

ARTICLE

Fluorescence Enhancement of Polyamine Derivatives of 1,8-Naphthalimide with Transition Metal Ions

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A series of fluorescent chemosensors **1-3** were synthesized to detect transition metal ions. At the room temperature, fluorescence intensities of these chemosensors in acetonitrile without transition metal ions were found to be very weak, due to the process of the efficient intramolecular photoinduced electron transfer (PET). However, after addition of the transition metal ions, the chemosensor **1-3** exhibits obvious fluorescence enhancement. Moreover, the intensity of the fluorescence emission of chemosensors increases significantly in the presence of Zn²⁺ and Cd²⁺. The fluorescent chemosensors with different polyamine as receptors show diverse affinity abilities to the transition metal ions and signal the receptor-metal ion interaction by the intensity change of fluorescence emission.

Key words: Transition metal ion, 1,8-naphthalimide, Photoinduced electron transfer, Fluorescence enhancement, Fluorescent chemosensor

I. INTRODUCTION

The interest in fluorescence devices which can selectively recognize and signal the presence of a special substrate by the change of their fluorescence emission has grown in the last ten years [1-3]. Among the various fluorescence devices, the photoinduced electron transfer (PET) type fluorescent chemosensors based on the switchable intramolecular PET fluorescence quenching mechanism are widely used and have been proven successful as direct fluorescent cation-sensing molecules [4-7]. The PET fluorescent chemosensors are generally multi-component systems containing a fluorophore as the signal moiety, a receptor as the guest binding site, and a spacer unit to connect the fluorophore and the receptor together. The electron rich amines are often chosen to be the receptors because of the efficient binding to the guest, e.g. proton or cation to be sensed [8,9]. The PET-type fluorescent chemosensor for proton, alkaline metal ions and alkaline-earth metal ions is an active field of present research [10-13]. Unlike alkaline metal ions and alkaline-earth metal ions, most of transition metal ions are known as quenchers of fluorescence. Fluorescence enhancement resulting from the suppression of PET is often disabled due to the inherent fluorescence quenching ability of these ions [14]. Therefore, the studies of PET fluorescent chemosensor for the transition metal ions are relatively few. In fact, the chemosensors for the detection of transition metal ions are really important because transition metal ions are essential trace elements in biological systems and a no-

torious pollutant in the environment [15,16]. Therefore, the development of PET chemosensors for transition metal ions is very significant.

Fluorescence enhancement is considered as an essential feature of a transition metal ions chemosensor because it enhances sensitivity and reduces the interference induced by other factors [17]. The toughest issue in the detection of transition metal ions is their quenching nature of fluorescence [18]. In this case, discovering how to inhibit the communication between the ion quenchers and the fluorophore is the key to design a PET fluorescent chemosensor for transition metal ions. There are two developed strategies to solve this problem. One is to design a proper receptor which binds the ions tighter than fluorophore does [19], thus the ions can not approach the fluorophore to quench the fluorescence. The other is to detect transition metal ions with an electron deficient fluorophore [20], which weakens the communication between the fluorophore and the transition metal ions. When the receptor binds a transition metal ion, the intramolecular PET communication between fluorophore and the nitrogen atom of the receptor is restrained and strong fluorescence will "switch on".

In our study, the electron deficient fluorophore, 1,8-naphthalimide, was chosen as a fragment in the design of the fluorescent chemosensor, based on two points: (i) 1,8-naphthalimide fluorophore has strong fluorescence and excellent photostability which is good for detection [21]; (ii) The electron deficient fluorophore could effectively weaken the PET interaction between transition metal ions and fluorophore. Polyamine compounds are well known as receptors for coordinating metal ions when the sufficient deprotonated amino groups are available [22,23]. Herein, some open polyamine chains, which can bind metal ions much freely resulting from

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their good flexibility, were applied in our investigation.

II. EXPERIMENTS

A. Materials

1,8-naphthalic anhydride was used without further purification. 1,2-diaminoethane, diethylene triamine, triethylene tetramine and *n*-butylamine were purified according to the reference [24]. The transition metal salts used in the investigation were in their chloride form and without any purification. Acetonitrile was spectroscopic grade; water was redistilled three times. The purified solvents were transparent in the spectral region of study.

B. Instrument

^1H and ^{13}C NMR spectra were recorded with a Bruker DMX-300 NMR spectrometer. Elemental analysis was performed on a Perkin-Elmer 240C analytical instrument. Absorption spectra were recorded on a Perkin-Elmer Lambda 45 UV-Vis spectrophotometer. Fluorescence emission spectra were measured with a CRT-970 spectrometer. Cyclic voltammetry measurements were carried out by using CHI 620A Electrochemical Analyzer. A glass carbon was used as the working electrode and the counter electrode was platinum wire, Ag/AgCl as reference electrode. CH_3CN (spectrophotometric grade and bubbled with N_2 before use) was used as solvent and 0.1 mol/L TBAP was used as the supporting electrolyte. The scanning speed was maintained at 100 mV/s.

C. Methods

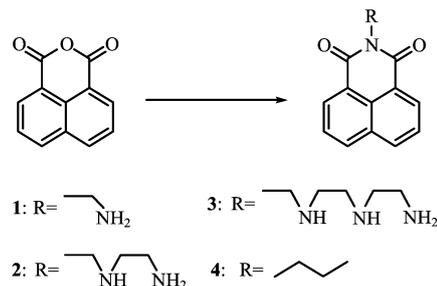
The fluorescence and UV-Vis spectrum were carried out by using $\sim 5 \mu\text{mol/L}$ solutions of the compounds. The effect of the metal ions on the fluorescence intensity was examined by adding a few μL of the stock solution of the metal ions to a known volume (10 mL) of the solution of the compound. The addition was limited to 100 μL so that the volume change was not significant.

The fluorescence quantum yields of the compounds were measured using 1,8-naphthalimide as the reference compound ($\Phi_f = 5.0 \times 10^{-2}$ in acetonitrile) [25]. The fluorescence spectra of all compounds were measured under the same operating conditions and settings, and the fluorescence quantum yields were determined by comparing the areas under the fluorescence spectra.

D. Synthesis

The compounds 1-4 (Scheme 1) were obtained using a similar synthesis procedure. Chemosensor 1 was prepared as follows: 1,2-diamino-ethane (0.80 mL, 12 mmol) was introduced to the solution of 1,8-naphthalic anhydride (2.4 g, 10 mmol) in 60 mL ethanol, and the suspension was refluxed for 8 h. After completion of the reaction, the mixture was cooled

to the room temperature. The precipitate was filtered, and the organic layer was washed with water (10 mL \times 3) and dried with anhydrous sodium sulfate. Then the solvent was removed by vacuum and the residue was purified by column chromatography (silica gel, 10:1 chloroform:methanol).



Scheme 1 The compounds 1-4.

The diethylene triamine and triethylene tetramine were used instead of 1,2-diaminoethane to synthesize 2 and 3 using the procedure mentioned above. The *n*-butylamine was used instead of the polyamine to synthesize compound 4.

1: Yield (80%), ^1H NMR (300 MHz, CDCl_3): δ 8.6 (2H,d), 8.2 (2H,d), 7.7 (2H,t), 4.2 (2H,t), 3.0 (2H,t), ^{13}C NMR (75 MHz, CDCl_3): 164.3, 134.3, 132.0, 131.7, 128.6, 127.2, 122.9, 42.8, 40.7. Element Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$ (%): C 69.99, H 5.03, N 11.66, Found (%) C 69.92, H 5.01, N 11.65.

2: Yield (78%), ^1H NMR (300 MHz, CDCl_3): δ 8.6 (2H,d), 8.2 (2H,d), 7.8 (2H,t), 4.3 (2H,t), 3.0 (2H,t), 2.8 (4H,m). ^{13}C NMR (75 MHz, CDCl_3): 164.3, 133.9, 131.4, 131.1, 128.0, 126.8, 122.5, 52.2, 47.5, 40.0, 38.5. Element Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_2$ (%): C 67.83, H 6.05, N 14.83; Found (%) C 68.02, H 6.07, N 14.91.

3: Yield (70%), ^1H NMR (300 MHz, CDCl_3): δ 8.6 (2H,d), 8.2 (2H,d), 7.7 (2H,t), 4.3 (2H,t), 3.0 (2H,t), 2.8 (2H,m), 2.7 (4H,m), 2.6 (2H,m). ^{13}C NMR (75 MHz, CDCl_3): 163.3, 133.1, 130.6, 130.3, 127.1, 126.1, 121.6, 52.7, 51.8, 48.5, 46.9, 41.1, 39.3. Element Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_4\text{O}_2$ (%): C 66.24, H 6.79, N 17.16; Found (%) C 66.35, H 6.83, N 17.24.

4: Yield (87%), ^1H NMR (300 MHz, CDCl_3): δ 8.6 (2H,d), 8.2 (2H,d), 7.7 (2H,t), 4.2 (2H,t), 1.7 (2H,t), 1.5 (2H,m), 1.0 (3H,t). ^{13}C NMR (75 MHz, CDCl_3): 164.3, 133.9, 131.7, 128.2, 127.0, 122.9, 40.4, 30.3, 20.5, 14.0. Element Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_2$ (%): C 75.87, H 5.97, N 5.53, Found (%) C 75.79, H 5.95, N 5.51.

III. RESULTS AND DISCUSSION

From UV-Vis spectra of 1-4 measured in CH_3CN at the room temperature, the shape and location of the absorption peaks of these compounds were found similar to those of the corresponding fluorophore, 1,8-naphthalimide (Table I). The similarity of the spectra data indicates that there is hardly any interaction between the fluorophore and receptor groups in the ground

TABLE I Absorption and fluorescence spectral data of the compounds in acetonitrile

	$\lambda_{\max}(\text{Abs.})/\text{nm}$			$\lambda_{\text{em}}(\text{Flu.})/\text{nm}$			$(\nu_A - \nu_F)/\text{cm}^{-1}$
	1	2	3	1	2	3	
1	321(s)	331	345	362(s)	381	401(s)	3965
2	318(s)	332	346	364(s)	380	401(s)	3805
3	319(s)	331	346	363(s)	380	400(s)	3896
4	321(s)	330	347	362(s)	375	401(s)	3636

state. When the solvents were changed from the 1,4-dioxane to the methanol, the absorption maxima are slightly red-shifted about 4 nm in comparison to those of the fluorophore. In most of the investigated cases, after titration of the transition metal ions, only small changes in the absorbance and the slight red shift of the maximum were observed.

The fluorescence spectra of these compounds **1-4** show structured emission at 380 nm. The typical UV-Vis and fluorescence spectra of **1** are shown in Fig. 1. The fluorescence maxima are not sensitive to the polarity variation of the solvents. The Stoke's shift, a parameter which indicates the differences in structure and properties of the compounds between the ground state S_0 and the first excited state S_1 , was detected in the range from 3636 cm^{-1} to 3965 cm^{-1} (in Table I).

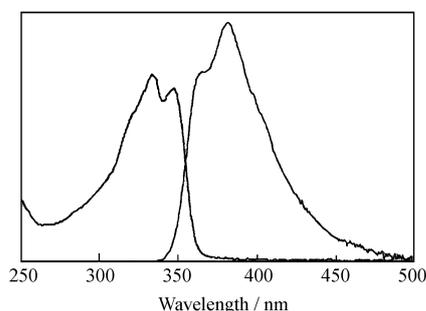


FIG. 1 Absorption spectra (left) and fluorescence spectra (right) of **1** in acetonitrile. The excitation wavelength was 320 nm.

The redox behaviors of these fluorescent chemosensors were investigated to test if the intramolecular PET process could take place in these systems. No oxidation peaks could be observed in the range of 0-2 V, showing that 1,8-naphthalimide is an electron deficient fluorophore. The measured redox potential and the fluorescence data are able to provide a quantitative estimation of the thermodynamic driving force. The ΔG values have been calculated using the equation, $\Delta G = 23.06(E_{\text{ox}(\text{receptor})} - E_{\text{red}(\text{fluorophore})}) - E_{00}$ [26], where $E_{\text{ox}(\text{receptor})}$ represents the oxidation potential of the amino moiety, $E_{\text{red}(\text{fluorophore})}$ indicates the reduction potential of the fluorophore and E_{00} denotes the energy of the fluorescent state. The E_{00} values used in the calculation of ΔG have been estimated from the location of the first peak in the fluorescence spectrum. $E_{\text{red}(\text{fluorophore})} = -1.00 \text{ V}$, and $E_{00} = -329.4 \text{ kJ/mol}$. $E_{\text{ox}(\text{receptor})}$ is 1.36 V for

chemosensor **1** and is 1.05 V for structure alike chemosensors **2** and **3**. The calculated ΔG values are -101.2 kJ/mol for **1** and -131.7 kJ/mol for chemosensors **2** and **3**. It is clear that the PET process is thermodynamically feasible for the present chemosensors.

Though the ΔG value proves the PET is thermodynamically feasible, other factors such as the distance between the receptor and the fluorophore, the suitable orientation of the two components, will also play important roles in the intramolecular PET process [27,28]. For example, through-space overlap of the nitrogen lone pair orbital with the π -orbital of the fluorophore was normally disturbed by the distance and orientation between two orbitals. The fluorescence quenching is induced by PET from the proximal amine to the fluorophore resulting from the better overlap of the orbits [29]. Herein, the proximal amine is the primary amine in chemosensor **1** and the secondary amine in the cases of **2** and **3**. Compared with the primary amine, the secondary amine has lower oxidation ability and more favorable thermodynamic driving force for the PET process. The actual extent of PET in these systems can be learned by comparing the fluorescence quantum yields.

The fluorescence quantum yield, Φ_f , usually reflects the extent of the PET communication between the receptor and the fluorophore. The values of Φ_f are 1.0×10^{-2} and **1**, 8.7×10^{-4} for **2** and **3**, and 3.4×10^{-2} for the reference compound **4**. The low values of fluorescence quantum yield illuminate that the PET processes are favorable and efficient in these chemosensor systems. The fluorescence quantum yield of compound **4**, which has no fluorescence quenching by the PET process in the molecule, is much higher than **1** and **2** or **3** by factors of 3.4 and 39.1 in acetonitrile respectively. In the other word, the PET process quenches the fluorescence emission intensity of compound **1** by 70.6% and that of compound **2** and **3** by 97.4%.

After the addition of transition metal salts, the lone electron pairs in amine of the receptors coordinate to metal ions, making the oxidation potential of the receptor increase [30-32]. The bound receptor is unavailable to donate an electron to the excited fluorophore, therefore the PET communication is interrupted and the recovery of fluorescence is expected. In fact, the observed values of the fluorescence enhancement of the chemosensors are significant (in Table II). The chemosensor **1** has good fluorescence enhancement effect but limited selectivity to the metal ions. The chemosensors **2** and **3** have good selectivity and the values of fluorescence enhance-

TABLE II The values of fluorescence enhancement of **1**, **2**, **3** as a function of different metal ions input in acetonitrile

	1		2		3	
	FE ^a	[M] ^b /(mol/L)	FE ^a	[M] ^b /(mol/L)	FE ^a	[M] ^b /(mol/L)
Zn ²⁺	82.9	2.8×10 ⁻⁴	73.2	2.5×10 ⁻⁴	184.1	3.4×10 ⁻⁴
Cd ²⁺	79.2	2.0×10 ⁻⁴	39.9	2.3×10 ⁻⁴	85.2	2.7×10 ⁻⁴
Cr ³⁺	74.5	9.5×10 ⁻⁵	16.0	8.2×10 ⁻⁵	27.3	1.2×10 ⁻⁴
Ni ²⁺	76.8	3.0×10 ⁻⁵	1.1	8.3×10 ⁻⁵	5.3	2.4×10 ⁻⁵
Co ²⁺	78.4	1.3×10 ⁻⁴	5.4	3.8×10 ⁻⁵	5.3	4.3×10 ⁻⁵
Cu ²⁺	61.1	2.9×10 ⁻⁵	8.7	1.5×10 ⁻⁵	4.1	2.2×10 ⁻⁵
Mn ²⁺	89.1	2.5×10 ⁻⁴	1.2	8.1×10 ⁻⁵	6.2	9.2×10 ⁻⁵
Hg ²⁺	89.0	2.7×10 ⁻⁴	3.4	2.5×10 ⁻⁴	10.8	3.1×10 ⁻⁴
Pb ²⁺	67.2	2.0×10 ⁻⁴	17.0	2.6×10 ⁻⁴	22.0	2.9×10 ⁻⁴

^a With reference to the fluorescence intensity of the respective compound in the absence of metal ion.

^b Represents the concentration of the transition metal ion for which maximum FE was observed.

ment vary in a wide range. The highest value (184.1) was gained when chemosensor **3** was treated with Zn²⁺ (see Fig.2). With the addition of Co²⁺, Ni²⁺ and Cu²⁺, the fluorescence enhancement values are low in the case of **2** and **3** due to non-radiative pathways, e.g. through charge transfer state. Co²⁺ and Ni²⁺ can also quench the fluorescence by energy transfer, electron transfer or the heavy-atom effect. However, the quenching processes are precluded when the electronic configuration of the metal ions, such as Zn²⁺ and Cd²⁺, is d¹⁰. Thus, the Zn²⁺ and Cd²⁺ have no electron transfer or energy transfer process with the fluorophore and their fluorescence enhancement is significant.

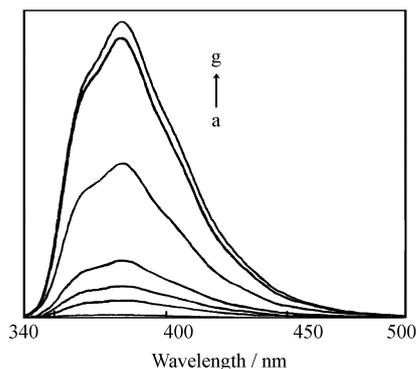


FIG. 2 Fluorescence spectra of **3** ($\sim 5 \mu\text{mol/L}$) in acetonitrile in the presence of Zn²⁺. Zn²⁺ concentration are (a) 0, (b) 5.0 $\mu\text{mol/L}$, (c) 10 $\mu\text{mol/L}$, (d) 20 $\mu\text{mol/L}$, (e) 40 $\mu\text{mol/L}$, (f) 0.5 mmol/L, (g) 0.75 mmol/L. $\lambda_{\text{ex}}=320 \text{ nm}$.

It is known that the protonation of the amino moiety of the receptor may cause fluorescence enhancement, and the hydrated metal ions are usually contaminated with protons (owing to partial hydrolysis of the salts). It is often argued that the enhancement results from the protonation of the receptor moiety. However, no obvious difference of the fluorescence enhancement values was observed between the crude salts and recrystallized

salts. This illustrates that even if the protons are assumed to contribute to the fluorescence enhancement of the chemosensors, the values should not exceed those predicted by suppression of PET.

In these systems, the chemosensors with different polyamine chains show diverse selectivities to the transition metal ions (see Fig.3). Chemosensor **1** may form complexes with more than one receptor because only one nitrogen atom exists in the receptor moiety. Under this situation, the transition metal ions cannot approach the fluorophore effectively. Hence, the selective recognition of the metal ions is weakened though the fluorescence enhancement is high. Chemosensors **2** and **3** show different response to the transition metal ions and the variation range of fluorescence enhancement is large. Among those ions, Zn²⁺ is a representative example, which is a soft ion and is easily coordinated with the soft nitrogen atoms. The quenching processes are precluded because of its stable electronic configuration. In the case of chemosensors **2** and **3**, the nitrogen atoms of the polyamine receptor can ligand to the metal ions with torsion of the polyamine chain to adopt the best orientation and spatial position. The coordination is so efficient that the PET from the nitrogen atoms to

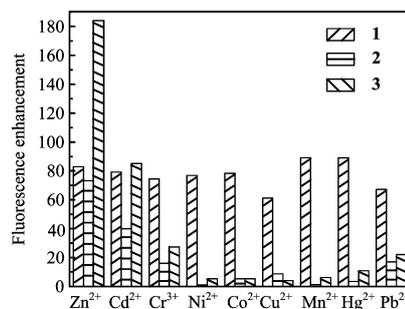


FIG. 3 A bar diagram of the signaling response of chemosensors **1**, **2**, **3** in acetonitrile with different transition metal ions.

the fluorophore is inhibited. Zn^{2+} and Cd^{2+} both have the d^{10} electronic configuration but the fluorescence enhancement of Zn^{2+} is larger than Cd^{2+} . This behavior could be attributed to the better ability of zinc ion to remove the electron density from the receptor, which is proportional to their charge density. Other transition metal ions such as Cu^{2+} , Co^{2+} and Ni^{2+} , have no remarkable fluorescence enhancement, which is possible due to their ability to quench fluorescence.

The interaction between transition metal ions and reference compound **4** were measured as well. Zn^{2+} and Cd^{2+} did not quench the fluorescence of **4**, while Cu^{2+} , Co^{2+} and Ni^{2+} did. In the presence of the metal ions, two opposite factors determine the net effect. One is that the binding interaction of the transition metal ions with receptor increases the fluorescence intensity. The other is that the fluorophore-metal ions interaction quenches the fluorescence. If receptor-metal ions interaction is stronger than fluorophore-metal ions interaction, a remarkable fluorescence enhancement could be observed. When the polyamine receptors bind to the metal ions, the metal ions get close to the fluorophore at the same time. Then, the quenching nature of the transition metal ions counteracts the fluorescence enhancement resulting from the suppression of the PET, and the net effect for other transition metal ions except Zn^{2+} and Cd^{2+} is not remarkable.

IV. CONCLUSION

In conclusion, fluorescent PET-type chemosensors **1-3** with polyamine as the receptor were synthesized. The fluorescence signaling behavior of the chemosensors has been observed with titration of some transition metal ions of biological and environmental importance. Even though the efficient transition metal ion quenchers were added to the solution of chemosensor **1**, strong fluorescence enhancement was still observed. It is worthy to note that chemosensors **2** and **3**, in which the polyamine acts as the receptor, show good selectivity to the transition metal ions. In our system, Zn^{2+} and Cd^{2+} have higher fluorescence enhancement values than other transition metal ions. The results provide a method to improve the fluorescence response and selectivity of structurally simple fluorophore-spacer-receptor fluorosensor systems by exploiting the electron deficient fluorophore and suitable receptors.

V. ACKNOWLEDGMENTS

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