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A Copper(II) Ion-Selective On−Off-Type Fluoroionophore Based on Zinc Porphyrin−Dipyridylamino

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A new copper(II) fluorescent sensor 5,10,15,20-tetra((*p*-*N*,*N*-bis(2-pyridyl)amino)phenyl)porphyrin zinc (**1**) has been designed and synthesized by the Ullmann-type condensation of bromoporphyrin zinc with 2,2′-dipyridylamine (dpa) under copper powder as a catalyst as well as with K_2CO_3 as the base in a DMF solution. It consists of two separately functional moieties: the zinc porphyrin performs as a fluorophore, and the dpa-linked-to-zinc porphyrin acts as a selected binding site for metal ions. It displays a high selectivity and antidisturbance for the Cu^{2+} ion among the metal ions examined (Na^+, Mg^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Fe^{3+}) and exhibits fluorescence quenching upon the binding of the Cu^{2+} ion with an "on−off"-type fluoroionophoric switching property. The detection limit is found to be 3.3×10^{-7} M (3s blank) for Cu^{2+} ion in methanol solution, and its fluorescence can be revived by the addition of EDTA disodium solution. The design strategy and remarkable photophysical properties of sensor **1** help to extend the development of fluorescent sensors for metal ions.

Introduction

The development of highly selective, sensitive, and low-detection-limit fluorescent sensors capable of reporting transition-metal ions has attracted considerable attention.[1−7] The design of fluorescent sensors for Cu^{2+} is actively investigated,[8−13] as it is a significant metal pollutant due to its widespread use,[14] but it is also an essential trace element in biological systems.[15] Although Cu^{2+} toxicity for human is rather low compared with other heavy-metal ions, certain microorganisms are affected by submicromolar concentrations of metallic materials. A fluorescent sensor of Cu^{2+} is used to clarify the physiological role of metal ion in vivo as well as to monitor its concentration in the metal-contaminated sources due to its high detection sensitivity and intrinsic operational simplicity.

The porphyrins have been widely utilized as fluorophores due to their high absorption coefficients in the visible region, tunable fluorescence emission, and high stability against light and chemical reactions.[16−22] Metalloporphyrins can be used

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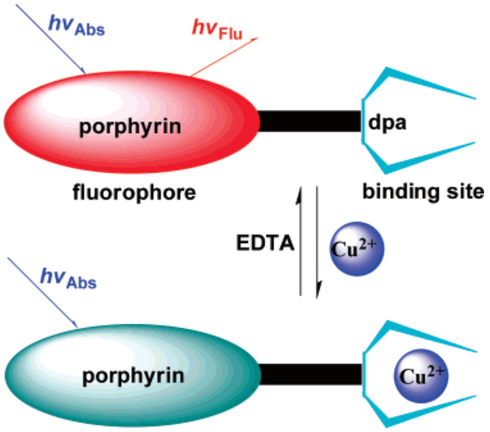
as colorimetric sensors for the detection of metal-ligating vapors and organic molecules because of their open coordination sites for the axial ligation, their large spectral shifts upon ligand binding, and their color changes.[23−25] On the other hand, molecular sensors based on porphyrins or metalloporphyrins would be constructed by the modification of a *meso*-porphyrin with appropriately functional groups that would act as both the recognition and the binding sites for the analytes via supramolecular interactions such as hydrogen bonding, electrostatics, and coordination bonding. Such interactions often lead to analyte-dependent changes in absorption and/or fluoresence properties of the sensors. Following this strategy, several sensors have been designed for certain analytes,[3] for example, a porphyrin−crown ether species as a sensor for peptides,[26] a porphyrin−tetrabrucin species for ATP,[27] a porphyrin−carbonylate species for nicotine and cotinine,[28] a porphyrin−tetraimidazolium species for sulfate,[29] and a porphyrin−quinone species for the yttrium ion.[30] However, the metal sensor constructed by porphyrin and polypyridyl is rare.

Herein, we report the synthesis of a new metal fluorescent sensor 5,10,15,20-tetra((*p*-*N*,*N*-bis(2-pyridyl)amino)phenyl)-porphyrin zinc (**1**). It consists of two separately functional moieties: the zinc porphyrin performs as a fluorophore due to its excellent photophysical properties, and 2,2′-dipyridylamine (dpa) linked to the zinc porphyrin acts as a recognition and binding site for the metal ions, as the dpa group possesses a remarkable binding ability to transition-metal ions.[31−33] Sensor **1** displays a high selectivity for Cu^{2+} among the metal ions examined and exhibits fluorescence quenching upon the binding of Cu^{2+} ion with an “on−off”-type fluoroionophoric switching property. Its fluorescent signals can be revived by the addition of ethylenediaminetetraacetic acid (EDTA) disodium solution, as outlined in Scheme 1.

Scheme 1. Schematic Representation of the Sensor **1** Interaction with the Cu(II) Ion



Experimental Section

Materials and Methods. All reagents and solvents employed for synthesis were commercially available and used as received without further purification. ^1H NMR spectra were recorded on a Varian Mercury-Plus 300 NMR spectrometer with chemical shifts (in ppm) relative to tetramethylsilane; ^{13}C NMR was measured at 75 MHz in a $CDCl_3$ solvent at room temperature. The FT-IR spectra were recorded from KBr pellets in the range of 4000−400 cm^{-1} on a Bruker-EQUINOX 55 FT-IR spectrometer. Electron spray ionization mass spectrometry (ESI-MS) was performed on a LCQ DECA XP quadrupole ion-trap mass spectrometer with methanol as the carrier solvent.

Synthesis of 5,10,15,20-Tetra(*p*-bromophenyl)porphyrin (3). The compound was synthesized according to the literature[34] in a yield of 10% and identified by spectral analysis. ^1H NMR (300 MHz, $CDCl_3$): δ 8.82 (s, 8H, pyrrole), 8.06 (d, $J = 8.4$ Hz, 8H, ph), 7.88 (d, $J = 8.4$ Hz, 8H, ph), −2.84 (s, br, 2H, N−H). ESI-MS: $m/z = 930.9$ $[M + H]^+$. FT-IR (KBr, cm^{-1}): ν 798 (s), 848 (s), 965 (s), 987 (s), 1011 (s), 1182 (s), 1471 (s), 1599 (s), 1584 (s), 2920 (s), 3082 (s), 3315 (s), 3438 (s).

Synthesis of 5,10,15,20-Tetra(*p*-bromophenyl)porphyrin Zinc (2). Compound **3** (0.193 g) and $Zn(OAc)_2 \cdot H_2O$ (0.050 g) were added to the solution mixture of $CHCl_3$ (50 mL) and MeOH (25 mL). The mixture was refluxed for 2 h, then the solution was removed. The zinc porphyrin was purified using a column chromatography (basic silica gel, $CHCl_3$ as eluent), then concentrated and dried. Yield: (80 mg, 80%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.92 (s, 8H, pyrrole), 8.06 (d, $J = 8.4$ Hz, 8H, ph), 7.89 (d, $J = 8.4$ Hz, 8H, ph). ESI-MS: $m/z = 995$ $[M + H]^+$. IR (KBr, cm^{-1}): ν 799 (s), 843 (s), 1001 (s), 1071 (s), 1077 (s), 1206 (s), 1337 (s), 1389 (s), 1481 (s), 1523 (s), 1586 (s), 2852 (s), 2922(s), 3431 (s).

Synthesis of 5,10,15,20-Tetra((*p*-*N*,*N*-bis(2-pyridyl)amino)-phenyl)porphyrin Zinc (1). Compound **2** (98 mg, 0.1 mmol), dpa (137 mg, 0.8 mmol), K_2CO_3 (83 mg, 0.6 mmol), and copper powder (32 mg, 0.5 mmol) were added to an anhydrous DMF (10 mL), then the suspended solution was refluxed for 24 h under a N_2 atmosphere (the reaction was monitored by thin-layer chromatography and ceased after the starting material disappeared). After the removal of DMF, the solid was extracted with chloroform. The

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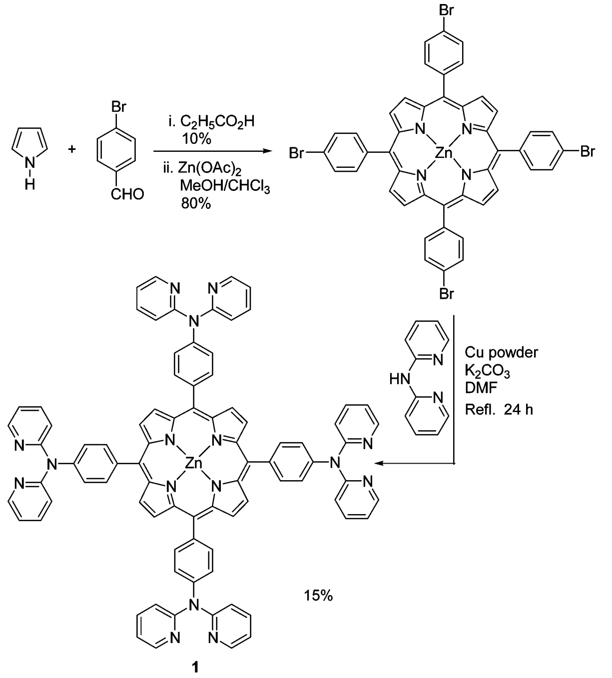
organic layer was dried over anhydrous sodium sulfate. The product was further purified on a chromatography column (basic silica gel, ethanol and $CHCl_3$ as eluent) and identified by NMR and ESI-MS. Yield: (20 mg 15%). Anal. Calcd for $C_{84}H_{56}N_{16}Zn$**1** (M_r = 1354.84): C, 74.47; H, 4.17; N, 16.54. Found: C, 74.10; H, 3.94; N, 16.18. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.10 (s, 8H, pyrrole), 8.45 (d, J = 4.5 Hz, 8H, py), 8.17 (d, J = 8.1 Hz, 8H, py), 7.72 (t, 8H, py), 7.53 (d, J = 8.1 Hz, 8H, ph), 7.31 (d, J = 8.4 Hz, 8H, ph), 7.05 (t, 8H, py). ^{13}C NMR (75 MHz, $CDCl_3$): δ 117.80, 118.83, 124.82, 132.33, 135.99, 138.06, 139.83, 144.63, 144.90, 148.99, 150.33, 158.52. ESI-MS: m/z 1355 $[M + H]^+$. FT-IR (KBr, cm^{-1}): ν 775 (s), 800 (s), 998 (s), 1098 (m), 1266 (s), 1327 (s), 1430 (s), 1468 (s), 1588 (s), 2853 (s), 2924 (s), 2961 (m), 3424 (m).

General Spectroscopic Methods. The solvents $CHCl_3$ and methanol used for the spectral experiments were purified via the standard methods. The water used for the titration experiment was double-distilled. Methanol solutions of Na^+ and Mg^{2+} were prepared from the sulfate salts, solutions of Cr^{3+}, Mn^{2+}, and Hg^{2+} were prepared from the chloride salts, solutions of Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} were prepared from the acetate salts, solutions of Ag^+ and Fe^{3+} were prepared from the nitrate salts, the solution of Fe^{2+} was prepared from ferrous ammonium sulfate and used immediately, and the solution of Cu^{2+} was prepared from copper(II) perchlorate. The binding constant determined by fluorescent titration was performed in duplicate, and the average is reported. All data were manipulated by using the *OriginLab* software package.

Optical Absorption and Fluorescence Spectroscopy. UV−vis spectra were acquired on a Shimadzu UV-315 UV−vis spectrophotometer at room temperature. Quartz cuvettes with a 1 cm path length and 3 mL volume were used for all measurements. For a typical metal-binding titration, 5 μL aliquots of a metal ion (2.5 mM in methanol) were added to a 3 mL solution volume of sensor **1** (25 μM in $CHCl_3$) by a syringe. Fluorescence excitation, emission spectra, quantum yield, and luminescence lifetime were measured on a Edinburgh-FLS 920 combined fluorescence lifetime and steady-state spectrometer at room temperature with a slit width of 1 nm. Quartz cuvettes with a 1 cm path length and 3 mL volume were used for all fluorescence measurements. The luminescence lifetime was measured in chloroform solution at 25 μM at room temperature and fit to a single-exponential decay function. The fluorescence quantum yield (ΦF) was estimated by calculating the integrated fluorescence intensity with the zinc tetraphenylporphyrin in chloroform as a standard (ΦF = 2.8%).[34] Fluorescence titration spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer with a slit width of 5 nm. For a typical experiment, 5 μL aliquots of a Cu^{2+} ion (2.5 mM in methanol) or a mixture of Cu^{2+} with other metal ion were added to a 3 mL solution volume of sensor **1** (25 μM in $CHCl_3$) by a syringe. For the recovered experiment, 5 μL aliquots of an EDTA disodium solution (0.01 M in water) were added to a 3 mL solution containing sensor **1** (25 μM) and Cu^{2+} ion (80 μM) in methanol solution by a syringe.[35] The metal ions dependent fluorescence intensity was obtained by monitoring the emission intensity at 610 nm. For all the experiments, the excitation wavelengths were fixed at 440 nm.

Scheme 2. Synthesis of **1**



Results and Discussion

Synthesis. The synthesis of the aimed sensor **1** is outlined in Scheme 2. The symmetric 5,10,15,20-tetra(p-bromophenyl)porphyrin was synthesized according to Longo's method[34] in ca. 10% yield. Its zinc complex **2** was obtained by the reaction of the free base porphyrin with zinc acetate in the solution mixture of $CHCl_3$ and MeOH in ca. 80% yield. The aimed-for product **1** was obtained by the directed reaction of the bromophenyl-porphyrin zinc with the dpa via the Ullmann-type coupling. We have tried the amination reaction of the bromoporphyrin zinc **2** with the dpa using Wang's method ($CuSO_4$ as a catalyst and K_2CO_3 or KOH as base) in the solid state at 200−220 °C,[32d] which has been successful applied in the synthesis of the aromatic substitution dpa via the solid-state reaction.[32,33] To our surprise, the mass spectra experiment showed that no targeted product was detected; instead, a large amount of unreacted materials were detected. These unsuccessful results might be attributed to the too-high melting point of **2** to mix with the other reagents homogeneously at the reaction temperature and led us to investigate the reaction in solution using a metal salt as a catalyst. We notice that the palladium-catalyzed amination reactions of aryl halides have been emerging as a powerful approach for the synthesis of triarylamines.[36] Indeed, Zhang's and other groups have successfully applied this method in the synthesis of *meso*-arylamino- and alkylamino-substituted porphyrins via the cross-coupling reactions of the preformed

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(35) The control experiments for various solvents were carried out. When methanol was added to the $CHCl_3$ solution of **1**, the absorbance spectra of **1** remained unchanged. Though the fluorescent intensity of **1** in methanol solution is slightly increased in comparison with that in $CHCl_3$ solution, the addition of a small amount of methanol to the solution of **1** in $CHCl_3$ did not induce a detectable change.

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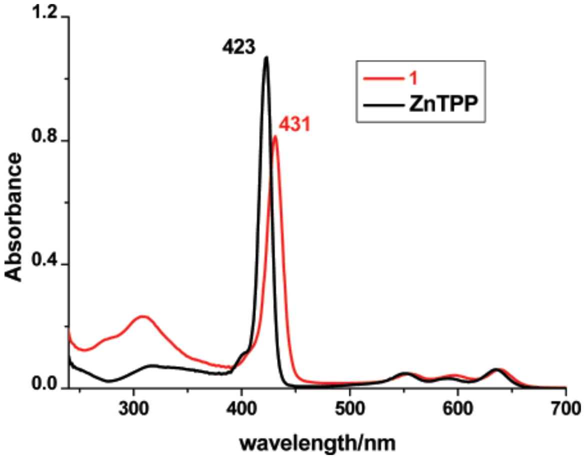

Figure 1. UV−vis absorption spectra of **1** and tetraphenylporphyrin zinc in $CHCl_3$. The concentrations of both complexes were 5 μM.

halogenated porphyrins and amines.[37,38] However, it is unfit for the coupling reaction of aryl halides with dpa due to the “electron-withdrawing-effect” of both 2-pyridyl groups.[39] On the other hand, cheap and commercially available copper powder has also been used as a catalyst to prepare tri-2-pyridylamine and its derivatives.[40] Therefore, the Ullmann-type condensation was employed to prepare the targeted product. Indeed, **1** was obtained in 15% yield using copper powder as a catalyst and K_2CO_3 as the base in DMF solvent at 150 °C.

Absorption Spectra and Titration. The absorption spectra of **1** in $CHCl_3$ exhibits a Soret band at 431 nm and Q bands at 556, 597, and 639 nm, slightly red-shifted compared with those of the tetraphenylporphyrin zinc at 423, 550, 587, and 634 nm, respectively, as shown in Figure 1. To examine the optical sensor property of **1** for metal ions, the tested metal ions representative of Na^+, Mg^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Fe^{3+} ions were added to the solution of **1**, respectively. Only the Cu^{2+} ion induces significant changes of the absorption spectra, implying that only the Cu^{2+} ion responds to **1** under the experimental condition. To investigate the binding property of **1** toward the Cu^{2+} ion, titration experiments were carried out as shown in Figure 2. The addition of Cu^{2+} ion to the solution of **1** induces the absorption intensity of the maximum absorption peak at 431 nm, assigned to the Soret band of the zinc porphyrin, gradually to decrease. On the other hand, the peak at 309 nm, probably assigned to the amine N by a ring charge transfer transition, is slightly red-shifted (5 nm) with a concomitant decrease in absorption intensity. The peak at 278 nm ascribed to pyridine-based (ligand center) transition progressively decreases, and a new absorption band at 250 nm develops.[33,41] The presence of very well-defined isosbestic points at 266, 315, 331, 407, and 420 nm indicates that there is a simple equilibrium involved. These changes are negligible up to the addition of 2 equiv of Cu^{2+} ion, implying that all the dpa groups in **1** coordinate to Cu^{2+} ion forming a **1**/Cu^{2+} complex in this case. The peak at 250 nm is a characteristic absorption band of the Cu^{2+}−dpa complex and can be used to diagnose whether the dpa group binds to Cu^{2+} ion or not.

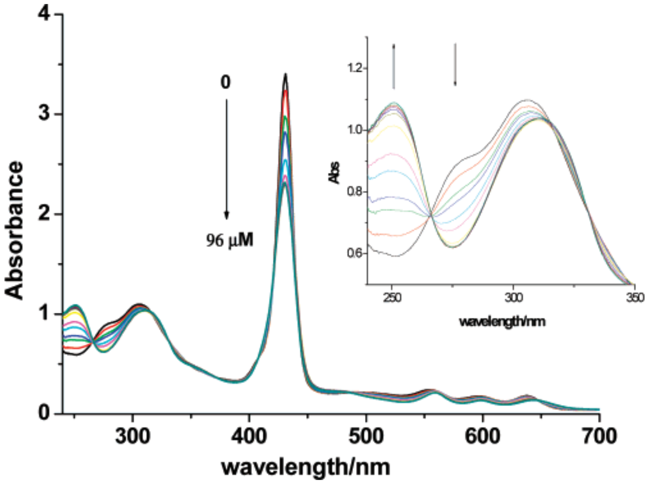

Figure 2. UV−vis titrations of **1** (25 μM) in $CHCl_3$ solution upon the addition of Cu^{2+} (0, 8, 16, 24, 32, 41, 49, 57, 65, 73, 80, 88, and 96 μM) in a MeOH solution. Inset: absorption spectra in the range of 230−350 nm.

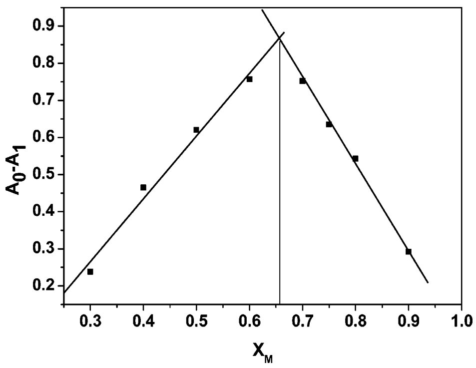

Figure 3. Job plot for determining the stoichiometry of **1** and Cu^{2+} ion in $CHCl_3$. The variation of the absorption at 431 nm was measured as a function of the molar ratio X_M ($[Cu^{2+}]/([Cu^{2+}] + [\mathbf{1}])$).

To determine the stoichiometry of the **1**/Cu^{2+} complex, Job’s method for the absorbance was applied, keeping the sum of the initial concentration of Cu^{2+} ion and **1** at 25 μM, and changing the molar ratio of Cu^{2+} ion ($X_M = [Cu^{2+}]/([Cu^{2+}] + [\mathbf{1}])$) from 0 to 1.[42] The absorbances of **1** in the absence (A_0) and presence (A_1) of Cu^{2+} ion were determined, respectively. A plot of ($A_0 - A_1$) versus X_M shows that the ($A_0 - A_1$) value goes through a maximum at a molar fraction of ca. 0.66 (see Figure 3), indicating a 1:2 stoichiometry complex formation. To further examine the stoichiometry,

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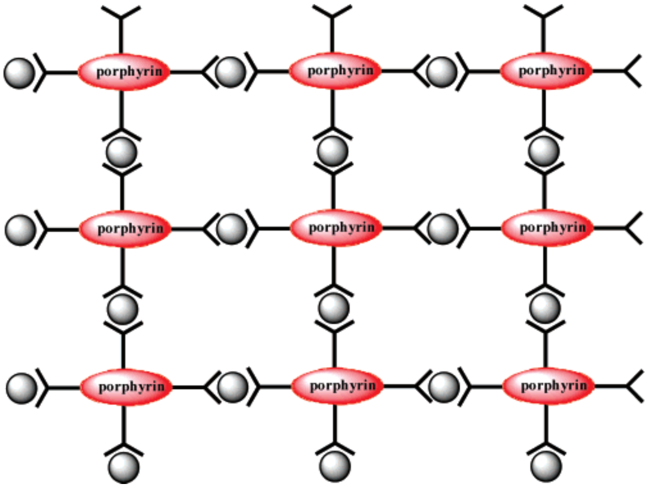
Scheme 3. The Probable (4,4) Network of **1**/(Cu^{2+})$_2$[a]



[a] The gray balls represent Cu^{2+} ions.

Job's method was also applied at different wavelengths of 250 and 278 nm (Figure S1, Supporting Information), and the same result was deduced. These experiments clearly show that the coordination reaches the end point at a 1:2 ratio of **1**/Cu^{2+}. On the basis of these observations, a probable polymeric structure may be the (4,4) network, in which each Cu^{2+} ion is coordinated by two dpa groups from two sensors **1** in four-coordination and each sensor **1** ligates four Cu^{2+} ions, as shown in Scheme 3. An attempt to get a single crystal of the **1**(Cu)$_2$ complex was unsuccessful.[43]

To confirm such a coordination model, a survey of the CSD[44] for Cu^{2+} complexes containing the aromatic substitution dpa reveals that such a coordination model is well-known in Cu^{2+}−dpa complexes.[45] Furthermore, a mono-dpa-substituted porphyrin, 5-(*p*-*N*,*N*′-bis(2-pyridyl)amino)phenyl-10,15,20-tris(*p*-methoxyphenyl)porphyrin zinc (mdpa), has been synthesized in a similar procedure to observe the coordination behavior of the Cu^{2+} ion with the dpa-substitution porphyrin.[46] When 2 equiv of Cu^{2+} ion was added to the solution of mdpa, its absorption band at 270 nm blue-shifted to 250 nm, matching well with those observations in the titration process of **1** with Cu^{2+} ion (see Figure S2, Supporting Information). The ESI-MS technique was employed to confirm the formation of the mdpa/Cu^{2+} complex. Its spectra give a very clear cluster of isotopic peaks centered at m/z = 1937.4. The mass spectrum of these clusters and the intensity ratio of different isotope peaks are in excellent agreement with the calculated isotope pattern for [(mdpa)$_2$Cu−H]$^+$ (C$_{114}$H$_{82}$N$_{14}$O$_6$Zn$_2$Cu, see Figure S3, Supporting Information), indicating that each Cu^{2+} ion is coordinated by two dpa groups from two mdpa ligands.

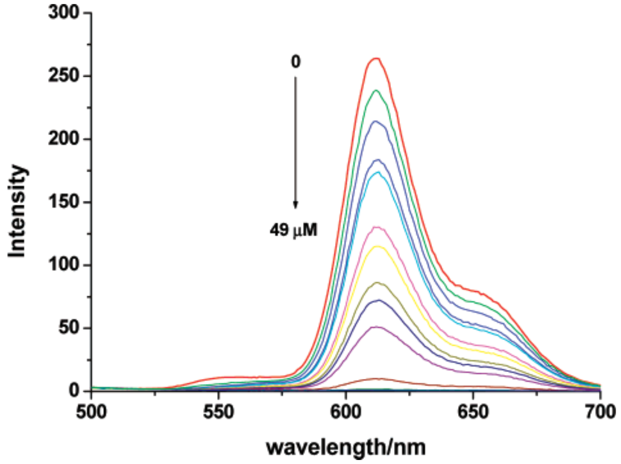


Figure 4. Fluorescent titrations emission spectra of **1** (25 μM) in CHCl$_3$ solution upon the addition of Cu^{2+} in MeOH solution ([Cu^{2+}] = 0, 4, 8, 12, 16, 20, 24, 28, 32, 37, 41, 45, and 49 μM). The excitation wavelength was 440 nm.

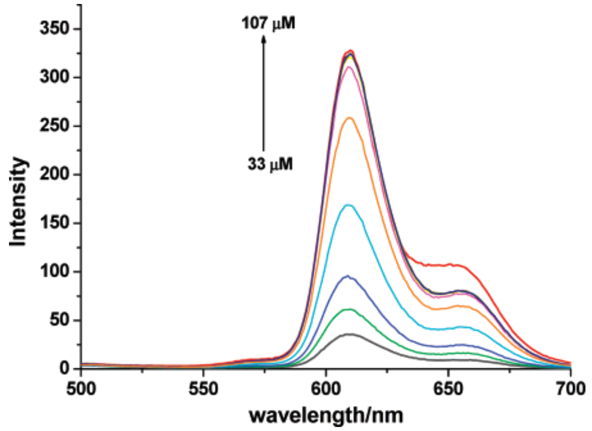


Figure 5. Fluorescent responses of **1** (25 μM) and Cu^{2+} (80 μM) in MeOH solution upon the addition of EDTA disodium (33, 50, 67, 84, 99, 115, 132, and 148 μM) in aqueous solution. The red line was the emission spectra of **1** in the mixed solution of MeOH and CHCl$_3$ (10:1, v/v). The excitation wavelength was 440 nm.

Fluorescence Spectra and Titration. The emission spectrum of **1** in CHCl$_3$ displays a sharp band with a maximum at 610 nm, and this fluorescence signal can be assigned to the vibronic transitions of zinc porphyrin (Figure S4, Supporting Information). When Cu^{2+} ion was added to the solution of **1**, complete fluorescence quenching in **1** was observed. To determine the amount of Cu^{2+} ion required to induce the complete quenching of fluorescence from **1**, titration experiments were carried out as shown in Figure 4. When 2 equiv of Cu^{2+} ion was added, the emission of **1** was almost completely quenched, indicating the binding of Cu^{2+} ion to the functional dpa groups forming a **1**/Cu^{2+} complex. The mole ratio method for the fluorescent intensity versus the number of equivalents of Cu^{2+} ions added was

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(43) The complex was synthesized by the addition of 2 equiv of Cu(ClO$_4$)$_2$ in MeOH to 1 equiv of **1** (1.0 mM) in CHCl$_3$. Anal. Calcd for C$_{84}$H$_{56}$N$_{16}$Cl$_4$O$_{16}$Cu$_2$Zn ([**1**·Cu$_2$](ClO$_4$)$_4$, M = 1878): C, 53.67; H, 3.00; N, 11.92; Cu, 6.76; Zn, 3.48. Found: C, 53.19; H, 2.53; N, 11.57; Cu, 6.35 (ICP method); Zn, 3.09 (ICP method).

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(46) The complex was identified by NMR and ESI-MS; calcd. for C$_{57}$H$_{41}$N$_7$O$_3$Zn ([M + H$^+$]): m/z 936.3; obsd., 936.4.

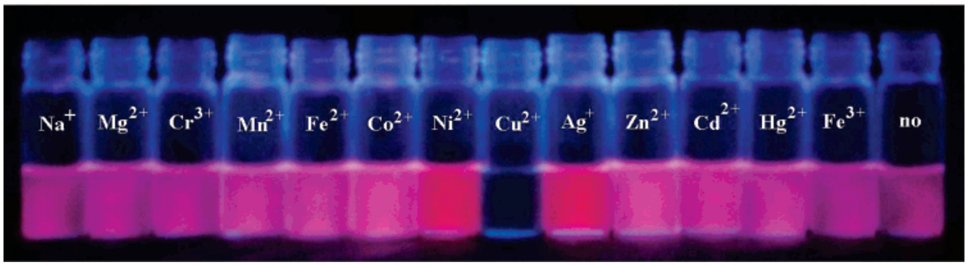

Figure 6. Fluorescence responses of **1** (25 μM) in $CHCl_3$ upon the addition of (160 μM) metal ions in MeOH excited at 365 nm using a UV lamp.

applied to examine the stoichiometry of the **1**/Cu^{2+} complex,[42] indicating a 1:2 stoichiometry of **1** to Cu^{2+} in the complex (see Figure S5, Supporting Information).

The quantum yield of **1** was also measured as 3.6% at room temperature in a $CHCl_3$ solution and slightly larger than that of the zinc tetraphenylporphyrin. The luminescence decay experiment was performed in a chloroform solution at room temperature. The lifetime yielded was 1.57 ± 0.01 ns by fitting the data to a single-exponential decay function (Figure S6, Supporting Information). To examine the reversibility of the binding of sensor **1** to the Cu^{2+} ion, aqueous solutions of EDTA disodium were added to the complexed solution of **1** (25 μM) and Cu^{2+} (80 μM) in methanol. As expected, fluorescence signals with a maximum at 610 nm are completely revived, as shown in Figure 5, demonstrating that the binding is really chemically reversible. The detection limit for Cu^{2+} ion with **1** was determined to be 3.3×10^{-7} M under the present conditions (3s blank).[47] These results indicate that **1** is a low-detection-limit fluorescence sensor for Cu^{2+} ion. To elucidate the quenching mechanism, the lifetimes of sensor **1** in the absence and presence of the Cu^{2+} ion were measured. Data fitting yielded the lifetimes of 1.57 ± 0.01, 1.56 ± 0.01, 1.62 ± 0.01, 1.62 ± 0.01, 1.58 ± 0.02, and 1.60 ± 0.02 ns, respectively, when Cu(II) ions (0, 8, 16, 24, 32, and 41 μM) were added to the solution of **1** (Figure S8, Supporting Information). The lifetime is almost unchanged under the experimental conditions. Combined with the observation in absorption titration experiments, in which the peak at 278 nm ascribed to pyridine-based (ligand center) transition is significant blue shifted to 250 nm when the dpa groups ligate the Cu^{2+} ion, a static quenching mechanism can be deduced.[1,5,48] The fluorophore **1** ligates Cu^{2+}, forming a nonfluorescent complex in the ground state.

Selectivity of Sensor 1. To examine the selectivity of sensor **1** toward metal ions, the influences of metal ions such as Na^+, Mg^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Fe^{3+} on the fluorescence spectra of **1** were investigated. The addition of the aforementioned metal ions to the solution of **1** resulted in negligible spectral change under the identical conditions of Cu^{2+} ion, as shown in Figures 6 and 7. Such a significant difference in fluorescence intensity between Cu^{2+} and the metal ions indicates that the functional group dpa in **1** is more suitable to bind to Cu^{2+} ion compared with the metal ions observed. Although the metal ions examined did not affect the fluorescence of **1** individually, to further exploit the utility of **1** as a selective fluorescence sensor for the Cu^{2+} ion, competition experiments were also performed. As shown in Figures 8 and 9, when the mixed solution of Cu^{2+} ion (50 μM) with the Na^+, Mg^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+},

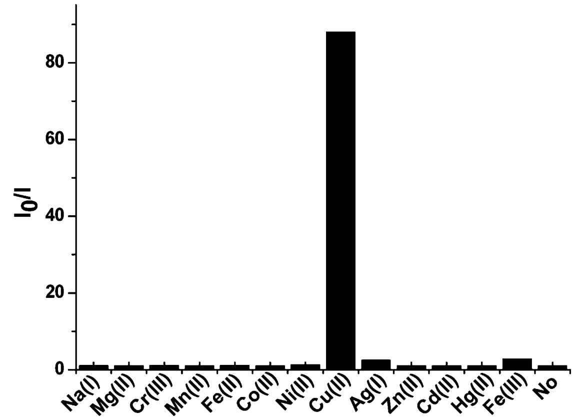

Figure 7. Responses of sensor **1** in $CHCl_3$ (25 μM) to different metal ions in MeOH (94 μM). The excitation was at 440 nm, and the emission was at 610 nm.

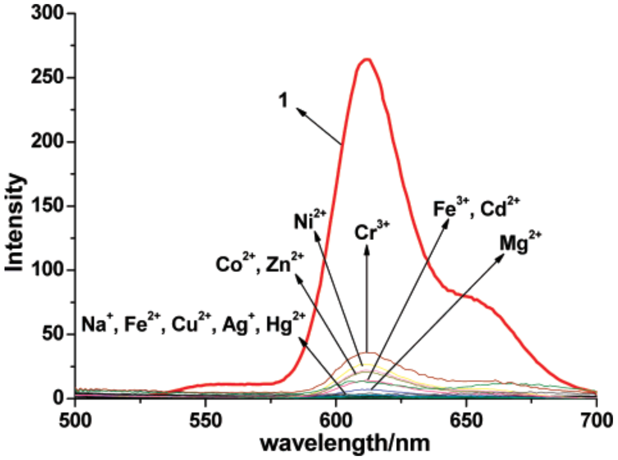

Figure 8. Fluorescence spectra of **1** (25 μM) in $CHCl_3$ solution (red line) and **1** in the presence of Cu^{2+} (50 μM) and Cu^{2+} (50 μM) plus other metal ions (160 μM) in MeOH solution: Cu^{2+} (black), Cu^{2+} and Ni^{2+} (yellow), Cu^{2+} and Co^{2+} (magenta), Cu^{2+} and Zn^{2+} (dark yellow), Cu^{2+} and Cd^{2+} (pink), Cu^{2+} and Hg^{2+} (purple), Cu^{2+} and Mn^{2+} (cyan), Cu^{2+} and Mg^{2+} (blue), Cu^{2+} and Na^+ (green), Cu^{2+} and Ag^+ (royal), Cu^{2+} and Cr^{3+} (wine), Cu^{2+} and Fe^{2+} (olive), and Cu^{2+} and Fe^{3+} (dark gray). The excitation was at 440 nm, and the emission was at 610 nm.

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(47) Detection limit (DL) is defined as the concentration corresponding to a signal 3 times the noise level of the background. DL = (0.03 × RSDB)/(x_A/c_0), where RSDB is the relative standard deviation of the background expressed as a percent and is the sensitivity (the slope of the calibration curve of intensity versus composition), x_A is the net analyte signal (i.e., the signal above background), and c_0 is the composition of the element in the sample. http://www.thespectroscopynet.com/Educational/detection_limit.htm.

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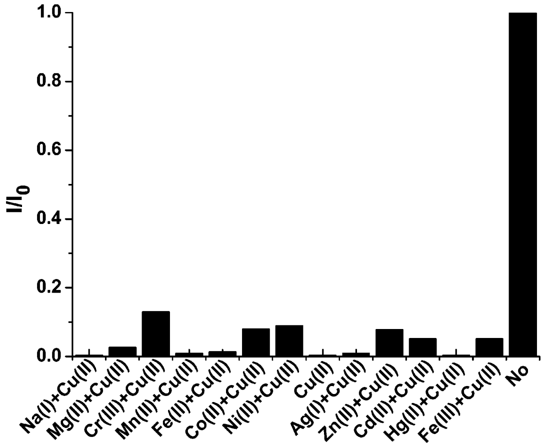

Figure 9. Fluorescent responses of **1** (25 μM) in $CHCl_3$ solution and **1** in the presence of Cu^{2+} (50 μM) and Cu^{2+} (50 μM) plus other metal ions (160 μM) in methanol solution, respectively. The excitation was at 440 nm, and the emission was at 610 nm.

or Fe^{3+} ions (160 μM) was added to the solution of **1** (25 μM), only the Cr^{3+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Fe^{3+} ions had a slight disturbance, though they are 3-fold in excess toward Cu^{2+} ion, indicating that the binding of the Cu^{2+} ion to **1** is much stronger than the binding of the other metal ions. To further examine the selectivity and antidisturbance of sensor **1**, Cu^{2+} ion (50 μM) was added respectively to the incubated solution of **1** (25 μM) containing much excess of Na^+, Mg^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, or Fe^{3+} ions (160 μM), in which the metal ions may occupy the four binding sites of **1**, almost complete fluorescence quenching was immediately induced in the solution of **1**, demonstrating that the Cu^{2+} ion can replace the other metal ions (if they bound to **1**). Therefore, the interferences from these metal ions are negligible, and **1** can be considered as a new, highly selective fluorescence sensor for Cu^{2+} ion with a low detection limit.

Conclusion

In conclusion, we have developed a new fluorescent sensor for Cu^{2+} with a high sensitivity and selectivity. Moreover, the *meso*-arylamino-substituted porphyrin featuring pyridyl groups can be synthesized by the Ullmann-type coupling of halogenated porphyrins and amines under Cu powder as a catalyst as well as with K_2CO_3 as the base. The design strategy and remarkable photophysical properties of sensor **1** will help to extend the development of fluorescent sensors for metal ions.

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Supporting Information Available: Fluorescent, NMR, and MS spectra; Job's plot and curve fitting (Figures S1−S12). This material is available free of charge via the Internet at http://pubs.acs.org.

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