nm[c]	525 nm[c]	450 nm[d]	610 nm[e]
None	398	401	450	453	1	1	1	1
Cd^{2+}	494	514	583	609	0.05	13.3	0.01	25.0
Cr^{3+}	495	523	585	610	0.02	16.0	0.01	25.4
Zn^{2+}	482	520	583	607	0.06	11.3	0.03	16.7
Mn^{2+}	490	518	583	607	0.06	8.6	0.07	16.9
Cu^{2+}	502	522	582	608	0.01	10.3	0.01	13.5
Fe^{3+}	498	520	584	608	0.01	10.8	0.01	35.6
H^+	479	515	565	607	0.02	15.7	0.01	35.0

[a] ±2 nm. [b] In acetonitrile, ±10%, the concentration of the metal ions for which the maximum output was observed was between 10^{-5} to 10^{-3} M. [c] $\lambda_{ex} = 360$ nm. [d] $\lambda_{ex} = 375$ nm. [e] $\lambda_{ex} = 435$ nm.

From the point of view of signaling, we first note that the metal ion signaling mechanism for the present systems is different from the conventional PET process.[2,5] The 'off-on' signaling ability of the current systems is the result of guest-induced *enhancement* of the communication between the fluorophore and the receptor components. Secondly, the 'switching on' of the new fluorescence takes place with simultaneous 'switching off' of the original fluorescence. Essentially, the systems serve as both 'off-on' and 'on-off' fluorosensors, depending on the monitoring wavelength. Even though a few systems have been reported that offer dual 'off-on' and 'on-off' signaling windows,[17] we are not aware of any system offering dual signaling windows for transition metal ions. As far as the signaling efficiency is concerned, when monitored at 400 nm, the fluorescence output of **I** decreases by a factor of 17–110 and increases by a factor of 9–16 at 525 nm in ACN (Table 1). For **II**, these factors are respectively 14–100 at 450 nm and 13–36 at 610 nm (Table 1). Moreover, the ability of the systems to detect low concentrations (10^{-5}–10^{-4} M) of metal ions is also quite noteworthy.

In summary, we have shown that 'off-on' signaling of the transition metal ions is based on a mechanism exploited for the first time. In addition, dual 'off-on' and 'on-off' windows and high signaling efficiency makes these simple systems really novel and attractive fluorosensors for transition metal ions.

Experimental

Absorption and fluorescence spectra (corrected) were recorded on Shimadzu (UV-3101PC) spectrophotometer and Spex (Fluormax 3) spectrofluorimeter, respectively. Time-resolved emission studies were performed using a IBH Model 5000 Time Correlated Single Photon Counting instrument.

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5 We have previously developed some simple 'off-on' signaling systems for transition metal ions following this strategy and exploiting the PET process. See: (*a*) B. Ramachandram and A. Samanta, *Chem. Commun.*, 1997, 1037; (*b*) B. Ramachandram and A. Samanta, *J. Phys. Chem. A.*, 1998, **102**, 10 579; (*c*) B. Ramachandram, G. Saroja, N. B. Sankaran and A. Samanta, *J. Phys. Chem. B.*, 2000, **104**, 11 824.

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7 Transition metal ions are notorious quenchers of fluorescence. See: A. W. Varnes, R. B. Dodson and E. L. Wehry, *J. Am. Chem. Soc.*, 1972, **94**, 946; (*a*) for recent reviews on fluorosensors for transition metal ions, see: L. Fabbrizzi, M. Licchelli and P. Pallavicini, *Acc. Chem. Res.*, 1999, **32**, 846; (*b*) L. Prodi, F. Bolletta, M. Montalti and N. Zaccheroni, *Coord. Chem. Rev.*, 2000, **205**, 59

8 Through-space interaction of two identical aromatic moieties leading to the formation of an excimer is a well-known phenomenon that also has been exploited for signaling of different species. See: Ref. 2(a) or a more recent article such as the following: Y. Nakahara, Y. Matsumi, W. Zhang, T. Kida, Y. Nakatsuji and I. Ikeda, *Org. Lett.*, 2002, **4**, 2641.

9 Hydrated perchlorate salts of the transition metal ions have been used.

10 A recent paper shows that bivalent transition metal ions form $[ML]^{2+}$, $[ML_2]^{2+}$, $[ML_3]^{2+}$ and $[ML_4]^{2+}$ complexes with 4-methylpyridine in acetonitrile. It also shows that the stability constants for the formation of the mono complexes follow the order $Mn^{2+} > Zn^{2+} > Cu^{2+}$. See: M. Kurihara, T. Kawashima and K. Ozutsumi, *Z. Naturforsch., B: Chem. Sci.*, 2000, **55**, 277.

11 (*a*) The new emission band could be observed with all the metal ions, though with some metal ions (*e.g.*, Mn^{2+}) the emission is not as intense. In the case of **II**, a similar behaviour is observed; however, the new fluorescence band is not as intense as in the case of **I**; (*b*) the fluorescence excitation spectrum corresponding to the new emission band is found to be identical to the long-wavelength absorption band of the system observed in the presence of the metal ions.

12 Since the concentration of the new emitting species is unknown, an exact estimate of ϕ_f could not be made. Time-resolved measurements suggest that the dominant component (88–99%) of the new emission band is associated with a sub-nanosecond lifetime.

13 That the new emission is not due to any exciplex formed between the metal ions and the fluorophore is evidentfrom the fact that unlike a typical exciplex emission, the new emission is as intense in a polar medium such as ACN as in the much less polar THF.

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