ORGANIC
LETTERS

2005
Vol. 7, No. 8
1573−1576

Attachment of Electron-Withdrawing 2,4-Dinitrobenzene Groups to a Cryptand-Based Receptor for Cu(II)/ H^+-Specific Exciplex and Monomer Emissions

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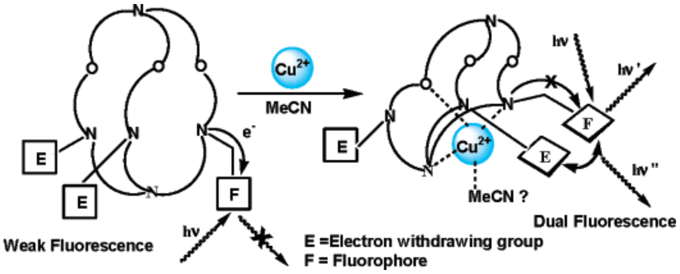
Received February 7, 2005

ABSTRACT



In a cryptand-based fluorescent signaling system with the configuration "fluorophore–spacer–receptor", attachment of the electron-withdrawing 2,4-dinitrobenzene groups to the cryptand receptor renders it highly selective for Cu(II). The system exhibits dual monomer and exciplex emissions in the presence of either of Cu(II) and H^+ as input with concomitant movements of one of the 2,4-dinitrobenzene groups.

Molecules exhibiting controlled movements of its parts due to external stimuli such as pH, temperature, photons, redox potential, metal ions, and so on are of considerable importance in several contemporary areas of research in chemistry and biology.[1] Herein, we report two fluorescent signaling systems in the format "fluorophore−spacer−receptor" that not only exhibit enhancement of fluorescence but also make a controlled movement of one of the sidearms in the presence of either Cu(II) or H^+ ion. The design and synthesis of ligands for chelation-enhanced fluorescence sensing[2] of a transition metal ion can be utilized for its detection in real-space and in real-time for biological, clinical, and environmental purposes. On the basis of the principles of supramolecular chemistry, most of the fluorescent chemosensors for these metal ions reported in various modular approaches use photoinduced electron transfer (PET) or energy transfer as the commonly exploited mechanism. Earlier, we had reported[3] that cryptands can be used as receptors for efficient fluorescence signaling of paramagnetic transition metal ions suppressing their quenching abilities. However, development of highly selective and sensitive chemosensors targeting biologically important transition metal ions such as Zn(II), Cu(II), Fe(II), etc. is still an area to be explored. The Cu(II) ion, despite being an essential element in biological systems, has a toxic impact[4] on the microorganisms at even submi-

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(1) (a) Badjic, J. D.; Balzani, V.; Credi, A.; Stoddart, J. F. *Science* **2004**, *303*, 1845. (b) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348. (c) Sauvage, J.-P. *Acc. Chem. Res.* **1998**, *31*, 611. (d) For reviews, please see the special issue on molecular machines: *Acc. Chem. Res.* **2001**, *34* (6). (e) Howard, J. *Nature* **1997**, *389*, 561. (f) Pascher, T.; Chesick, J. P.; Winkler, J. R.; Grey, H. B. *Science* **1996**, *271*, 1558.

(2) (a) *Fluorescent Chemosensors of Ion and Molecule Recognition*; Czarnik, A. W., Ed.; ACS Symposium Series 538; American Chemical Society: Washington, DC, 1993. (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) Bharadwaj, P. K. *Prog. Inorg. Chem.* **2003**, *51*, 251. (d) Ramachandram, B.; Saroja, G.; Sankaran, N. B.; Samanta, A. *J. Phys. Chem. B* **2000**, *104*, 11824.

(3) (a) Ghosh, P.; Bharadwaj, P. K.; Roy, J.; Ghosh, S. *J. Am. Chem. Soc.* **1997**, *119*, 11903. (b) Bag, B.; Bharadwaj, P. K. *J. Lumin.* **2004**, *110*, 1−2, 85.

(4) Beyersmann, D. In *Metals and Their Compounds in the Environment*; Merian, E., Ed; VCH: Weinheim, 1991.

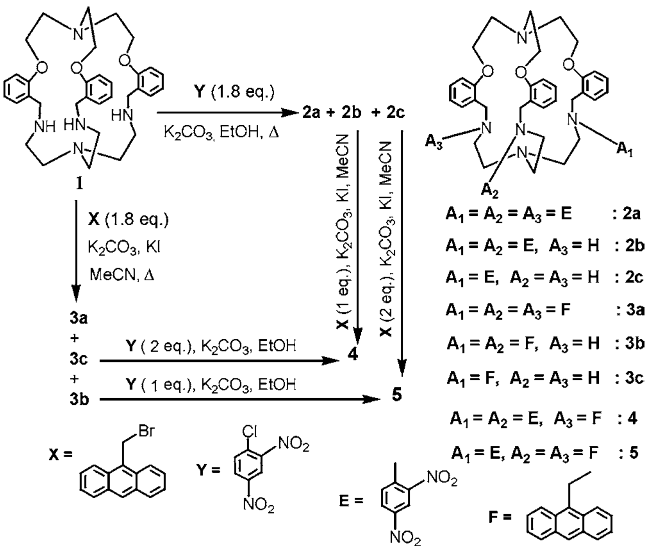
10.1021/ol050254v CCC: $30.25

cromolar concentrations. So, development of selective fluorescent sensors for Cu(II) by employing various synthetic strategies varying ligand topology and exploiting the host−guest ensemble has attracted a lot of attention[5] in recent years.

The two compounds described here give dual monomer and exciplex emissions in the presence of paramagnetic Cu(II) ion in a coordinating solvent like acetonitrile that usually quenches exciplex emission. In other less coordinating solvents such as THF, CH_2Cl_2, etc., neither monomer nor exciplex emission is observed. A recent report is available where a fluorescent signaling system exhibits dual emissions in the presence of Zn(II) ion.[6]

Synthetic routes to **4** and **5** are given in Scheme 1. In the first route, aromatic nucleophilic substitution (ArSN) reaction of the parent cryptand[7] **1** with 1-chloro-2,4-dinitrobenzene in a 1:1.8 molar ratio affords tris-, bis-, and monofunctionalized products **2a**, **2b**, and **2c**, respectively. This partial derivatization strategy was followed in order to avoid multistep protection and deprotection of amines and to produce all three products in one pot by variation of the stoichiometry of the reactants. These products are separated in a silica gel column (100−200 mesh) with a chloroform and methanol mixture as the eluent. Subsequent derivatization of **2b** and **2c** with 9-(bromomethyl) anthracene[8] in MeCN gives **4** and **5**, respectively, in good yields. In the second route, the parent cryptand is derivatized with 9-(bromomethyl)anthracene (in a 1:1.8 molar ratio) to obtain tris-, bis-, and monosubstituted products **3a**, **3b**, and **3c**, respectively, which are separated and purified through column chromatography. Subsequent reaction of **3b** and **3c** with 1-chloro-2,4-dinitrobenzene results in **4** and **5**, respectively. The compounds are characterized by elemental analysis and ^1H NMR, and ^{13}C NMR, and FAB-mass spectroscopy. They can be crystallized from mixed acetone−petroleum ether solutions by slow evaporation at room temperature.

Scheme 1. Synthetic Route to Compounds **4** and **5**



The photophysical properties of **4** and **5** are studied in different solvents.[9] Absorptions observed in the 340−400 nm region for the metal-free compounds are due to a combination of two different types of transitions: (i) anthracene $S_0 \rightarrow S_1$ with a (0,0) band appearing at 386 nm along with Franck−Condon vibrational structures at 368 and 350 nm and (ii) intramolecular charge transfer (ICT) from donor N atom to the acceptor nitro groups through the aromatic spacer. The ICT band overlaps with the anthacence $\pi-\pi^*$ transitions, and both are found to be nonsolvatochromic in nature. To investigate the binding properties of **4** and **5** toward metal ions, hydrated perchlorate salts of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), and Ag(I) are used. Upon complexation with a transition metal ion in MeCN, a small shift ($\Delta\lambda = 2-5$ nm) of the (0,0) band with concomitant decrease in the molar extinction coefficient is observed for both systems. However, in the presence of Cu(II), the Franck−Condon vibrational structures of ligand absorption become modulated (Figure 1a), shifting λ_{max} from 369 to 350 nm, whereas in the presence of other transition metal ions, the spectral features remain unchanged with decreased intensity. This is indicative of a different binding mode of **4** and **5** with Cu(II) in the ground state in contrast to other metal ions under investigation.

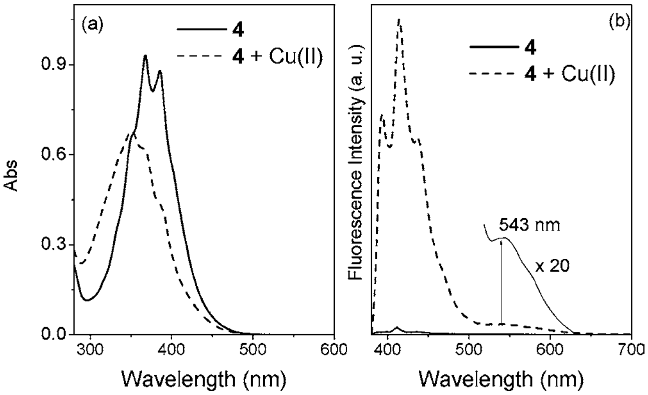


Figure 1. (a) Absorption (concn = 2×10^{-5} M, MeCN) and (b) fluorescence (MeCN, concn = 1×10^{-6} M, 298 K) spectra of **4** alone and in the presence of Cu(II).

Cation-free **4** and **5** exhibit monomer emission in different solvents typical of 9-substituted anthracene at 298 K, as the ICT operative here is nonemitting in nature. The

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[5] (a) Fernandez, Y. D.; Gramatges, A. P.; Amendola, V.; Foti, F.; Mangano, C.; Pallavicini, P.; Patroni, S. *Chem. Commun.* **2004**, 1650. (b) Clares, M. P.; Aguilar, J.; Aucejo, R.; Lodeiro, C.; Albelda, M. T.; Pina, F.; Lima, J. C.; Parola, A. J.; Pina, J.; de Melo, J. S.; Soriano, C.; García-España, E. *Inorg. Chem.* **2004**, *43*, 6114. (c) Rurack, K.; Kollmannsberger, M.; Resch-Genger, U.; Daub, J. *J. Am. Chem. Soc.* **2000**, *122*, 968. (d) Dujols, V.; Ford, F.; Czarnik, A. W. *J. Am. Chem. Soc.* **1997**, *119*, 7386.

[6] Bencini, A.; Bianchi, A.; Lodeiro, C.; Masotti, A.; Parola, A. J.; Pina, F.; de Melo, J. S.; Valtancoli, B. *Chem. Commun.* **2000**, 1639.

[7] Raghunathan, K. G.; Bharadwaj, P. K. *Tetrahedron Lett.* **1992**, *33*, 7581.

[8] Bullpit, M.; Kitching, W.; Doddrell, D.; Adcock, W. *J. Org. Chem.* **1976**, *41*, 760.

[9] For details, please see Supporting Information.

fluorescence quantum yields (ϕ_F) are found to be very low due to the highly efficient intramolecular photoinduced electron transfer (PET) process operative from the HOMO of the donor tertiary N to the anthracene. Higher quantum yields are observed in nonpolar solvents compared to polar ones as expected.[10] Neither compound shows an exciplex in the cation-free state. However, with Cu(II) in MeCN, the monomer emission exhibits a ~160-fold increase along with an exciplex emission centering at ~540 nm (Figure 1b). With other transition metals, the enhancement hardly reaches ~25-fold, while with Cu(I) it is only <2-fold. With protons, the increment factor is ~85 for **4** and ~160 for **5**. The excitation spectra monitoring both monomer ($\lambda_{max} \sim 420$ nm) and the broad emission band ($\lambda_{max} \sim 540$ nm) in acetonitrile are found to be similar and consistent with the absorption spectra. The specificity of **4** and **5** (Figure 2a) toward Cu(II) may be attributed to complex formation with the metal in preference over others following Irving−Williams order of stability, which was observed earlier in aza-macrocycle-[11] and aza-cyclophane-based[12] receptors. Fluorescence titration of either **4** or **5** with Cu(II) in MeCN (Figure 2b) indicates[9] formation of a 1:1 complex. The low stability constant[13] values obtained for **4** and **5** with Cu(II) compared to that of the parent cryptand **1** suggests[14] that Cu(II) binds **4** and **5** from outside the cavity.

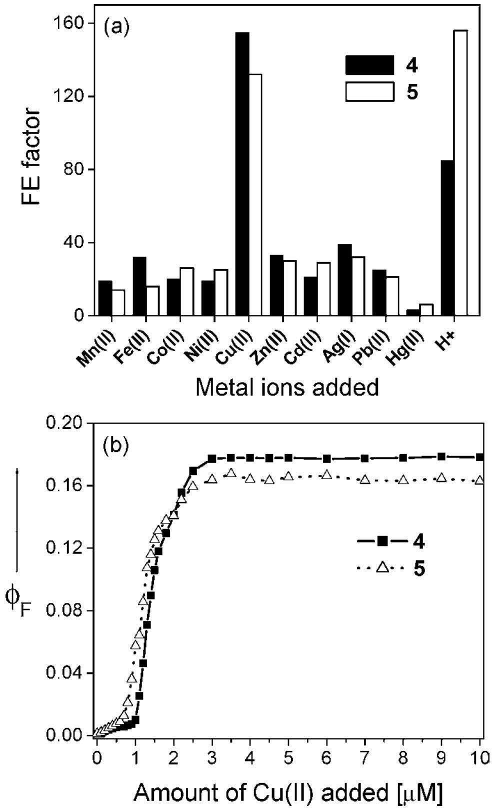

Figure 2. (a) Extent of fluorescence enhancement factors in the presence of various metal ions. (b) Plot of total fluorescence quantum yield (ϕ_{FT}) of **4** (2.5×10^{-6} M) and **5** (2.0×10^{-6} M) as a function of the amount of Cu(II) added in dry acetonitrile.

Interestingly, with $Cu(ClO_4)_2{\cdot}6H_2O$ salt as input, no significant fluorescence enhancement is observed (Figure 3) in a less coordinating solvent such as THF or CH_2Cl_2. However, addition of MeCN to the above solution leads to monomer enhancement of up to about ~130-fold along with an exciplex at ~540 nm, suggesting participation of MeCN in the binding of Cu(II) to **4** or **5** (Figure 3). When a coordinating counteranion like SCN^- is added to the solution of **4** containing $Cu(ClO_4)_2{\cdot}6H_2O$ in THF, the fluorescence enhancement (~160-fold) is found to be same as when MeCN was used as the solvent. Fluorescence recovery on addition of SCN^- suggests that Cu(II) binds **4** from outside the cavity with SCN^- taking part[15] in coordination. When $AgBF_4$ is added to the solution of **4** containing Cu(II) and SCN^-, the fluorescence is quenched, almost to the level of metal-free **4**. This is due to preferential binding of Ag(I) to SCN^- leaving the Cu(II) with BF_4^- anion when Cu(II) does not bind to **4** and allows PET to be restored. Thus, a reversibility in Cu(II) binding to the systems can be induced with the coordinating tendencies of the counteranions. However, further addition of SCN^- to the solution enhances the fluorescence to ~40-fold, which may be due to the change in the ionic strength of the solution. When the Cu(II) chloride salt is used as the input, the dual emission with comparable enhancement is observed in THF as well.

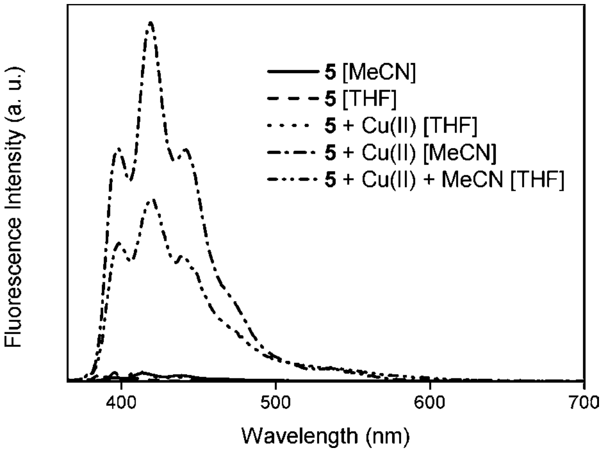

Figure 3. Fluorescence of **5** alone and in the presence of perchlorate salt of Cu(II) in THF and/or MeCN. $\lambda_{ex} = 368$ nm, ex and em band-pass = 5 nm, concn = 1×10^{-6} M, 298 K.

Although attempts to grow single crystals of the Cu(II) complexes remained unsuccessful, the protonated **4** and **5**

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(10) The PET process is considerably enhanced in polar medium due to charge−dipole and H-bonding interactions causing a lower fluorescence quantum yield. For more examples, see: (a) Bag, B.; Bharadwaj, P. K. *Inorg. Chem.* **2004**, *43*, 4626. (b) de Silva, A. P.; Gunaratne, H. Q. N.; Habib-Jiwan, J.; McCoy, C. P.; Rice, T. E.; Soumillion, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1728.

(11) Boiochhi, M.; Fabbrizzi, L.; Licchelli, M.; Sachhi, D.; Vázquez, M.; Zampa, C. *Chem. Commun.* **2003**, 1812.

(12) Bernardo, M. A.; Pina, F.; García-España, E.; LaTorre, J.; Luis, S. V.; Llinares, J. M.; Ramírez, J. A.; Soriano, C. *Inorg. Chem.* **1998**, *37*, 3935.

(with $HClO_4$) afford X-ray quality crystals. The solid-state structures of **[4.H].ClO_4.2MeCN** (**6**) and **[5.2H].$(ClO_4)_2$·3MeCN·H_2O** (**7**) show that one of the 2,4-dinitrobenzene groups moves on protonation; aligns parallel to the anthracene ring showing $\pi-\pi$ stacking interactions (Figure 4 a,b). In **6**, the distance between the anthracence and one of the 2,4-dinitrobenzene group is reduced to ~3.59 Å from 14.566 Å in **4**. In case of **7**, the same is found to be 3.776 Å. While the $\pi-\pi$ stacking interaction accounts for the exciplex emission, attachment of a proton to the N atom connected to the anthryl moiety leads to monomer emission due to blockage of PET. The solid-state photoluminescence spectra of **6** and **7** also exhibit an exciplex at ~660 nm in addition to the monomeric emission at ~550 nm. The intensity of exciplex emission in the presence of Cu(II) in MeCN either in **4** or **5** is higher compared to the corresponding protonated species.

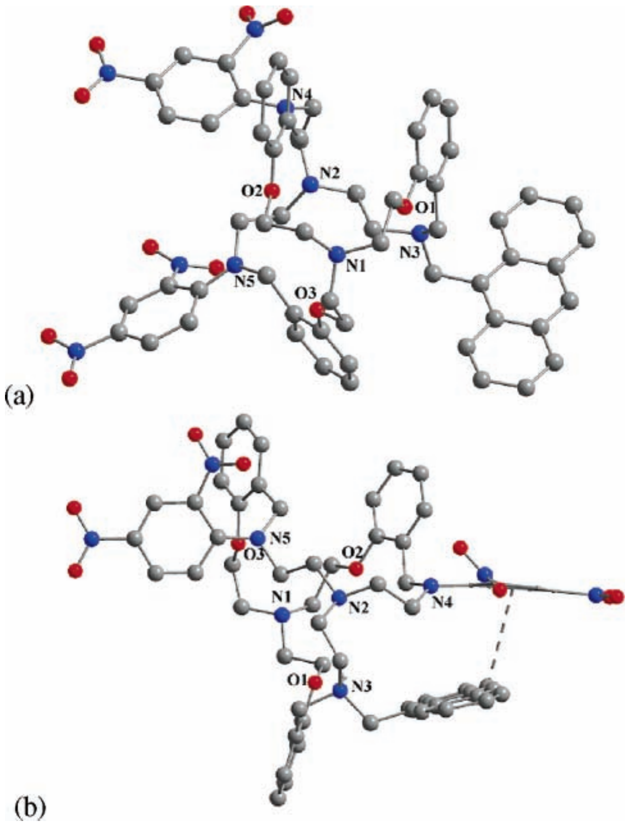

Figure 4. Perspective views of the X-ray structures of **4** (a) and [**4**.H^+] (b). Color code: N, blue; O, red; C, grey. Hydrogen atoms are omitted for clarity.

Thus, the occurrence of dual emissions in the presence of Cu(II) points to the fact that the metal ion engages the lone-pair on the N attached to the anthryl group and supresses PET, while at the same time controlled movement of the sidearms takes place leading to $\pi-\pi$ stacking between the 2,4-dinitrobenzene and the anthracene groups. Such controlled movement of groups in a molecule by external agents such as pH or a metal ion can be potentially useful in designing molecular machines.

In conclusion, we have shown that attachment of electron-withdrawing 2,4-dinitrobenzene group(s) to the cryptand receptor results in two new and unique fluorescent signaling systems; this not only brings about the selectivity with high fluorescent enhancement upon Cu(II) complexation but also results in the formation of an exciplex only in MeCN due to controlled movement of the sidegroups. The Cu(II)-induced exciplex emission in a polar solvent like MeCN is quite unusual. The specificity in fluorescent signaling is brought out by varying the structural rigidity of the receptor upon attachment of electron-withdrawing 2,4-dinitrobenzene group-(s). Our present research efforts are directed toward the design and synthesis of similar systems with other receptors for specificity toward different metal ions.

Acknowledgment. Financial support from DST, New Delhi, India, is gratefully acknowledged. B.P.B. thanks CSIR, New Delhi, for a senior research fellowship.

Supporting Information Available: Detailed synthesis, spectroscopic data, and crystallographic information (CIF) of **4**, **5**, **6**, and **7**. This material is free of charge via the Internet at http://pubs.acs.org. The CCDC numbers for crystal structures **4**, **5**, **6**, and **7** are 258795, 258796, 258797, and 258798, respectively.

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(13) Complex stability constants (*K*) were determined from the increase in fluorescence quantum yields as a function of added ionic input concentrations in MeCN according to the reported procedures. (a) de Silva, A. P.; McClean, G. D.; Pagliari, S. *Chem. Commun*. **2003**, 2010. (b) Fery-Forgues, S.; Le Bris, M.-T.; Guetté, J.-P.; Valeur, B. *J. Phys. Chem*. **1988**, *92*, 6233.

(14) Complex stability constant determined for **4** (log K [$Cu^{2+} \subset$ **4**] = 5.7) and **5** (log K [$Cu^{2+} \subset$ **5**] = 5.8) with Cu(II) was found to be much lower than that for **1** (log K [$Cu^{2+} \subset$ **1**] = 15.22). The higher K value for **1** with Cu(II) is attributed to the *cryptate effect* of the formed inclusion complex. For K determined for **1** with different metal ions, please see: Bazzicalupi, C.; Bencini, A.; Bianchi, A.; Bharadwaj, P. K.; Bandyopadhyay, P.; Giorgi, C.; Vatancoli, B.; Biswas, D.; Butcher, R. J. *Eur. J. Inorg. Chem.* **2000**, 2111.

(15) Mukhopadhyay, P.; Sarkar, B.; Bharadwaj, P. K.; Nättinen, K.; Rissanen, K. *Inorg. Chem.* **2003**, *42*, 4955.