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Cerium ion-induced fluorescence enhancement of a tripodal fluoroionophore

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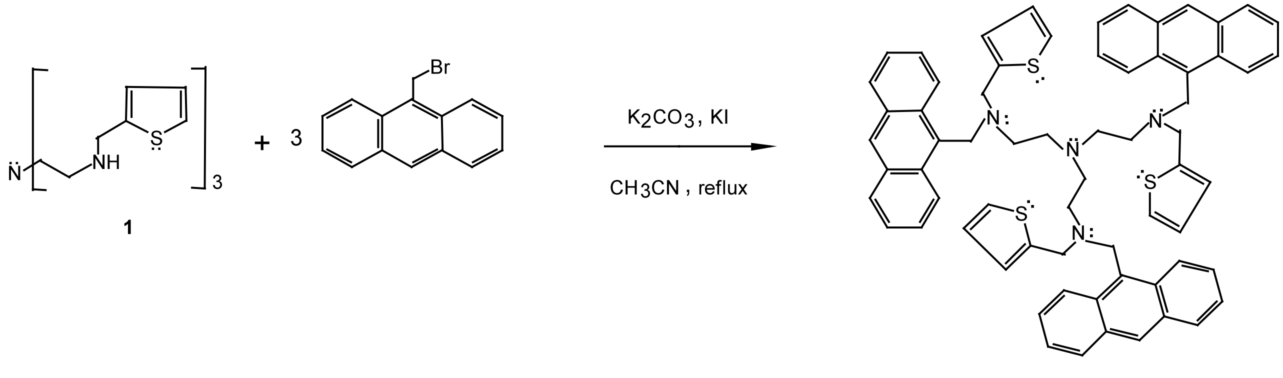
Abstract—A new tripodal ligand, *N*-anthracen-9-ylmethyl-*N'*,*N'*-bis-[2-(anthracen-9-ylmethyl-thiophen-2-ylmethylamino)ethyl]-*N*-thiophen-2-ylmethyl-ethane-1,2-diamine **2** was synthesized. Selective fluorescence enhancement was observed in the presence of Ce^{3+} for this newly synthesized ionophore in dry tetrahydrofuran (THF). © 2002 Elsevier Science Ltd. All rights reserved.

Fluorescent signaling of ions is of considerable interest from the viewpoint of application as chemosensors[1] and as molecular switches.[2] Chemosensors for alkali, alkaline earth and d^{10} metal ions are well established.[1] Recently much attention has been focused on the design and synthesis of chemosensors for heavy, transition and lanthanide metal ions.[3] In most of the reported molecular systems, these metal ions quench the fluorescence strongly via different mechanisms,[4–6] but there are only few examples wherein complexation of these cations results in an enhancement of the fluorescence.[7–12] Our earlier reports on metal ion-induced fluorescence enhancement systems show enhancement of fluorescence in the presence of lanthanide ions but similar enhancement was also found with transition metal ions.[8] Recently, Aoki et al. have reported a cyclen-based fluorescence probe for Y^{3+} and La^{3+}.[13] A tripodal ligand containing the dansyl chromophore has also been designed as a luminescent chemosensor for d-block metal ions.[14] However, the selectivity of fluorescent chemosensors for metal cations remains a significant challenge. We report herein cerium ion selective fluorescence enhancement with the new tripodal ligand **2** in dry THF. To the best of our knowledge this is the first example of a sensor which exhibits fluorescence enhancement in the presence of cerium ions.

Fluoroionophore **2** was prepared from an *N*-thiophen-2-ylmethyl-*N'*,*N'*-bis-{2-[(thiophen-2-ylmethyl)-amino]-ethyl}-ethane-1,2-diamine **1**, wherein each secondary amino group is derivatized with an anthryl moiety connected via a methylene spacer **2** (Scheme 1). Thiophene derivatized tris(2-aminoethyl)amine compound **1** was synthesized by a Schiff base condensation



Scheme 1.

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reaction between tris(2-aminoethyl)amine (2 mmol) and thiophene 2-aldehyde (6 mmol) followed by $NaBH_4$ reduction in dry MeOH. The trianthryl derivative was prepared by refluxing **1** (1 mmol) with 9-bromomethyl anthracene (3 mmol) in presence of anhydrous K_2CO_3 and a catalytic amount of KI in dry acetonitrile, followed by the usual work up to give the fluoroionophore **2** (Scheme 1). Fluoroionophore **2** was purified by column chromatography using silica-gel with $CHCl_3$ and 2% CH_3OH eluant. The pale-yellow major fraction was collected and dried in vacuo to obtain pure product. *Selected data* for **2**: light yellow solid, yield 53%, mp 88±2°C. Anal. calcd for $C_{66}H_{60}N_4S_3$: C, 78.65; H, 6.26; N, 5.56. Found: C, 77.91; H, 6.13; N, 5.56. ^1H NMR (200 MHz, $CDCl_3$) δ: 2.3 (m, 12H), 3.6 (s, 6H), 4.2 (s, 6H), 6.9–8.3 (m, 36H). ESMS: $m/z = 1005.2$ (M^+).

Photo-induced electron transfer (PET)-based fluorescent sensors for metal ions are widely used.[1] In most of these systems, the fluorophore and receptor are linked via a methylene spacer. In the absence of any guests, PET will occur between the fluorophore and the electron rich receptor, which results in the maximum quenching of the fluorescence. Upon binding of the guest to the receptor molecule, PET gets turned off which leads to regeneration of the fluorescence of the system. Here the system *N*-anthracen-9-ylmethyl-*N′*,*N′*-bis-[2-(anthracen-9-ylmethyl-thiophen-2-ylmethyl-amino)-ethyl]-*N*-thiophen-2-ylmethyl-ethane-1,2-diamine, **2** (Scheme 1) containing a fluorophore–spacer–receptor configuration shows a low intense well-resolved anthracene monomer emission[15] (band positions are at 394, 416 and 440 nm). The quantum yield (ϕ_F) of the system is 0.017 in tetrahydrofuran (THF) at 298 K versus ϕ_F of 0.297 for free anthracene under same experimental conditions, i.e. a reduction by a factor of about 18. The fluorescence quenching of the ionophore **2** is assumed to be due to PET from the nitrogen and sulfur lone pairs to the excited state of the anthracene. Literature reports suggest that such electron transfer processes occur both through bond and through space.[1] The ionophore **2** contains four tertiary nitrogen atoms along with the three weak sulfur donor atoms from the thiophene moieties, which would be expected to promote coordination with transition, lanthanide and heavy metal ions.[16] We investigated the influence of different salts[17] of alkali, alkaline earth, transition, lanthanide and heavy metal ions on the fluorescence behavior of **2** in THF. The ionophore **2** shows appreciable fluorescence enhancement only in the presence of Ce^{3+} or with H^+ input (Fig. 1). The monomer emission band positions of **2** in presence of Ce^{3+} input are at 397, 420 and 442 nm and the ϕ_F is 0.12. The fluorescence enhancement factor (FEF) compared to that of ionophore **2** is about 7, whereas no fluorescence enhancement was observed for other lanthanide metal ions (La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} and Dy^{3+}). The fluorescence output of these other lanthanide metal ions were similar to the ionophore **2**.

Moreover, **2** also shows a negligible effect of fluorescence with the input of transition metal ions (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Rh^{3+} and Ag^+), d^{10} metal ion (Zn^{2+}), heavy metal ions (Pb^{2+}, Hg^+), alkali (Li^+, Cs^+), and alkaline earth metal (Ca^{2+}) ions under the same experimental conditions. In the case of Ru^{2+}, a further quenching of the fluorescence by a factor of 5 was observed (Fig. 1). We have also verified the influence of different inputs on the excitation behavior of fluoroionophore **2**. Excitation spectra behavior was similar to the fluorescence spectra with different inputs. Therefore, fluoroionophore **2** distinctly distinguishes Ce^{3+} from other lanthanide metal ions (La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} and Dy^{3+}), alkali, alkaline, transition and heavy metal ions in the periodic table. However, the observed difference within the lanthanide series is more difficult to rationalize. The decrease in metal ion size along the series, might cause the expulsion of one of the soft donor groups from a multidentate ligand **2** and decrease the stability of the complex. This point could be reached at different places along the series depending upon the geometry and steric requirements of multidentate ligand.[18a] Moreover, acidity of Ln^{3+} series increases down the group which disfavors coordination[18b] with the lone pairs of N_4S_3 soft donor sets in the ligand **2**. With this account, it may be inferred that Ce^{3+} is strongly bound to the lone pairs of the heteroatoms in ionophore **2** in dry THF compared to other Ln^{3+} except La^{3+}. This is the likely reason for the 4 nm red shift in the case of Ce^{3+}, which was not found for the other lanthanide ions. The oxidation states of cerium are important in influencing the magnitude of fluorescence enhancement. Ce^{4+} shows only ~3-fold fluorescence enhancement without any appreciable change in band positions, which is presumably due to the hard nature of Ce^{4+}. We do not observe Ce^{3+}-induced fluorescence enhancement of the fluoroionophore **2** in acetonitrile or water medium. The FEF in acetonitrile or water is negligible (FEF = 1–2) in the presence of lanthanide metal ions including Ce^{3+}. This may be due to the low complex formation ability of Ce^{3+} with fluoroionophore **2** in these solvent systems.

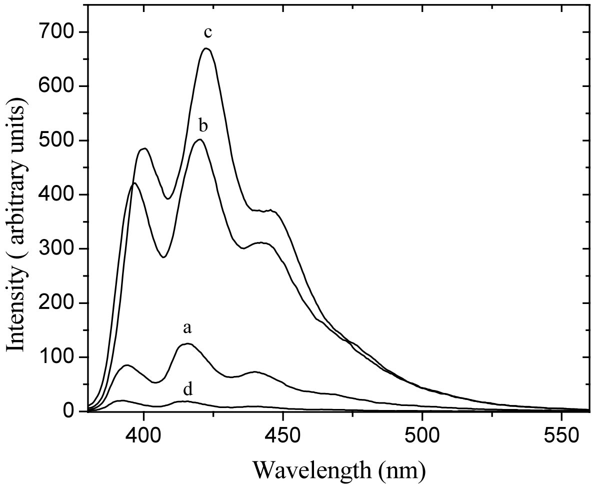

Figure 1. Emission spectra of **2** (a), and **2** in the presence of Ce^{3+} (b), H^+ (c) and Ru^{3+} (d) in dry THF at 298 K.

We have also studied the effect of mixed metal ions. In the presence of a mixture of input ions like Ce^{3+}, Ni^{2+} and Pb^{2+} (100-fold each), fluoroionophore **2** still shows about 3-fold fluorescence enhancement which indicates that Ce^{3+} has a stronger affinity in comparison to Ni^{2+} and Pb^{2+}, although some influence of the latter on **2** is evident.

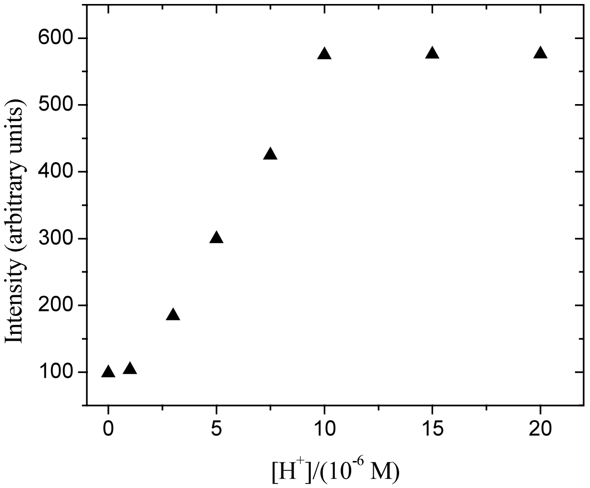

Figure 2. A [H$^+$] concentration profile of the emission spectra of **2** (9.4×10^{-7} M) in dry THF at 298 K.

It is of interest that protons, also effect fluorescence enhancement of a high magnitude in dry THF as found with Ce^{3+} with a similar red shift (~7 nm) of the fluorescence (Fig. 1). However, these may be of different origin as it is unlikely that the proton can tie up all the heteroatoms, as in the case of Ce^{3+}. Fig. 2 shows the concentration profile for protonation of **2** in dry THF. It is clear from the profile that noticeable fluorescence enhancement takes place only when [H$^+$] is three times the ligand concentration. At this point there is basically no shift in the fluorescence peak positions due to protonation. The intensity of fluorescence increases with the gradual increase of the acid concentration—this increase is associated with a red shift of the fluorescence. Intensity reaches a maximum value after the addition of 10-fold excess of acid.

In conclusion, the present study demonstrates that PET system **2** bearing three thiophene units in close proximity to the fluorophores is a viable candidate for sensing of Ce^{3+} in dry THF. We have synthesized a number of similar tripodal ligands with different coordination sites in close proximity to the fluorophores to probe with a number of transition/inner-transition metal ions. These systems will be investigated to find out the effect of different coordination sites attached, close to the PET unit.

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References

1. (a) Prodi, L.; Bolletta, F.; Montalti, N. M.; Zaccheroni, N. *Coord. Chem. Rev.* **2000**, *205*, 59; (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**, *97*, 1515; (c) *Chemosensors of Ion and Molecule Recognition*; Desvergne J. P.; Czarnik, A. W., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997.
2. (a) de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. *Nature* **1993**, *364*, 42; (b) de Silva, A. P.; Dixon, I. M.; Gunaratne, H. Q. N.; Gunnlaugsson, J. T.; Maxwell, P. R. S.; Rice, T. E. *J. Am. Chem. Soc.* **1999**, *121*, 1393; (c) Fabbrizzi, L.; Licchelli, M.; Pallavicini, P. *Acc. Chem. Res.* **1999**, *32*, 846.
3. (a) Bergonzi, R.; Fabbrizzi, L.; Licchelli, M.; Mangano, C. *Coord. Chem. Rev.* **1998**, *170*, 31; (b) Alfimov, M. V.; Gromov, S. P.; Fedorov, Y. V.; Fedorova, O. A.; Vedernikov, A. I.; Churakov, A. V.; Kuz'mina, L. G.; Howard, J. A. K.; Bossmann, S.; Braun, A.; Woerner, M., Jr.; Sears, D. F.; Saltiel, J. *J. Am. Chem. Soc.* **1999**, *121*, 4992.
4. Varnes, A. W.; Dodson, R. B.; Wehry, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 946.
5. Akkaya, E. U.; Huston, M. E.; Czarnik, A. W. *J. Am. Chem. Soc.* **1990**, *112*, 3590.
6. (a) Fabbrizzi, L.; Licchelli, M.; Pallavicini, P.; Perotti, A.; Taglietti, A.; Sacchi, D. *Chem. Eur. J.* **1996**, *2*, 75; (b) Krämer, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 772.
7. Ghosh, P.; Bharadwaj, P. K.; Mandal, S.; Ghosh, S. *J. Am. Chem. Soc.* **1996**, *118*, 1553.
8. Ghosh, P.; Bharadwaj, P. K.; Roy, J.; Ghosh, S. *J. Am. Chem. Soc.* **1997**, *119*, 11903.
9. Ramachandram, B.; Samanta, A. *Chem. Commun.* **1997**, 1037.
10. (a) Rurack, K.; Kollmannsberger, M.; Resch-Genger, U.; Daub, J. *J. Am. Chem. Soc.* **2000**, *122*, 968; (b) Hennrich, G.; Walther, W.; Resch-Genger, U.; Sonnennschein, H. *Inorg. Chem.* **2001**, *40*, 641.
11. Sakamoto, H.; Ishikawa, J.; Nakao, S.; Wada, H. *Chem. Commun.* **2000**, 2395.
12. Czarnik, A. W. *Chem. Biol.* **1995**, *2*, 423.
13. Aoki, S.; Kawatani, H.; Goto, T.; Kimura, E.; Shiro, M. *J. Am. Chem. Soc.* **2001**, *123*, 1123.
14. Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. *Eur. J. Inorg. Chem.* **1999**, 455.
15. Experimental conditions: medium, dry THF; concentration of **2**, 10^{-6} M; concentration of ionic input, 10^{-4} M; excitation at $\lambda_{\max}$ value, 368 nm with excitation band-pass, 3 nm and emission band pass, 3 nm; temperature 298 K. ϕ_F calculated by comparison of the spectrum with that of anthracene ($\phi_F=0.297$), taking the area under the total emission. The error in ϕ_F is within 5% in each case. The UV spectra of **2** are characteristic of 9-monoalkyl substituted anthracene with well-resolved structures with (0,0) band appearing at 388.0 nm and vibrational struc-

tures at 368 nm, 350 nm and 334 nm. The ε value at λ_{max} of **2** is 2.9×10^{-4} mol^{-1} cm^{-1} and this value is almost the same for **2** in the presence of lanthanide metal ions except Ce^{3+} where the ε value is $\sim2.0\times10^{-4}$ mol^{-1} cm^{-1}. Excitation spectra were recorded at 415 nm emission wavelength with emission and excitation band pass, 3 nm; temperature 298 K.

16. (a) Cattrall, R. W.; Gregorio, C. G.; Webster, R. D. *Anal. Chem.* **1997**, *69*, 3353; (b) Dujols, V.; Ford, F.; Czarnik, A. W. *J. Am. Chem. Soc.* **1997**, *119*, 7386.
17. The following metal salts have been used as inputs: LiCl, CsCl, $CaSO_4$, $MnCl_2\cdot4H_2O$, $FeSO_4\cdot7H_2O$, $Co(NO_3)_2\cdot6H_2O$, $NiCl_2\cdot6H_2O$, $Cu(NO_3)_2\cdot2.5H_2O$, $Zn(NO_3)_2\cdot6H_2O$, $RuCl_3\cdot3H_2O$, $RhCl_3\cdot3H_2O$, $AgClO_4\cdot H_2O$, $HgCl_2$, $Pb(NO_3)_2$, $Ce_2(SO_4)_3$, $(NH_4)_2Ce(NO_3)_6$, $La_2(NO_3)_3\cdot6H_2O$, $DyCl_3\cdot6H_2O$, $SmCl_3\cdot6H_2O$, $EuCl_3\cdot6H_2O$, $PrCl_3\cdot7H_2O$, $Nd_2(SO_4)_3\times H_2O$, $HClO_4$. In all cases the input concentration was 100-fold excess compared to the fluoroinophore for complete complexation. All the salts were dried under vacuum before use.
18. (a) Kepert, D. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds.; Pergamon: Oxford, UK, 1987; Vol. 1, p. 83; (b) Moeller, T.; Martin, D. F.; Thompson, L. C.; Ferrus, R.; Feistel, G. R.; Randall, W. J. *Chem. Rev.* **1965**, *65*, 1.