Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Photochemistry and Photobiology A: Chemistry 173 (2005) 264–270
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Highly selective sensing of lead ion based on α-, β-, γ-, and δ-tetrakis(3,5-dibromo-2-hydroxylphenyl)porphyrin/β-CD inclusion complex

Ying Zhang [a], WangChu Xiang [b], RongHua Yang [a,*], Feng Liu [a], KeAn Li [a]

[a] *College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*
[b] *Hunan City University, Hunan, Yiyang 413500, China*

Available online 13 May 2005

Abstract

α, β, γ, δ-Tetrakis(3,5-dibromo-2-hydroxylphenyl)porphyrin (TDBHPP) was synthesized and used for the fluorimetric determination of trace amount of lead ion in aqueous solution based on the inclusion interaction of the porphyrin with β-cyclodextrin (β-CD). In aqueous solution, the interaction of β-CD with TDBHPP caused a large enhancement of the porphyrin fluorescence intensity. In addition, the increased fluorescence of TDBHPP by β-CD was sensitive to metal ion following the fluorescence quenching of TDBHPP at its maximum emission wavelength. The quenching of TDBHPP fluorescence at room temperature was fast and nearly complete upon lead ion interaction. The organizing ability of the β-CD medium and the protection of the ligand from the micro-environment conferred in increased sensitivity, selectivity and detection limit, and allowed the determination of 2.8×10^{-7} to 7.4×10^{-5} mol/L lead compared with those obtained in the absence of β-CD. The method was applied in the analysis of synthetically biological samples with satisfactory results.

Keywords: Fluorimetry; Porphyrin; Cyclodextrin; Lead ion; Inclusion complex

1. Introduction

There is a great demand for monitoring of lead ion for environmental or biomedical applications because this toxic metal is widely dispersed in the environment, and exposure to it can give rise to a number of adverse health effects [1]. Due to the toxicity of Pb^{2+}, the determination of lead in biological and environmental samples plays an important role in the diagnosis of clinical disorders as well as in the monitoring of environmental pollution. Several methods have been published in the last decade for lead analysis such as atomic absorption spectrometry (AAS) [2], inductively coupled plasma mass spectrometry [3], anodic stripping voltammetry [4], and reversed-phase high-performance liquid chromatography coupled with UV–vis or fluorescence detection [5], of which AAS is most common used. With regard to sensitivity and accuracy, the mentioned methods are efficient tools for Pb^{2+} detection, however, they are time-consuming or require expensive and sophisticated equipment [6]. Since there is an increasing demand for reliable monitoring of lead ion during the analysis of environmental or biological samples, more simple and sensitive techniques are required [7]. Considering these, optical sensors involving fluoroionophores are becoming popular [8,9]. A large number of chromogenic reagents used for the determination of lead are available [10–14], whereas fluorometric methods are to be favored over other spectrophotometric methods, thanks to the high sensitivity and straightforward application to fiber optical-based remote detection. Many efficient fluoroionophores have been developed for alkali metals [15–17], alkaline earth metals [18] and Zn^{2+} [19–23], however, the number of Pb^{2+}-selective fluoroionophores is still limited [24,25].

In the past decades, porphyrin compounds have attracted much attention as analytical reagents and particularly as chromogenic ligands for various metal ions [26–30]. The inherent aromaticity, planarity and rigidity of the porphine nucleus give its fluorimetric potential. However, there is a serious

* Corresponding author. Tel.: +86 10 62752475; fax: +86 10 62751708.
E-mail address: yangrh@pku.edu.cn (R. Yang).

1010-6030/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2005.04.005

draw-back when porphyrins are used as fluorigenic ligand for metal ions in aqueous solution: (i) the solubility of porphyrin in water is poor, and thus, the fluorescence quantum yield is low, and (ii) the rate of metal complexation of porphyrin is very slow. In order to overcome these problems, several sophisticate methods have been proposed, including heating, solvent extraction, addition of auxiliary complexing agents (catalyst method) and application of metal ion substitution reaction [3–5,10–14,26–28]. Recently, we have been intrigued in the inclusion interaction of alkylated β-CD with porphyrin and the fluorescence sensing property of this inclusion complex to metal ion [31]. It provides a novel and effective method for the fluorometric assay of metal ion in water.

In this work, a new porphyrin compound, α, β, γ, δ-tetrakis (3,5- dibromo-2-hydroxylphenyl)porphyrin (TDBHPP) was synthesized, and its interaction with β-CD as well as the fluorescence sensing property of the inclusion complex to lead ion in aqueous solution were studied. The results showed that the fluorescence of TDBHPP in water was greatly increased by β-CD. In addition, it was found that the increased fluorescence would be quenched by lead ion, and the quenching of TDBHPP fluorescence is fast and complete at room temperature. Thus, a simple and highly sensitive fluorimetric method for Pb^{2+} was developed. Although aqueous β-CD solutions have been applied as molecular "organizing" media for both fluorimetric and phosphorimetric analysis and for the determination of several organic analytes, the analytical potential of β-CD as host molecules and as organizing media to promote fluorescent coordination reactions between organic ligands and metal ions has less been exploited [31,32].

2. Experimental

2.1. Apparatus and reagents

All fluorescence measurements were made with a Hitachi F-4500 fluorescence spectrometer (Kyoto, Japan) using a quartz cell ($1.0 \times 1.0\,cm^2$). The spectrofluorimeter was equipped with a high-pressure Xenon lamp. pH of solution was measured with a pH meter (Model PHS-3C, Shanghai, China) and adjusted if necessary. Data processing was performed on a Pentium III computer with Sigmaplot software.

β-CD (A. R., obtained from Sigma Chemical Co.) was crystallized twice from boiling water. Stock solution (0.01 mol/L) of β-CD was prepared by dissolving the material in doubly distilled water. Solution of TDBHPP/β-CD inclusion complex was prepared by evaporating of THF from 5 mL of 2×10^{-3} mol/L TDBHPP and diluting with 0.01 mol/L β-CD to 250 mL. A stock solution of 1.5×10^{-3} mol/L Pb^{2+} was prepared by dissolving lead (II) nitrate, $Pb(NO_3)_2$ (Fluka A.G.) in 0.1 mol/L nitric acid and diluted with doubly distilled water. Lower concentrations of Pb^{2+} solutions were obtained by serial dilution of the stock solution in water and stored at room temperature. Unless otherwise stated, all solutions were prepared with doubly distilled water. All other chemicals were of analytical-reagent grade and were used without further purification or treatment.

2.2. Procedure

In a 10 mL volumetric flask, aliquots of lead solutions sufficiently to ensure final concentrations between 5×10^{-7} and 2.0×10^{-4} mol/L were added to a mixed solution containing 5 mL 4×10^{-5} mol/L TDBHPP and 2.0 mL buffer solution (pH 9.0, 0.1 mol/L Tris/HCl). The mixture was then diluted to 10 mL with 0.01 mol/L β-CD solution. After the mixture had been allowed to stand for 5 min at room temperature, the fluorescence intensity was measured at 655 nm with an excitation wavelength of 420 nm.

2.3. Determination of lead added to biological samples

Hair samples (1 g) were dried and carbonized in an electric furnace. Samples of blood or urine (10 mL) were concentrated by boiling to about 2 mL, and then digested with a mixture of 2.5 mL of concentration hydrochloric acid and 5 mL of concentration nitric acid in a Berghof pressure digestor at 150 °C for 20 min. The hair samples were subjected to the same treatment. The volumes of the sample solutions were made up to 50 mL with doubly distilled water to give clear acidic solutions. To aliquots of these samples acidic solutions, 1 mL of 1% solution of dimethylglyoxime in ethanol and 1 mL of 1.0×10^{-4} mol/L potassium cyanide solution were added. Drops of 5 mol/L sodium hydroxide were added to give neutral or weakly alkaline solutions, which were subjected to the general procedure.

2.4. Synthesis of TDBHPP

3,5-Dibromo-2-hydroxylbenzdehyde [33]: In a three-necked flask, salicylaldehyde (4.5 g) was dissolved in absolute ethanol (15 mL). At 5 °C, to this solution were added dropwise 0.1 mol/L $KBrO_3$–0.1 mol/L KBr solution (90 mL) and HCl (0.1 mol/L, 60 mL) simultaneously with stirring. After stirring for 1 h at 15 °C, the reaction mixture was left to stand for 12 h at 0 °C. A crude residue was isolated by washing the filtrate several times with 0.1 mol/L NaOH and water separately to give an neutral or weakly alkaline solution. The 3,5-dibromo-2-hydroxylbenzdehyde solid was dissolved in 50 mL 95% ethanol, heated on a boiling water bath until crystal formed, left to stand for 30 min and filtered, the pure 3,5-dibromo-2-hydroxylbenzdehyde was obtained with yield of 78%. Its structure was verified by IR and ^1H NMR spectrometry (Fig. 1).

2.4.1. TDBHPP

TDBHPP was prepared from 3,5-dibromo-2-hydroxylbenzdehyde and pyrrole using a standard procedure [34]. Pyrrole (0.9 mL) was added dropwise to a refluxing solution

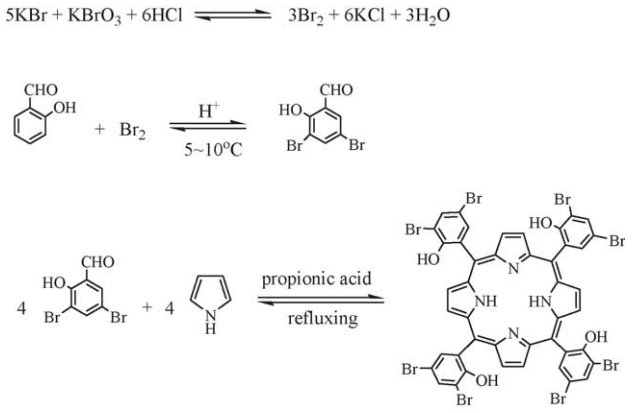

Fig. 1. Synthetic mechanism of α-, β-, γ-, δ-tetrakis(3,5-dibromo-4-hydroxylphenyl) porphyrin.

of 3,5-dibromo-2-hydroxylbenzdehyde (3.0 g) in 100 mL of propionic acid. After complete addition of the pyrrole, the reaction mixture was refluxed for 1 h at 165 °C on an oil-bath. The mixture was cooled, and left for 12 h at room temperature. After filtering and washing with methanol and ethyl acetate separately, the crude product was obtained. The product was dried at 100 °C in vacuum and purified by silica gel column chromatography with ethyl acetate as eluent to give TDBHPP as a blue-violet solid in 9.3% yield. ^{1}H NMR ($CDCl_3$) δ: −2.80 (s, 2H, pyrrole NH), 4.20 (br, 4H, hydroxyl), 8.11 (d, 4H, *o*-phenyl), 8.34 (d, 4H, *p*-phenyl), 8.89 (s, 8H, β-pyrrole NH).

3. Results and discussion

3.1. Inclusion complex

When organic molecules are included within a β-CD cavity in aqueous solution, the water is expelled. This strong hydrophobic interaction produces stable inclusion complexes. The stability derives from the polar character of the guest molecule and the functional group that attaches to it. Molecules that are included with the host cavity may have enhanced fluorescence and modified spectra. This type of interaction occurs with molecules that have greater affinity for the hydrophobic interior of the β-CD molecule than for aqueous phase.

Fig. 2 shows the fluorescence spectra of TDBHPP in aqueous solution in the absence and presence of 0.001 mol/L β-CD at pH 9.0 (curves of a and b). It can be seen that host–guest complexation produces fluorescence enhancement of TDBHPP. This change results from the binding of the TDBHPP molecule to the interior of the β-CD cavity in a particular orientation, which in turn, decreases the rotational freedom of the included molecule and mitigates non-radiative deactivated processes that occur in aqueous solution.

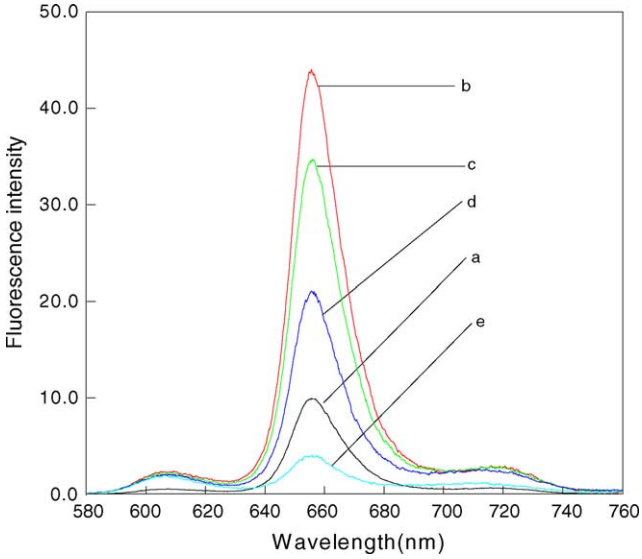

Fig. 2. Fluorescence emission spectra of TDBHPP at different experimental conditions: (a) TDBHPP at pH 9.0; (b) (a) + 0.001 mol/L β-CD; (c) (b) + 1.5×10^{-6} mol/L Pb^{2+}; (d), (b) + 1.5×10^{-5} mol/L Pb^{2+}; (e) (b) + 1.5×10^{-4} mol/L Pb^{2+}.

If the complexation of β-CD and porphyrin forms a 2:1 host–guest complex [35], the inclusion constant (K) can be obtained by the Benesi–Hildebrand method, and is expressed as [36]:

$$\frac{1}{I - I_0} = \frac{1}{(I_\infty - I_0)K[\beta\text{-CD}]^2} + \frac{1}{I_\infty - I_0} \quad (1)$$

where I_0 and I are the fluorescence intensity of TDBHPP in the absence and presence of β-CD, respectively, and I_∞ is the fluorescence intensity of TDBHPP when all porphyrin molecules are complexed by β-CD molecule. Plotting $1/(I - I_0)$ versus $1/[\beta\text{-CD}]^2$ gives a linear pattern (the plot is not shown). The slope of the linear relationship between $1/(I - I_0)$ and $1/[\beta\text{-CD}]^2$ gives K to be 1.7×10^3 M^{-2}, which implies that a strong inclusion complex is formed. Based on the 1:1 porphyrin–metal ligandated complex [37], a possible molecular modeling structure of the three-component complex was proposed (Fig. 3), which showed the opposing phenyl substituents of porphyrin binding within the hydrophobic cavity of the cyclodextrin.

3.2. Fluorescence response of the inclusion complex to lead ion

Metal ion may interact with free base porphyrin to form metalloporphyrin compound following the spectroscopic variations [26–30]. However, the rate of metal interaction at room temperature is very slow. In contrast, it was observed that the formation of β-CD/porphyrin inclusion complex results in a significant increase of the porphyrin metallation rate. Fig. 2 shows the effects of Pb^{2+} concentration on the fluorescence emission of TDBHPP in the inclusion system,

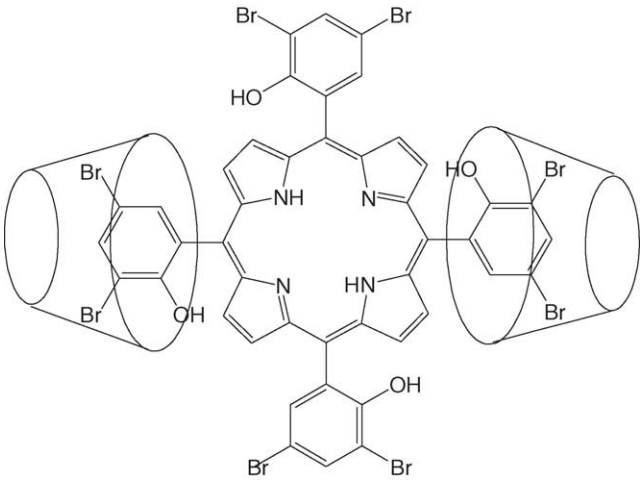

Fig. 3. Schematic graph of β-CD/porphyrin inclusion complex and lead ion.

fluorescence measurements were carried out at room temperature within 5 min. The fluorescence emission spectra of TDBHPP at room temperature are sensitive to the presence of Pb^{2+} (curves c–e in Fig. 2). In the presence of different concentrations of lead ion, significant fluorescence quenching of TDBHPP is observed, and the TDBHPP fluorescence quenching at 655 nm is fast and nearly complete upon Pb^{2+} interaction.

The effects of addition of other metal cationic ions such as Na^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Hg^{2+} and Fe^{3+} to the β-CD/porphyrin inclusion system were also examined. The fluorescence intensity changes of TDBHPP at 655 nm in the presence of these metal ions are shown in Fig. 4, where I_0 and I are fluorescence intensity of TDBHPP in the absence and presence of 1.5×10^{-4} mol/L of metal ions. The TDBHPP fluorescence is quenched by the addition of Pb^{2+} as well as that of Hg^{2+}, Mn^{2+}, Cu^{2+}, Co^{2+} and Fe^{3+}. In contrast, the fluorescence is less quenched by complex of Na^+, Ca^{2+}, Mg^{2+}, Ba^{2+} and Cd^{2+}. The quenching of TDBHPP fluorescence by transition metal ion or heavy metal may be attributed to the π-interaction between the heavy atom and the electron-rich aromatic rings in the porphyrin framework via spin-orbital coupling [38]. In the absence of β-CD, the quenching of TDBHPP fluorescence by metal ions is not significant.

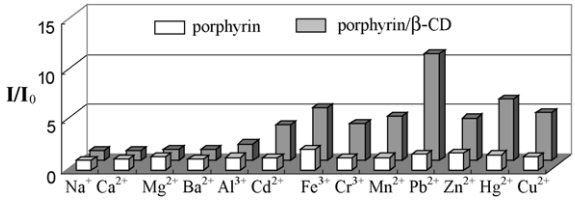

Fig. 4. Responses of the β-CD/porphyrin inclusion complex (gray) and TDBHPP (white) to different metal ions (*x*-axis markers) at pH 9.0. Excitation was at 420 nm and emission was monitored at 655 nm. Metal ion concentration was 1.5×10^{-4} mol/L.

3.3. Rate of complex formation

Under the same experimental conditions, the reactions of TDBHPP with Pb^{2+} in the absence or presence of β-CD were examined. The results clearly demonstrated that the fluorescence quenching of TDBHPP by Pb^{2+} was markedly accelerated by β-CD. In the absence of β-CD, even after 2 h, the TDBHPP fluorescence changes can hardly be observed. However, the formation of β-CD/porphyrin inclusion complex "catalyzes" the insertion of metal ion. Similar behaviors were observed for the system when other transition metal ions were employed in place of Pb^{2+}.

A reasonable explanation for this "catalysis" effect is that the aggregation of TDBHPP in water should suppress the accessibility of the metal ions to the porphine "core" owing to the porphyrin face-to-face arrangement [39]. Whereas the formation of inclusion complex reduces the aggregation of TDBHPP and increases the rigidity of the porphine core that leads to the effective incorporation of the metal ions into the ring. These hypotheses are in good agreement with the previous results reported by Purrello et al. [40].

3.4. Conditions for measurement of lead ion

Fig. 5 shows the pH-dependence of TDBHPP fluorescence in the inclusion system and the fluorescence response of the inclusion complex to lead ion. It shows that the fluorescence intensity of β-CD/porphyrin complex is constant at pH 6.30–10.0 (curve 1 in Fig. 5). At lower pH, the neutral form of porphyrin (H_2L) can be successively protonated to form mono-(H_3L^+) and dicationic (H_4L^{2+}) forms, both of which result in shifts of the maximum emission wavelength of the porphyrin, and thus, decreasing the fluorescence intensity at 655 nm. The decrease in TDBHPP intensity above pH 10.0 is not reversible but is a consequence of the breakdown

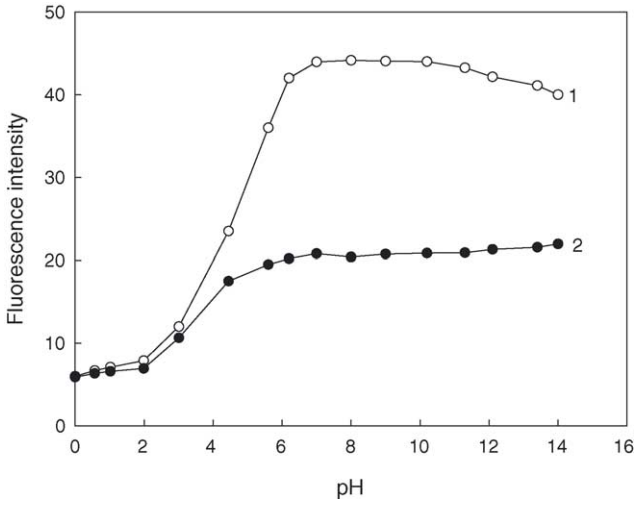

Fig. 5. The pH-dependence of TDBHPP fluorescence in the inclusion system in the absence (blank) and presence (solid) of lead ion. Lead ion concentration was 1.5×10^{-5} mol/L. Excitation was at 420 nm and emission was monitored at 655 nm.

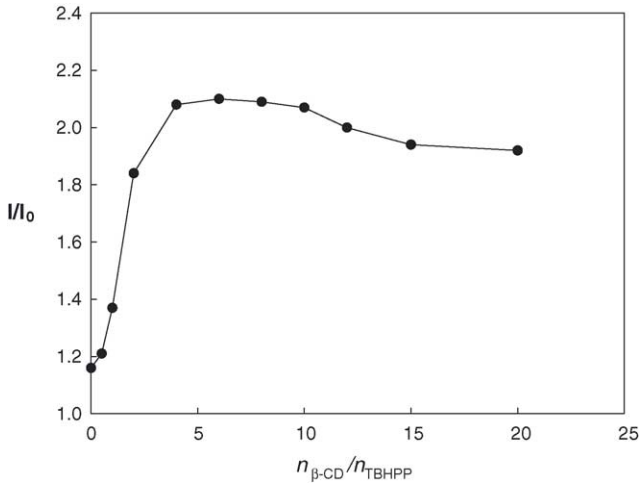

Fig. 6. Effect of the amount of β-CD in the inclusion complex on the TDBHPP fluorescence response to lead ion. Other conditions are the same to Fig. 5.

[41] of the β-CD capsule. Fig. 5 also shows the influence of pH on the fluorescence response of the inclusion complex to 1.5×10^{-5} mol/L lead ion (curve 2). As can be seen, curve 2 has similar shape of curve 1, while the fluorescence signal values are smaller. Taking the sensitivity and the absolute values of fluorescence signal into accounts, a final pH 9.0 is chosen as an ideal experimental condition.

The amount of β-CD in the inclusion complex influences the TDBHPP fluorescence intensity and its response to metal ion. Low concentration of β-CD in the system leads to the relative weak blank fluorescence intensity of TDBHPP. Thus, it will decrease the sensitivity and detection range. However, the amount of β-CD in the system should not be too high. Otherwise, an inner filter effect would be expected. Fixing the concentration of TDBHPP in the mixture at about 0.1 mM, Fig. 6 shows the fluorescence response of TDBHPP to 1.5×10^{-5} mol/L Pb^{2+} in the presence of different amounts of β-CD. It is clear that when the molar ratio of β-CD to TDBHPP reaches 6, the value of I/I_0 levels off at maximum. Higher β-CD concentrations produce only small changes in I/I_0. Taking the analytical range and the sensitivity (I/I_0) into accounts, the molar ratio of β-CD to TDBHPP in the system was fixed at 8.

No fluorescence decrease was produced by an excess of reagent at least up to 1.0×10^{-5} mol/L, accordingly, 5 mL of 4.0×10^{-5} mol/L TDBHPP solution was used in a final volume of 10 mL. No changes in fluorescence were observed when the sequence of addition was changed. The complex formed quickly and the fluorescence remained stable for at least 5 h. There was no temperature effect in the range 10–35 °C.

3.5. Calibration curve and detection range

The interaction of porphyrin with metal ion was verified to form a 1:1 metalloporphyrin complex [37], which can be expressed in terms of the equilibrium:

$$H_2L + M^{2+} \overset{K}{\rightleftharpoons} ML + 2H^+ \tag{2}$$

The corresponding association constant can also be expressed as:

$$K = \frac{[ML][H^+]^2}{[M^{2+}][H_2L]} \tag{3}$$

$$\frac{K}{[H^+]^2} = \frac{[ML]}{[M^{2+}][H_2L]} = \frac{[ML]}{\{[M^{2+}]_0 - [ML]\} \cdot \{[H_2L]_0 - [ML]\}} \tag{4}$$

where K is the association constant of the reaction, and $[M^{2+}]_0$ and $[H_2L]_0$ are initial concentrations of metal ion and porphyrin, respectively. The degree of complexation is described as α, defined as the ratio of the metal complex concentration, [ML], to the initial concentration of the porphyrin, $[H_2L]_0$

$$\alpha = \frac{[ML]}{[H_2L]_0} \tag{5}$$

From Eqs. (4) and (5), the following equation could be derived:

$$[M^{2+}]_0 = \frac{\alpha}{1-\alpha}\frac{K}{[H^+]^2} + \alpha[H_2L]_0 \tag{6}$$

It is known (i) the variations in fluorescence signals is proportional to the porphyrin concentration and (ii) in the case of high lead ion concentration, almost all porphyrin molecules are complexed with the metal ion, α is connected to the fluorescence intensity of the porphyrin as following:

$$\alpha = \frac{I_0 - I}{I_0 - I_1} \tag{7}$$

where I is the fluorescence intensity of porphyrin actually measured at a defined metal concentration, and I_0 and I_1 are the fluorescence intensities of porphyrin in the absence and presence of excess of metal ion, respectively.

The relationship between I and $[M^{2+}]_0$ as expressed by Eqs. (6) and (7) is the basis for quantitative determination of lead ion concentration in aqueous solution. In Fig. 7, α is given as a function of the logarithm of $[Pb^{2+}]$ at pH 9.0. The experimental data points were fitted to Eq. (6) by adjusting K values. The best curve fitting was obtained with $\log K = 3.06$. The fitting curve can serve as the calibration curve for the determination of Pb^{2+} concentration. A sufficient response to Pb^{2+} is obtained from 2.8×10^{-7} to 7.4×10^{-5} mol/L ($0.05 \leq \alpha \leq 0.95$) [42]. The detection limit is determined to be 5.0×10^{-8} mol/L.

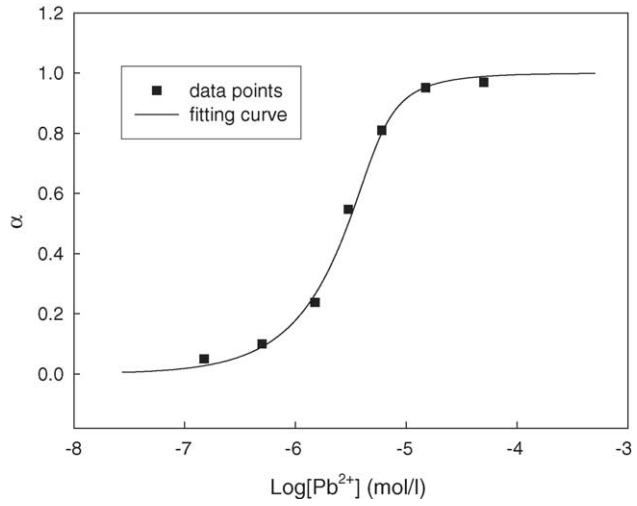

Fig. 7. The fluorescence response, α, as a function of log [Pb^{2+}] at pH 9.0. The curve fitting for experimental data was calculated from Eq. (6).

3.6. Interference study

The effect of foreign ion was examined by adding different amounts of potentially interfering species to the solutions containing 1.5×10^{-5} mol/L Pb^{2+}. Cations were added as chlorides, nitrates or sulphates, anions were added as their sodium, potassium or ammonium salts. The tolerance limit was taken as the concentration causing an error of ±5% in the determination of Pb^{2+}. The results obtained are summarized in Table 1, which shows that most anions do not interfere even when they are added in fairly large amounts, and most cations such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+}, Cd^{2+}, Cr^{3+} and Zn^{2+} do not interfere, whereas the tolerance limits for Cu^{2+}, Fe^{3+}, Mn^{2+}, Hg^{2+} and Ni^{2+} are not high. It can be concluded that a significant improvement in selectivity is gained by the proposed method compared with the determination of the metal ion simply using porphyrin [28]. The improved selectivity can be attributed to the protection conferred to the porphyrin by β-CD. The interferences of Co^{2+}, Mn^{2+}, Cr^{3+}, Fe^{2+} and Fe^{3+} can be avoided by adding 1 mL of 1% solution of dimethylglyoxime in ethanol, and Cu^{2+}, Zn^{2+} and Hg^{2+} can be masked with 1.0×10^{-4} mol/L potassium cyanide since cyano anion shows no interference with the determination of lead ion.

Table 1
Effect of foreign ions on the determination of 1.5×10^{-5} mol/L Pb^{2+}

Foreign ions	Concentration (mol/L)	Pb^{2+} found (10^{-5} mol/L)	Relative error (%)
Na^+	0.1	1.54	2
Mg^{2+}	0.001	1.57	4
Ba^{2+}	0.05	1.53	1
Ca^{2+}	0.05	1.55	3
Cd^{2+}	5.0×10^{-4}	1.56	3
Al^{3+}	0.001	1.54	2
Cu^{2+}	2.0×10^{-4}	1.51	1
Mn^{2+}	8.0×10^{-5}	1.47	−2
Co^{2+}	5.0×10^{-4}	1.55	3
Fe^{2+}	1.0×10^{-4}	1.58	5
Fe^{3+}	5.0×10^{-5}	1.57	4
Zn^{2+}	5.0×10^{-4}	1.46	−3
Cr^{3+}	3.0×10^{-4}	1.54	2
Hg^{2+}	1.0×10^{-4}	1.53	1
F^-, Cl^-	0.01	1.56	3
I^-	0.002	1.57	4
CO_3^{2-}	0.1	1.46	−2
SCN^-	0.001	1.48	−1

Table 2
Determination of lead added to biological samples

Samples	Pb^{2+} added (mol/L, 10^{-6})	Pb^{2+} found (mol/L, 10^{-6})	
		Present method[a]	AAS
Serum	1.5	1.53 ± 0.04	1.56 ± 0.02
	5.0	5.04 ± 0.18	5.10 ± 0.24
Hair	1.5	1.55 ± 0.11	1.49 ± 0.07
	5.0	4.98 ± 0.20	5.08 ± 0.29
Urine	1.5	1.48 ± 0.09	1.52 ± 0.12
	5.0	5.11 ± 0.33	4.96 ± 0.25

[a] The results expressed are mean of five determination ± standard deviation.

3.7. Recovery determination

The method proposed was applied to the determination of lead added to biological samples. Table 2 summarizes the results, from which it can be concluded that acceptable accuracy and precision can be obtained in the analysis of final solution containing 1.5×10^{-6} mol/L or 5.0×10^{-6} mol/L Pb^{2+}. Unfortunately, the level of lead in these natural samples is too low to detect. However, it would be suitable for monitoring subjects exposed to abnormal lead level. The results show reasonable agreement with the results obtained by atomic absorption spectrometry.

4. Conclusions

A new way of employing porphyrin in the fluorimetric determination of metal ions is described, which overcomes solubility and reaction time problems of the ligand and which eliminates the needs for liquid-liquid extraction and heating. In addition, the apparently good fit of the porphyrin within the β-CD cavity provides improved quantum yields because of the increased order and stability in the protected microenvironment which, in turn, permits better detection limits. The method is economic, simple, rapid, reproducible and selective.

Acknowledgement

Financial support from the National Science Foundation of China (Grant No. 20475005) is gratefully acknowledged.

References

[1] H.L. Needleman, Human Lead Exposure, CRC Press, Boca Raton, FL, 1992.
[2] J.E. Tahan, V.A. Granadillo, R.A. Romero, Anal. Chim. Acta 295 (1994) 187.
[3] R.J. Bowins, R.H. Mcnutt, J. Anal. At. Spectrom. 9 (1994) 1233.
[4] B.J. Feldman, J.D. Osterioh, B.H. Hata, A. D'Alessandro, Anal. Chem. 66 (1994) 1983.
[5] X.J. Xu, H.S. Zhang, C.Y. Zhang, J.K. Cheng, Anal. Chem. 63 (1991) 2532.
[6] H.A. Mckenzie, L.E. Smythe (Eds.), Quantitative Trace Analysis of Biological Materials, Elsevier, New York, 1998.
[7] X. Yu, H. Yuan, T. Górecki, J. Pawliszyn, Anal. Chem. 71 (1999) 2998.
[8] A.P. de Silva, D.B. Fox, A.J.M. Huxley, T.S. Moody, Coord. Chem. Rev. 205 (2000) 41.
[9] V. Adendota, L. Fabbrizzi, M. Licchelli, C. Mangano, P. Pallavicini, L. Parodi, A. Poggi, Coord. Chem. Rev. 192 (2000) 649.
[10] J.F. Tertoolen, D.A. Detmar, C. Buijze, Z. Anal. Chem. 167 (1959) 401.
[11] N. Trinder, Analyst 91 (1966) 587.
[12] T. Hongo, A.O. Azaki, L. Terada, T. Kiba, Fresen. J. Anal. Chem. 331 (1988) 647.
[13] M.N. Bale, D.P. Dave, A.D. Sawant, Talanta 42 (1995) 1291.
[14] Z. Li, Z. Zhun, Y. Chen, C.-G. Hsu, J. Pan, Talanta 48 (1999) 511.
[15] H. He, M.A. Mortellaro, M.J.P. Leiner, R.J. Fraats, J.K. Tusa, J. Am. Chem. Soc. 125 (2003) 1468.
[16] T. Hayashita, S. Taniguchi, Y. Tanamura, T. Uchida, S. Nishizawa, N. Teramae, Y.S. Jin, J.C. Lee, R.A. Bartsch, J. Chem. Soc., Perkin Trans. 2 (2000) 1003.
[17] H. Ueyama, M. Takagi, S. Takenaka, J. Am. Chem. Soc. 124 (2002) 14286.
[18] A. Miyawaki, J. Llopis, R. Heim, J.M. McCaffery, J.A. Adams, M. Ikura, R.Y. Tsien, Nature 388 (1997) 882.
[19] T. Hirano, K. Kikuchi, Y. Urano, T. Higuchi, T. Nagano, J. Am. Chem. Soc. 122 (2000) 12399.
[20] T. Hirano, K. Kikuchi, Y. Urano, T. Higuchi, T. Nagano, J. Am. Chem. Soc. 124 (2002) 6555.
[21] K.R. Gee, Z.-L. Zhou, W.-J. Qian, R. Kennedy, J. Am. Chem. Soc. 124 (2002) 776.
[22] S.C. Burdette, S.J. Lippard, Inorg. Chem. 41 (2002) 6816.
[23] S. Bhattacharya, A. Gulyani, Chem. Commun. (2003) 1159.
[24] C.-T. Chen, W.-P. Huang, J. Am. Chem. Soc. 124 (2002) 6246.
[25] S. Deo, H.A. Godwin, J. Am. Chem. Soc. 122 (2000) 174.
[26] X. Xu, H. Zhang, C. Zhang, J. Cheng, Anal. Chem. 63 (1991) 2529.
[27] S. Igarashi, T. Yotsuyanagi, Anal. Chim. Acta 281 (1993) 347.
[28] M. Tabata, M. Kumamoto, J. Nishimoto, Anal. Chem. 68 (1996) 758.
[29] Z. Li, Z.Z. Zhu, T. Jan, T.M. Pan, Analyst 124 (1999) 1227.
[30] Q.F. Hu, G.Y. Yang, J.Y. Yin, Y. Yao, Talanta 57 (2002) 751.
[31] R.H. Yang, K.A. Li, K.M. Wang, F. Liu, N. Li, F.L. Zhao, Anal. Chim. Acta 469 (2002) 285.
[32] A. Yamanchi, T. Hagashita, S. Nishizawa, M. Watanabe, N. Teramae, J. Am. Chem. Soc. 121 (1999) 2319.
[33] A. Syamal, D. Kumar, J. Indian Chem. Soc. 65 (1988) 112.
[34] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Org. Chem. 32 (1967) 476.
[35] R.H. Yang, K.M. Wang, D. Xiao, X.H. Yang, Spectrochim. Acta A 57 (2001) 1595.
[36] C.C. Catena, F.V. Bright, Anal. Chem. 61 (1988) 905.
[37] M. Tabta, M. Tanaka, Trends Anal. Chem. 10 (1991) 128.
[38] C. Wieser, C.B. Dieleman, D. Matt, Coord. Chem. Rev. 165 (1997) 93.
[39] C.A. Hunter, J.K.M. Sanders, J. Am. Chem. Soc. 112 (1990) 5525.
[40] R. Purrello, S. Gurrieri, R. Lauceri, Coord. Chem. Rev. 190/192 (1999) 683.
[41] G..S. Cox, N.J. Turro, N.C. Yang, M.J. Chen, J. Am. Chem. Soc. 106 (1984) 422.
[42] M.M.F. Choi, X. Wu, Y.R. Li, Anal. Chem. 71 (1999) 1342.