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A colorimetric probe for copper(II) ion based on 4-amino-1,8-naphthalimide

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ABSTRACT

A novel fluorescent probe with naphthalimide as fluorophore and di(2-picolyl)amino unit as receptor for Cu(II) was designed and synthesized. In water/acetonitrile solution, the presence of Cu^{2+} ions induced significant blue shift on the maximum absorption band as well as complete fluorescence quenching due to the formation of a 1:1 metal–ligand complex. It exhibited high selectivity toward Cu(II) and no interference from other metal ions was observed. The structure of the complex was characterized by single crystal X-ray diffraction experiments. The results of this research demonstrate successfully that excellent sensing properties can be achieved by a small organic compound with very simple structure. This is also the first single crystal structure which reveals directly the coordination pattern of fluorescent probe bearing di-2-picoly-amine unit with Cu(II).

1. Introduction

Fluorescent probes for sensing and monitoring chemical analytes are topical and attractive due to their high sensitivity and simplicity [1]. The design and synthesis of highly effective fluorescent probes is thus a fundamental task for organic and analytical chemists. To make a useful probe, a compound must contain a "receptor", which can selectively interact with the analytes, and a "signaling site", normally a strongly emitting fluorophore [2]. Among the numerous mechanisms which induce visual signal changes upon binding of analytes, intramolecular charge transfer (ICT) has been widely used in the design of new sensors [3], which usually display distinctive changes on absorption and fluorescence spectra.

4-Aminonaphthalimide has recently generated great interest in the field of fluorescent probes because of its desirable properties, such as excellent photo stability, high luminescence efficiency, large stock's shifts and easy modification on the molecular structure. Qian and co-workers reported recently an ICT-based fluorescent chemosensor for Cu(II) based on 1,8-naphthalimide, which displayed red-shifted absorption and emission bands in the presence of Cu(II) due to deprotonation of the secondary amine in the molecule [4]. But the fluorescence quantum yields of this probe were very small. Another fluorescent probe containing 4,5-di-2-picoly-amine as receptor for Cu(II) showed a blue-shifted emission with small intensity change, which was ascribed to the reduced ICT process [5]. Additionally, a fluorescent probe based on 1,8-naphthalimide for Zn(II) showed red-shifted fluorescence and absorption spectra, but with an inferior selectivity [6]. Anyway, the 1,8-naphthalimide based ICT fluorescent probe, which displays not only remarkable change on absorption and emission spectrum, but also high selectivity towards analyst, is promising but less developed.

Herein, we report another fluorescent probe, N-*n*-butyl-4-N′-di(2-pyridylmethyl)amino-1,8-naphthalimide (**1**) with naphthalimide as the fluorophore, and di(2-picolyl)amino unit (DPA) as the receptor. According to the literature, the fluorescent chemosensors containing DPA as receptor showed excellent selectivity towards transitional metal ions, such as Zn^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} [3i,l,7]. As long as the DPA receptor moiety is not involved in metal ion binding, it can act as strong electron donor, and thus a push–pull typed naphthalimide with ICT characteristic can be achieved. In the case of binding with a given metal ion, because of the decrease on the electron donating ability of DPA, the ICT process will be affected significantly and ultimately the color as well as the fluorescence of the probe will be changed.

2. Results and discussion

2.1. Molecular design and synthesis

The synthesis of **1** is depicted in Scheme 1. The reaction of *n*-butylamine with 4-bromo-1,8-naphthalic anhydride in refluxing ethanol gave compound **3** in ca. 85% yield as an off-white powder. Compound **2** was easily synthesized by condensation of 2-aminomethyl pyridine with compound **3** in 2-methoxyethanol solution with a yield of 78%. By using anhydrous potassium carbonate as base and hexadecyltrimethylammonium

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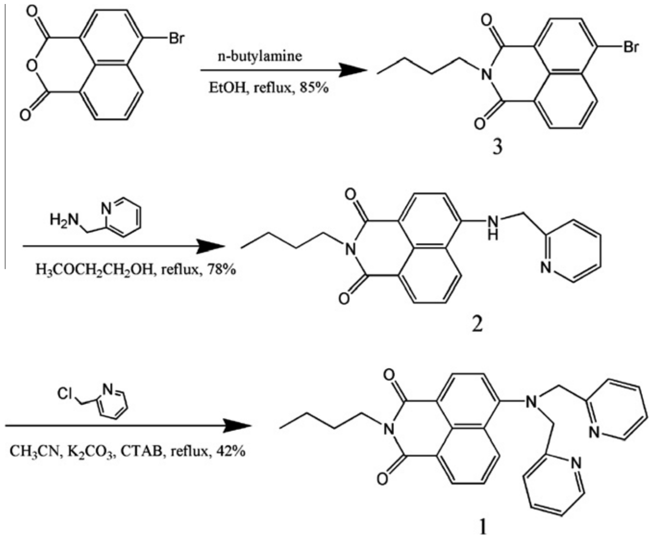

Scheme 1. Synthesis of probe **1**.

chloride as a phase transfer catalyst, the probe **1** was prepared by the reaction of picolyl chloride with compound **2** in acetonitrile with 42% yield. The molecular structure of probe **1** was fully characterized by ^{1}H and ^{13}C NMR, and ESI-TOF mass spectra.

*2.2. Absorption and fluorescence spectra of probe **1***

The absorption and fluorescence spectra of probe **1** were recorded in a mixed solvents of acetonitrile/water (8:2, v/v). In the absorption spectra of probe **1**, an intense absorption band centered around 405 nm ($\varepsilon = 1.25 \times 10^4\ \mathrm{M^{-1}\ cm^{-1}}$) was observed, which is responsible for the yellow color of the solution. Meanwhile, a strong fluorescence emission band with a maximum at 527 nm ($\Phi = 0.72$) was presented in the fluorescence spectra, which is typical for 1,8-naphthalimide derivatives with amino group connected at 4-position of the naphthalene imide ring [8]. The results suggest that the connection of DPA group at the 4-position induces ICT characteristics for the excited states of naphthalimide.

*2.3. Absorption and fluorescence response of probe **1** to different metal cations*

The absorption and fluorescence spectra of **1** in the presence of different metal ions (5 equiv.) were recorded in the mixed solvents of acetonitrile/water (8:2, v/v). As shown in Fig. 1, the most distinctive changes of the absorption spectra upon addition of Cu^{2+} ion is that the lowest-energy absorption band of probe **1** shifts hypsochromically about 80 nm from 403 to 330 nm, which leads to an eye-perceived color change from yellow to colorless as shown in the photograph **1b**. More importantly, the presence of other metal ions including Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} produced negligible absorption changes under identical experimental conditions.

The fluorescence of probe **1** is quenched completely in the presence of Cu^{2+} ($\Phi < 0.01$). As can be seen from the photograph in Fig. 2, the distinct green fluorescence of **1** disappears in the presence of Cu^{2+} ions. But the presence of other metal ions induces no significant change on the emission spectra. The fluorescence intensity is enhanced slightly while adding Hg^{2+}. The abovementioned results suggest that **1** coordinate with copper ions with high stability and selectivity among the various ions tested. This has also been found in other DPA containing probes [7j,p].

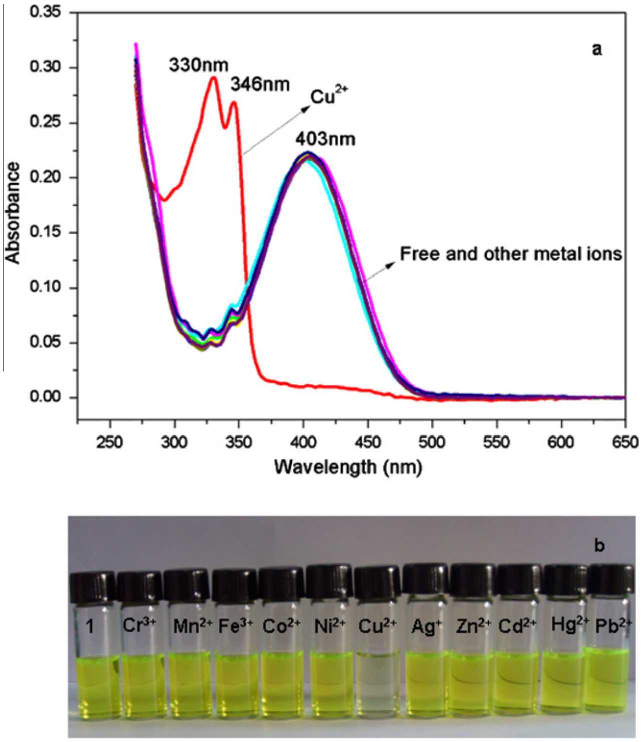

Fig. 1. (a) Absorption spectra change of **1** (20 μM) upon addition of different metal cations (5 equiv.) in an acetonitrile/water mixed solvents (8:2, v/v). (b) Color change of **1** in the presence of various metal cations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

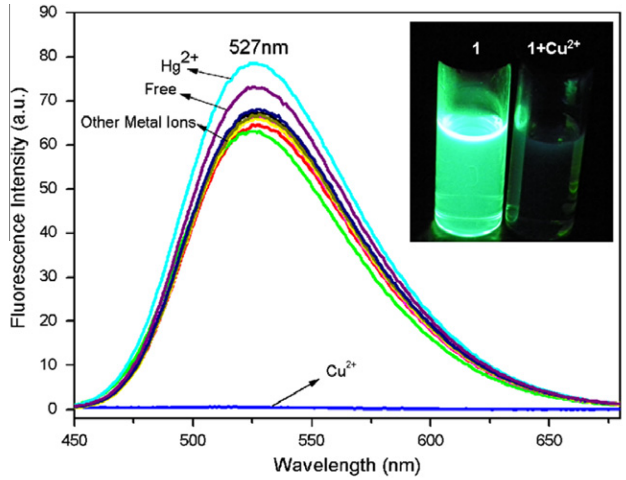

Fig. 2. Fluorescence spectra changes of **1** (20 μM) upon addition of different metal cations (5 equiv.) in an acetonitrile/water mixed solvent (8:2, v/v). The excitation wavelength was 357 nm. Inset: Photograph of **1** and **1** in the presence of excess amount of copper ions(II) under a 365 nm UV light.

2.4. Fluorescence and absorption titration experiments

Fig. 3a shows the changes of the absorption spectra of **1** as the function of the concentration of Cu^{2+} in acetonitrile/water (8/2, v/v) solution at room temperature. With the sequential addition of Cu^{2+}, the intensity of the absorption maximum of **1** at 405 nm decrease gradually following the formation of a new bands centered at 330 nm ($\varepsilon = 1.5 \times 10^4\ \mathrm{M^{-1}\ cm^{-1}}$). A clear isobestic point at 357 nm is observed. The results indicate that the coordination of

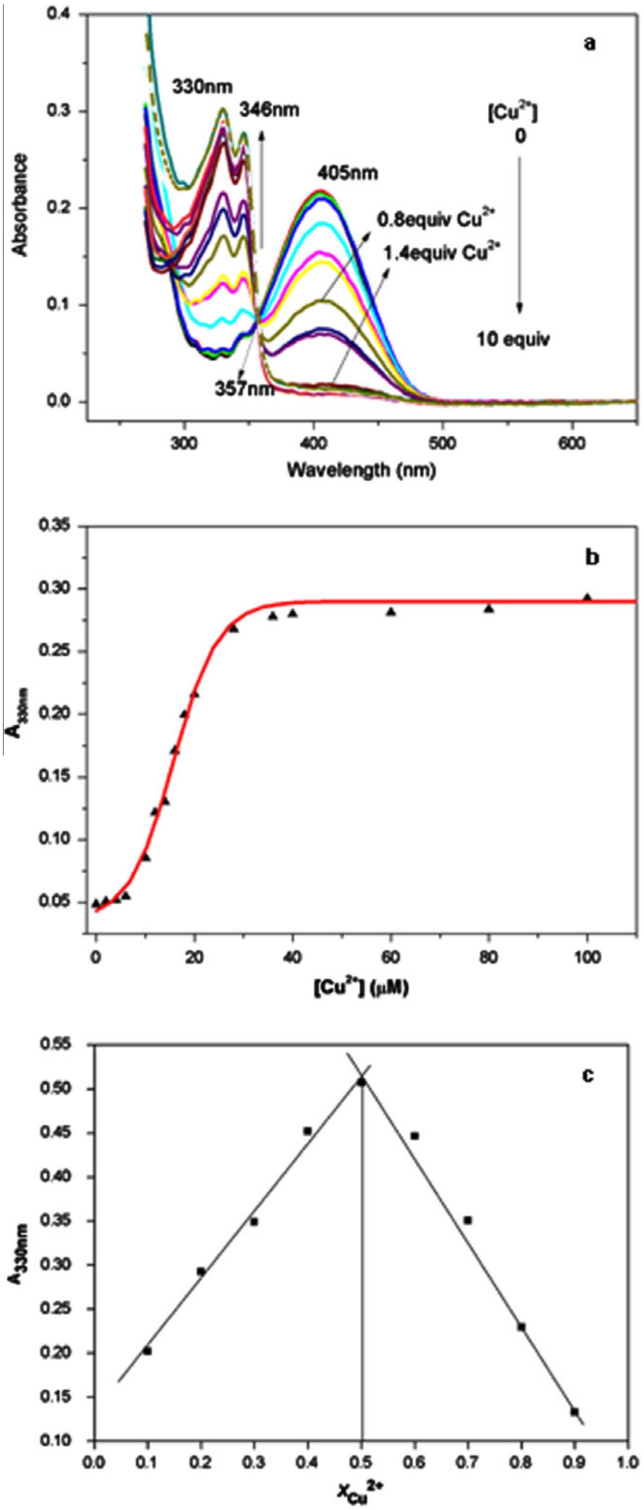

Fig. 3. (a) Absorption spectra of **1** (20 μM) in the presence of increasing Cu^{2+} concentrations (0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0, 1.4, 1.8, 2.0, 4.0, 5.0, 7.0, 8.0, 10 equiv.) in an acetonitrile/water mixed solvent (8:2, v/v). (b) The titration profile of **1** according to the absorbance at 405 nm. (c) Job's plot of 1:1 complex of **1** and Cu^{2+}, where the absorption at 330 nm was plotted against the mole fraction of copper ions, and the mole fraction of copper ions $X_{Cu}{}^{2+}$ was $[Cu^{2+}]/([Cu^{2+}] + [\mathbf{1}])$. The total concentration of copper ions with **1** was 100 μM.

Cu^{2+} with the tridentate receptor DPA reduces the electron-donating ability of the nitrogen atom in the DPA moiety, and thus the ICT process in **1** is suppressed. Consequently, a large blue shift in the absorption maximum was observed upon Cu^{2+} binding.

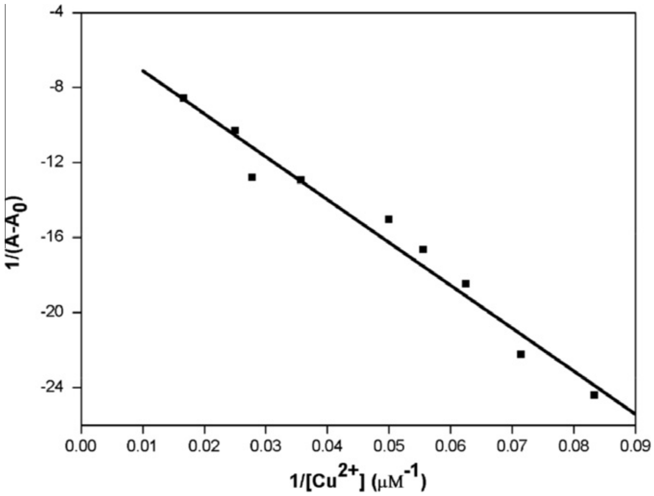

Fig. 4. Benesi–Hildebrand plot (absorbance at 405 nm) of **1**, assuming 1:1 stoichiometry for association between **1** and Cu^{2+}.

The Job's plot, as shown in Fig. 3c, reveals clearly that the stoichiometry of the complex formed by **1** and Cu^{2+} is 1:1. The Benesi–Hildebrand equation (1) was used to estimate the stability of the complex.

$$\frac{1}{A - A_0} = \frac{1}{K_a \cdot (A_{\min} - A_0) \cdot [Cu^{2+}]} + \frac{1}{A_{\min} - A_0} \qquad (1)$$

A_0 and A are the absorption of **1** at 405 nm in the absence and presence of Cu^{2+}, respectively. $A_{\min}$ is the absorption obtained with a large excess of Cu^{2+}, K_a is the association constant of the complex, and $[Cu^{2+}]$ was the concentration of Cu^{2+}. As shown in Fig. 4, the plot of $1/(A - A_0)$ against $1/[Cu^{2+}]$ is linear. From the slop of the Benesi–Hildebrand plot, the association constant K_a is determined to be $4.5 \times 10^4\ M^{-1}$, this confirmed the high copper affinity of **1** as speculated.

Similarly, the fluorescence spectra of **1** change significantly along with the concentration increase of Cu^{2+} as shown in Fig. 5. The intensity of the fluorescence band centered at 527 nm of **1** (excited at 357 nm) decreased progressively along with the concentration increase of Cu^{2+}, and it was quenched almost completely after the addition of 1 equiv. Cu^{2+}.

2.5. Crystal structure of the complex

To investigate the binding mode between **1** and Cu^{2+} in aqueous acetonitrile solution, a single crystal of the complex, which is suitable for the single crystal X-ray diffraction experiment, was grown by adding equivalent of $CuCl_2$ to **1** in CH_3CN and then evaporating the solvents slowly at room temperature. The structure of the complex is investigated by X-ray diffraction experiment and the result is shown in Fig. 6. The crystal structure reveals clearly 1:1 stoichiometry between metal and ligand, which is in accordance with the results of Job's plot. The coordination number of metal center Cu^{2+} is 5 and a trigonal bipyramid geometry is found for the complex. Cu^{2+} coordinates with totally three nitrogen atoms, with two (N2, N3) of them belong to pyridine rings and the last one (N4) is the nitrogen connected directly at the 4-position of the naphthalene ring. Two chloride atoms (Cl1, Cl2) as counter ions coordinate with copper ion too. As far as we know, although several Cu^{2+} sensors with DPA as receptor were reported in literature, but the crystal structure of DPA–Cu^{2+} complex was never reported before. The crystal structure obtained in this research represents the first example.

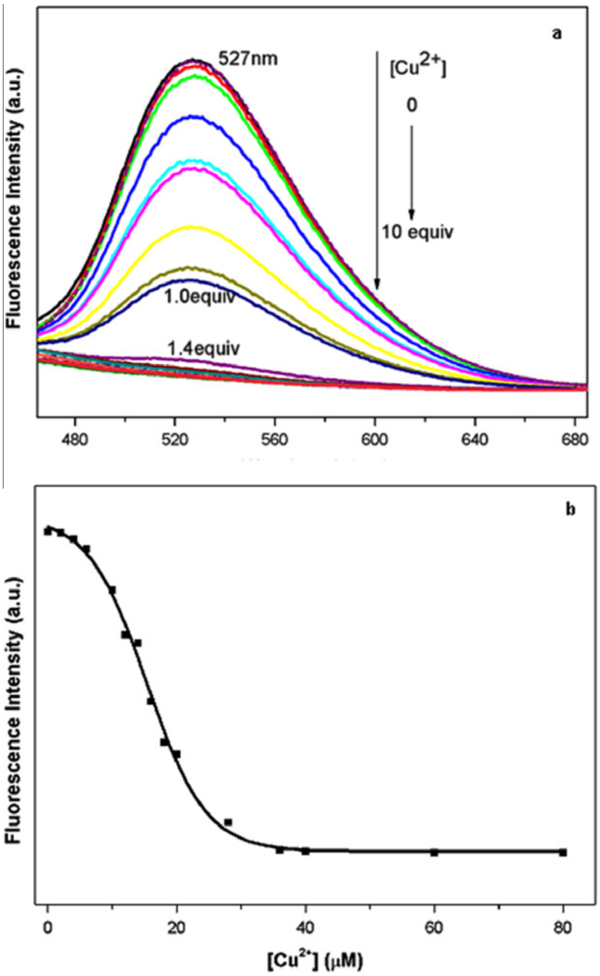

Fig. 5. (a) Changes on the fluorescence spectra of **1** (20 μM) in the presence of increasing Cu^{2+} concentrations in acetonitrile/water mixed solvents (8:2, v/v). The excitation wavelength was 357 nm. (b) The fluorescence intensity (integrated area from 440 to 700 nm) vs. the concentration of Cu^{2+}.

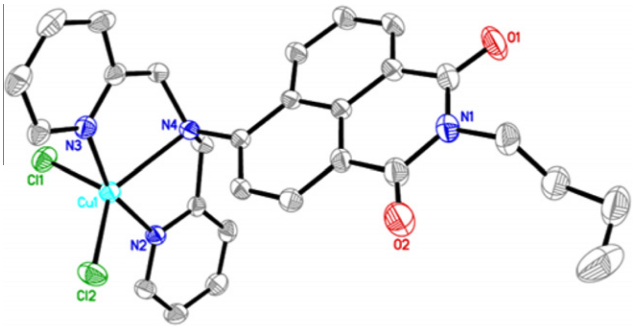

Fig. 6. Crystal structure of [**1**–Cu]Cl_2. H atoms are omitted for clarity. Selected bond length (Å) and angles (°): Cu1–N2 1.975(3), Cu1–N3 1.978(3), Cu1–N4 2.289(3), Cu1–Cl1 2.2908, Cu1–Cl2 2.3413, Cl1–Cu1–N4 105.07(8), Cl2–Cu1–N4 130.16(8), Cl1–Cu1–Cl2 124.77(4), Cl1–Cu1–N3 93.42(9), Cl2–Cu1–N3 95.14(9), N4–Cu1–N3 80.45, Cl1–Cu1–N2 93.54(9), Cl2–Cu1–N2 95.56(9), N4–Cu1–N2 80.43(11), N2–Cu1–N3 160.76(12).

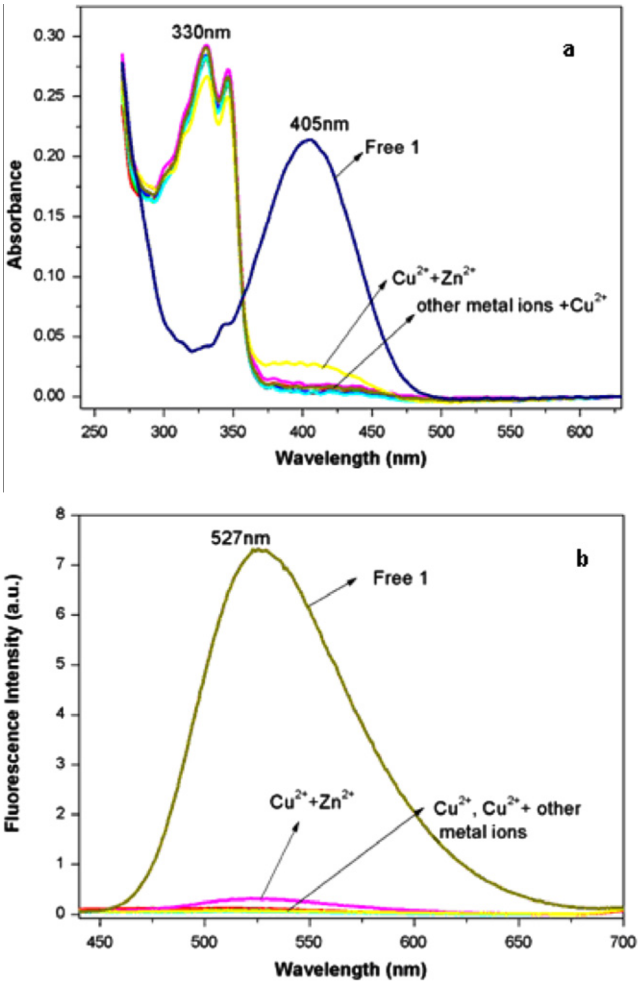

Fig. 7. (a) Absorption and (b) emission spectra of **1** (20 μM) and **1** (20 μM) upon addition of Cu^{2+} (3 equiv.) and subsequent addition of different metal ions (6 equiv.) in an acetonitrile–water solution (8:2, v/v).

2.6. Competition experiment

To further explore the utility of probe **1** as an "on–off" fluorescence probe for Cu^{2+} with naked-eye detective change, the competition experiments were conducted. Fig. 7 shows the absorption and fluorescence responses of **1**–Cu^{2+} complex in the presence of other metal ions, such as Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Ag^{+}, Zn^{2+},Cd^{2+}, Hg^{2+}, and Pb^{2+}. Addition of Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}, Pb^{2+} do not interfere with the absorption and fluorescence spectra of **1**–Cu^{2+} complex. Only Zn^{2+} presents a slight disturbance when its concentration is 3-fold excess as compared to the concentration of Cu^{2+}. The results confirm that the selectivity of **1** towards Cu^{2+} is extremely high even in the presence of other metal ions.

3. Conclusion

In summary, 1,8-naphthalimide derivative **1** appending a di(2-picolyl)amine as the receptor was successfully prepared and structurally characterized. Its sensing capabilities for transitional metal ions were examined. Compound **1** exhibited high selectivity towards Cu^{2+} in the presence of various metal cations including Zn^{2+}, Cd^{2+} and Ni^{2+} which were expected to interfere with. The coordination between **1** and Cu^{2+} hindered the ICT process and led to large blue shift on the absorption spectra and eye detectable color alteration. On the other hand, the fluorescence of **1** was remarkably quenched upon addition of Cu^{2+}. Binding mode between Cu^{2+} and **1** was clearly uncovered by the single crystal structure, which indicates that the DPA moiety enables efficient tridentate coordination for Cu^{2+}. To the best of our knowledge, this is the first example of a naphthalimide-based “on–off” fluorescent probe for Cu^{2+} with significant color change.

4. Experimental

4.1. Materials

The salts used in stock solutions of metal ions were NaCl, $CrCl_3 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $CdCl_2 \cdot 2.5H_2O$, $HgCl_2$, $Pb(NO_3)_2$ and $AgNO_3$. Compound **3** was synthesized according to literature method. Other chemicals were purchased from commercial sources. Solvents were of analytical grade and purified by standard methods.

4.2. General methods

^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer and the chemical shifts were reported in ppm (in $CDCl_3$, TMS as internal standard). ESI mass spectra were recorded on a Varian/Ionspec QFT-7 Fourier-transform ion-cyclotron-resonance (FT-ICR) mass spectrometer with a Micromass Z-spray ESI ion source. Absorption spectra were measured on HITACHI U-4100 spectrophotometer. Fluorescence emission spectra were measured on an ISS K2 system. Single crystal of the complex for X-ray diffraction analysis with suitable dimensions was mounted on a glass rod, and the crystal data were collected on a Bruker SMART CCD diffractometer with a Mo $K\alpha$ sealed tube (λ = 0.71073 Å) at 293 K, using the ω scan mode. The structure solution and refinement of the data were handled with the SHELXS-86 and SHELXL-97 programs.

4.3. Preparation

4.3.1. Synthesis of N-n-butyl-4-(2-pyridylmethyl)amino-1,8-naphthalimide (**2**)

To a solution of **3** (1 g, 3.32 mmol) in 2-methoxyethanol (40 ml), 2-aminomethyl pyridine (900 mg, 8.32 mmol) was added at room temperature. After reflux for 24 h, the cooled reacting mixture was dissolved in dichloromethane and washed with water. The collected organic phase was dried over anhydrous $MgSO_4$. After evaporation of solvent, the crude product was purified by column chromatography on silica gel (200–300 mesh) using 1000:6 (v/v) $CHCl_3$/MeOH as eluent, compound **2** (845 mg, 2.35 mmol) was obtained as yellow solid in 78% yield; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.68 (d, 1H), 8.60 (m, 1H), 8.48 (d, 1H), 8.33 (d, 1H), 7.76 (m, 1H), 7.67 (m, 1H), 7.37 (d, 1H), 7.30 (m, 1H), 7.18 (b, 1H; *NH*), 6.73 (d, 1H), 4.67 (d, 2H; NHCH_2), 4.18 (t, 2H; NCH_2), 1.72 (m, 2H; $NCH_2$$CH_2$), 1.46 (m, 2H; $CH_3$$CH_2$), 0.98 (t, 3H; CH_3); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 165.0, 164.2, 155.1, 153.7, 149.1, 148.9, 136.9, 136.6, 134.4, 131.1, 129.8, 126.4, 124.8, 123.2, 122.8, 122.3, 121.9, 120.6, 110.7, 104.7, 47.4, 39.9, 30.3, 20.4, 13.9; MS (ESI): *m/z*: 360.1734 [$M+H^+$]; Calc. for $C_{22}H_{21}N_3O_3$: 359.1634.

4.3.2. Synthesis of N-n-butyl-4-di(2-pyridylmethyl)amino-1,8-naphthalimide (**1**)

A mixture of 2-chloromethylpyridine hydrochloride (450 mg, 2.74 mmol), compound **3** (220 mg, 0.62 mmol), hexadecyltrimethylammonium chloride (400 mg) and anhydrous potassium carbonate (500 mg) in acetonitrile (50 mL) was refluxed for 24 h. After the solvent was evaporated, the residue was dissolved in dichloromethane and washed with water. The collected organic phase was dried over anhydrous $MgSO_4$. After evaporation of solvent, the brownish crude product was purified by column chromatography on silica gel (200–300 mesh) using 200:3 (v/v) $CHCl_3$/MeOH as eluent. Compound **1** was collected as a green oil (117 mg, 0.26 mmol, 42%); ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.90 (m, 1H), 8.60 (m, 3H), 8.38 (d, 1H), 7.71 (m, 1H), 7.59 (m, 2H; pyridyl), 7.36 (d, 2H; pyridyl), 7.19 (m, 3H), 4.74 (s, 4H; CH_2pyridyl), 4.18 (t, 2H; NCH_2), 1.74 (m, 2H; $NCH_2$$CH_2$), 1.46 (m, 2H; $CH_3$$CH_2$), 0.98 (t, 3H; CH_3); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 164.5, 164.0, 157.4, 153.6, 149.6, 136.7, 131.9, 131.1, 130.3, 130.1, 126.7, 125.9, 123.5, 122.5, 122.3, 117.6, 116.7, 59.9, 40.1, 30.3, 20.4, 13.9; MS (ESI): *m/z*: 451.2135 [$M+H^+$], 473.1950 [$M+Na^+$]; Calc. for $C_{28}H_{26}N_4O_2$: 450.2056.

4.3.3. Preparation of single crystal of complex **1**–$CuCl_2$

To a solution of **1** (42 mg, 0.093 mmol) in CH_2Cl_2/EtOH (4:1, 10 ml), $CuCl_2$ in EtOH (20 mM, 4.6 ml) was added dropwise. After stirring for 30 min at room temperature and filtering, the solvent was removed through evaporation. The residual was redissolved in CH_3CN (6 ml). After standing for 2 days, the green crystal was obtained.

4.4. Absorption and fluorescence response experiments

Stock solutions (0.5 mM) of each metal salts, probe **1** (0.2 mM) in acetonitrile were prepared. Test solutions were prepared by placing 1 ml of the probe’s stock solutions into a test tube, adding an appropriate aliquot of each metal stock solution, and then diluting the solution to 10 ml with acetonitrile and 2 ml distilled water to give the final concentration. After complete mixing for 10 min, measurements of UV–Vis absorption and fluorescent emission were carried out on above mentioned spectrophotometers with a 1 cm standard quartz cell.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.07.039.

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