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Tetrahedron
Tetrahedron 64 (2008) 1294–1300
www.elsevier.com/locate/tet

FRET-derived ratiometric fluorescence sensor for Cu^{2+}

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Received 29 September 2007; received in revised form 17 November 2007; accepted 20 November 2007
Available online 22 November 2007

Abstract

New *N*-(pyrenylmethyl)naphtho-azacrown-5 (**1**) was synthesized as an 'On–Off' fluorescent chemosensor for Cu^{2+}. Excited at 240 nm corresponding to the absorption of naphthalene unit (energy donor) of **1**, emission at 380 nm from pyrene unit (energy acceptor) is observed, indicating that intramolecular fluorescence resonance energy transfer (FRET-On) occurs in **1**. When Cu^{2+} is added to a solution of **1**, however, the fluorescence of pyrene is strongly quenched (FRET-Off) whereas that of naphthalene group is revived. Such FRET 'On–Off' behavior of **1** is observed only in the case of Cu^{2+} binding, but not for other metal cations. The high selectivity of **1** toward Cu^{2+} can be potentially applied to a new kind of FRET-based chemosensor. The FRET On–Off behavior is supported by computational studies. The calculated molecular orbitals of HOMO and LUMOs suggest the excited-state interactions leading to FRET from naphthalene to pyrene in **1**, but no electron density changes in $\mathbf{1}\cdot Cu^{2+}$ complex.

1. Introduction

During recent two decades, there has been a great emergence of interests in the development of fluorescent probes for various metal cations.[1–3] On account of their importance in many biological and environmental processes, especially transition metal ions have received an increasing concern.[4,5] Heavy metal cations such as Cu^{2+}, Pb^{2+} and Zn^{2+} ions are widely considered as pollutants as well as the essential trace elements in biological systems.[6–10] In particular, the recognition and detection of Cu^{2+} is of growing interest because they are considered as highly noxious elements.[6–8] Accordingly, the design and synthesis of fluorescent chemosensors for the Cu^{2+} ion have become very active research areas.[6–8] However, only a few reports are available for fluorescence enhancing chemosensors upon Cu^{2+} ion encapsulation [6] because the Cu^{2+} ion is known as inherent quenching metal ion.[16,17c,d]

Fluorescent sensors offer several distinct advantages such as sensitivity, selectivity, time response and spatial resolution. Photo-physical sensing processes are diverse: photo-induced electron transfer (PET),[11] photo-induced charge transfer (PCT), [12] fluorescence resonance energy transfer (FRET),[13] perturbation of optical transitions, and polarizabilities, excimer/exciplex formation,[14a,b] modification of redox potentials in ground or excited states, and photo-regulation of binding properties.

The FRET is defined as an excited-state energy interaction between two fluorophores in which excited donor (D) energy is transferred to an acceptor (A) part without any photon-emission.[13] So, the FRET requires a certain degree of spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor. In pursuit of the FRET-based metal cation sensors, here we report a new receptor **1** in which naphthalene unit as an energy donor and pyrene group as an energy acceptor are anchored with 15-monoazacrown-5, displaying changes in FRET behavior upon the Cu^{2+} cation encapsulation. Furthermore, density functional theory (DFT) calculations provide the complexation mechanism of the ligand–Cu^{2+} ion and qualitative explanation for the observed FRET *On–Off* phenomena.

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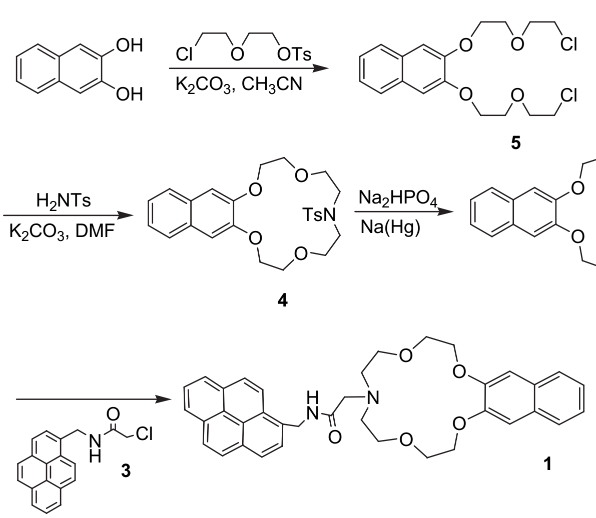
doi:10.1016/j.tet.2007.11.063

2. Results and discussion

Our synthesis began with a preparation of naphthalene derivative **5**[14c,d] as shown in Scheme 1. Under N_2 atmosphere, treatment of **5** with *p*-toluenesulfonamide and K_2CO_3 in DMF led to **4** in 78% yield. Subsequently, **2**[14e] was obtained in 85% yield after tosyl group was removed by the use of 6% Na(Hg) amalgam. Finally, **1** was synthesized in 73% yield from the reaction of **2** with **3** in the presence of the K_2CO_3 in CH_3CN. Their molecular structures were fully characterized by the ^1H NMR, ^{13}C NMR, MS, and elemental analyses (see Section 4 and Supplementary data).



Scheme 1. Synthetic pathway to **1**.

Figure 1 displays a collection of absorption and emission spectra of **1**–**3** and **1**·Cu^{2+} complex along with excitation wavelengths for the fluorescence measurements denoted by arrows. To investigate the role of the individual constituent chromophores in the photodynamics of **1**, we examined absorption and emission spectra of **2** (naphthalene) and **3** (pyrene), shown in Figure 1a and b. Most notably, the emission spectrum of naphthalene overlaps with the absorption spectrum of pyrene, achieving a favorable condition for the FRET-On. Figure 1b also shows that pyrene *alone* exhibits very weak fluorescence at ~380 nm upon excitation at 240 nm. When both naphthalene and pyrene are incorporated in **1**, the emission band of pyrene appears upon excitation at 240 nm (naphthalene absorption band) as shown in Figure 1c, indicative of an efficient intramolecular FRET from naphthalene to pyrene in **1**. When Cu^{2+} is added to **1**, however, the pyrene emission is completely quenched, then the naphthalene emission is solely observed at ~330 nm [Fig. 1d].

The FRET efficiency (ϕ) of naphthalene/pyrene system is determined by Eq. 1, where F_{DA} and F_D denote the fluorescence intensities of naphthalene (energy donor) in the presence and absence of pyrene (energy acceptor), respectively:[15a]

$$\phi = 1 - F_{DA}/F_D \tag{1}$$

The FRET efficiency ϕ becomes **1** (the maximum FRET efficiency) when the energy transfer works 100% and thus fluorescence from the donor is completely extinguished in the presence of the energy acceptor (F_{DA}=0) whereas ϕ becomes 0 (the minimum FRET efficiency) when the energy transfer does not occur at all (F_{DA}=F_D). We measured ϕ=0.85 for free **1**, but noticed that upon addition of Cu^{2+} ion it decreased to ϕ=0.08.

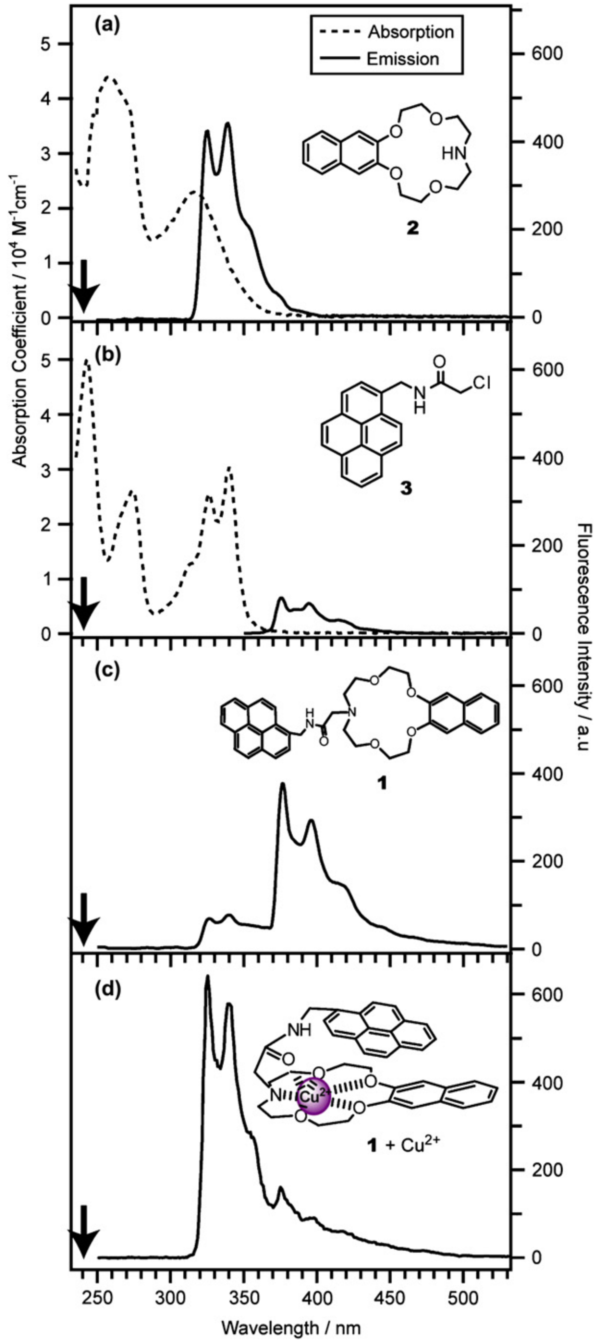


Figure 1. Absorption (dashed line) and emission (solid line) spectra of (a) **2** and (b) **3**. Emission spectra of (c) **1** and (d) **1** (6.0 μM) with 0.72 mM of $Cu(ClO_4)_2$ in CH_3CN. The emission spectra were acquired with an excitation at 240 nm marked by downward arrows.

In addition, we also measured quantum yields (Φ_f) of both **1**, **2** and their Cu^{2+} ion complexes (Table 1). For **2**, the fluorescence quantum yield was observed to decrease 2.3-fold in the presence of Cu^{2+} ions, probably due to the heavy metal

Table 1
Quantum yields (Φ_f) of both **1**–**3** and their Cu^{2+} ion complexes[15b]

Compound	Ligand		Ligand+Cu^{2+}	
	310–365 nm (naphthalene)	365–480 nm (pyrene)	310–365 nm (naphthalene)	365–480 nm (pyrene)
1	0.000704	0.380	0.0811	0.0433
2	0.528	—	0.229	—
3	—	0.473	—	0.0995

ion effect.[16,17c,d] We, however, found that in **1** the quantum yield of the naphthalene unit increases 115.0-fold with the Cu^{2+} ions, indicating the FRET-Off. Judging from the quantum yield data in Table 1, we inferred that for the fluorescence changes of the naphthalene unit, the metal ion-induced FRET On–Off effect is predominent over the heavy metal ion factor. These *FRET On–Off* phenomena can be also explained by comparison to the quantum yield of free **3** and its complex.

The fluorescence changes of **1** also show a high selectivity toward Cu^{2+} over other metal cations as seen in Figure 2. While the FRET is *turned off* upon addition of Cu^{2+}, resulting in the fluorescence shift to ~330 nm, other metal ions such as Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, and Zn^{2+} ions (720 μM, 120 equiv) do not induce any changes in the fluorescence spectrum of **1**.

We measured the fluorescence spectral changes as a function of Cu^{2+} concentration. Figure 3 shows that the fluorescence band switches from ~380 nm (pyrene) to ~330 nm (naphthalene) by the addition of Cu^{2+} ion, implicating that indeed the complexation of Cu^{2+} suppresses the FRET behavior in **1**. The spectral band switch completes with the addition of ~120 equiv of Cu^{2+} and the excessive amount of Cu^{2+} (>120 equiv) quenches both pyrene and naphthalene emission, mainly due to a heavy metal ion effect.[16,17c,17d] According to the extent of the fluorescence emission changes, we could obtain the association constants[17e] of **1** ($K_a = 1.04 \times 10^4\ M^{-1}$) for Cu^{2+} ion.

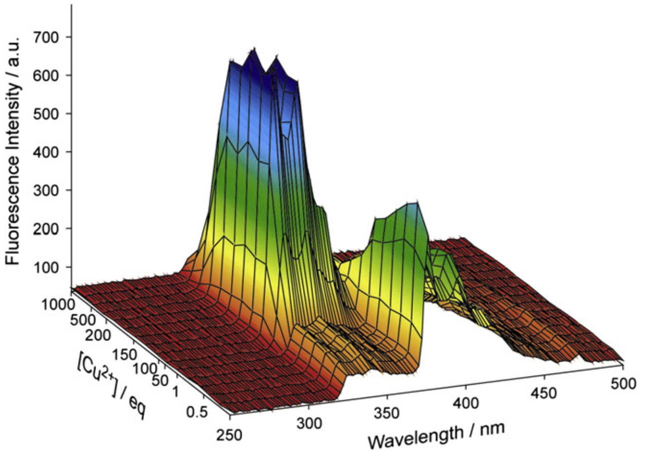


Figure 3. Fluorescence spectra of **1** (6.0 μM) upon addition of various concentrations of $Cu(ClO_4)_2$ in CH_3CN with excitation at 240 nm.

To quantify the compelxation ratio between **1** and Cu^{2+} ion, the Job plot measurement was executed by varying the concentration of both **1** and Cu^{2+} ion (Fig. S1). The maximum point appears at the mole fraction of 0.54, close to the typical ligand mole fraction (0.5) for 1:1 ligand-to-metal complex. This suggests that the Cu^{2+} be entrapped by the monoazacrown-5 to form a $\mathbf{1}\cdot Cu^{2+}$ complex.[17a,b] Mass spectrum also confirms the formation of the $\mathbf{1}\cdot Cu^{2+}$ complex (Fig. S2). There are two major peaks at *m*/*z* 651 and 750, corresponding to $[\mathbf{1}+Cu]^{2+}$ and $[\mathbf{1}+Cu(ClO_4)]^+$, respectively.

To investigate the structure of $\mathbf{1}\cdot Cu^{2+}$ complex and the origin of Cu^{2+}-induced FRET-Off, we have performed density function theory (DFT) calculations using Gaussian 03 suite.[18] The Becke-3–Lee–Yang–Parr (B3LYP) exchange functionals[19] and LANL2MB basis sets[20] were employed to compromise the computation time and the accuracy. Calculations either failed to converge or took too long when we used various other basis sets including 3-21G, 6-31G(d) and

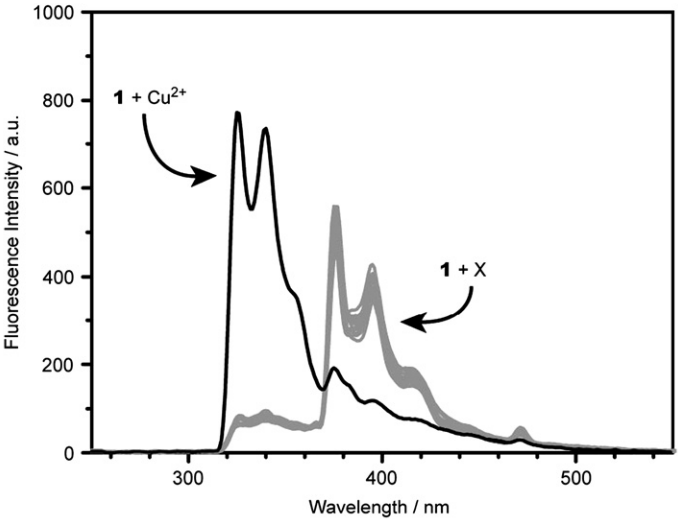


Figure 2. Fluorescence spectra of **1**+Cu^{2+} (dark line) and **1**+X (gray lines) where X=Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, and Zn^{2+}. The gray spectrum also includes the fluorescence of free **1**. The concentrations of metal ions used were 720 μM in CH_3CN, corresponding to 120 equiv of the free **1**. The spectra were obtained by excitation at 240 nm.

LANL2DZ. For LANL2MB, we tried other forms of initial geometry to confirm that the optimized geometry is a global minimum, given the calculation method and basis set.

Figure 4 presents the optimized geometry of free **1**, and **1**·Cu^{2+} complex. The free ligand has a structure where naphthalene and pyrene are positioned perpendicular to each other (T-shaped structure) with center-to-center distance ~6.5 Å. Van der Waals interactions between the pyrene-H and the naphthalene π electrons make the major contribution in stabilizing the overall geometry. Previous computation studies on a similar system (naphthalene–anthracene)[21] suggest that the parallel-displaced structure be slightly more stable than the T-shaped structure. For **1**, however, a constrained amide spacer keeps pyrene and naphthalene farther apart and the resulting longer interplanar distance makes the H–π interaction preferable to the π–π interaction, yielding the T-shaped structure, as shown in Figure 4a.

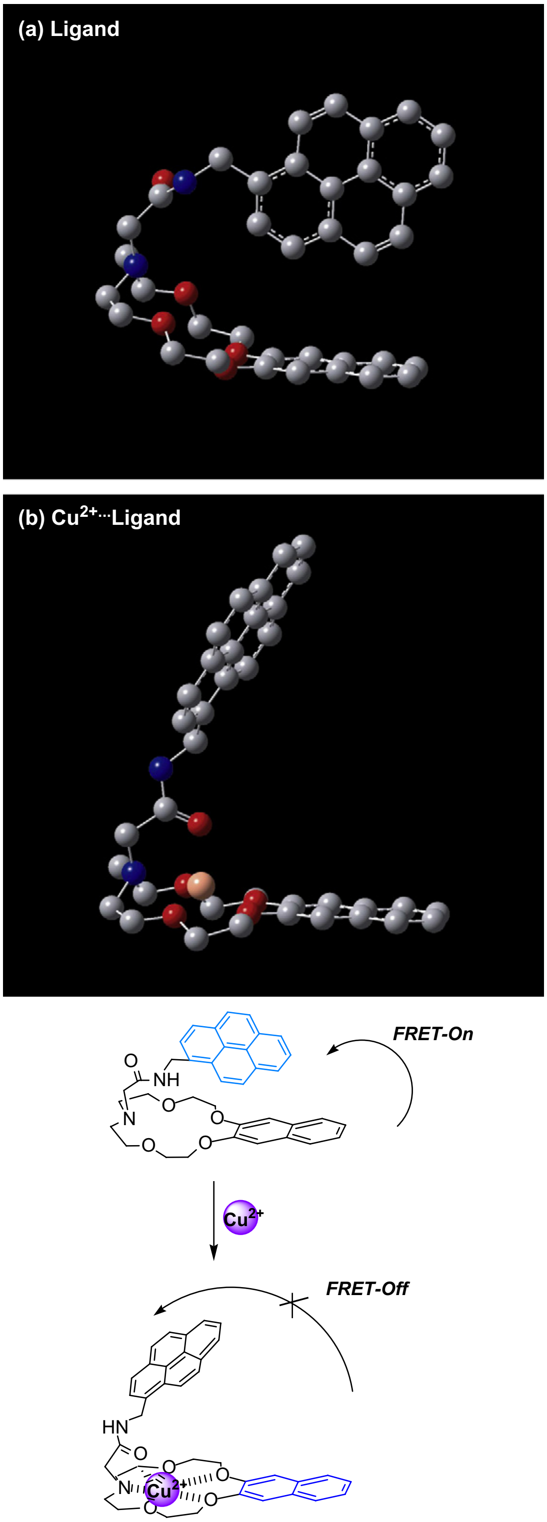


Figure 4. Optimized geometry of (a) free **1** and (b) **1**·Cu^{2+} complex. Hydrogen atoms are omitted for clarity.

Upon binding Cu^{2+} ion, **1** undergoes dramatic structural changes. Strong carbonyl oxygen–Cu^{2+} complexation pulls in the carbonyl group and subsequently rotates the pyrene moiety to form the tilted parallel structure between pyrene and naphthalene group. The strong interaction between the carbonyl oxygen and Cu^{2+} is further evidenced by the red shift of the C=O stretching band from 1674 to 1646 cm^{-1} in IR spectra upon addition of Cu^{2+} (Fig. S3).

With the optimized geometries of **1** and **1**·Cu^{2+} complex, we explored the mechanism of Cu^{2+}-induced FRET-Off. We first considered the change in the distance between the energy donor and the acceptor. FRET depends on R^{-6} where R is the inter-chromophore distance.[15] Upon Cu^{2+} binding, the distance between naphthalene and pyrene increases from ~6.5 Å to ~11 Å as shown in Figure 4. However, since the Förster distance at which the energy transfer efficiency falls to 50% is typically ~20 Å (e.g., 16 Å for naphthalene–anthracene),[21] Cu^{2+}-induced distance change is not sufficient enough to turn off the FRET.

Another possibility is the change of electronic structure arising from the Cu^{2+} complexation. Figure 5 shows the HOMO and LUMOs of the free **1** and the **1**·Cu^{2+} complex. Most interestingly, the LUMO for **1** is localized on the pyrene group while the next LUMO (LUMO-1), 23 kcal/mol higher than LUMO, is dominantly on naphthalene. Upon irradiation at 240 nm as in the experiment, LUMO-1 is excited and the excited-state interaction between LUMO and LUMO-1 causes the electronic energy transfer from naphthalene to pyrene, producing a fluorescence being emitted from the pyrene group, consistent with our experimental observations. Then we also found that the molecular orbital structure of **1**·Cu^{2+} is markedly different from that of **1**. The localized electron density of LUMO, LUMO-1, and LUMO-2 all remain on the pyrene moiety, leaving no possibility for energy transfer between the chromophores. Calculated geometry and the molecular orbital picture consistently explain the experimental results.

3. Conclusions

A fluorogenic compound **1** bearing both naphthalene and pyrene units has been newly synthesized. In free **1**, the intramolecular FRET is observed from the energy donor (naphthalene) to the energy acceptor (pyrene) arising from a spectral overlap between absorption band of pyrene and emission

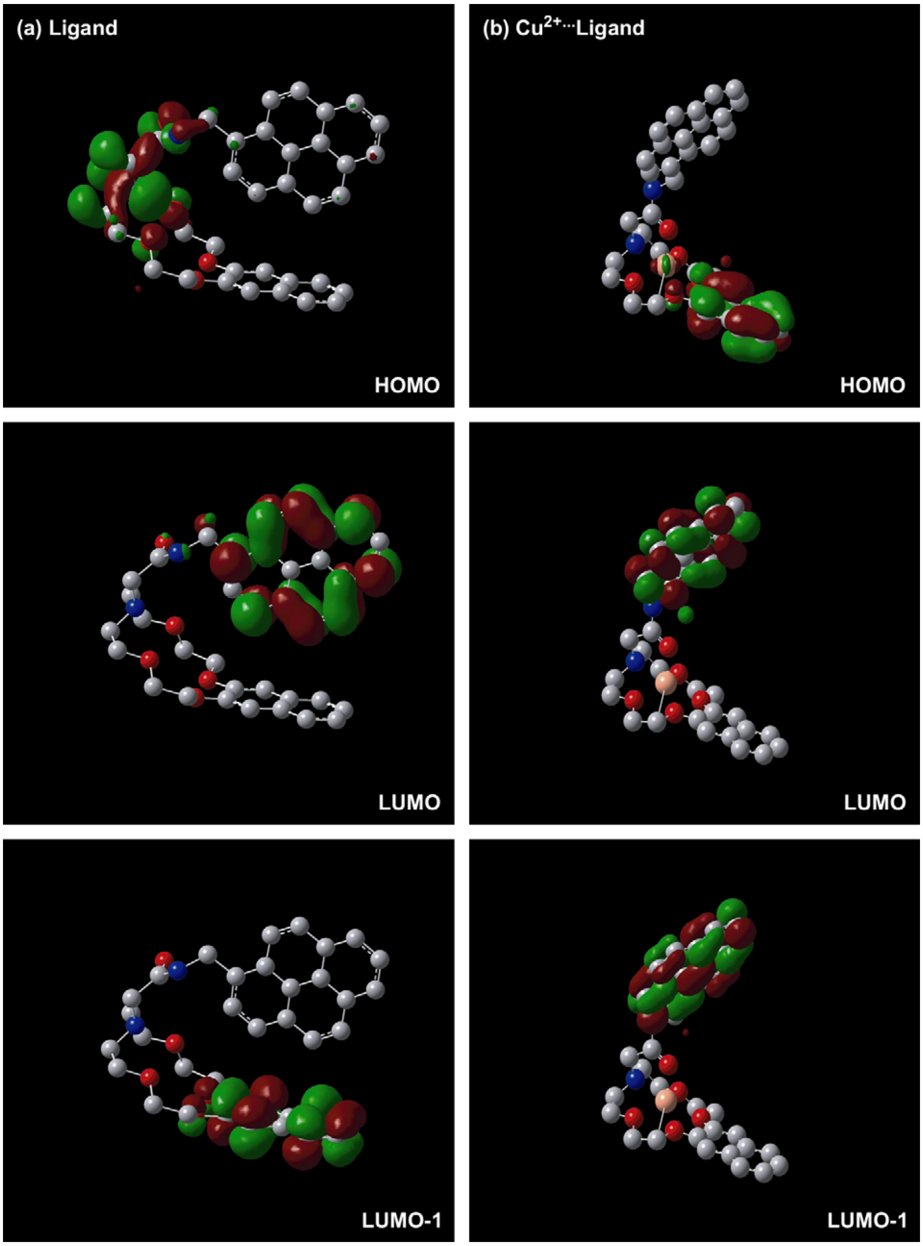


Figure 5. Molecular orbitals of HOMO, LUMO, and the second excited LUMO (LUMO-1) of (a) free ligand **1** and (b) **1**$\cdot$Cu^{2+} complex.

band of naphthalene. However, upon addition of Cu^{2+}, the FRET is suppressed and the emission of naphthalene is only observed. Density functional theory calculations show that **1** has a T-shaped structure with pyrene and naphthalene perpendicular to each other by the H—π interaction. Cu^{2+} ion entrapped by the azacrown ether strongly binds to the carbonyl oxygen and induces the structural changes of **1** from the T-shape to the tilted parallel structure. The molecular orbitals of **1** and **1**$\cdot$Cu^{2+} complex suggest that the excited-state interactions between pyrene and naphthalene in **1** cause the FRET to occur while no excited energy exchange between the chromophores inhibits the FRET for **1**$\cdot$Cu^{2+} complex. Such high selectivity of compound **1** presents itself as a potential new material for the selective Cu^{2+} ion sensor.

4. Experimental section

4.1. Synthesis

4.1.1. *N-(Pyrenylmethyl)naphtho-azacrown-5 (**1**)*

To a mixture of 0.50 g (1.57 mmol) of 2,3-naphtho-azacrown-5 (**2**)[14e] and 0.96 g (3.14 mmol) of *N*-(1-pyrenylmethyl)chloroacetamide (**3**)[16] in 50 mL of dry CH_3CN, anhydrous K_2CO_3 (0.24 g, 1.57 mmol) and a catalytic amount of NaI were added. The reaction mixture was refluxed for 2 days. After removal of the solvent in vacuo, the resulting solid was dissolved in CH_2Cl_2 (100 mL) and the organic layer was washed three times with water. The organic layer was dried over $MgSO_4$ and evaporated in vacuo. Column chromatography on silica gel with EtOAc–hexane (1:1) as eluent gave 0.82 g (73%) of **1** as a white solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.55 (s, 1H, N*H*, pyrene), 7.99–7.54 (m, 9H, Ar*H*, pyrene), 7.26–7.19 (m, 2H, $\mathrm{Ar_{naph}}H$), 7.08–7.03 (m, 2H, $\mathrm{Ar_{naph}}H$), 6.51 (s, 2H, $\mathrm{Ar_{naph}}H$), 4.86–4.83 (d, 2H, $\mathrm{CONHC}H_2$, *J*=5.79 Hz) 3.53–3.51 (d, 4H, $\mathrm{ArOC}H_2$–, *J*=3.79 Hz), 3.41–3.34 (m, 8H, $\mathrm{ArOCH_2C}H_2\mathrm{OC}H_2\mathrm{CH_2}$–), 3.28 (s, 2H, $-\mathrm{NC}H_2\mathrm{CO}$–), 2.64–2.59 (t, 4H, $\mathrm{OCH_2C}H_2\mathrm{NH}$, *J*=4.69 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 177.8, 148.8, 131.3, 130.9, 130.6, 129.3, 128.6, 127.5, 127.4, 127.0, 126.5, 126.3, 125.9, 125.2, 125.0, 124.7, 124.4, 124.2, 122.9, 108.2, 69.0, 68.4, 56.6, 41.3 ppm. FABMS *m/z* (M^+): calcd, 588.6, found, 589.0. Anal. Calcd for $C_{37}H_{36}N_2O_5$: C, 75.49; H, 6.16. Found: C, 75.51; H, 6.15.

*4.1.2. 2,3-Naphtho-azacrown-5-p-toluensulfonate (**4**)*

Under nitrogen, a mixture of *p*-toluenesulfonamide (0.91 g, 5.35 mmol), K_2CO_3 (0.74 g, 5.35 mmol), and DMF (100 mL) was heated to 80 °C for 30 min. 2,3-Bis(2-(2-chloroethoxy)-ethoxy)naphthalene (**5**) (2.00 g, 5.35 mmol) dissolved in DMF (20 mL) was added dropwise over a period of 3 h. After refluxing for 24 h, the mixture was dissolved in CH_2Cl_2 (100 mL) and treated with 10% aqueous $NaHCO_3$ (100 mL). The organic layer was washed with water (100 mL) and dried over anhydrous $MgSO_4$ and filtered to give 1.97 g of **4** as an oil in 78% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.70–7.58 (m, 4H, $\mathrm{Ar_{naph}}H$, Ar*H*-tosyl), 7.31–7.22 (m, 4H, $\mathrm{Ar_{naph}}H$, Ar*H*-tosyl), 7.05 (s, 2H, $\mathrm{Ar_{naph}}H$), 4.16–4.12 (t, 4H, $\mathrm{ArOC}H_2$–, *J*=3.69 Hz), 3.95–3.85 (m, 4H, $\mathrm{ArOCH_2C}H_2\mathrm{O}$–), 3.70–3.65 (t, 4H, $\mathrm{OC}H_2\mathrm{CH_2N}$–, *J*=4.59 Hz), 3.35–3.28 (t, 2H, $\mathrm{OCH_2C}H_2\mathrm{N}$–, *J*=6.29 Hz), 2.96–2.91 (t, 2H, $\mathrm{OCH_2C}H_2\mathrm{N}$–, *J*=4.59 Hz), 2.38 (s, 3H, $\mathrm{ArC}H_3$-tosyl); ^{13}C NMR (50 MHz, $CDCl_3$): 148.9, 143.2, 136.0, 129.7, 129.2, 127.8, 127.1, 124.2, 107.6, 69.4, 69.1, 66.0, 45.9, 21.5 ppm. FABMS *m/z* (M^+) calcd 471.17, found 471.25. Anal. Calcd for $C_{25}H_{29}NO_6S$: C, 63.67; H, 6.20. Found: C, 63.62; H, 6.25.

4.2. General procedure for fluorescence studies

Fluorescence spectra were recorded with a RF-5301PC spectrofluorophotometer. Stock solutions (1.00 mM) of metal perchlorate salts were prepared in CH_3CN. Stock solutions of free **1**–**3** (0.060 mM) were prepared in CH_3CN. Excitations were carried out at 240 nm (for **1** and **3**) with all excitation and emission slit widths at 3 nm. Titration experiments were performed with 6.0 μM solutions of **1** in CH_3CN and various concentrations of metal perchlorates in CH_3CN. For the Job plot experiment, **1** (6.0 μM) in CH_3CN and $Cu(ClO_4)_2$ (6.0 μM) in CH_3CN were prepared as stock solutions. The concentrations of each CH_3CN solution were varied, but the total volume was fixed at 4.0 mL. After the mixture was shaken for 2 h, the fluorescence emission at 240 nm was recorded.

Acknowledgements

This work was supported by the SRC program (R11-2005-008-02001-0(2007)), the Korea Research Foundation grant (KRF-2006-331-C00141) and Seoul Fellowship for H.J.K.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.11.063.

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