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Selective and Sensitive Fluorescent Chemosensors for Cu^{2+} Ion Based upon Bis-1,8-naphthalimide Dyads

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A series of new fluorescent chemosensors **5a**—**5e**, composed of two aminonaphthalimide fluorophores and 2,6-bis((*N*-aminoalkyl)aminocarboxy)pyridines, were prepared, characterized, and their fluorescent properties towards heavy and transition metal (HTM) ions were investigated. Chemosensors **5c**—**5e** exhibited high selectivity and sensitivity for Cu^{2+} ion over other HTM ions with fluorescent quenching (green to colourless). It clearly demonstrated that the length of the linkers (diamines) between the aminonaphthalimides and 2,6-dicarboxypyridine of **5a**—**5e** was very important for their sensitivity and selectivity for Cu^{2+} ion over other HTM ions.

Keywords　fluorescence, sensors, 1,8-naphthalimide, metal ion, selectivity

Introduction

Since heavy and transition metal (HTM) ions play an important role in many biological and environmental processes, the design and synthesis of fluorescent sensors with high selectivity and sensitivity for the detection and measurement of HTM ions nowadays are of significant importance.[1] For example, Cu^{2+} ion has been shown to have an important role in the enzymatic defense against oxygen toxicity, and identified as an environmental pollutant, consequently, the development of fluorescent chemosensors with high selectivity and sensitivity for Cu^{2+} ion over other HTM ions is still a challenge.[2]

Due to their fluorescent properties and special interactions with some biomolecules, mono-1,8-naphthalimides are frequently used as the fluoroionophores to prepare fluorescent chemosensors for metal cations and protons in recent years.[3] Meanwhile, the fluorescent properties of bis-1,8-naphthalimide derivatives have also recently received much attention, for example, a series of new kind of chemosensors **A** (Figure 1) have been prepared and exhibited the excellent and selective recognition for the HTM ions.[4] However, to our knowledge, little attention has been paid to the fluorescent properties of another kind of chemosensors **B** based upon the bis-1,8-naphthalimide dyads. Only Grabchev and coauthors described the behavior and spectral characteristics of **B1** and **B2** (Figure 1), two bis-1,8-naphthalimide derivatives linked by a diethylenetriamine bridge, in the presence of different HTM ions.[5] Although the selectivity of the reported sensors **B1** and **B2** for different HTM ions was not good, this encouraging

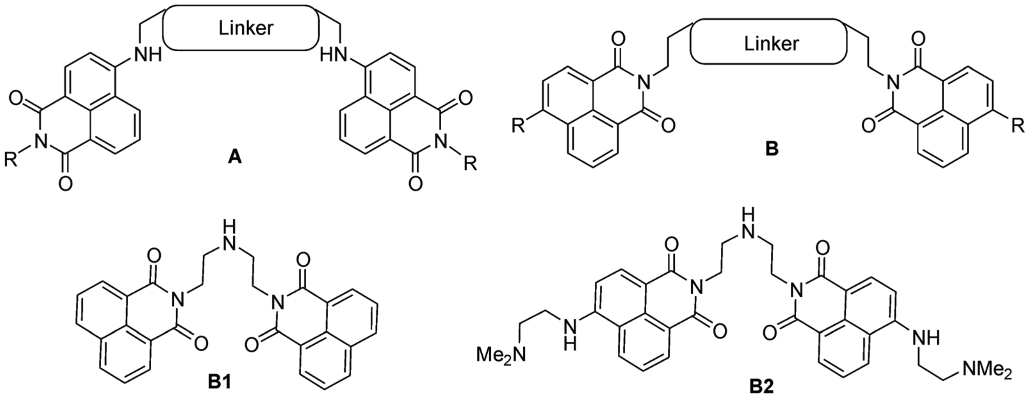

Figure 1　Chemical structures of chemosensors.

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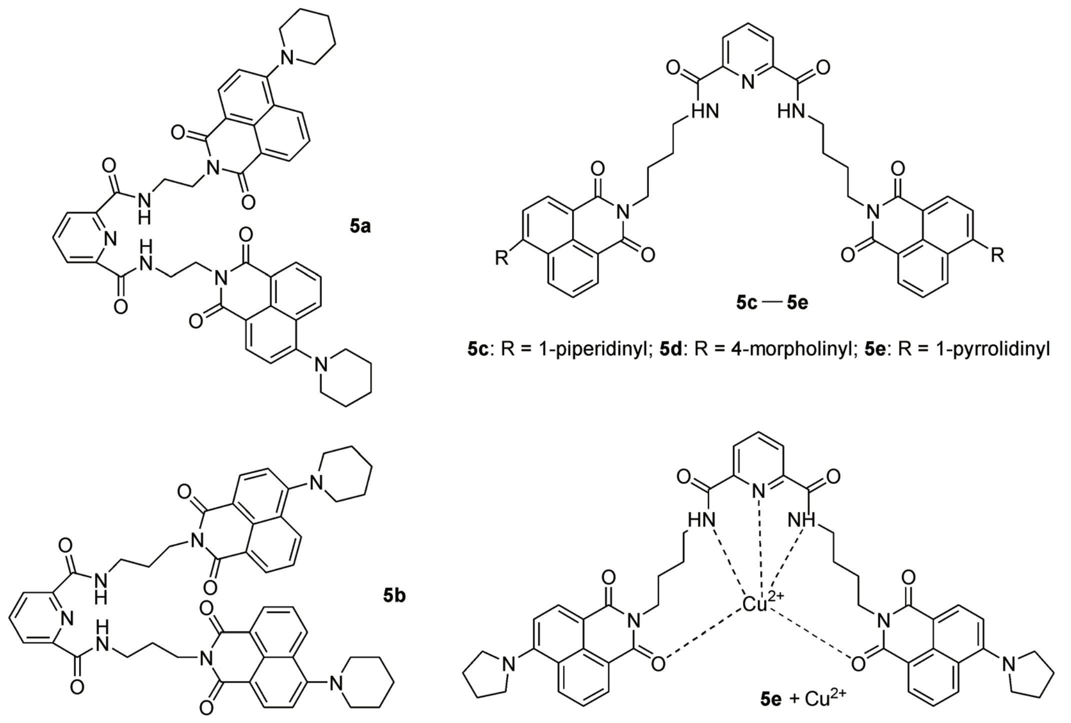
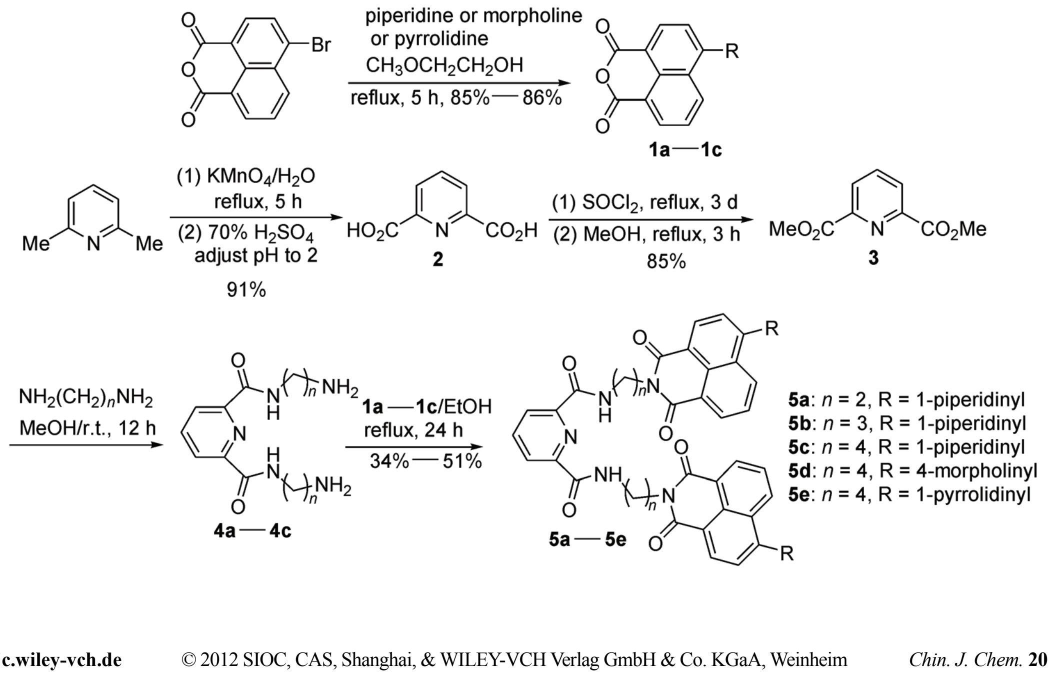
results prompted us to further study other bis-1,8-naphthalimide derivatives of **B** as the fluorescent sensors. Therefore, based on the aforementioned results, in the present paper we designed a series of new chemosensors **5a**—**5e** (Figure 2), which were composed of two aminonaphthalimide fluorophores and 2,6-bis((*N*-aminoalkyl)aminocarboxy)pyridines. We expected that **5a**—**5e** could adopt the semirigid V-shaped conformation, which might be selectively binding with a metal cation. Meanwhile, the nitrogen atoms of 2,6-bis((*N*-aminoalkyl)aminocarboxy)pyridines and oxygen atoms of aminonaphthalimides were both the ion receptors. Moreover, according to the length of the linkers (diamines) between the aminonaphthalimides and 2,6-dicarboxypyridine of **5a**—**5e**, the size of the cavity for binding HTM ions could be regulated to some degree. To our delight, **5a**—**5e** displayed highly selective and sensitive response toward Cu^{2+} ion over other HTM ions. The synthetic route of **5a**—**5e** was shown in Scheme 1.



5c: R = 1-piperidinyl; **5d**: R = 4-morpholinyl; **5e**: R = 1-pyrrolidinyl

Figure 2 Chemical structures of target chemosensors **5a**—**5e**.

Scheme 1 Synthetic routes of **5a**—**5e**



5a: *n* = 2, R = 1-piperidinyl
5b: *n* = 3, R = 1-piperidinyl
5c: *n* = 4, R = 1-piperidinyl
5d: *n* = 4, R = 4-morpholinyl
5e: *n* = 4, R = 1-pyrrolidinyl

Experimental

All solvents and reagents were used as obtained from commercial sources without further purification. The solutions of metal ions were prepared from $Zn(ClO_4)_2•6H_2O$, $Fe(ClO_4)_2•6H_2O$, $Ca(ClO_4)_2•4H_2O$, $Mg(ClO_4)_2$, $Ba(ClO_4)_2$, $Pb(ClO_4)_2$, $Cd(ClO_4)_2$, $Cu(ClO_4)_2$, $Hg(ClO_4)_2$, and $AgPF_4$, respectively, and were dissolved in distilled THF. Analytical thin-layer chromatography (TLC) and preparative thin-layer chromatography (PTLC) were performed with silica gel plates using silica gel 60 GF_{254} (Qingdao Haiyang Chemical Co., Ltd.). Melting points are uncorrected. Nuclear magnetic resonance spectra (NMR) were recorded on a Bruker Avance DMX 300 or 400 MHz instrument in $CDCl_3$ (^1H at 300 or 400 MHz and ^{13}C at 75 or 100 MHz) using TMS (tetramethylsilane) as the internal standard. High-resolution mass spectra (HR-MS) and mass spectra (EI-MS) were carried out with APEX II Bruker 4.7T AS instrument and HP 5988 instrument, respectively. Electrospray iontrap mass spectrometry (ESI-MS) was carried out with Thermo Scientific LCQ Fleet mass spectrometer. Fluorescent spectra were determined on a Hitachi F-4500 spectrophotometer. UV-visible spectra were determined on a Hitachi U-3310 spectrophotometer.

Synthesis of compounds 1a—1c

A mixture of 4-bromo-1,8-naphthalic anhydride (2.77 g, 10.0 mmol), and piperidine or morpholine or pyrrolidine (20 mmol) in 2-methoxyethanol (25 mL) was refluxed for 5 h, then the reaction mixture was cooled to room temperature to afford a yellow solid after filtration, which was purified by recrystallization from ethanol to give **1a**—**1c** in 85%—86% yields as the orange needles.

1a: CAS: 87223-12-9. m.p. 170—171 ℃ (lit.[6] 175—176 ℃); ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.58 (d, $J=$7.6 Hz, 1H), 8.50 (d, $J=$8.4 Hz, 1H), 8.44 (d, $J=$8.8 Hz, 1H), 7.73 (t, $J=$7.6 Hz, 1H), 7.20 (d, $J=$8 Hz, 1H), 3.31 (t, $J=$5.6 Hz, 4H), 1.88—1.93 (m, 4H), 1.74—1.78 (m, 2H); EI-MS m/z: 281 (M^+, 83), 280 ($[M-1]^+$, 100).

1b: CAS: 31837-36-2. m.p. 210—212 ℃ (lit.[7] 220—221 ℃); ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.56 (d, $J=$7.2 Hz, 1H), 8.50 (d, $J=$8.0 Hz, 1H), 8.46 (d, $J=$8.8 Hz, 1H), 7.73 (t, $J=$8 Hz, 1H), 7.26 (d, $J=$1.6 Hz, 1H), 4.03 (t, $J=$4.4 Hz, 4H), 3.31 (t, $J=$4.8 Hz, 4H); EI-MS m/z: 283 (M^+, 48).

1c: CAS: 99024-08-5. m.p. 220—222 ℃; ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.64 (d, $J=$8.4 Hz, 1H), 8.51 (d, $J=$7.2 Hz, 1H), 8.33 (d, $J=$8.4 Hz, 1H), 7.52 (t, $J=$8.4 Hz, 1H), 6.77 (d, $J=$8.8 Hz, 1H), 3.84 (s, 4H), 2.14 (s, 4H); MS (ESI-TRAP) m/z: 268 ($[M+1]^+$, 100).

Synthesis of compound 2 A mixture of $KMnO_4$ (8.848 g, 56 mmol) and 2,6-dimethylpyridine (1.2 mL, 10 mmol) in water (85 mL) was refluxed for 5 h, and filtered. Then the filtrate was concentrated to the 1/5 of original volum. Finally, when the pH value of the mixture was adjusted to 2 by using 70% H_2SO_4, compound **2** (1.519 g) was obtained as a white solid. CAS: 499-83-2. Yield 91%, m.p. 226—227 ℃ (lit.[8] 227—228 ℃).

Synthesis of compound 3 A mixture of **2** (1.67 g, 10 mmol) and $SOCl_2$ (7.1 mL) was refluxed for 3 d. Then the excess $SOCl_2$ was removed under normal pressure. After the reaction mixture was cooled to room temperature, methanol (50 mL) was added and the mixture was refluxed for 3 h in the dry atmosphere. Finally, some solvent was removed and 1.633 g of compound **3** was precipitated as a white solid. CAS: 5453-67-8. Yield 85%, m.p. 130—131 ℃ (lit.[9] 130—132 ℃); ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.33 (dd, $J=$8.0, 1.6 Hz, 2H), 8.03—8.07 (m, 1H), 4.04 (s, 6H), EI-MS m/z: 195 (M^+, 2).

General procedure for the synthesis of 5a—5e To a solution of diamine (5 mmol) in dried MeOH (5 mL) under argon at 0 ℃, a solution of **3** (97.5 mg, 0.5 mmol) in dried MeOH (20 mL) was added dropwise. After adding, the above mixture was stirred for 12 h at room temperature, and the solvent and excess of diamine were removed under reduced pressure to give the residues **4a**—**4c**, which were used directly for the next step without further purification. Then a mixture of **4a**—**4c** and **1a**—**1c** (1.25 mmol) in EtOH (20 mL) was refluxed under argon, and after 24 h, the solvent was evaporated under reduced pressure to give the residue, which was seperated by preparative thin-layer chromatography (PTLC) to give the pure products **5a**—**5e**.

5a: Yield 49%, yellow solid, m.p. 152—153 ℃; ^1H NMR ($CDCl_3$, 400 MHz) δ: 9.04 (s, 2H), 8.20—8.38 (m, 8H), 7.91—7.95 (m, 1H), 7.55—7.59 (m, 2H), 7.02 (t, $J=$8.8 Hz, 2H), 4.02—4.03 (m, 4H), 3.83 (s, 4H), 3.17 (s, 8H), 1.86—1.87 (m, 8H), 1.71 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 164.9, 164.5, 163.9, 157.3, 148.3, 138.6, 132.7, 131.0, 130.7, 129.7, 125.9, 125.2, 124.0, 122.7, 115.3, 114.5, 54.4, 39.2, 39.0, 26.1 24.2; IR ν: 3456, 2936, 2852, 1690, 1649, 1588, 1533, 1235 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{44}N_7O_6$ $[M+H]^+$ 778.3348, found 778.3351.

5b: Yield 51%, yellow solid, m.p. 147—148 ℃; ^1H NMR ($CDCl_3$, 400 MHz) δ: 9.36 (t, $J=$5.6 Hz, 2H), 8.42 (d, $J=$7.2 Hz, 2H), 8.36 (d, $J=$7.6 Hz, 2H), 8.32 (d, $J=$7.6 Hz, 2H), 8.21 (d, $J=$8.4 Hz, 2H), 8.00 (t, $J=$7.6 Hz, 1H), 7.53 (t, $J=$7.6 Hz, 2H), 7.06 (d, $J=$8.4 Hz, 2H), 4.34 (t, $J=$6.4 Hz, 4H), 3.58—3.62 (m, 4H), 3.16 (s, 8H), 2.12—2.15 (m, 4H), 1.87 (s, 8H), 1.72 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 164.7, 164.3, 163.6, 157.2, 148.7, 138.6, 132.6, 130.9, 130.6, 129.7, 125.8, 125.1, 124.3, 122.6, 115.3, 114.5, 54.3, 37.5, 36.2, 27.9, 26.1, 24.2; IR ν: 3373, 2935, 2852, 1691, 1651, 1587, 1532, 1236 cm^{-1}; HRMS (ESI) calcd for $C_{47}H_{48}N_7O_6$ $[M+H]^+$ 806.3661, found 806.3670.

5c: Yield 47%, yellow solid, m.p. 143—144 ℃; ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.61 (s, 2H), 8.32—8.46 (m, 8H), 7.96 (t, $J=$7.6 Hz, 1H), 7.59 (t, $J=$7.8 Hz, 2H), 7.12 (d, $J=$8 Hz, 2H), 4.14 (s, 4H), 3.59—3.61 (m, 4H), 3.22 (m, 8H), 1.73—1.89 (m, 20H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 164.5, 164.1, 163.9, 157.2, 149.0, 138.6, 132.6, 130.9, 130.7, 129.7, 126.0, 125.2, 124.7, 122.8, 115.5, 114.6, 54.5, 39.5, 39.4, 26.1, 25.5, 24.3; IR ν: 3463, 2935, 2854, 1693, 1654, 1587, 1535 cm^{-1}; HRMS (ESI) calcd for $C_{49}H_{52}N_7O_6$ $[M+H]^+$ 834.3974, found 834.3982.

5d: Yield 41%, yellow solid, m.p. 141—142 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.64 (s, 2H), 8.46 (d, J=7.2 Hz, 2H), 8.41 (d, J=7.2 Hz, 2H), 8.34—8.36 (m, 4H), 7.99 (s, 1H), 7.63 (t, J=7.2 Hz, 2H), 7.18 (d, J=7.2 Hz, 2H), 4.13 (s, 4H), 4.01 (s, 8H), 3.60 (s, 4H), 3.25 (s, 8H), 1.79 (s, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 164.3, 163.9, 163.8, 155.6, 148.9, 138.6, 132.4, 131.0, 130.1, 129.6, 125.9, 125.7, 124.7, 123.0, 116.7, 114.8, 66.8, 53.3, 39.5, 39.4, 26.1, 25.5; IR ν: 3462, 2958, 2856, 1693, 1652, 1588, 1536, 1236 cm^{-1}; HRMS (ESI) calcd for $C_{47}H_{48}N_7O_8$ $[M+H]^+$ 838.3559, found 838.3550.

5e: Yield 34%, yellow solid, m.p. 146—147 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.87 (s, 2H), 8.46 (d, J=8 Hz, 2H), 8.38 (d, J=6.8 Hz, 2H), 8.32 (d, J=6.8 Hz, 2H), 8.22 (d, J=8.4 Hz, 2H), 7.98 (s, 1H), 7.42—7.44 (m, 2H), 6.68 (d, J=8 Hz, 2H), 4.11 (s, 4H), 3.74 (s, 8H), 3.6 (s, 4H), 2.09 (s, 8H), 1.78 (s, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 164.7, 163.9, 152.9, 149.1, 138.4, 133.2, 131.8, 130.9, 130.8, 124.6, 122.8, 122.2, 110.2, 108.4, 53.1, 39.4, 39.3, 25.9, 25.5; IR ν: 3463, 2927, 2867, 1676, 1636, 1587, 1530; HRMS (ESI) calcd for $C_{47}H_{48}N_7O_6$ $[M+H]^+$ 806.3661, found 806.3647.

Results and Discussion

As described in Scheme 1, **5a**—**5e** were smoothly obtained by the reaction of 4-piperidine/morpholine/pyrrolidine-1,8-naphthalimides (**1a**—**1c**) with the corresponding 2,6-bis((N-aminoalkyl)aminocarboxy)pyridines (**4a** — **4c**), which were prepared from 2,6-dimethylpyridine and the corresponding diamines. The chemical structures of **5a**—**5e** were well characterized by IR, m.p., ^{1}H NMR, ^{13}C NMR, and HRMS.

Due to the good solubility for HTM ions and the fluorescent quantun yields (Φ_F), tetrahydrofuran (THF) was chosen as the solvent for all the measurements. The absorption spectra of **5a**—**5e** in THF were shown in Figure 3. The respective fluorescence responses of **5a**—**5e** in the presence of Hg^{2+}, Ag^+, Zn^{2+}, Fe^{3+}, Cd^{2+}, Pb^{2+}, Ca^{2+}, Cu^{2+}, Mg^{2+} and Ba^{2+} ions were presented in Figures 4—8. When Cu^{2+} ion was added to the solution of **5a**—**5e**, respectively, a decrease of the fluorescent intensity was detected. However, the addition of other metal ions, *e.g.*, Hg^{2+}, Ag^+, Zn^{2+}, Fe^{3+}, Cd^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+} and Ba^{2+} ions, did not lead to a clear change of the fluorescent intensity of **5a**—**5e**. Especially when Cu^{2+} ion was added to the solution of **5c**—**5e**, all with four carbon linkers, the significant changes in the fluorescent intensity were observed. For example, after addition of Cu^{2+} ion to the solution of **5c**—**5e**, the corresponding fluorescent intensities were sharply decreased more than fivefold as compared with the controls. It suggested that the length of the linkers (diamines) between the aminonaphthalimides and 2,6-dicarboxypyridine of **5a**—**5e** was very crucial for sensitivity and selectivity for Cu^{2+} ion. But the effect of substituents (*e.g.*, 1-piperidinyl, 4-morpholinyl, and 1-pyrrolidinyl groups) at the 4-position of **5c**—**5e** on their fluorescent intensity changes for Cu^{2+} ion was not obvious.

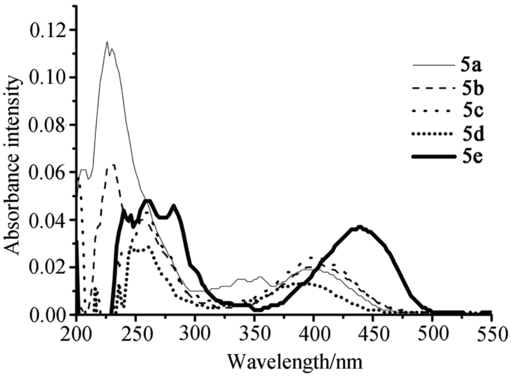


Figure 3 Absorbance intensities of **5a**—**5e** (1×10^{-6} mol•L^{-1}) in THF at 288 K.

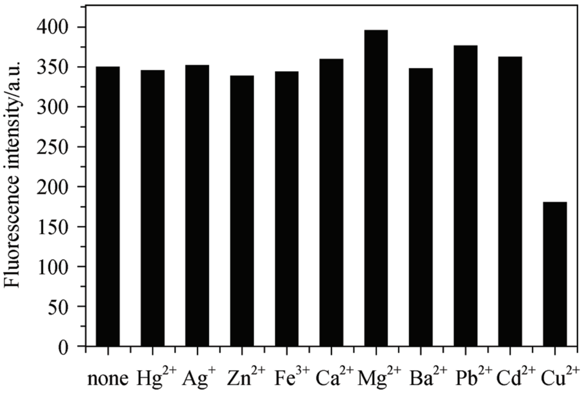


Figure 4 Variation of the fluorescent intensity at λ_{max} (522 nm) of **5a** (1×10^{-6} mol•L^{-1}) in THF in the presence of 5.0 equiv. of the respective metal cations.

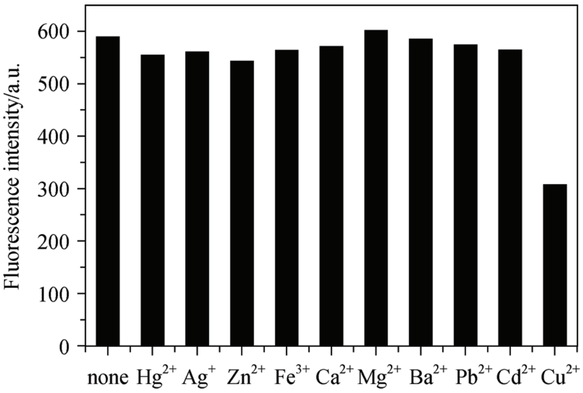


Figure 5 Variation of the fluorescent intensity at λ_{max} (522 nm) of **5b** (1×10^{-6} mol•L^{-1}) in THF in the presence of 5.0 equiv. of the respective metal cations.

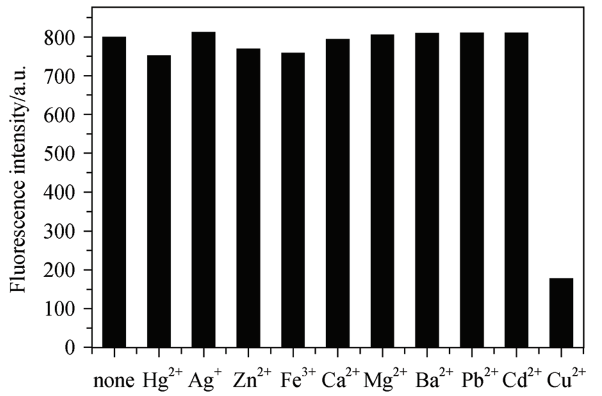


Figure 6 Variation of the fluorescent intensity at λ_{max} (519 nm) of **5c** (1×10^{-6} mol•L^{-1}) in THF in the presence of 5.0 equiv. of the respective metal cations.

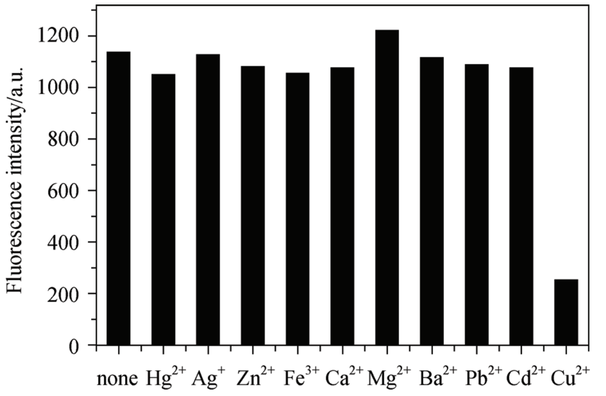


Figure 7 Variation of the fluorescent intensity at λ_{max} (516 nm) of **5d** (1×10^{-6} mol•L^{-1}) in THF in the presence of 5.0 equiv. of the respective metal cations.

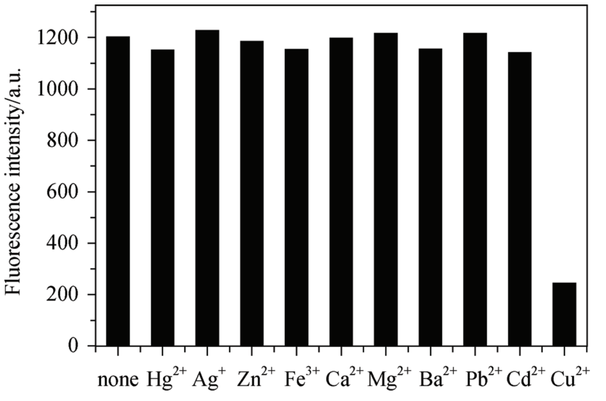


Figure 8 Variation of the fluorescent intensity at λ_{max} (513 nm) of **5e** (1×10^{-6} mol•L^{-1}) in THF in the presence of 5.0 equiv. of the respective metal cations.

Subsequently, the sensitivity of the fluorescent emission response of **5e** toward Cu^{2+} ion was typically investigated with various Cu^{2+} ion concentrations (0—7 $\times10^{-6}$ mol•L^{-1}) (Figure 9). The sensor exhibited high sensitivity for Cu^{2+} ion probably attributed to the formation of a **5e**-Cu^{2+} ion complex (Figure 2). The inset in Figure 9 displayed the changes of fluorescent intensity ($I_{513\ nm}$) of **5e** to the concentrations of Cu^{2+} ion. The photo in Figure 9 showed the colour change of **5e** after addition of 10 equiv. of Cu^{2+} ion (green to colourless). However, the increasing amounts of Cu^{2+} ion had almost no effect on the absorption spectra in this paper (Figure 10).

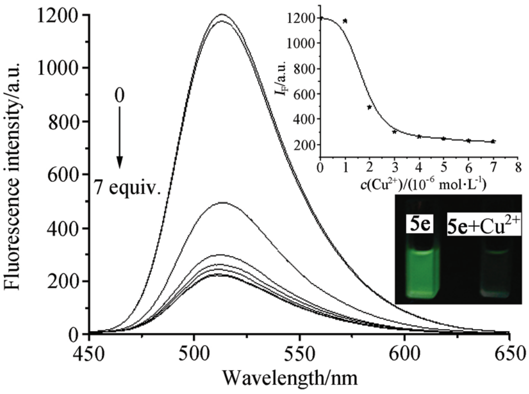


Figure 9 Fluorescent spectra of **5e** (1×10^{-6} mol•L^{-1}) in THF in the presence of increasing amounts of $Cu(ClO_4)_2$ (from 0 to 7 equiv.). λ_{ex}=440 nm. Inset: (1) the plot of the fluorescent intensity ($I_{513\ nm}$) vs. the concentration of $Cu(ClO_4)_2$; (2) the photo of **5e** before and after addition of 10.0 equiv of $Cu(ClO_4)_2$ under UV light illumination (365 nm).

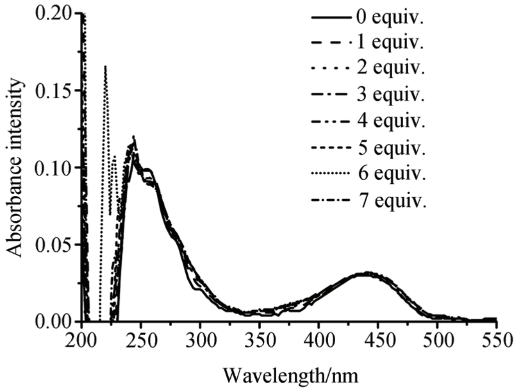


Figure 10 Variation of the absorbance intensity of **5e** (1×10^{-6} mol•L^{-1}) in the presence of increasing amounts of $Cu(ClO_4)_2$ (from 0 to 7 equiv.) in THF at 288 K.

To explore further the utility of **5e** as an ion-selective fluorescent chemosensor for Cu^{2+} ion, the competition experiments were conducted in the presence of Cu^{2+} ion (5×10^{-6} mol•L^{-1}) mixed with Hg^{2+}, Ag^{+}, Zn^{2+}, Fe^{3+}, Cd^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}, and Ba^{2+} ions at 5×10^{-6} mol•L^{-1}, respectively. As outlined in Figure 11, as compared with that only in the presence of Cu^{2+} ion, no obvious variation in its fluorescent intensity was detected in the presence of the mixture of Cu^{2+} ion with other metal ions. It implied that the selectivity of **5e** for Cu^{2+} ion was remarkable.

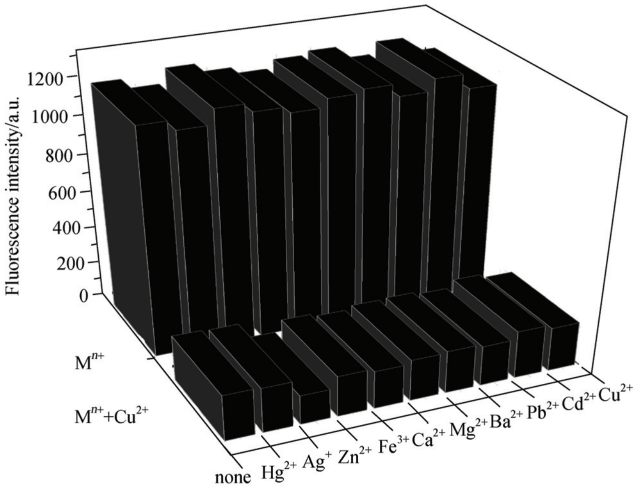


Figure 11 Variation of the fluorescent intensity at $\lambda_{\max}$ (513 nm) of **5e** (1×10^{-6} mol•L^{-1}) in THF in the presence of different metal cations (M^{n+}, 5×10^{-6} mol•L^{-1}). [Cu^{2+}]: 5×10^{-6} mol•L^{-1}.

Conclusions

In summary, based on bis-1,8-naphthalimide dyads, we have developed a novel series of fluorescent chemosensors **5c**—**5e** for Cu^{2+} ion with high sensitivity and selectivity. It is noteworthy that the length of the linkers (diamines) between the aminonaphthalimides and 2,6-dicarboxypyridine of **5a**—**5e** was very important for their sensitivity and selectivity for Cu^{2+} ion over other HTM ions. Moreover, it clearly demonstrated that another kind of bis-1,8-naphthalimides **B** could also display the good selectivity for the HTM ions via introduction of the appropriate groups on the linker.

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