Pergamon

Tetrahedron 56 (2000) 7041–7044

TETRAHEDRON

Fluorescence Signalling of Transition Metal Ions by Multi-Component Systems Comprising 4-Chloro-1,8-naphthalimide as Fluorophore

B. Ramachandram, N. B. Sankaran, R. Karmakar, S. Saha and A. Samanta*

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

Received 17 February 2000; revised 12 March 2000; accepted 14 March 2000

Abstract—Fluorescence of **1a** and **1b** is '*switched on*' by the quenching transition metal ions and the extent of fluorescence enhancement is found to be considerably higher than that expected on the basis of photoinduced intramolecular electron transfer in the systems. The observation has been rationalised taking into account the hydrated nature of the transition metal salts and preferential solvation of the fluorophore by the water molecules. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

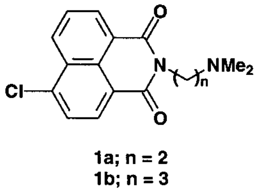
There has been a great deal of current interest in the design and development of molecular systems capable of performing functions of various kinds.[1,2] A molecular device is essentially an assembly of suitably organised molecular components capable of performing some logic function characteristic of the assembly. Of particular interest are the fluorosensors, which are molecular devices powered by light and response of these systems are based on fluorescence. Fluorosensors are generally multi-component systems comprising a signalling moiety (fluorophore), a guest binding site (usually termed as receptor) and a spacer group. The components are so chosen that photoinduced intramolecular electron transfer (PIET) between the receptor and fluorophore results in 'switching off' of the fluorescence. However, in presence of a guest, which ties up the lone pair electrons of the receptor, PIET communication between the receptor and fluorophore gets cut-off and the fluorescence of the system is 'switched on'. Thus, the presence of a guest is signalled by fluorescence enhancement (FE) of the system.

During our previous investigations,[3–5] it was noted that structurally simple fluorophore–spacer–receptor system that comprises an electron deficient fluorophore can exhibit fluorescence 'off-on' signalling even in the presence of transition metal ions, well known for their fluorescence quenching abilities.[6,7] The present investigation deals with two simple multi-component systems (Chart 1) involving 4-chloro-1,8-naphthalimide (CNP) as the fluorophore. Despite the fact that fluorophore–spacer–receptor systems involving 4-amino-1,8-naphthalimide (ANP) display rather poor sensing behaviour,[3] CNP has been chosen as the fluorophore component in view of its electron deficient nature and higher singlet state energy (vide later) compared to ANP. Both these properties are likely to make PIET much more efficient in **1a** and **1b** compared to that in structurally similar systems involving ANP. In this context it is to be noted that while a number of photophysical studies have been carried out on 1,8-naphthalimide derivatives,[8] the signalling ability of these systems towards the transition metal ions has not been investigated until very recently.[5]

Experimental

Materials and methods

N,*N*-Dimethylethylenediamine and *N*,*N*-dimethylpropylenediamine (Aldrich) and 4-chloro-1,8-naphthalic anhydride (Acros Organics) were used without any further purification. Hydrated transition metal salts of analytical grade were procured locally and were used without any purification. Anhydrous salt of cobalt was prepared from $Co(H_2O)_6Cl_2$ following a standard procedure[9] according to which the hydrated salt (once recrystallised) was refluxed



1a; n = 2
1b; n = 3

Chart 1.

Keywords: photoinduced electron transfer; fluorosensors; transition metals; naphthalimides.

* Corresponding author. E-mail: assc@uohyd.ernet.in

0040–4020/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.

PII: S0040-4020(00)00527-5

with excess of dimethoxypropane for 6 h and subsequently the solvent was removed in vacuum. The solvents, tetrahydrofuran (THF) and acetonitrile (ACN) used in the spectral studies, were rigorously purified by standard procedures.

Synthesis of 1a

N,*N*-Dimethylethylenediamine (0.29 ml, 2.6 mmol) was added to a suspension of CNP (0.5 g, 2.15 mmol in 5 ml ethanol) and the mixture was refluxed for 6 h. The suspended CNP dissolved slowly with the progress of the reaction. The reaction mixture was allowed to cool to room temperature after completion of reaction. The desired product, that crystallised out on cooling, was recrystallised several times from ethanol to obtain the spectroscopic purity. Yield 95%. IR (KBr, cm^{-1}): 2968, 2858, 1697, 1658, 1379, 1037 and 779. ^1H NMR ($CDCl_3$): δ 2.4 (s, 6H), 2.6 (t, 2H), 4.3 (t, 2H), 7.9 (t, 2H) and 8.5–8.7 (m, 3H).

Synthesis of 1b

1b was obtained by following a procedure similar to that used for **1a** using *N*,*N*-dimethylpropylenediamine instead of *N*,*N*-dimethylethylenediamine. Yield 90%. **IR** (KBr, cm^{-1}): 2947, 2780, 1699, 1653, 1348 and 783. ^1H NMR ($CDCl_3$): δ 1.9 (m, 2H), 2.25 (s, 6H), 2.4 (t, 2H), 4.2 (t, 2H), 7.8 (t, 2H) and 8.5–8.7 (m, 3H).

Instrumentation

The IR and NMR spectra of the compounds were recorded on JASCO FT-IR/5300 and Bruker ACF-200 spectrometer respectively The absorption and fluorescence spectra were recorded on JASCO UV–vis spectrophotometer (Model 7800) and JASCO spectrofluorimeter (Model FP-777) respectively. Cyclic voltammetric measurements were made with Cypress Model CS-1090/CS-1087 electroanalytical system employing Ag/AgCl as the reference electrode, a glassy carbon as the working electrode and a Pt wire as the auxiliary electrode. The redox potentials were measured in N_2 bubbled acetonitrile using 0.1 M TBAP as the supporting electrolyte. The scanning speed was maintained at 100 mV/s. The fluorescence quantum yields were measured using 1,8-naphthalimide as the reference compounds ($\phi_f = 5.0 \times 10^{-2}$ in acetonitrile).[8f]

Results and Discussion

While ANP exhibits oxidation at 1.27 V, no oxidation could be observed for 4-chloro-*N*-butyl-1,8-naphthalimide between 0–2 V. This suggests that the chosen fluorophore is relatively electron deficient and hence, a better choice as the fluorophore component for the design of multicomponent sensor systems. The reduction of the fluorophore was observed at −0.85 V. The thermodynamic driving force for PIET in **1a** and **1b** has been estimated in terms of the free energy change (ΔG) using, $\Delta G = 23.06[E_{ox}\text{ (recep)} - E_{red}\ (\textit{fluor})] - E_{0,0}$, where, E_{ox} (recep) represents the oxidation potential for the receptor moiety, E_{red} (fluor) represents the reduction potential for the fluorophore component and $E_{0,0}$ denotes the energy of the fluorescent state. The $E_{0,0}$ value used in the calculation of ΔG has been estimated from the location of the first peak in the fluorescence spectrum (76.9 kcal/mol). The oxidation potential of triethylamine (0.49 V) has been used as E_{ox} (recep).[10] The ΔG value associated with PIET is estimated to be −46.0 kcal/mol.

Even though PIET is thermodynamically feasible, the actual extent of PIET in **1a** and **1b** can only be ascertained by measuring the fluorescence yield of the systems. The fluorescence quantum yield of **1a** and **1b** is estimated to be lower than that of the constituent fluorophore by a factor of 105 and 18 respectively in THF and 110 and 38 respectively in ACN. This immediately suggests that PIET in **1a** is more efficient than in **1b**, presumably due to a more favourable fluorophore–receptor distance and orientation of the two components.[11]

The changes in the fluorescence response of the multicomponent systems induced by the transition metal salts have been illustrated in Fig. 1 using a typical example. Addition of the metal salts leads to an increase in the fluorescence intensity of the system. For a certain concentration of the metal ion (in the submillimolar range) the FE value reaches a maximum and further addition results in fluorescence quenching. No significant spectral shift could be noticed.

The maximum FE values obtained for **1a** and **1b** in the presence of different metal ions in THF and ACN are collected in Table 1. As can be seen, the observed FE values are unusually high in most cases. The highest FE value could be observed with **1a** in the presence of the nonquenching Zn^{2+}. It is noteworthy that even the most efficient quenching metal ions such as Fe^{3+} and Cr^{3+} give rise to excellent FE.

The most interesting observation of the present study is that the FE values are considerably higher than the expected values. Since the factor by which the fluorescence yield of a given multi-component system is lower than that of its

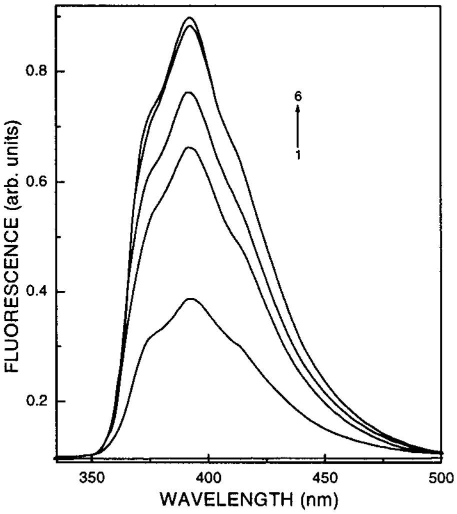


Figure 1. Fluorescence response of **1a** (10^{-5} M) in THF in the presence of $Ni(H_2O)_6(ClO_4)_2$. Ni^{+2} concentrations are (1) 0, (2) 1.1×10^{-4}, (3) 2.2×10^{-4}, (4) 4.3×10^{-4}, (5) 1.3×10^{-3} and (6) 1.6×10^{-3} M. $\lambda_{ex} = 320$ nm.

Table 1. Fluorescence output of **1a** and **1b** as a function of different metal ion input in THF and ACN (2×10^{-5} M solution of the compounds in THF or CAN was used at 298 K, $\lambda_{exc} = 320$ nm; the concentration of the metal ions were in the submillimolar range; the fluorescence output values are relative to the fluorescence intensities of the same system in the absence of the metal ion, ±15%)

	Cr^{3+}	Mn^{2+}	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
			1a				
In THF	185	725	655	295	660	195	735
In ACN	260	375	315	375	380	320	430
			1b				
In THF	30	70	60	40	70	40	70
In ACN	90	120	115	125	130	100	115

constituent fluorophore is a good measure of the extent of PIET in the system, then assuming full recovery of fluorescence on complete suppression of PIET by the transition metal ions, one can expect maximum $\sim$110 fold FE for **1a** and $\sim$40 fold for **1b**. However, as can be seen from Table 1, the FE values are much higher than those expected on the basis of PIET in **1a** and **1b**. The result suggests that additional mechanism of FE is operative in the presence of transition metal salts. In an earlier investigation, we noted that addition of the transition metal salts, which are available in the hydrated form, may increase the polarity around the fluorophore.[5b,5c] Hence, if the chosen fluorophore is such whose fluorescence efficiency is higher in polar media (compared to that in nonpolar media) then the FE of the corresponding multi-component results not only due to the modulation of the PIET interaction between the fluorophore and the receptor but also arises due to a change in the microscopic polarity surrounding the fluorophore.

In order to find out whether or not the above is responsible for high FE of the present systems, we have measured the fluorescence efficiency of the fluorophore as a function of the solvent polarity and the values are shown in Table 2.

As can be seen, the fluorescence yield of the fluorophore is considerably higher in polar media. The observation is very similar to that observed with bare 1,8-naphthalimide.[5b] If it is assumed that the water molecules from the hydrated salts used in the study preferentially solvates the fluorophores by forming hydrogen bonds and thereby create an environment similar to that in water, then taking into consideration of the two mechanisms of FE, the expected values of FE for **1a** and **1b** (using the results presented in Results and Discussion and the data shown in Table 2) in THF are ≈790 (7.5×105) and 135 (7.5×18). Even though these values are not very different from those observed experimentally, it should be noted that the expected and observed values differ significantly in ACN. This is understandable when taken into consideration the fact that the microscopic polarity around the fluorophore is largely unknown and there could be additional mechanism of FE. What is shown in this paper is that the change in the polarity around the fluorophore is definitely one of the mechanisms of FE for the present systems. The fact that a change in the microscopic polarity around the fluorophore induced by the water molecules of the hydrated salts indeed leads to high FE values of the systems is also supported by the fact that multi-component systems comprising structurally similar naphthalimides, whose fluorescence yield is not sensitive to the solvent polarity, exhibit FE values very similar to those expected from consideration of PIET in the systems. That our reasoning is valid is also evident from the fact that anhydrous metal salts do not lead to FE values higher than PIET expected values.[5b,5c]

Table 2. Fluorescence quantum yield (unless otherwise mentioned, ±10%) of 4-chloro-*N*-butyl-1,8-naphthalimide as a function of the solvent

1,4-Dioxane	Tetrahydrofuran	Acetonitrile	Methanol	Water[a]
2.4×10^{-2}	2.0×10^{-2}	6.0×10^{-2}	0.14	0.15

[a] ±15%, because of poor solubility of these systems in aqueous solution.

In conclusion, it has been shown that it is possible for a fluorophore–spacer–receptor PIET system to exhibit FE much higher than that expected on consideration of PIET mechanism alone. The results provide a means of improving the signalling ability of simple multi-component systems by exploiting the solvent sensitive fluorescence properties of the fluorophore.

Acknowledgements

Financial support for this research was obtained from Council of Scientific and Industrial Research (CSIR) and University Grants Commission.

References

1. (a) *Molecular Electronic Devices*; Carter, F. L., Siatkowski, R. E., Wohltjen, H., Eds.; Elsevier: Amsterdam, 1988. (b) *Supramolecular Chemistry*; Lehn, J. M., Ed.; VCH: Weinheim, 1995. (c) Balzani, V.; Juzis, A.; Venturi, A. M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.

2. (a) *Chemosensors of Ion and Molecular Recognition*; Desvergene, J. P., Czarnik, A. W., Eds.; NATO ASI Series; Kluwer Academic: Dordrecht, 1997; Vol. C492. (b) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, 1515. (c) Valeur, B. In *Topics in Fluorescence Spectroscopy*; Lakowicz, J. R., Ed.; Plenum: New York, 1994; Vol. IV, p 21. (d) James, T. D.; Linnane, P; Shinkai, S. *J. Chem. Soc. Chem. Commun.* **1996**, 281. (e) Fabbrizzi, L.; Licchelli, M.; Pallavicini, P.; Sacchi, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1975.

3. Ramachandram, B.; Samanta, A. J. *Chem. Soc. Chem. Commun.* **1997**, 1037.

4. (a). Ramachandram, B.; Samanta, A. *Chem. Phys. Lett.* **1998**, *290*, 9. (b) Ramachandram, B.; Samanta, A. *J. Phys. Chem. A* **1998**, *102*, 10579.

5. (a). Ramachandram, B.; Sankaran, N. B.; Samanta, A. *Res. Chem. Intermed.* **1999**, *25*, 843. (b) Ramachandram, B. PhD Thesis, University of Hyderabad,1999. (c) Ramachandram, B.; Saroja, G.; Sankaran, N. B.; Samanta, A. Submitted for publication.

6. Varnes, A. W.; Dodson, R. B.; Wehry, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 946.

7. Kemlo, J. A.; Shepherd, T. M. *Chem. Phys. Lett.* **1977**, *47*, 158.

8. (a) Demeter, A.; Bérces, T.; Biczók, L.; Wintgens, V.; Valat, P.; Kossanyi, J. *J. Phys. Chem.* **1996**, *100*, 2001 and references

therein. (b) Valat, P.; Wintgens, V.; Kossanyi, J.; Biczók, L.; Demeter, A.; Bérces, T. *J. Am. Chem. Soc.* **1992**, *114*, 946. (c) Pardo, A.; Martin, E.; Poyato, J. M. L.; Camacho, J. J.; Guerra, J. M.; Weigand, R.; Brana, M. F.; Castellano, J. M. *J. Photochem. Photobiol. A: Chem.* **1989**, *48*, 259. (d) Pardo, A.; Poyato, J. M. L.; Martin, E.; Camacho, J. J.; Reyman, D. *J. Lumin.* **1990**, *46*, 381 and references therein. (e) Yuan, D.; Brown, R. G. *J. Chem. Res. (M)* **1994**, 2337. (f) Saroja, G.; Samanta, A. *J. Photochem. Photobiol. A: Chem.* **1994**, *84*, 19. (g) Samanta, A.; Ramachandran, B.; Saroja, G. *J. Photochem. Photobiol. A: Chem.* **1996**, *101*, 29. (h) Aveline, B. M.; Matsugo, S.; Redmond, R. W. *J. Am. Chem. Soc.* **1997**, *119*, 11785. (i) Daffy, L. M.; de Silva, A. P.; Gunaratne, H. Q. N.; Huber, C.; Lynch, P. L. M.; Werner, T.; Wolfbeis, O. S. *Chem. Eur. J.* **1998**, *4*, 1810.

9. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry: A Comprehensive Text*, Wiley-Interscience: New York, 1988 (p 552).

10. *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: New York, 1988; Part C, p 6. Reported E_{ox} data (measured vs SCE) are corrected by subtracting 0.27 V.

11. (a). Ref. 10, Parts A–D. (b) Weller, A.; Staerk, H.; Trichel, R. *Faraday Discuss. Chem. Soc.* **1984**, *79*, 271. (c) Gust, D.; Moore, T. A. In *Photoinduced Electron Transfer*; Mattey, J., Ed.; Topics in Current Chemistry 159; Springer: New York, 1991; Vol. III, pp 105. (d) Verhoeven, J. W. *Pure Appl. Chem.* **1990**, *62*, 1585. (e) Jordan, K. D.; Paddon-Row, M. N. *Chem. Rev.* **1992**, *92*, 395. (f) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.