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A fluorescent probe for zinc ions based on *N*-methyltetraphenylporphine with high selectivity

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ABSTRACT

N-Methyl-α,β,γ,δ-tetraphenylporphine (NMTPPH) has been used to detect trace amount of zinc ions in ethanol–water solution by fluorescence spectroscopy. The fluorescent probe undergoes a fluorescent emission intensity enhancement upon binding to zinc ions in EtOH/H_2O (1:1, v/v) solution. The fluorescence enhancement of NMTPPH is attributed to the 1:1 complex formation between NMTPPH and Zn(II) which has been utilized as the basis for the selective detection of Zn(II). The linear response range covers a concentration range of Zn(II) from 5.0×10^{-7} to 1.0×10^{-5} mol/L and the detection limit is 1.5×10^{-7} mol/L. The fluorescent probe exhibits high selectivity over other common metal ions except for Cu(II).

1. Introduction

Zinc is the second abundant transition metal after iron in human body with the range of normal concentration from sub-nM to ~0.3 mM [1]. It plays an important role in various biological systems such as gene expression, protein–protein interaction and neurotransmission [2,3]. However, zinc is an environmental pollutant, significant concentrations of which may reduce the soil microbial activity causing phytotoxic effect [4,5]. Thus, the determination of trace zinc ion is of considerable importance for both biological and environmental applications.

Though several analytical techniques such as UV–vis spectroscopy [6], potentiometry [7] and flame atomic absorption spectrometry [8] have been reported for zinc ion assay in various samples, the available detection methods of Zn(II) are still limited due to its $3d^{10}4s^0$ electron configuration not giving any spectroscopic or magnetic signals. Owing to the advantages of simplicity, high sensitivity and low cost, past decades have seen increasing interest in the development of fluorescent probes for zinc ions. The Zn(II)-selective receptors in general include the derivatives of quinoline [1,9–12], di-2-picolylamine [13–18], acyclic and cyclic polyamine [19–25], terpyridine [26,27], and iminodiacetate [28–30]. Although some of these fluorescent probes can be applied to detect zinc ions in environmental or biological samples, they have the disadvantages such as insufficient selectivity or sensitivity. These fluorescent probes usually have interference problems caused by other transition metals cations such as Ni(II), Co(II) or Fe(III). Especially, among the reported fluorescent probes for Zn(II), many cannot distinguish Cd(II) from Zn(II) [31–33] because Zn(II) and Cd(II) have similar chemical properties. Searching for new fluorophores which would react with Zn(II) with sufficient high selectivity is still an active field as well as a challenge for the analytical chemistry research effort. Examples of recent advances along this line have been the synthesis of some new fluorescent probes which show selectively binding with Zn(II) not affected by Cd(II) [34–36].

In the past decades, porphyrins have gained increasing interest as analytical regents for various metal ions [37–39]. The porphyrins possess some characteristic features such as aromaticity, planarity and rigidity. In addition, the porphyrins exhibit nice photophysical properties including strong fluorescence, large Strokes shifts and relatively long excitation (>400 nm) and emission (>600 nm) wavelengths that minimize the effects of the background fluorescence. These make porphyrins potential fluorophores for several metal ions. However, the very slow rate of metal insertion into porphyrin limits the use of porphyrins as fluorogenic ligands for metal ions. To accelerate the reaction rate, several methods have been employed [38,40–42]. In addition, some supramolecular complexes of porphyrin have been used to detect zinc making use of the catalyzing effect of the complexes toward the Zn(II) insertion [43,44]. However, the non-covalent supramolecular complexes of meso-tetrakis(4-*N*-methylpyridyl)porphine on polyglutamate [43] are less robust than those obtained by covalent approach. Besides, as reported in the literature [44], Cd(II) influences on the fluorescence emission spectra of supramolecular complexes of porphyrin

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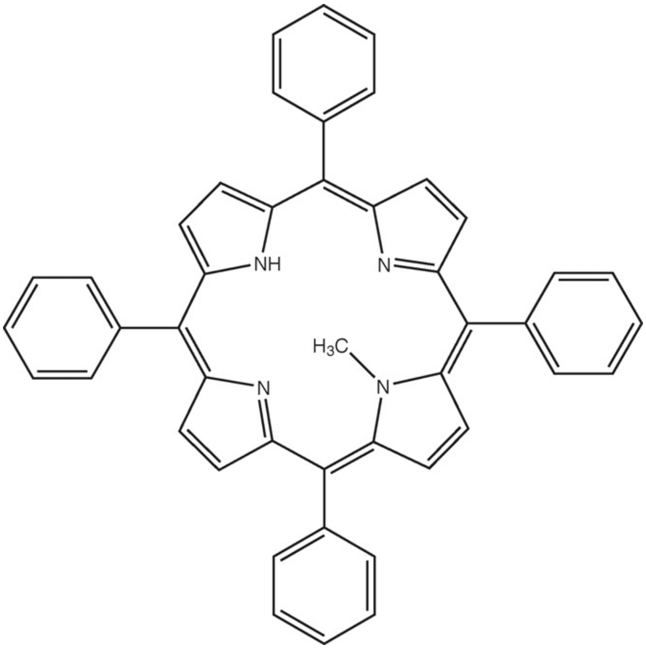

Fig. 1. The structure of NMTPPH.

in the same way as Zn(II) and interferes with the determination of Zn(II).

Herein, we report a selective fluoroionophore for Zn(II) based on *N*-methyltetraphenylporphyrin, which is barely affected by various metal ions except Cu(II). The *N*-methylporphyrins are a class of porphyrins with a nonplanar coordination site of pyrrolic nitrogens and the rate of complexation of the metal with *N*-methylporphyrin is much more quickly than that with non-methylated porphyrin [45,46]. The metal complexes of *N*-methylporphyrin exhibit very similar visible absorption spectra [47,48]. Lavallee et al. [49] investigated the fluorometric properties of *N*-methyltetraphenylporphyrin and several derivatives and chose their zinc complexes as standards for determination of chlorophyll a. Tanaka et al. [50] used *N*-methyltetrakis(4-sulfonatophenyl)porphyrin for kinetic determination of copper and zinc by UV–vis spectroscopy in serum. Making use of its relatively fast complexation rate, we studied in detail the use of *N*-methyl-α,β,γ,δ-tetraphenylporphine (NMTPPH, Fig. 1) as a fluorescent probe for zinc ions and showed its outstanding characteristics including large Stokes shifts, nice sensitivity and selectivity for zinc over other metal ions.

2. Experimental

2.1. Reagents

$CF_3SO_2OCH_3$ was obtained from Aldrich Chemical Co. Doubly distilled water was used throughout all experiments. CH_2Cl_2 was distilled from calcium hydride and stored over molecular sieves. Before being used, benzaldehyde was simply distilled from K_2CO_3. Pyrrole was distilled at atmospheric pressure from CaH_2. Unless otherwise stated, all other chemicals were of analytical reagent grade and used without further purification. α,β,γ,δ-tetraphenylporphine ($TPPH_2$) was prepared from pyrrole and benzaldehyde according to previously described method [51]. NMTPPH was synthesized from tetraphenylporphyrin ($TPPH_2$) and $CF_3SO_2OCH_3$ according to documented procedures [49].

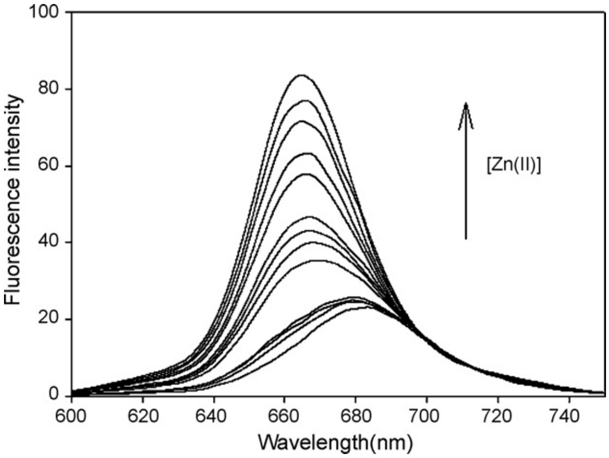

Fig. 2. Fluorescence emission spectra of NMTPPH (1.0×10^{-5} mol/L) in the presence of increasing concentration of Zn(II). The concentration of Zn(II) (from bottom to top): 0, 0.5, 0.7, 1, 3, 3.5, 4, 4.5, 5, 6, 7, 8 and 10 μM. Measured at 25 °C in $CH_3CH_2OH–H_2O$ (1:1, v/v) and Tris–HCl (0.05 mol/L) buffer (pH 7.10), with λ_{ex} = 432 nm.

2.2. Preparation of solutions

A stock solution of 2×10^{-5} mol/L NMTPPH was obtained by dissolving NMTPPH in absolute ethanol. A stock solution of 1×10^{-2} mol/L Zn(II) was prepared by dissolving $Zn(OAc)_2 \cdot 2H_2O$ in doubly distilled water. The stock solution of Zn(II) was diluted to lower concentrations of 1×10^{-3} to 1×10^{-7} mol/L stepwise.

The wide pH range solutions were prepared by adjustment of 0.05 mol/L Tris–HCl solution with HCl or NaOH solution.

The complex solution of Zn(II) and NMTPPH was obtained by mixing 12.5 mL of the stock solution of NMTPPH and 2.5 mL of Zn(II) solution of the different concentrations and diluting the mixture to 25 mL in a volumetric flask. In the solution thus obtained, the concentrations were 1×10^{-5} mol/L in NMTPPH and 1×10^{-4} to 1×10^{-8} mol/L in Zn(II). Blank solution of NMTPPH was prepared under the same conditions without Zn(II).

2.3. Apparatus

UV–vis absorption spectra were scanned on a Shimadzu MultiSpec-1501 spectrophotometer. All fluorescence measurements were taken on a PerkinElmer LS 55 Luminescence Spectrometer with excitation slit set at 10.0 nm and emission at 15.0 nm. The measurements of pH were carried out on a Mettler-Toledo Delta 320 pH meter. Data processing was performed on a Pentium IV computer with software of SigmaPlot.

2.4. Measurement procedures

The fluorescence intensity was measured at the maximum of excitation wavelength of 432 nm with the emission wavelength varied over 600–750 nm. Before the fluorescence measurement, the complex solution of NMTPPH/Zn(II) was allowed to stand for a few minutes to allow complete formation of metal–ligand complex.

3. Results and discussion

3.1. Spectral characteristics

The fluorescence emission spectra were recorded from 1×10^{-5} mol/L solution of NMTPPH at 25 °C in $CH_3CH_2OH–H_2O$ (1:1, v/v) and Tris–HCl (0.05 mol/L) buffer (pH 7.10). Fig. 2 shows