

Highly selective ratiometric fluorescent sensor for Cu(II) with two urea groups

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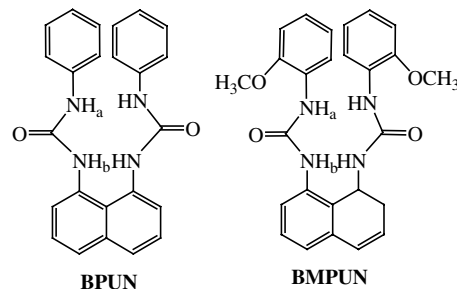
Abstract—A new Naphthalene derivative with two urea groups, 1,8-bis[*N*-(*o*-methoxyphenyl)ureido]naphthalene (**BMPUN**), was synthesized for detecting Cu(II) ratiometrically. Complexation between urea groups of **BMPUN** and Cu(II) with high selectivity gives rise to a great red-shift from 380 to 440 nm in the emission spectra. The introduction of electron donating groups is helpful to increase the electron density of the nitrogen atom of urea groups and then enhance the ability of complexation for Cu(II). © 2006 Elsevier Ltd. All rights reserved.

Design and synthesis of new chemosensors for transition and heavy metal ions have been of interest to chemists for many years because these ions play important roles in the areas of biological, environmental and chemical systems.^{1,2} Among these, the colorimetric and fluorescent chemosensors have been developed quickly for their simplicity and high sensitivity. Recently, ratiometric measurements with the changes in the ratio of the intensities of absorption or emission at two wavelengths have been utilized to increase the selectivity and sensitivity.³ Especially, ratiometric fluorescent probes greatly increase the dynamic range and provide built-in correction for environmental effects.

As we know, Cu(II) ion is one of the most important environmental pollutants and an essential trace element in various biological systems. To detect Cu(II), some receptors showing remarkable colorimetric,⁴ electrochemical⁵ and fluorescent responses⁶ have been generally investigated. Since Cu(II) is well known to be quenched effectively by fluorescence,⁷ most of fluorescent sensors for Cu(II) were designed by fluorescence quenching strategy.⁸ Only a few sensors in which the binding of Cu(II) caused an increase in the fluorescence

emission have been reported.⁹ Sensors with ratiometric fluorescence measurements have scarcely been reported.¹⁰ Therefore, the development of new ratiometric receptors capable of recognizing Cu(II) has attracted our great interests.

As one type of important receptors, urea groups have been widely adapted as fluorescent and colorimetric receptors of anion sensors based on the hydrogen-bonding mechanism.¹¹ For example, Lee et al. reported that **BPUN** (Scheme 1) could recognize fluoride anion.^{11d} However, urea receptors have rarely attracted interest in recognizing metal ions.¹² Herein, we report a naphthalene derivative **BMPUN** (Scheme 1) with two urea groups, which shows a unique ratiometric fluorescence emission in the presence of Cu(II).



Scheme 1. Molecular structures of **BPUN** and **BMPUN**.

Keywords: Fluorescent sensor; Ratiometry; Cu²⁺ sensor.

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BMPUN was easily synthesized according to the reported procedure¹³ and characterized by ¹H NMR and elemental analysis. To a solution of 1,8-diaminonaphthalene (0.24 g, 1.5 mmol) in 10 mL of DMF, a solution of 1-isocyanato-2-methoxybenzene (6.0 mmol) in 20 mL of THF was dropwise added over 30 min. The reactant was refluxed for 6 h in a nitrogen atmosphere. Then the solid product was filtered and washed with THF and acetone to give 0.62 g **BMPUN** (90% yield).¹⁴ **BPUN** was also prepared for a comparison research.

The cation binding properties were investigated by UV–vis absorption and fluorescence spectroscopy. The titration experiments were carried out in CH₃CN–DMSO system (9:1, v/v) by adding aliquots of Cu(II). Herein, Cu(NO₃)₂ was used as a Cu(II) source.

As shown in Figure 1, **BMPUN** possessed two intensive absorption bands centred at 290 and 314 nm, which can be contributed to $\pi \rightarrow \pi^*$ transition.¹⁵ Notably, the absorption of **BMPUN** was gradually increased at the red edge of the spectra (~ 360 nm) and was broadened upon the addition of Cu(II), suggesting the interaction between **BMPUN** and Cu(II).

Comparing with the change of absorption spectra, the response of **BMPUN** to Cu(II) was more remarkable in its fluorescence emission spectra. When Cu(II) was added to the solution of **BMPUN**, dramatic fluorescent change from purple to blue was observed by the naked eye under the excitation of handled-UV lamp. As shown in Figure 2, upon complexation with Cu(II), the characteristic strong fluorescence emission band of **BMPUN** at 380 nm was greatly decreased, and a new band centred at 440 nm was increased. About 60 nm red-shift in emission spectra occurred with this cation binding event and an isoemission point at 394 nm was found for **BMPUN**. By plotting the changes in the ratio of fluorescence intensity at 440 nm to that at 380 nm (I_{440}/I_{380}) as a function of Cu(II), sigmoidal curve was obtained and

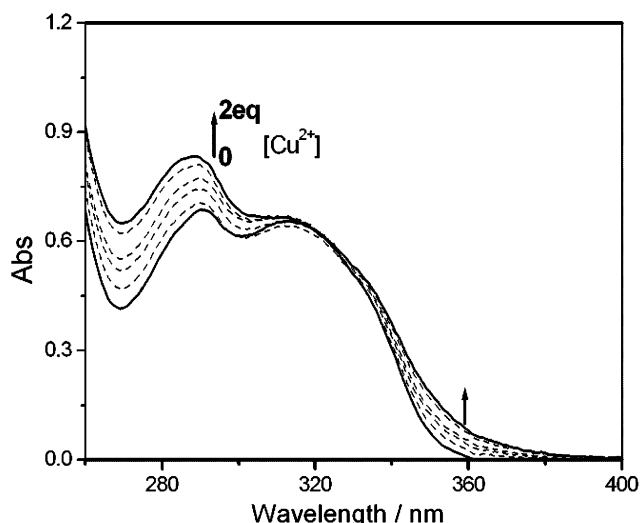


Figure 1. Changes in the UV–vis spectra of **BMPUN** (50 μ M) upon addition of Cu(II) (0–100 μ M) in CH₃CN/DMSO (9:1, v/v).

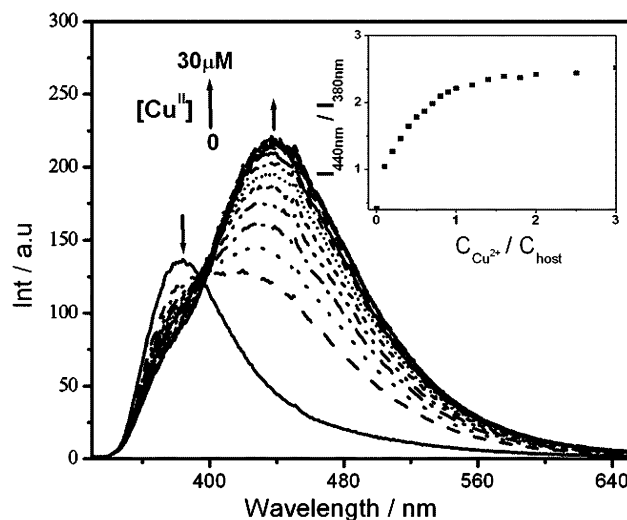


Figure 2. Changes in emission spectra of **BMPUN** (10 μ M) at 20 °C in CH₃CN/DMSO (9:1, v/v) upon addition of Cu(II) (0–30 μ M) (λ_{ex} : 310 nm). Inset: Plots of fluorescence intensity ratio between 380 and 440 nm (I_{440}/I_{380}) as a function of Cu(II) concentration.

shown in Figure 2 inset. We speculated the formation of a 1:1 stoichiometry Cu(II) complex, which was supported by linear relationship obtained in the Benesi–Hildebrand plot. The binding constant for **BMPUN** with Cu(II) was determined from the fluorescence titration curves to be 304,000 M⁻¹ at 20 °C in THF, which was comparable to that of Cu(II)-sensor reported previously.² In addition, the 1:1 stoichiometry complex of **BMPUN** to Cu(II) was confirmed by the electrospray ionization mass (ESI-MS) spectrum (Supplementary data). The main peak at m/z 581.0 was assignable to the cationic species, [CuBMPUN(NO₃)]⁺. Fluorescence quantum yields (ϕ_F) were determined to be 0.019 and 0.031 for the free **BMPUN** and **BMPUN**/Cu²⁺ adduct (1:1), respectively.¹⁶

For comparison, the recognition of **BPUN** to Cu(II) was also investigated. However, the binding constant of **BPUN** with Cu(II) was determined as only 73,000 M⁻¹ according to the similar procedure mentioned above. Then it was seemed that the *o*-methoxy groups of **BMPUN** played an important role in recognizing Cu(II). From the data of ¹H NMR, an obvious shift of NH was observed for **BMPUN** in comparison with **BPUN**. H_a showed a significant peak shifted up-field by $\Delta\delta = 0.41$ ppm. This fact indicated that the electron density of nitrogen atom for **BMPUN** increased after the introduction of the *o*-methoxy groups, which enhanced the complexation ability of **BMPUN** for Cu(II) ion.

To examine the selectivity of **BMPUN**, we investigated its affinity for other metal cations. The influence of various metal cations on the fluorescence behaviour of **BMPUN** was shown in Figure 3. No obvious changes in the fluorescence intensity ratio were observed, even though double equivalents of other metal cations such as K(I), Ca(II), Mg(II), Fe(III), Co(II), Ni(II), Zn(II), Cr(II), Cd(II), Hg(II), Ag(I) or Pb(II) were added.

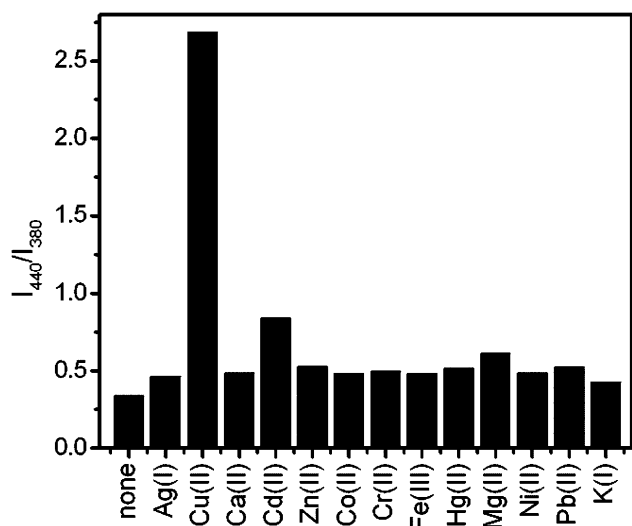


Figure 3. Fluorescent ratiometric responses of **BMPUN** (10 μM) upon addition of cations (20 μM) (λ_{ex} : 310 nm).

To explore practical applicability of **BMPUN** as a Cu(II)-selective fluorescent chemosensor, competition experiments were also performed in the presence of Cu(II) at 25 μM mixed with 25 μM background metal cations such as Fe(III), Co(II), Ni(II), Zn(II) (Fig. 4). The fluorescence intensity ratios (I_{440}/I_{380}) of solutions containing both background metal cations and Cu(II) showed no obvious variation comparing with that only containing Cu(II). Importantly, the presence of Ag(I) and Cd(II) did not affect the selectivity of **BMPUN** for Cu(II). To examine the effects of different counteranions on the sensing function of Cu(II), the fluorescence responses of **BMPUN** to CuSO₄, CuCl₂ and Cu(NO₃)₂ solution were recorded under the same condition. The experimental data showed no obvious difference in the fluorescent responses of **BMPUN** to all these Cu(II) sources. All these results indicated that **BMPUN** could be used as a potential candidate of fluorescent chemosensor for Cu(II) with very high selectivity.

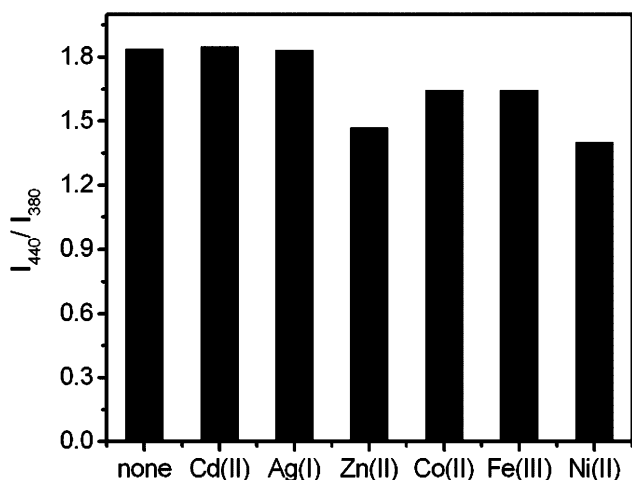


Figure 4. Fluorescent ratiometric responses of **BMPUN** (10 μM) containing 25 μM Cu(II) and the background cations (25 μM) (λ_{ex} : 310 nm).

In conclusion, we developed a highly selective fluorescent sensor **BMPUN** for Cu(II) using the naphthalene urea group as the receptors. The recognition of Cu(II) gave rise to the ratiometric change at the ratio of the fluorescent intensity of 380 and 440 nm for the complexation. Such a design strategy would be of great interest in the development of other chemosensors for heavy and transition metal cations.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.02.126.

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14. **MBPUN**: ^1H NMR (DMSO- d_6 , ppm): δ 9.12 (s, 2H, NH), 8.44 (s, 2H, NH), 8.09 (dd, 2H, $J = 8.0$ Hz, ArH), 7.66 (dd, 4H, $J = 7.6$ Hz, ArH), 7.45 (t, 2H, $J = 8.0$ Hz, ArH), 6.805–6.935 (m, 6H, ArH), 3.65 (s, 6H, CH₃). Anal. Calcd for C₂₆H₂₄N₄O₄: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.01; H, 5.26; N, 12.14. **BPUN**: ^1H NMR (DMSO- d_6 , ppm): δ 9.02 (s, 2H, NH), 8.85 (s, 2H, NH), 7.70 (dd, 4H, $J = 8.0$ Hz, ArH), 7.46 (t, 2H, $J = 8.0$ Hz, ArH), 7.40 (d, 4H, $J = 8.0$ Hz, ArH), 7.22 (t, 4H, $J = 7.2$ Hz, ArH), 6.92 (t, 2H, $J = 7.2$ Hz, ArH).
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