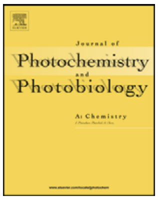
Journal of Photochemistry and Photobiology A: Chemistry 204 (2009) 1–6

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Optical sensing of heavy metal ions in anionic micellar solution using a Pd porphyrin phosphorescent probe

Shuang Hu [a,b], Hongsheng Mao [c], Yu Wang [a,*]

[a] *School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, PR China*
[b] *School of Pharmacy, Shanxi Medical University, Taiyuan 030001, PR China*
[c] *Graduate Department, Shanxi Medical University, Taiyuan 030001, PR China*

ARTICLE INFO

Article history:
Received 28 June 2008
Received in revised form 9 December 2008
Accepted 2 February 2009
Available online 21 February 2009

Keywords:
Room temperature phosphorescence
Micelle
Palladium porphyrin
Heavy metal ion
Quenching

ABSTRACT

Using sodium sulfite as an oxygen scavenger, meso-tetra (4-N,N,N-trimethylanilinium) porphyrin-Pd (Pd-TAPP) emits strong and stable room temperature phosphorescence (RTP) in sodium dodecyl sulfate (SDS) micellar solution. Heavy metal ions, including Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}, can efficiently quench the phosphorescence of Pd-TAPP. The Stern–Volmer constants increased in the order $Fe^{2+} < Co^{2+} < Cu^{2+} < Ni^{2+}$, directly reflecting the relative sensitivity of the method for these ions. The detection limits calculated following the 3σ IUPAC criteria are: 2.3×10^{-7} mol/L for Cu^{2+}, 3.4×10^{-7} mol/L for Co^{2+}, 1.2×10^{-7} mol/L for Ni^{2+} and 2.1×10^{-6} mol/L for Fe^{2+}. The addition of these ions also resulted in reduction of the lifetime (τ) of Pd-TAPP. The linear relationship between the concentration of Fe^{2+}, Co^{2+}, Ni^{2+} or Cu^{2+} ions and τ_0/τ indicated the dynamic quenching mechanism.

1. Introduction

Heavy metal ions are the most toxic environmental pollutants threatening the health of humans and natural ecosystem alike. Therefore, the detection and quantification of heavy metal ions are of great importance in many practical applications such as environmental or process monitoring and waste management. Among various techniques used for the determination of heavy metals, fluorimetry has received much attention over the past few years due to its high selectivity and sensitivity [1–9]. As a complementary method for fluorimetry, room temperature phosphorimetry has several advantages over fluorescence as a detection mode for optical sensing [10,11]. Compared with fluorescence, phosphorescence is a less usual phenomenon and exhibits superior selectivity. The phosphorescence emission band is located at a much longer wavelength than fluorescence, which results in a larger Stokes shift and thereby simplify the spectral separation between the excitation light and the phosphorescence emission. In addition, phosphorescence has a longer decay time from about 10^{-4} to 10 s and the interferences from short-lived scattering light and possible fluorescence signals can be easily avoided by using an appropriate delay time. Consequently, there is a possibility to lower the detection limits of phosphorimetry. Also, longer lifetime of the phosphorescent state facilitates the design of relatively inexpensive optical sensing systems based on decay-time measurements. Actually, RTP has been widely used in many fields such as pharmaceutical analysis, environmental monitoring of pesticide residue and detection of polyaromatic hydrocarbons [12–15]. However, there have been relatively few reports on phosphorescent probes for heavy metal ions [16–21]. Therefore, development of sensitive and selective phosphorescent probes for detection of heavy metal concentrations would be desirable.

Taking advantage of the ability of surfactant micelles to bind or solubilize a wide range of compounds in aqueous solutions and to stabilize the triplet state of some molecules, micelle-stabilized room temperature phosphorescence (MS-RTP) technique was first developed by Kalyanasundaram et al. [22] and has been successfully applied to the determination of a wide variety of lumophors [14,15,23–28]. The MS-RTP characteristics of Pd-porphyrin complexes, a kind of metal porphyrins, have been investigated in different organized media including micelles [29,30]. The presence of heavy atom Pd can facilitate the S1 → T1 intersystem crossing and thus induce strong phosphorescence of porphyrins [31]. These complexes show a very high phosphorescence quantum yield even in an aqueous environment at room temperature. Furthermore, Pd-TAPP emits phosphorescence at near infrared wavelength and can be excited at either Soret or Q bands. These characteristics make the Pd-porphyrin complexes very useful as room temperature phosphorescent probes.

---

[*] Corresponding author. Tel.: +86 351 7010319; fax: +86 351 7011688.
E-mail address: wangyu1168@sxu.edu.cn (Y. Wang).

1010-6030/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2009.02.004

Previous reports revealed that metal ions as quenchers can quench the luminescence of micelle-solubilized probes and the quenching efficiency is critically dependent on the nature of the micellar aggregate [32–34]. These results prompted us to investigate the effect of a variety of metal ions on the RTP of Pd-TAPP in anionic sodium dodecyl sulfate (SDS) micelles. Some heavy metal ions were found to efficiently quench both the RTP intensity and lifetime of Pd-TAPP, which can be used for the detection of these heavy metal ions.

2. Experimental

2.1. Apparatus

UV–visible measurements were performed on a TU-1901 UV–vis spectrophotometer (Purkinje General Instrument Co., Ltd, Beijing, China). All luminescence measurements were made on a Cary Eclipse luminescence spectrometer (Varian Co., USA) equipped with a pulsed xenon lamp. The excitation and emission slits were both set at 15 nm. The delay time and the gate time were set at 0.10 and 2.0 ms, respectively. For the lifetime measurements, the delay time was set at 0.10 ms while the gate time was typically set at 0.20 ms. The pH measurements were carried out on a pHS-3C acidometer (Shanghai Precision & Scientific Instrument Co., Ltd, China).

2.2. Reagents

Meso-tetra (4-N,N,N-trimethylanilinium) porphine tetrachloride (TAPP) was purchased from Strem Chemicals (USA). $PdCl_2$ was obtained from Shanghai Chemicals Co. (China) and used as received. A stock solution of 8.4×10^{-5} mol/L Pd-TAPP was prepared in dimethyl formamide (DMF). All the metal salts, mainly chloride, were analytical grade. Al^{3+} was tested as acetate and Fe^{2+} as sulfate. Bi^{3+}, Ag^{+} and Tl^{+} were nitrates. All metal stock solutions were prepared by dissolving the appropriate amounts of metals with doubly distilled water. Freshly prepared sodium sulfite solution (1 mol/L) was used for the RTP measurements. Britton-Robinson (B-R) buffer solutions of different pH were prepared by mixing appropriate amounts phosphoric, acetic and boric acids at the same concentration (0.040 mol/L) and then adjusting to desired pH with 0.20 mol/L sodium hydroxide.

2.3. Synthesis of palladium porphyrin

Pd-TAPP was prepared following a literature procedure [35]. The reaction was monitored by UV–vis absorption and fluorescence spectra. The gradual disappearance of the original bands at 412 nm and the subsequent appearance of new bands at 429 nm (Soret band) and 532 nm (Q-band) indicated the formation of metal porphyrin. The observed fluorescence quenching of porphyrin also confirmed the insertion of Pd into free base porphyrin.

2.4. General procedure

Into a comparison tube were added 0.1 mL of Pd-TAPP stock solution, 0.5 mL of 3.0×10^{-2} mol/L SDS stock solution, 2 mL of B-R buffer solution and 40 μL of sodium sulfite solution sequentially. The mixture was diluted to the final volume of 5 mL with water. After thorough mixing, the mixture was allowed to stand for 5 min before absorption and phosphorescence measurements. The titrations of Pd-TAPP with metal ions were performed by directly adding different volumes of cation stock solution to the above Pd-TAPP working solution in the quartz cell. The total volume change after addition of metal ion solution was less than 10%.

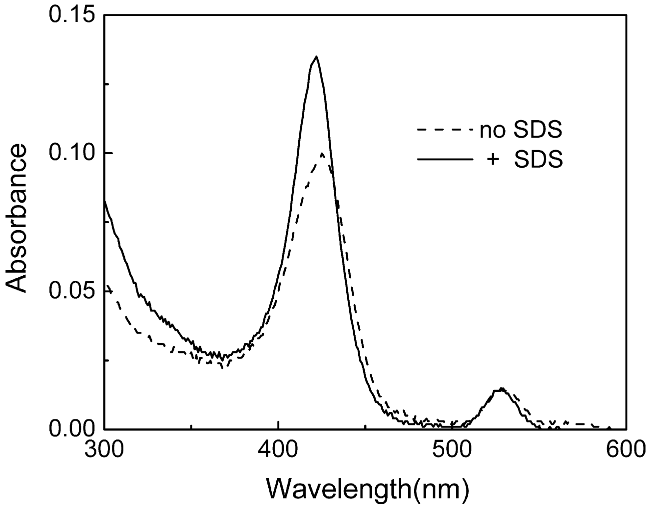


Fig. 1. UV–vis spectra of Pd-TAPP in the presence and absence of SDS. [Pd-TAPP] = 2.3×10^{-6} mol/L; [Na_2SO_3] = 8.0×10^{-3} mol/L; [SDS] = 3.0×10^{-3} mol/L.

3. Results and discussion

3.1. RTP of Pd-TAPP in the SDS solution

Fig. 1 shows the absorption spectra of Pd-TAPP in the presence and absence of SDS. The absorbance of Pd-TAPP at 426 nm increased upon adding of SDS and the absorption peak blue-shifted to 421 nm, indicating that Pd-TAPP was effectively incorporated into the SDS micelle.

After the removal of dissolved oxygen by Na_2SO_3, Pd-TAPP displayed strong phosphorescence in SDS media. As shown in Fig. 2, the maximum excitation and emission peaks lied at 420 and 708 nm, respectively. This result indicated that SDS micelles provide a protecting microenvironment for the RTP emission. The average occupation number of a micelle by a solute obeys Poisson statistics. When the ratio of the concentration of solute versus the concentration of micelle is less than 5, under the conditions of Fig. 2, 99% of the micelles are occupied by no more than one Pd-TAPP complex molecule [36]. This means that the micellar aggregates compartmentalize and separate the phosphorescent molecules from each other and from potential quencher molecules as well, thereby stabilizing the excited triplet state. By comparison, no RTP signals were observed in nonionic Brij30 and Brij35 micelles, indicating that the electrostatic binding of the electropositive groups of Pd-

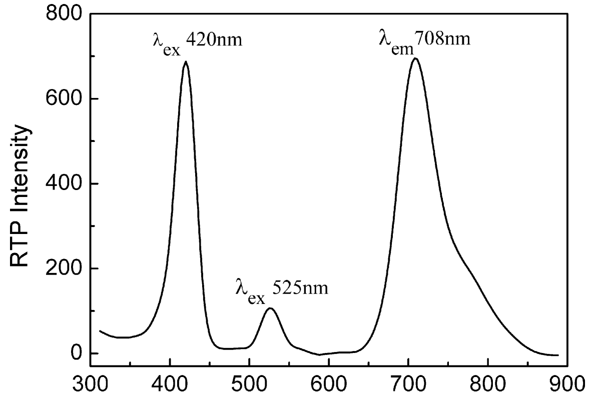


Fig. 2. Phosphorescence spectra of Pd-TAPP. [Pd-TAPP] = 1.5×10^{-6} mol/L; [Na_2SO_3] = 8.0×10^{-3} mol/L; [SDS] = 3.0×10^{-3} mol/L.

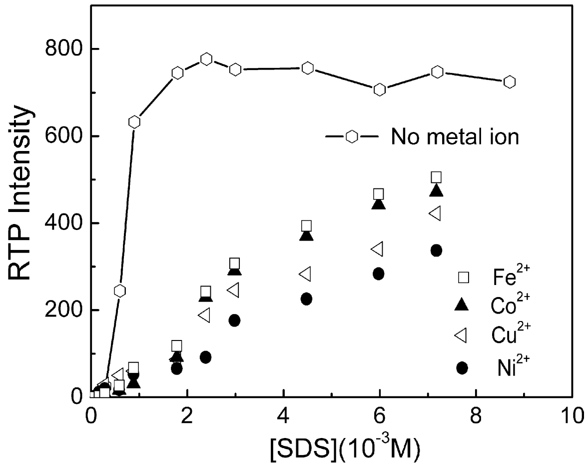


Fig. 3. Effect of SDS concentration on the RTP intensity of Pd-TAPP. [Pd-TAPP] = 1.5×10^{-6} mol/L; [Na_2SO_3] = 8.0×10^{-3} mol/L; [M^{2+}] = 2.0×10^{-5} mol/L.

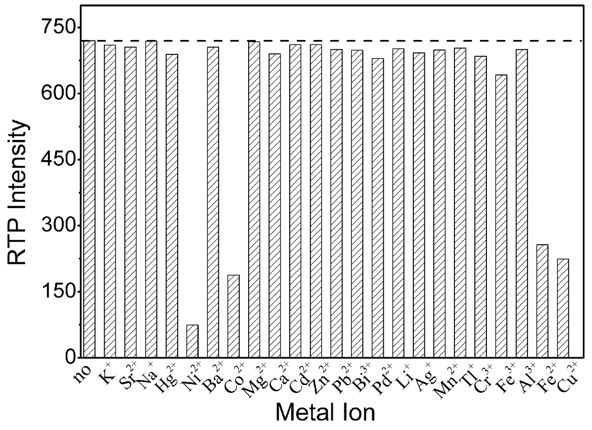


Fig. 5. Effect of various metal ions on the RTP intensity of Pd-TAPP in SDS micellar solution. [Pd-TAPP] = 1.5×10^{-6} mol/L; [Na_2SO_3] = 8.0×10^{-3} mol/L; [SDS] = 3.0×10^{-3} mol/L; Metal ion concentration: 2.0×10^{-5} mol/L. Excitation wavelength: 420 nm; emission wavelength: 708 nm.

TAPP with negatively charged SDS micelles plays an important role in the solubilization and stabilization of Pd-TAPP.

As can be seen in Fig. 3, the RTP intensity of Pd-TAPP sharply increased with the increase of SDS concentration. This change became slow and tended to reach a plateau when the concentration of SDS was more than 1.8 mM, which is much lower than the critical micelle concentration (cmc) value of 8 mM for SDS [37]. It is well known that cmc value depends largely on the surfactant structure, counterion type and concentration, and the presence of other solutes such as organic additives, co-ions or cosurfactants [37–39]. Previous reports have shown that cation porphyrins can change aggregation of anion surfactant SDS and lowered its cmc to ~1.0×10^{-3} mol/L [40,41]. From Fig. 3, it is approximately estimated that the cmc value of SDS was less than 2 mM in the presence of Pd-TAPP. This value is in agreement with the previous reports. When the surfactant concentration increases, it is more difficult to remove the dissolved oxygen which is more soluble in surfactant solutions than in water and could effectively quench the phosphorescence [42]. Taking the RTP intensity and the time required for the deoxygenation of micellar by sodium sulfite into account, a 3 mM concentration of SDS was selected in our experiment.

The effect of pH from 4 to 8.5 on the RTP of Pd-TAPP was examined in B-R buffer solution. As shown in Fig. 4, the RTP signals were not appreciable in either strong acidic or alkaline solutions. It increased slowly to a plateau with the increase of pH from 6 to 7.5. Then, the RTP intensity dropped sharply and disappeared when pH was over 7.9. A final pH of 7.0 was selected for phosphorescence development.

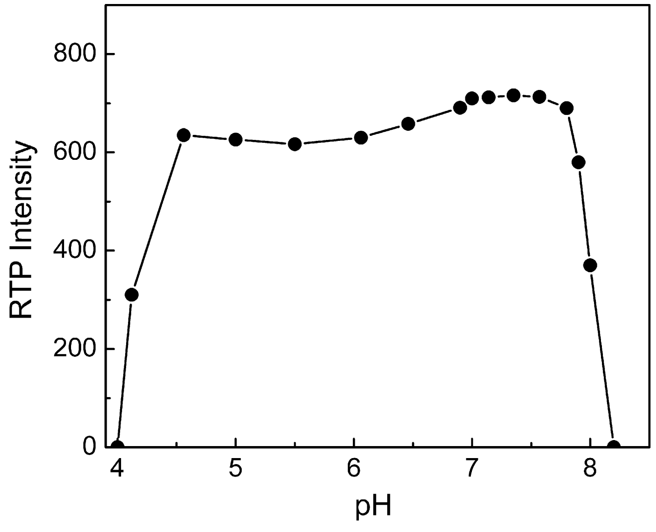


Fig. 4. Effect of pH on the RTP intensity of Pd-TAPP in SDS micellar solutions. [Pd-TAPP] = 1.5×10^{-6} mol/L; [Na_2SO_3] = 8.0×10^{-3} mol/L; [SDS] = 3.0×10^{-3} mol/L.

3.2. Phosphorescence quenching of Pd-TAPP by heavy metal ions

Under optimum conditions, phosphorescence titrations of Pd-TAPP with various metals were performed. Among the metallic ions studied, only Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} quenched the RTP emission of Pd-TAPP efficiently, whereas Hg^{2+}, Ca^{2+}, Ag^{+} and Cr^{3+} were found to have a lesser degree of quenching (Fig. 5). No spectral shifts were observed. In addition, changing the counterions of the quenching metal ions to acetate or nitrate induced no obvious spectral changes, indicating the effect of the anions is negligible. Fig. 6 is a typical example with the addition of Ni^{2+}. It can be seen from Fig. 6 that the luminescence intensity decreased with increasing heavy transition metal (HTM) ions concentrations, which can be used to monitor the concentration of these ions.

A quantitative analysis of the phosphorescence data was made as a function of the metal ion concentration. The quenching data fit the Stern–Volmer relationship with high correlation (Fig. 6), which is particularly convenient for analytical purposes. Table 1 compares the data obtained for several metal ions of interest. The apparent Stern–Volmer constants decreased in the order

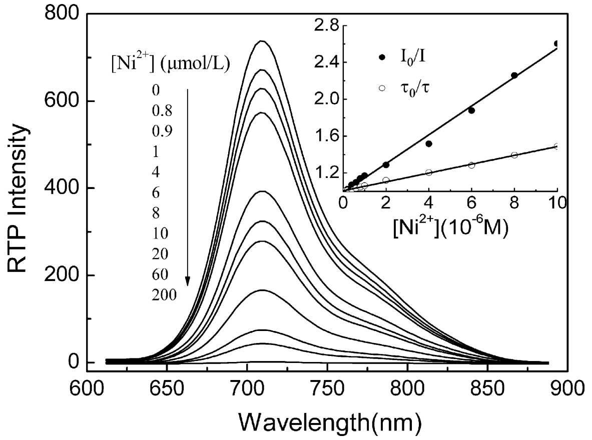


Fig. 6. Phosphorescence spectra change of Pd-TAPP under various concentrations of Ni^{2+}. Inset: the corresponding Stern–Volmer plots.

Table 1
The Stern–Volmer constants for quenching metal ions.

Quenchers	K_{SV} (L mol^{-1})	k_q (L mol^{-1} s^{-1})	r^2	Linear range (mol L^{-1})	Limits of detection (mol L^{-1})
Cu^{2+}	1.0×10^5	2.8×10^8	0.9972	3.0×10^{-7} to 2.1×10^{-5}	2.3×10^{-7}
Co^{2+}	5.6×10^4	1.6×10^8	0.9942	4.1×10^{-7} to 1.0×10^{-5}	3.4×10^{-7}
Ni^{2+}	1.6×10^5	4.4×10^8	0.9942	1.8×10^{-7} to 2.0×10^{-5}	1.2×10^{-7}
Fe^{2+}	1.7×10^4	4.8×10^7	0.9961	2.5×10^{-6} to 1.0×10^{-5}	2.1×10^{-6}
Hg^{2+}	6.1×10	1.7×10^5	0.9971	1.2×10^{-4} to 1.2×10^{-3}	1.0×10^{-4}
Ca^{2+}	1.3×10	3.7×10^4	0.9956	4.3×10^{-4} to 2.8×10^{-3}	3.7×10^{-4}
Ag^{+}	5.5×10	1.5×10^5	0.9928	2.1×10^{-4} to 2.2×10^{-3}	1.5×10^{-4}
Cr^{3+}	7.1×10	2.0×10^5	0.9950	1.8×10^{-4} to 2.0×10^{-3}	1.3×10^{-4}

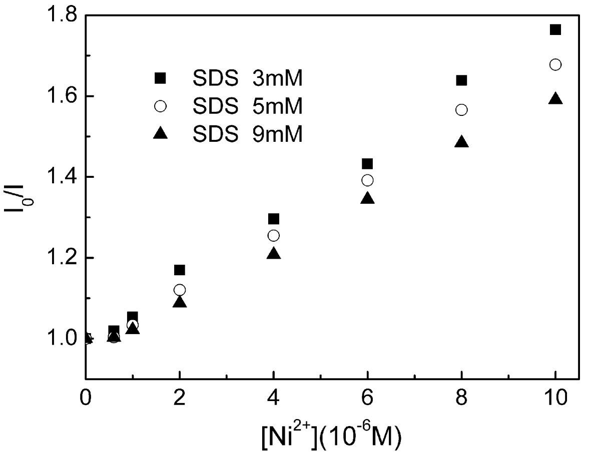
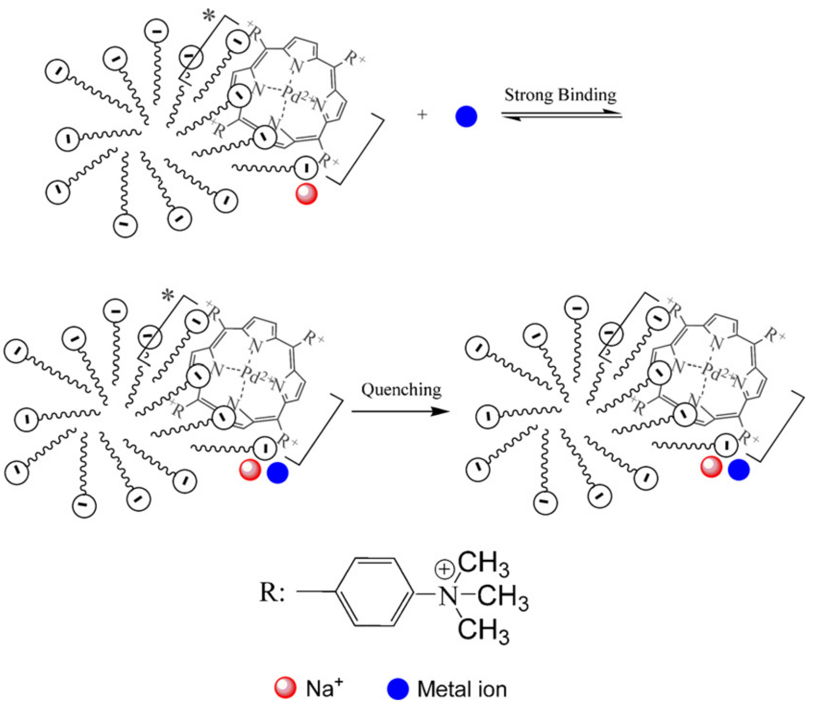


Fig. 7. Effect of SDS concentration on the RTP intensity of Pd-TAPP in the presence of coexisting metal ions (Ni^{2+}). [Pd-TAPP] = 1.5×10^{-6} mol/L; [Na_2SO_3] = 8.0×10^{-3} mol/L.

$Ni^{2+} > Cu^{2+} > Co^{2+} > Fe^{2+} > > Cr^{3+} > Hg^{2+} > Ag^{+} > Ca^{2+}$, directly reflecting the relative sensitivity of the method for these ions. It is obvious that Hg^{2+}, Ca^{2+}, Ag^{+} and Cr^{3+} showed substantially lower quenching rates, their Stern–Volmer constants being 2–4 order of magnitude lower than that of Ni^{2+}, Cu^{2+}, Co^{2+} and Fe^{2+}. Therefore, the interference effect of these four ions on the detection of Ni^{2+}, Cu^{2+}, Co^{2+} and Fe^{2+} was negligible over the concentration range studied. Good linear relationships ($r^2 > 0.9942$) were observed up to concentrations of at least 1.0×10^{-5} mol/L for Ni^{2+}, Cu^{2+}, Co^{2+} and Fe^{2+}. The standard deviation of five replicate measurements at 3.0×10^{-6} mol/L of four chosen HTM ions were between 0.86% and 1.2%. The detection limits of 2.3×10^{-7}, 3.4×10^{-7}, 1.2×10^{-7} and 2.1×10^{-6} mol/L were achieved for Cu^{2+}, Co^{2+}, Ni^{2+} and Fe^{2+}, respectively. These detection limits are comparable to or lower than those previously reported method [4,32,43–46]. Accordingly, the method proposed here should be acceptable as a simple and fast screening method for these metal ions, although it is not a specific one.

The experimental results clearly show that the degree of quenching by the four metal ions (Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}) all decreased with the increase of SDS concentration (Fig. 3). Fig. 7 shows typical Stern–Volmer plots obtained for the quenching of Pd-TAPP phosphorescence upon the addition of Ni^{2+}. As can be seen from Fig. 7, the quenching efficiency decreased with increasing SDS concentration, which means that the sensitivity of the method decreases as the concentration of SDS increases. Due to the ability of the metal ions to replace sodium ions from the Stern layer of the micelles, a close proximity of metal ions and phosphorophore was obtained. Increasing SDS concentration would result in an increase in the volume of the micellar phase and a decrease in the local concentration of the heavy metal ion at the micellar surface. Thus, the binding effi-



Scheme 1. Schematic representation showing the quenching of RTP of Pd-TAPP bound to negatively charged SDS micelles by heavy metals exchanged with sodium counterions.

cacy of quenching metal ions on the SDS–Pd-TAPP complex plays an important role in the efficiency of RTP quenching.

3.3. *Possible quenching mechanism*

The linear Stern–Volmer plots of the quenching data obtained above are indicative of the presence of either purely static or dynamic quenching. The absorption spectrum of Pd-TAPP showed no change upon addition of the heavy metal ions, indicating the absence of ground state complex formation between Pd-TAPP and the metal quenchers. The phosphorescence lifetime of Pd-TAPP was found to significantly decrease with increasing of the heavy metal ions. The RTP lifetime values of Pd-TAPP as a function of the four metal ions concentration have been analyzed according to the equation, $\tau_0/\tau = 1 + k_q\tau_0[Q]$, where τ_0 and τ represent the lifetimes without and with quenchers, k_q is the quenching rate constant, and $[Q]$ is the concentration of quenchers. All the quenching process obeyed a single exponential decay. In the case of dynamic quenching, lifetime changes with quencher concentration, whereas static quenching would not affect the lifetime. Therefore, the linear relationship between τ_0/τ and the concentration of metal ion shown in Fig. 6 reflects the dynamic process. The τ_0 is 0.366 ± 0.011 ms and the k_q values obtained from the plot of τ_0/τ versus $[Q]$ are listed in Table 1.

Common dynamic quenching mechanisms include Förster energy transfer, electron transfer, or charge transfer, etc. Lacking significant overlap between the RTP emission of Pd-TAPP and absorbance of quenchers, the possibility of energy transfer mechanism can be excluded. In combination with the previously proposed quenching mechanism [47–51], the quenching of luminescence of Pd-TAPP by paramagnetic Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} could be attributed to ion binding to the negatively charged SDS micelles via exchange of heavy metals and Na^+ or hydronium ions at the micellar surface, followed by an electron exchange or electron transfer process between these metal ions and Pd-TAPP located near the headgroup of the micelle (Scheme 1). Another possibility is that the energy difference between the lowest triplet and singlet states of the phosphorescent complex could be increased by the inhomogeneous magnetic field of these paramagnetic metal ions, which may lead to a lower transition probability such that the long-lived triplet states are more easily quenched [36]. Additional research is still needed to determine the exact mechanism of quenching.

4. Conclusions

In summary, the effect of a variety of metal ions on the room temperature phosphorescence of Pd-TAPP was investigated in anionic SDS micelle solution. Among all the metallic ions studied, only Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} effectively quenched the RTP emission of Pd-TAPP, demonstrating its capability to detect these ions with wide linear rang, low detection limits and good precision. The proposed method could be potentially used for rapid screening of these metal ions in water samples.

Acknowledgements

We thank the Natural Science Foundation of Shanxi Province (No. 2008011015-1) and the project sponsored by Shanxi Province for the Returned Overseas Chinese Scholars (2007) for financial support.

References

[1] A. Rahmalan, M.Z. Abdullah, M.M. Sanagi, M. Rashid, Determination of heavy metals in air particulate matter by ion chromatography, J. Chromatogr. A 739 (1996) 233–239.

[2] R.H. Yang, K.A. Li, K.M. Wang, F.L. Zhao, N. Li, F. Liu, Porphyrin assembly on β-cyclodextrin for selective sensing and detection of a zinc ion based on the dual emission fluorescence ratio, Anal. Chem. 75 (2003) 612–621.

[3] G.E. Tumambac, C.M. Rosencrance, C. Wolf, Selective metal ion recognition using a fluorescent 1,8-diquinolylnaphthalene-derived sensor in aqueous solution, Tetrahedron 60 (2004) 11293–11297.

[4] R.H. Yang, Y. Zhang, K.A. Li, F. Liu, W.H. Chan, Fluorescent ratioable recognition of Cu^{2+} in water using a pyrene-attached macrocycle/γ-cyclodextrin complex, Anal. Chim. Acta 525 (2004) 97–103.

[5] J. Ishikawa, H. Sakamoto, S. Nakao, H. Wada, Silver ion selective fluoroionophores based on anthracene-linked polythiazaalkane or polythiaalkane derivatives, J. Org. Chem. 64 (1999) 1913–1921.

[6] A.M. Josceanu, P. Moore, S.C. Rawle, P. Sheldon, S.M. Smith, 1,4,8,11-Tetrakis {(2,2′-bipyridyl-5′-ylmethyl)-bis (2,2′-bipyridyl) ruthenium (II)}-1,4,8,11-tetraazacyclotetradecane (L^1), a macrocyclic pH and transition metal ion fluorescence sensor. Equilibrium, and stopped-flow kinetic, fluorimetric studies of the reactions of L^1 with nickel(II) and copper(II) ions in aqueous solution at neutral pH, Inorg. Chim. Acta 240 (1995) 159–168.

[7] R.B. Thompson, Z.F. Ge, M. Patchan, C.C. Huang, C.A. Fierke, Fiber optic biosensor for Co(II) and Cu(II) based on fluorescence energy transfer with an enzyme transducer, Biosens. Bioelectron. 11 (1996) 557–564.

[8] A. Singh, Q.W. Yao, L. Tong, W.C. Still, D. Sames, Combinatorial approach to the development of fluorescent sensors for nanomolar aqueous copper, Tetrahedron Lett. 41 (2000) 9601–9605.

[9] D. Delmarre, R. Méallet, C. Bied-Charreton, R.B. Pansu, Heavy metal ions detection in solution, in sol-gel and with grafted porphyrin monolayers, J. Photochem. Photobiol. A: Chemistry 124 (1999) 23–28.

[10] I. Sánchez-Barragán, J.M. Costa-Fernández, M. Valledor, J.C. Campo, A. Sanz-Medel, Room-temperature phosphorescence (RTP) for optical sensing, Trends Anal. Chem. 25 (2006) 958–967.

[11] J. Kuijt, F. Ariese, U.A.Th. Brinkman, C. Gooijer, Room temperature phosphorescence in the liquid state as a tool in analytical chemistry, Anal. Chim. Acta 488 (2003) 135–171.

[12] A.S. Carretero, C.C. Blanco, M.I. Ramírez García, B.C. Díaz, A.F. Gutiérrez, Simple and rapid determination of the drug naproxen in pharmaceutical preparations by heavy atom-induced room temperature phosphorescence, Talanta 50 (1999) 401–407.

[13] L.F. Capitán-Vallvey, M.D. Fernández Ramos, R. Avidad, M.K.A. Deheidel, Determination of the pesticide morestan by means of a single-use phosphorimetric sensor, Anal. Chim. Acta 440 (2001) 131–141.

[14] W.J. Jin, C.S. Liu, Luminescence rule of polycyclic aromatic hydrocarbons in micelle-stabilized room-temperature phosphorescence, Anal. Chem. 65 (1993) 863–865.

[15] J.A. Murillo Pulgarin, A. Alañón Molina, M.T. Alañón Pardo, Determination of nafcillin by room temperature phosphorescence, Anal. Chim. Acta 423 (2000) 85–93.

[16] H. Linschitz, L. Pekkarinen, The quenching of triplet states of anthracene and porphyrins by heavy metal ions, J. Am. Chem. Soc. 82 (1960) 2411–2416.

[17] C.O. Hill, S.H. Lin, Quenching of phosphorescence by paramagnetic molecules in rigid media. II. Quenching of perdeuderated naphthalene by Co^{++}, Cr^{3+}, Cu^{++}, and Ni^{++}, J. Chem. Phys. 53 (1970) 608–612.

[18] H.F. Wasgestian, R. Ballardini, G. Varani, L. Moggi, V. Balzani, Quenching of the tris (ethylenediamine) chromium (III) phosphorescence by some transition metal ions in aqueous solutions, J. Phys. Chem. 77 (1973) 2614–2617.

[19] Y. Wang, J.J. Wu, Y.F. Wang, L.P. Qin, W.J. Jin, Selective sensing of Cu(II) at ng ml^{-1} level based on phosphorescence quenching of 1-bromo-2-methylnaphthalene sandwiched in sodium deoxycholate dimer, Chem. Commun. 5 (2005) 1090–1091.

[20] J.M. Liu, A.H. Wu, H.H. Xu, Q.H. Wang, L.D. Li, G.H. Zhu, Determination of trace mercury by solid substrate room temperature phosphorescence quenching method based on lead carboxymethyl cellulose ($Pb(CMC)_2$) particles containing luminescent salicyl fluorones molecules, Talanta 65 (2005) 501–504.

[21] M.L. Ho, Y.M. Cheng, L.C. Wu, P.T. Chou, G.H. Lee, F.C. Hsu, Y. Chi, Probing Pb^{2+} cation via the iridium based phosphorescent dye, Polyhedron 26 (2007) 4886–4892.

[22] K. Kalyanasundaram, F. Grieser, J.K. Thomas, Room temperature phosphorescence of aromatic hydrocarbons in aqueous micellar solutions, Chem. Phys. Lett. 51 (1977) 501–505.

[23] M.E. Diaz Garcia, A. Sanz-Medel, Facile chemical deoxygenation of micellar solutions for room temperature phosphorescence, Anal. Chem. 58 (1986) 1436–1440.

[24] W.J. Jin, C.S. Liu, Study on five polycyclic aromatic hydrocarbons by chemical deoxygenation micelle-stabilized room temperature phosphorimetry, Microchem. J. 48 (1993) 94–103.

[25] Y.S. Wei, W.J. Jin, C.S. Liu, H.P. Zhou, H.B. Tong, N.C. Zhang, Study on micelle stabilized room temperature phosphorescence behaviour of pyrene by laser induced time resolved technique, Spectrochim. Acta Part A 53 (1997) 1405–1410.

[26] J.A. Murillo Pulgarín, A. Alañón Molina, P. Fernández López, M.T. Alañón Pardo, Fast determination of propranolol in urine and pharmaceutical preparations by stopped-flow and micellar-stabilized room-temperature phosphorescence: validation of the method, Anal. Biochem. 312 (2003) 167–174.

[27] J.A. Murillo Pulgarín, A. Alañón Molina, M.T. Alañón Pardo, Simplex optimization of the variables affecting the micelle-stabilized room temperature phosphorescence of 6-methoxy-2-naphthylacetic acid and its kinetic determination in human urine, Anal. Biochem. 339 (2005) 157–164.

[28] L.D. Li, W.G. Huang, Room temperature phosphorescence properties of dansyl chloride and its derivatives, Anal. Chim. Acta 312 (1995) 345–350.

[29] G.R. Li, J.J. Wu, W.J. Jin, J.W. Xie, Anti-oxygen-quenching room temperature phosphorescence stabilized by deoxycholate aggregate, Talanta 60 (2003) 555–562.

[30] M. Roza-Fernández, M.J. Valencia-González, M.E. Díaz-García, Room-temperature phosphorescent palladium-porphine probe for DNA determination, Anal. Chem. 69 (1997) 2406–2410.

[31] A.M. Brun, A. Harriman, Energy- and electron-transfer processes involving palladium porphyrins bound to DNA, J. Am. Chem. Soc. 116 (1994) 10383–10393.

[32] L.V. Vargas, J. Sand, Tiago, A.S. Brandão, F.H. Fiedler, H.D. Quina, F. Nome, Determination of environmentally important metal ions by fluorescence quenching in anionic micellar solution, Analyst 130 (2005) 242–246.

[33] F.H. Quina, E.A. Lissi, Photoprocesses in microaggregates, Acc. Chem. Res. 37 (2004) 703–710.

[34] I.R. Could, P.L. Kuo, N.J. Turro, Quenching of pyrene fluorescence by cesium ions in micellar systems. Protection by surface-active crown ethers, J. Phys. Chem. 89 (1985) 3030–3034.

[35] Y. Amao, I. Okura, An oxygen sensing system based on the phosphorescence quenching of metalloporphyrin thin film on alumina plates, Analyst 125 (2000) 1601–1604.

[36] M.E.D. Garcia, M.R. Fernfindez de la Campa, W.L. Hinze, A. Sanz-Medel, Room temperature phosphorescence decay of metal chelates in micellar media, Mikrochim. Acta 3 (1988) 269–282.

[37] D. Myers, Surfactant Science and Technology, second ed., VCH Publishers, New York, 1992.

[38] B.C. Paul, S.S. Islam, K. Ismail, Effect of acetate and propionate co-ions on the micellization of sodium dodecyl sulfate in water, J. Phys. Chem. B 102 (1998) 7807–7812.

[39] A. Chatterjee, S.P. Moulik, S.K. Sanyal, B.K. Mishra, P.M. Puri, Thermodynamics of micelle formation of ionic surfactants: a critical assessment for sodium dodecyl sulfate, cetyl pyridinium chloride and dioctyl sulfosuccinate (Na salt) by microcalorimetric, conductometric, and tensiometric measurements, J. Phys. Chem. B 105 (2001) 12823–12831.

[40] Y.T. Wang, W.J. Jin, H-aggregation of cationic palladium-porphyrin as a function of anionic surfactant studied using phosphorescence, absorption and RLS spectra, Spectrochim. Acta Part A 70 (2008) 871–877.

[41] R.H. Zhu, W.J. Jin, Principles and Applications of Phosphorescence Spectroscopy, Science Press, Beijing, 2006.

[42] I.B.C. Matheson, R. Massoudi, Photophysical and photosensitized generation of singlet molecular oxygen ($^1\delta_g$) in micellar solutions at elevated pressures. Measurement of singlet molecular oxygen solvent to micelle transfer rates via both molecular diffusion and energy transfer, J. Am. Chem. Soc. 102 (1980) 1942–1948.

[43] H.S. Kim, H.S. Choi, Spectrofluorimetric determination of copper(II) by its static quenching effect on the fluorescence of 4,5-dihydroxy-1,3-benzenedisulfonic acid, Talanta 55 (2001) 163–169.

[44] D.S.K. Peker, O. Turkoglu, M. Soylak, Dysprosium(III) hydroxide coprecipitation system for the separation and preconcentration of heavy metal contents of table salts and natural waters, J. Hazar. Mater. 143 (2007) 555–560.

[45] F.V. Bright, G.E. Poirier, G.M. Hieftje, A new ion sensor based on fiber optics, Talanta 35 (1988) 113–118.

[46] S.A. Wallington, T. Labayen, A. Poppe, N.A.J.M. Sommerdijk, J.D. Wright, Sol–gel entrapped materials for optical sensing of solvents and metal ions, Sens. Actuators B 38–39 (1997) 48–52.

[47] G.J. Hoijtink, The influence of paramagnetic molecules on singlet–triplet transitions, Mol. Phys. 3 (1960) 67–70.

[48] S.E. Peterson-Kennedy, J.L. McGourty, J.A. Kalweit, B.M. Hoffman, Temperature dependence of and ligation effects on long-range electron transfer in complementary [Zn,Fe^{III}]hemoglobin hybrids, J. Am. Chem. Soc. 108 (1986) 1739–1746.

[49] H. Koloczek, T. Horie, T. Yonetani, H. Anni, G. Maniara, J.M. Vanderkooi, Interaction between cytochrome *c* and cytochrome *c* peroxidase: excited-state reactions of zinc- and tin-substituted derivatives, Biochemistry 26 (1987) 3142–3148.

[50] F.K. Klemens, D.R. McMillin, Room-temperature phosphorescence from azurin derivatives. Phosphorescence quenching in oxidized native azurin, Photochem. Photobiol. 55 (1992) 671–676.

[51] M.D.P. De Costa, W.A.P.A. Jayasinghe, Detailed studies on complexation behaviour and mechanism of fluorescence quenching of naphthalene linked hydroxamic acid with transition metal ions by UV–visible and fluorescence spectra, J. Photochem. Photobiol. A: Chemistry 162 (2004) 591–598.