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A new selective fluorescent chemosensor for Cu(II) ion based on zinc porphyrin-dipyridylamino

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Abstract

A new fluorescent chemosensor 5-(p-N,N'-bis(2-pyridyl)amino)phenyl-10,15,20-tris(*p*-methoxyphenyl)porphyrin zinc has been designed and synthesized by the Ullmann-type coupling. It displays high selectivity for Cu²⁺ ion and exhibits fluorescence quenching upon binding of Cu²⁺ ion with an "on-off" type fluoroionophoric switching property, and its fluorescence can be revived by addition of EDTA disodium solution.

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The development of high selective, sensitive and low detection limit fluorescent sensors for Cu^{2+} ion has been actively investigated [1–7], since copper is a significant metal pollutant due to its widespread use [8], but it is also required as a cofactor in nearly 20 enzymes and an essential micronutrient for all known life forms. Fluorescent sensor of Cu^{2+} ion is used to clarify the physiological role of the metal in vivo as well as to monitor its concentration in the metal-contaminated sources due to its high detection sensitivity and intrinsic operation simplicity.

Porphyrins have been widely utilized as fluorophores due to their high absorption coefficients at visible region, tunable fluorescence emission, high stability against light and chemical reactions [9]. Metalloporphyrins can also be used as colorimetric sensors for detection of metalligating vapours and organic molecules because of their open coordination sites for axial ligation, their large spectral shifts upon ligand binding, and their color change [10,11]. On the other hand, molecular sensors based on porphyrins or metalloporphyrins can also be constructed by modification

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of the porphyrin *meso*-positions with appropriately functional groups that create both the recognition and binding sites for the analytes. Such interactions may lead to the analyte-dependent changes in the absorption and/or fluoresence properties of the sensors. Following this strategy, several sensors have been developed for certain analytes [12–15]. Herein, we designed and synthesized a new metal fluorescent sensor 5-(p-N,N'-bis(2-pyridyl)amino)phenyl-10,15,20-tris(*p*-methoxyphenyl)porphyrin zinc (1, Scheme 1). The sensor is constructed via two functional moieties: zinc porphyrin acts as a fluorophore for its excellent photophysical property, and 2,2'-dipyridylamine (dpa) linked to zinc porphyrin provides the recognition and binding site for metal ions [16-18]. Indeed, 1 displays high selectivity for Cu²⁺ ion among the metal ions examined and exhibits fluorescence quenching upon binding of Cu^{2+} ion with an "on-off" type fluoroionophoric switching property. Its fluorescent signal can be revived by the addition of EDTA disodium solution.

The targeted product **1** was synthesized by the direct reaction of 5-(*p*-bromophenyl)-10,15,20-tris(*p*-methoxy-phenyl)porphyrin zinc with dpa via the Ullmann-type coupling using copper powder as a catalyst and K₂CO₃ as base in the dry DMF solvent at 150 °C [19].

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Scheme 1. Structure of 1.

Absorption spectra of 1 in CHCl₃ exhibits a Soret band at 427 nm, which is slightly red shift compared with that of the tetraphenylporphyrin zinc at 423 nm (Fig. S1). To observe the optical sensor property of 1 for metal ions, the tested metal ions representative of Na⁺, Mg²⁺, Cr³⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Ag⁺, Zn²⁺, Cd²⁺, Hg²⁺ and Fe³⁺ were added to the solution of 1, respectively. The spectra showed negligible changes, when the metal ions (four equivalent) were added to the solution of 1, respectively.

Emission spectrum of 1 in CHCl₃ displays a sharp band at 608 nm with a shoulder at 656 nm upon excition at 435 nm (Fig. S2). To screen the fluorescent sensor property, the responses of 1 to the aforementioned metal ions were examined. Only Cu^{2+} ion caused a significant fluorescence quenching as shown in Figs. 1 and 2. Such a significant difference in fluorescence intensity between Cu^{2+} and other metal ions indicates that the function group dpa of 1 is more suitable to bind Cu^{2+} than other metal ions observed. This may be attributed to complex formation with the metal ion in preference over others following Irving–Williams order of stability [20]. The fluorescence quenching was most probably caused by the binding of Cu^{2+} at dpa moiety [21].

To examine the binding properties of 1 toward Cu^{2+} ion, titration experiments were carried out and the results are shown in Fig. 3. Addition of Cu^{2+} to the solution of 1 caused a decrease of emission intensity, and about 76%



Fig. 1. The fluorescence responses of 1 (25 μ M) in CHCl₃ upon addition of (160 μ M) metal ions in MeOH excited at 365 nm using UV lamp. Final solvent composition is CHCl₃:MeOH = 18:1 in volume.



Fig. 2. Responses of sensor 1 in CHCl₃ (25μ M) to different metal ions in MeOH (125μ M). Excitation at 435 nm and emission at 608 nm. Final solvent composition is CHCl₃:MeOH = 20:1 in volume.

intensity loss in 1:1 molar ratio. Continuous addition of Cu^{2+} ion, emission intensity of **1** decreased slowly and was about 10% of the original one when the molar ratio of Cu^{2+} to **1** increased to 2. The mole ratio method was applied to examine the stoichiometry [22], indicating a 1:1 complex formed (Fig. S3), which was further confirmed by ESI-MS (Fig. S4) [23]. The binding constant, *K*, determined by fluorescence titration is appropriate $6.31 \times 10^5 \text{ M}^{-1}$, comparable to the report [22,24].

Quantum yield of 1 was 5.8% measured at room temperature in CHCl₃ solution, which is larger than that of zinc tetraphenylporphyrin (2.8%) [25]. Luminescence decay experiment was performed in chloroform solution at room temperature. The lifetime yield in 1.53 ns by fitting the data to a single exponential decay function (Fig. S5).



Fig. 3. Fluorescent titrations emission spectra of 1 ($25 \,\mu$ M) in CHCl₃ solution upon addition of Cu²⁺ in MeOH solution [Cu²⁺] = 0, 4, 8, 12, 16, 20, 24, 28, 32, 37, 41, 45, 49 μ M. The excitation wavelength was 435 nm. Final solvent composition is CHCl₃:MeOH = 50:1 in volume.

To examine the reversibility of sensor 1 to Cu^{2+} ion, aqueous solution of EDTA disodium was added to the complexed solution of 1 (25 µM) and Cu^{2+} (50 µM) in methanol. As expected, fluorescence signal with a maximum at 608 nm was completely recovered (Fig. S6), demonstrating the binding is really chemically reversible. This is very important for the preparation of sensor device. The detection limit for Cu^{2+} ion with 1 is determined to be 1.5×10^{-6} M under the present conditions (3s blank) [26]. These results indicate that 1 can function as a fluorescence sensor for Cu^{2+} ion.

The competition experiments of Cu^{2+} and other metal ions were also performed. As shown in Fig. 4, when the mixed solution of Cu^{2+} ion (25 μ M) with other metal ions (125 μ M) were added to the solution of 1 (25 μ M), respectively, only Co^{2+} , Zn^{2+} , Cd^{2+} and Fe^{2+} ions had a slight disturbance under their much excess. The results indicate that the binding of Cu^{2+} ion to 1 is much stronger than that of other metal ions, though the latter is fivefold to Cu^{2+} ion.

To further examine the selectivity and anti-disturbance of sensor 1, Cu^{2+} ion (25 μ M) was added, respectively, to the incubated solution of 1 (25 μ M) containing much excess of the aforementioned metal ions (125 μ M), in which the metal ions may occupy the binding sites of 1. Nearly complete fluorescence quenching caused immediately, demonstrating that Cu^{2+} ion can replace the other metal ions (if they bind to 1). Therefore, the interference from those metal ions could be neglected and 1 can be considered as a high selective fluorescence sensor for Cu^{2+} ion with low detection limit.

In conclusion, we have developed a new fluorescent sensor for Cu^{2+} ion with high sensitivity and selectivity. The design strategy and remarkable photophysical properties



Fig. 4. Fluorescent responses of $1 (25 \,\mu\text{M})$ in CHCl₃ solution and 1 in the presence of Cu²⁺ (25 μ M) plus other metals ions (125 μ M) in methanol solution, respectively. The excitation was at 435 nm and emission was at 608 nm. Final solvent composition is CHCl₃:MeOH = 15:1 in volume.

of sensor **1** would help to extend the development of fluorescent sensors for metal ions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006. 12.023.

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(300 MHz, CDCl₃): δ 9.02 (d, J = 4.5 Hz, 2H, pyrrole), 8.90–8.80 (m, 6H, pyrrole), 8.09 (d, J = 8.4 Hz, 2H), 8.03–8.00 (m, 6H), 7.71 (t, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.29–7.27 (m, 2H), 7.20 (m, 2H), 7.15–7.12 (m, 6H), 7.03 (m, 2H), 4.08 (s, 9H, OCH₃).¹³C NMR (75 MHz, CDCl₃): δ 158.1, 157.5, 152.1, 149.5, 149.2, 147.8, 146.0, 143.3, 139.1, 136.8, 136.5, 134.8, 134.7, 134.5, 130.9, 123.6, 119.8, 119.3, 117.5, 116.6, 115.2, 111.0, 110.7, 54.7. ESI-MS: m/z calcd. for C₅₇H₄₁N₇O₃Zn ([M + H⁺]): 936.3, obsd. 936.4; IR (KBr, cm⁻¹): 771 (s), 799 (s), 846 (s), 1173 (s), 1245 (s), 1432 (s), 1466 (s), 1508 (s), 1600 (s), 1655 (s), 2851 (s), 2922 (s), 3030 (s), 3305 (s).

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observed, which can be assigned the species of $[1 + H]^+$ and $[1 \cdot (Cu)(OH)]^+$, respectively.

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