ORIGINAL ARTICLE



Synthesis of a tetrapyrazinoporphyrazine-based fluorescent sensor for detection of Cu^{2+} ion

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Received: 16 December 2016 / Accepted: 3 July 2017 © Springer Science+Business Media B.V. 2017

Abstract In this study, a novel tetrapyrazinoporphyrazine-based fluorescent sensor for Cu²⁺ ion was synthesized and fully characterized by ¹H NMR, MALDI-TOF MS, and elemental analysis. A tetrapyrazinoporphyrazine substituent was used as the reporting group and a 2,2'-dipyridylamine moiety was employed as the recognition group. The effects of various metal ions on the absorption and emission spectra of the designed molecule were investigated, demonstrating that this compound shows selectivity and sensitivity toward the Cu²⁺ ion. Upon addition of Cu²⁺ ion, a fluorescent intensity of the tetrapyrazinoporphyrazine-based sensor decreased gradually at 655 nm. To confirm a selective binding ability of 2,2'-dipyridylamine moiety toward Cu²⁺ ion, a comparative study was performed using tetrapyrazinoporphyrazine derivative with bromine instead of 2,2'-dipyridylamine moiety. Furthermore, association constant and detection limit value of the synthesized compound toward Cu²⁺ ion were derived from a repetitive titration experiment. Also, a reversibility of the prepared sensor was confirmed through additional test using compound and ethylenediaminetetraacetic acid.

Keywords Fluorescence spectroscopy \cdot Tetrapyrazinoporphyrazine \cdot Chemosensor \cdot Cu²⁺ ion

Electronic supplementary material The online version of this article (doi:10.1007/s10847-017-0735-3) contains supplementary material, which is available to authorized users.

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Introduction

Copper, a soft transition metal, is the third most abundant essential trace element in the human body, and the Cu^{2+} ion is commonly found in natural water [1]. However, ingestion of excess copper can cause liver and kidney damage, as well as neurodegenerative diseases including Menkes', and Wilson's, Alzheimer's, and prion diseases [2–5]. Copper is also a significant environmental pollutant due to its widespread use in industry and agriculture [6, 7]. Therefore, detection of this transition metal in biological and environmental samples is of considerable importance for human and environmental health.

Among the many available methods for the detection of copper ion, fluorescent sensing is a valuable technique with significant advantages, including high sensitivity, instantaneous response, and operational simplicity. Over the past few years, many studies concerning fluorescent sensing of copper have been conducted [7–9].

Tetrapyrazinoporphyrazines, the aza-analog of phthalocyanines in which the benzene rings are replaced with pyrazines, have been studied for use in diverse application including liquids crystals [10], electrochemical capacitors [11], dye-sensitized solar cells [12] and photodynamic therapy [13], due to their outstanding photo-chemical and physical properties. In particular, their strong absorption and emission abilities in the red to near-infrared region show good transmission, low autofluorescence, and deep tissue penetration, all ideal qualities for application in biological systems [14, 15].

Though a number of researchers have attempted to develop fluorescent sensors with superb performance, tetrapyrazinoporphyrazine-based fluorescent sensors for Cu^{2+} are relatively rare. Herein, we report a novel A₃B-type zinc tetrapyrazinoporphyrazine for fluorescent sensing.

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This compound uses a strongly emissive zinc tetrapyrazinoporphyrazine unit as the reporting group and a 2,2'-dipyridylamine moiety as the recognition group for Cu^{2+} . The synthesized compound displays selective and sensitive response toward Cu^{2+} ion in a fluorescent spectrum.

Experimental

General

All reagents and solvents were purchased commercially and used without further purification. 1-(4-bromophenyl)-2-(4-(tert-butyl)phenyl)ethane-1,2-dione (1) and 3,3-dimethyl-2-oxobutanal (4) were prepared according to the methods described in literature [16, 17].

The synthesized compounds were identified, and their properties were measured using the following techniques. Flash chromatography was performed using Merck-EM type 60 (230–400 mesh) silica gel. Melting points were measured using an SMP30 apparatus (Stuart Equipment). Proton NMR spectra were recorded on a VARIAN Unity Inova 300 MHz FT-NMR spectrometer. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis was conducted on a Waters Limited MALDI-TOF spectrometer using a dithranol matrix. The UV–Visible absorption and emission spectra were measured by a Scinco S-4100 and Fluoromate FS-2 spectrophotometers, respectively. Elemental analyses were performed with a CE Instruments-EA 1112 Automatic Element Analyzer.

Synthesis

1-(4-tert-butylphenyl)-2-[4-(dipyridin-2-ylamino)phenyl] ethane-1,2-dione (2)

A mixture of 2,2'-dipyridylamine (2.0 g, 11.7 mmol), 1-(4-bromophenyl)-2-(4-(tert-butyl)phenyl)ethane-1,2-dione (6.1 g, 17.5 mmol), anhydrous potassium carbonate (3.2 g, 23.4 mmol), cupric sulfate (0.35 g, 2.2 mmol), 18- crown-6 (0.1 g, 0.5 mmol), and phenyl ether (25 mL) was heated at 180 °C under N2. After 48 h, the mixture was cooled and diluted with dichloromethane and methanol. The solution was then passed through a pad of Celite and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using chloroform/ethyl acetate (20:1) as eluent to produce a yellow liquid (4.5 g, yield 88% based on 2,2'-dipyridylamine). Yield 88%. ¹H NMR (d-chloroform), δ: 1.34 (9 H, s); 7.04–7.08 (4 H, m); 7.18 (2 H, d, J=8.4 Hz); 7.52 (2 H, d, J=8.4 Hz); 7.63–7.68 (2 H, t, J=7.2 Hz); 7.89–7.93 (4 H, d, J=8.4 Hz); 8.39 (2 H, d, J=7.2 Hz).

Anal. Calcd. (%) for C₂₈H₂₅N₃: C, 77.22; H, 5.79; N 9.65. Found (%): C, 77.32; H, 5.79; N 9.65.

5-(4-tert-butylphenyl)-6-[4-(dipyridin-2-ylamino)phenyl] pyrazine-2,3-dicarbonitrile (3)

Compound **2** (4.5 g, 10.4 mmol), diaminomaleonitrile (1.69 g, 15.6 mmol), methanol (30 ml) and a catalyst amount of *p*-toluenesulfonic acid were combined in a onenecked flask and refluxed for 3 h. After cooling, the solvent was evaporated and crystallized in chloroform. The precipitate was filtered and the filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel using chloroform/methanol (20:1) as eluent to produce a yellowish brown solid. (4.0 g). Yield 75%, Mp 63–65 °C. ¹H NMR (d-chloroform), δ : 1.32 (9 H, s); 7.01–7.10 (6 H, m); 7.41 (2 H, d, *J*=8.4 Hz); 7.54–7.57 (6 H, m); 8.37 (2 H, d, *J*=7.2 Hz). Anal. Calcd. (%) for C₃₂H₂₅N₇: C, 75.72; H, 4.96; N, 19.32. Found (%): C, 75.74; H, 4.99; N, 19.25.

5-(tert-butyl)pyrazine-2,3-dicarbonitrile (5)

3,3-Dimethyl-2-oxobutanal **4** (17.12 g, 0.15 mol) was refluxed with diaminomaleonitrile (12.5 g, 0.17 mol) in the presence of *p*-toluenesulfonic acid as catalyst for 3 h. After cooling, the mixture was passed through a pad of Celite and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using using ethyl acetate/hexane (1:3) as eluent to produce a yellowish brown solid (15.0 g). Yield 49%. Mp 160–162 °C. ¹H NMR (d-chloroform), δ : 1.45 (9 H, s); 8.94 (1 H, s). Anal. Calcd. (%) for C₁₀H₁₀N₇: C, 64.50; H, 5.41; N, 30.09. Found (%): C, 64.56; H, 5.39; N, 30.02.

Metal-free A_3B tetrapyrazinoporphyrazine (6)

A suspension of magnesium turnings (1.8 g, 75.0 mmol) and a small amount of iodine and n-butanol (120 ml) were refluxed for 4 h. After cooling to room temperature, 3 (2.03 g, 4.0 mmol) and 5 (2.6 g, 14.0 mmol) were added together. The mixture was refluxed for 6 h. After the resulting mixture was cooled, and diluted with chloroform, it was filtered through a Celite pad, and the filtrate was concentrated in vacuo. The residue was crystallized in ether, yielding a crude Mg phthalocyanine. The crude solid and p-toluenesulfonic acid (16.2 g, 95.4 mmol) in THF (70 ml) were stirred for 3 h at room temperature. The mixture was then evaporated under reduced pressure and extracted with chloroform and water. The organic layer was dried by sodium sulfate and concentrated in vacuo. The residue was purified by column chromatography on silica gel using chloroform/ methanol (15:1) as the eluent to produce metal-free A₃B

tetrapyrazinoporphyrazine (0.9 g). Yield 21%. Mp > 350 °C. ¹H NMR (d-chloroform), δ : -2.5 (2 H, br); 1.48 (9 H, s); 1.96 (27 H, s); 7.04–7.09 (2 H, m); 7.17–7.22 (2 H, m); 7.33–7.40 (2 H, m); 7.61–7.73 (4 H, m); 8.11–8.16 (4 H, m); 8.46 (2 H, br); 9.53–9.64 (3 H, m). MALDI-TOF MS : [M+H]⁺ 1068.24 calculated for C₆₂H₅₇N₁₉ 1068.31. Anal. Calcd. (%) for C₆₂H₅₇N₁₉: C, 69.71; H, 5.38; N, 24.91. Found (%): C, 69.75; H, 5.41; N, 24.82.

Zinc A_3B *-type tetrapyrazinoporphyrazine (7)*

A mixture of **6** (0.11 g, 0.1 mmol) and zinc acetate (0.09 g, 0.5 mmol) in pyridine (10 ml) was refluxed for 4 h. The resulting mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was diluted with chloroform and washed with water. The organic layer was dried with anhydrous sodium sulfate, and evaporated. The residue was purified by column chromatography on silica gel using chloroform/methanol (10:1) to afford **7** (93 mg). Yield 80%. Mp>350 °C. ¹H NMR (d-chloroform), δ : 1.48 (9 H, s); 1.98 (27 H, s); 7.09 (6 H, br); 7.71 (8 H, br); 8.46 (2 H, br); 9.64 (3 H, br). MALDI-TOF MS : [M+H]⁺ 1131.64 calculated for C₆₂H₅₅N₁₉Zn 1131.72. Anal. Calcd. (%) for C₆₂H₅₅N₁₉Zn: C, 65.80; H, 4.90; N, 23.52. Found (%): C, 65.84; H, 4.93; N, 23.49.

Spectroscopic methods

The salts used for testings were LiClO₄, NaClO₄, KClO₄, AgNO₂, CuCl₂, CoCl₂, FeCl₂, Hg(ClO₄)₂, MgSO₄, MnCl₂, NiCl₂, SnCl₂, Pb(NO₂)₃ and ZnCl₂. Quartz cuvettes with 1 cm length and 3.3 ml volume were used for all measurements. For a typical metal-binding titration, 0.3 ml metal ion solution (62.5 µmol in methanol) was added to a 3 ml solution volume of **7** (6.25 µmol in CHCl₃) by micropipette. The metal-dependent fluorescence intensity was obtained by monitoring the emission intensity at 655 nm. The excitation wavelengths were fixed at 599 nm. For fluorescence titration test, various concentration of CuCl₂ solution in methanol (6.94, 15.63, 26.79, 41.67, 62.5, 93.75, 145.83, 250 and 562.5 µmol) were used.

Results and discussion

Synthesis

The synthetic route to prepare the compound is presented in Scheme 1. The starting material (1) was treated with the commercially-available 2.2'-dipyridylamine in phenyl ether according to the reported method [18]. The condensation of the 1,2-dicarbonyl compounds (2 and 4) with diaminomaleonitrile (DAMN) produced 2,3-dicyanopyraizne substituents (3 and 5). The two dicyanopyrazine precursors then underwent cyclic tetramerization in the magnesium butoxide suspension and produced various kinds of asymmetrical tetrapyrazinoporphyrazines, including a component ratio of each monomer (A₄, A₃B, A₂B₂, AB₃, B₄) as well as structural isomers of the tert-butyl and diaryl substituents. After demetallization, the target material A₃B was separated by purification through column chromatography on silica gel and subsequently reacted with zinc acetate, yielding A₃B-type zinc tetrapyrazinoporphyrazine. The compound was identified using ¹H-NMR, and MALDI-TOF mass spectroscopy. ¹H-NMR spectra show broad peaks due to isomeric compounds. Nine protons of tert-butyl groups in the peripheral position and three protons for tert-butyl groups at the para position of the phenyl ring were confirmed around 1.98 and 1.48 ppm, respectively. Protons for the 2,2'-dipyridyl amine moiety were found around 8.42 and 7.10 ppm. In the MALDI-TOF mass spectrum, a clear peak was exhibited at 1129.4, corresponding to $[M]^+$ of 7.

Fluorescent probe for Cu²⁺

Figure S1 shows the absorption spectrum of 7 in diverse organic solvents. Compound 7 displays a monomeric absorption band with a Soret band at 358 nm and a sharp Q-band at 643 nm in DMF and DMSO, but exhibits little aggregation behavior in THF. In particular, very broad Q-bands were observed in chloroform and toluene due to J-aggregation [19].

On the other hand, the J-aggregation band at 689 nm was not observed after the addition of methanol to the chloroform solution. Thus, the addition of a coordinating solvent disrupts the J-aggregation as a result of the competitive coordination of methanol molecules with the central zinc atoms [20]. Moreover, the Lambert–Beer law could apply in a chloroform–methanol solvent for **7** in concentrations ranging from 0.1 to 7 μ M (Fig. 1).

The absorption spectrum of 7 upon addition of various metal ions was recorded in chloroform–methanol solvent (10:1 v/v). Figure 2a shows few absorption changes for Li⁺, Na⁺, K⁺, Ag⁺, Co²⁺, Fe²⁺, Hg²⁺, Mg²⁺, Mn⁺, Ni²⁺, Sn²⁺, Pb²⁺ and Zn²⁺, whereas only the Cu²⁺ ion caused a slight decrease in the intensity of the Q-band, indicating that the Cu²⁺ ion responds to 7.

The fluorescence spectra of 7 in Fig. 2b exhibited a significant difference between Cu^{2+} ion and the other metal ions. Addition of Cu^{2+} ion effectively reduced the emission intensity at 655 nm due to electron transfer [21], while the other metal ions displayed negligible spectral change, indicating that the 2,2'-dipyridylamine moiety is more suitable for sensing Cu^{2+} ions than the other metals. (The



Scheme 1 Synthesis of A₃B-type zinc tetrapyrazinoporphyrazine



Fig. 1 Absorption spectra of 7 in $CHCl_3/MeOH$ (10:1 v/v) binary solvent at different concentrations. The inset plots the Q-band absorbance versus the concentration of 7

absorbance and fluorescence spectra of the each interfering metal ion and table were demonstrated in Supplementary material.) To investigate the chemosensing properties of 7, fluorescence titration experiments for the complexation of 7 with Cu^{2+} ion were implemented as indicated in Fig. 3. Upon the addition of Cu^{2+} ion to the solution of 7, the intensity of the maximum absorption band around 642 nm gradually decreased. Fluorescence titration for the complexation of 7 with Cu^{2+} ion allowed the emission intensity at 655 nm to gradually decrease upon the addition of Cu^{2+} ion, indicating that there is an interaction between Cu^{2+} and receptor in the ground state [22].

A 1:1 complexation stoichiometry between 7 and Cu²⁺ was indicated by Job's plot [23]. (Fig. 4) From the fluorescence titration data, the association constant was determined to be 8.4×10^5 M⁻¹ from a Benesi–Hildebrand plot [24]. The detection limits of 7 for Cu²⁺ ion was found to be 1.0×10^{-6} M [23]. These values are comparable to reported examples [7, 23–25].

To further investigate the sensing ability of the 2,2'-dipyridylamine moiety for Cu^{2+} , 8 bearing bromine instead of the 2,2'-dipyridylamine moiety was prepared in a similar way to 7. (Details are described in the Supplementary material) Changes in emission intensity ratio according to concentration of Cu^{2+} ion are presented in



Fig. 2 a UV-visible absorption spectra and b fluorescence spectra of 7 (5.68 μ mol) treated with various metal ions (5.68 μ mol) in CHCl₃/MeOH (10:1 v/v)



Fig. 3 Fluorescent spectra of 7 (5.68 μ mol) upon the addition of Cu²⁺ ion (0, 0.63, 1.42, 2.43, 3.79, 5.68, 8.52, 13.25, 22.72, 51.12 μ mol) in CHCl₃/MeOH (10:1 v/v). The excitation wavelength was 599 nm

Fig. 5. As shown in Fig. 5, the value of I/I_0 for 8 changed no more than a few percent under one equivalence, whereas that of 7 was reduced by almost half, supporting that 2,2'-dipyridylamine moiety has a capability to selectively detect the Cu²⁺ ion.

Considering the finding that addition of ethylenediamineteraacetic acid (EDTA) to a solution of $7-Cu^{2+}$ leads to regeneration of 7, we performed additional tests. Fig. S8 shows that the emission intensity of $7-Cu^{2+}$ was steadily increased upon the addition of EDTA. This result suggests the possibility of using 7 as a reversible fluorescent sensor.



Fig. 4 Job plot for the binding of 7 with Cu^{2+} . Fluorescence intensity at 655 nm was plotted as a function of the molar ratio $[Cu^{2+}]/([7] + [Cu^{2+}])$



Fig. 5 Fluorescent intensity ratio of 7 and 8 (5.68 μ mol) upon the addition of Cu²⁺ ion (0–1 eq) in CHCl₃/MeOH (10:1 v/v) (The excitation wavelength was 599 nm.) and structure of compound 8

Conclusion

We described the synthesis methods and characterization of a novel zinc A_3B -type tetrapyrazinoporphyrazine (7) bearing a 2,2'-dipyridylamine functional group that can be used as a fluorescent sensor for Cu²⁺ ions. The addition of Cu²⁺ ion causes the emission intensity of 7 to decrease drastically, indicating its high selectivity toward Cu²⁺ ion among other tested metal ions. Titration demonstrated the sensitivity of 7 with a good association constant and detection limit value. Moreover, the binding ability of the 2,2'-dipyridylamine moiety and the reversibility of the prepared sensor were confirmed through additional tests using 8 and EDTA, respectively.

Acknowledgements This work was supported by the Technology Innovation Program (No. 10047756, Development of tetra-pyrrole type for Color, light-emitting, detecting Devices) funded by the Ministry of Trade, Industry & Energy (MI, Korea).

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