Available online at www.sciencedirect.com

ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry 188 (2007) 351–357

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

A novel pyrene-based film: Preparation, optical properties and sensitive detection of organic copper(II) salts

Jing Hu, Fengting Lü, Liping Ding, Shujuan Zhang, Yu Fang*

Key Laboratory of Macromolecular Science of Shaanxi Province, School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, PR China

Received 2 October 2006; received in revised form 19 December 2006; accepted 19 December 2006

Available online 27 December 2006

Abstract

A novel fluorescent sensing film for organic copper(II) salts was developed by covalently attaching pyrene moieties onto glass slide surfaces via a long flexible spacer. Fluorescence measurements demonstrated that the emission of the film was efficiently quenched by organic copper(II) salts, including copper acetate, cupric tartrate and cupric citrate. Presence of any of other divalent metal acetates, such as $Ni(Ac)_2$, $Co(Ac)_2$, $Pb(Ac)_2$, $Cd(Ac)_2$ and $Zn(Ac)_2$, has little effect upon the emission of the film. The quenching efficiency of $Cu(Ac)_2$, however, was reduced moderately in the presence of these similar divalent metal acetates. The interference of these salts to the sensing of organic copper(II) salts was attributed to the competition of the complexation sites in the spacer, which may be one of the reasons that enhance the enrichment of Cu(II) into the spacer layer. The detection limit of the film to $Cu(Ac)_2$ is 0.26 μM, which is much lower than those reported earlier. The quenching by copper acetate of the emission of the film is static in nature due to complexation of the spacers to the metal ions. Furthermore, the sensing process is fully reversible.

Keywords: Pyrene; Fluorescence; Film sensor; Organic copper(II) salts; Chelating effect

1. Introduction

Considerable efforts have been devoted to develop chemosensors for Cu(II) over the last few decades [1–9]. This intense research interest is strongly related to the analytical significance of trace Cu(II) found in environmental and biological processes [1]. As it is well known, the species is a paramagnetic ion with an empty d shell and can strongly quench the emission of a fluorophore via a photoinduced metal-to-fluorophore electron or energy transfer mechanism [2–4]. In addition, among the relevant transition metal ions, Cu(II) has a particularly high thermodynamic affinity for ligands with “N” or “O” as chelating element, and furthermore the chelating is a fast process [5]. On the basis of fluorescence quenching and chelating effect, a number of fluorescent sensors for Cu(II) has been prepared and reported [1,4,5]. Most of them, however, are molecular sensors, and used in aqueous or polar organic solvents [6–10]. Clearly, these sensors can be used only once, and use of them will contaminate sample solutions. Chemical immobilization of the molecular sensors on suitable solid substrate surfaces might solve the problems mentioned above [11].

Self-assembled monolayers (SAMs) on glass are widely used as a platform to sequentially deposit fluorophores or small molecules for sensing studies. Furthermore, SAMs provides a convenient way to produce surfaces with specific chemical functionalities that allow the precise tuning of surface properties [12]. The advantages of SAMs for surface confined sensing are fast response, ease and reproducibility of synthesis. A number of research groups led by Reinhoudt and co-workers [13–15], Fox [16] and Blanchard and co-workers [17,18] have focused on preparing film sensors for several years due to the advantages of this methodology.

During the last few years, our group has been engaging in developing fluorophore functionalized SAM films, and investigating their photophysical properties and sensing applications. It was found that these films are sensitive to various analytes including sodium nitrite, nitromethane, dicarboxylic acids and nitroaromatics, etc. [19–24]. Recently, we reported some selective film sensors for organic copper(II) salts based on the screening effect of the long, flexible spacer [25–27]. Unfortunately, the

---

* Corresponding author. Tel.: +86 29 85310081; fax: +86 29 85310079.
E-mail address: yfang@snnu.edu.cn (Y. Fang).

1010-6030/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2006.12.035

sensitivity of these films is low. In fact, a common goal in sensory materials is increased sensitivity, which has led to great interest in fluorescence-based chemosensors [28]. According to the works conducted in our laboratory, it was known that the sensing performance of the films with similar structures depends strongly on the structures of the spacers connecting the substrate and the fluorophores. For example, for selective sensing of dicarboxylic acids, imino units, which can form hydrogen bonds with the carboxyhydroxy groups of the acids, were intentionally introduced into the spacers. It was found that the analytes, dicarboxylic acids, could insert into the space between neighboring spacers, altered the distribution of the sensing molecules on the substrate surface, and resulted in changes in the profile of the fluorescence spectra of the films. The sensitivity and selectivity of the film with spacer containing diethylenetriamine to dicarboxylic acids were greatly improved when compared with the films with spacers containing ethylenediamine [23], or 1,3-diaminopropane [21]. Inspired by these results, a new fluorescent sensing film for organic copper(II) salts was designed and fabricated. Diethylenetriamine was introduced into the spacer of this film in order to increase the association constant of the binding event [29]. As expected, the sensitivity and selectivity of the new film to organic copper(II) salts were enhanced greatly if compared with the one containing 1,3-diaminopropane units in its spacer [25]. The details are reported in this paper.

2. Experimental

2.1. Chemicals

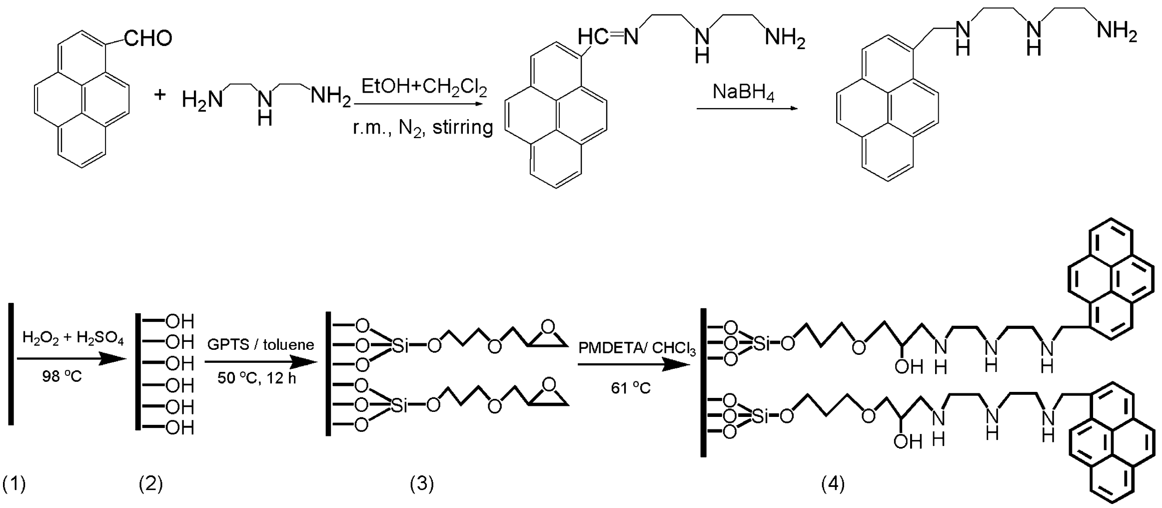
Pyrene carboxyldehyde (Alfa, 99%), sodium borohydride (München, 96.0%), diethylenetriamine (DETA, Acros, 98.5%) and 3-glycidoxypropyltrimethoxy silthoxysilane (GPTS, Acros, 97%) were used directly without further purification. *N*-(2-Aminoethyl)-*N*′-pyrene-1-ylmethylethane-1,2-diamine (AEPMEDA) was synthesized according to a literature method [30]. ^{1}H NMR (CDCl$_3$-d): δ (ppm) 8.0–8.3 (9H), 4.4–4.5 (2H), 2.6–2.9 (8H). All the solvents were of analytical grade and used without further purification. Water used throughout was de-ionized and then double distilled. The solutions of metal ions were prepared by dissolving $C_6H_4Cu_2O_7{\cdot}2.5H_2O$, $C_4H_4CuO_6{\cdot}3H_2O$, $Cu(Ac)_2{\cdot}H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $CuCl_2$, $CuSO_4$, $Pb(Ac)_2{\cdot}3H_2O$, $Zn(Ac)_2{\cdot}2H_2O$, $Cd(Ac)_2$, $Ni(Ac)_2{\cdot}4H_2O$ and $Co(Ac)_2{\cdot}3H_2O$, respectively, into double-distilled water. Other chemicals, including disodium ethylenediamine tetraacetate (EDTA), sodium acetate and trifluoroacetic acid are of analytic grade.

2.2. Instrumentation

All fluorescence measurements were conducted on a time-correlated single photon counting fluorescence spectrometer (Edinburgh Instruments FLS 920) which is equipped with a 450-W Xenon arc lamp for steady-state fluorescence measurement. A front face method was adopted throughout the measurements. The contact angles with water for the glass slide surfaces were measured by using a home-made JY-82 contact angle goniometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a SCA PHI5400 (Perkin-Elmer) photoelectron spectrometer using a monochromatic Mg Kα X-ray source. The ^{1}H NMR spectra of the samples were obtained on a Bruker AV 300 NMR spectrometer.

2.3. Fabrication of pyrene-functionalized film

Glass slides were activated by immersion in boiling “piranha solution” (98%H_2SO_4/30%H_2O_2, 7/3, v/v; 98 °C, 1 h) (*caution*: piranha is a very strong oxidant and reacts violently with many organic materials). After that, they were rinsed thoroughly with double-distilled water and air dried immediately prior to performing the formation of the monolayer. Then the freshly cleaned substrates were exposed to a warm (50 °C) toluene solution, containing GPTS (0.6%, v/v) and a trace of water (0.12%, v/v), for 24 h to give the desired epoxy-terminated SAM. After the treatment, they were rinsed with toluene to remove excess silane and avoid polymerization. The attachment of the fluorophores to the epoxy-terminated SAM was achieved by



Scheme 1. Synthesis of *N*-(2-aminoethyl)-*N*′-pyrene-1-ylmethylethane-1,2-diamine and chemical coupling of pyrene on the glass surface.

refluxing the slides in tricholoromethane solution of AEPMEDA for 10 h. Finally, the pyrene-functionalized slides were washed with plenty of fresh $CHCl_3$ and then rinsed with ethanol and water successively. The whole coupling process is schematically shown in Scheme 1.

3. Results and discussion

3.1. Characterization of the films

Contact angle measurement provides a convenient way to characterize surface polarity and then reflects surface functionality [31]. Table 1 shows the advancing contact angle data of the surface and water at 18 °C. With reference to the table, it is revealed that the contact angle decreased significantly from 20.9° to 11.5° after treatment with the "piranha solution". Further treatment of the surface with GPTS resulted in a sharp increase in the data (from 11.5° to 53.6°), indicating the surface becoming less hydrophilic. The angle slightly increased further after treatment with AEPMEDA. These results are consistent with the expectation from the chemical composition of the surface, of which the composition changed from a less hydroxyl group, more hydroxyl group, epoxy group and pyrene along with the treatment (c.f. Scheme 1).

XPS technique provides detailed information on the elemental composition of surface layers in different coupling steps (c.f. Fig. 1). As for surface (2), the spectrum is dominated by the peaks of O 1s (531.2 eV), Si 2s (153.4 eV) and Si 2p (103.3 eV) due to the silicon oxide substrate. The intensity of peak C 1s (284.6 eV) of surface (3) dramatically increases and is much larger than that shown in surface (2), which apparently comes from the introduction of organosilanes onto the surface. In addition to the further increase in the intensity of peak of C 1s, the spectrum of surface (4) exhibits peaks of N 1s (400.8 eV) after modification with AEPMEDA. Consequently, these results further confirmed that the fluorophores and the ion-binding sites were successfully attached on the glass slide surface.

Loading density of fluorophores on the glass surface was performed on FLS 920 according to literature [31]. It was determined that the density of the fluorophore is 0.85 pyrene moieties per $100\ \text{Å}^2$, which is about 14.7% of the theoretical value [25].

Table 1
Advancing contact angles (θ) of various glass plate surfaces and water

Glass plates	Advancing contact angles (°)
(1)	20.9° ± 1.3°
(2)	11.5° ± 1.2°
(3)	53.8° ± 1.6°
(4)	55.5° ± 1.8°

(1) The original clean glass plate, (2) the activated glass plate with hydroxyl surface, (3) the glass plate with epoxy surface and (4) the plate with pyrene surface.

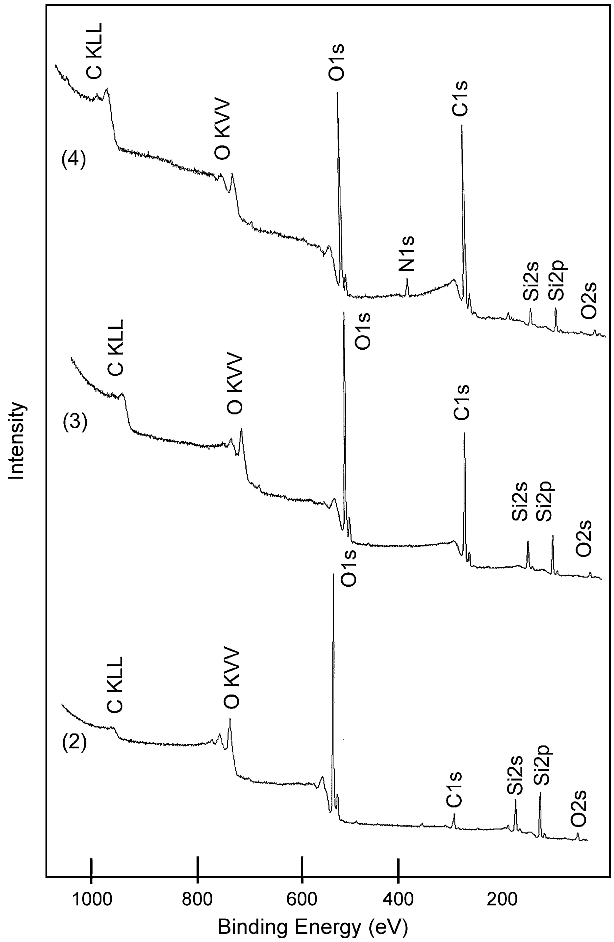


Fig. 1. X-ray photoelectron spectra of the glass plates of various surface structures.

The excitation and emission spectra of the film (c.f. Fig. 2) were recorded at different analysis wavelength or different excitation wavelength. According to Kasha's rule, the sensing molecules are quite homogeneously distributed on the substrate surfaces because the profiles of the two spectra are analysis wavelength or excitation wavelength independent. With reference to the figure reveals that the emission spectra are dominated by monomer emission. This can be explained by low loading density of the sensing molecules on the substrate surface which minimizes their chances to associate with each other. And as revealed before for a long and relatively hydrophobic spacer, it

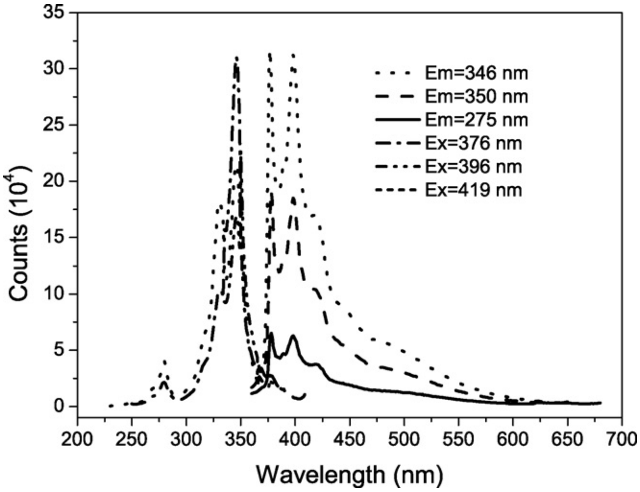


Fig. 2. Excitation and emission spectra of the sensing film in aqueous medium.

may adopt coiled conformation and wrap the sensing element within it when immersed in a polar solvent, and thereby prevents the formation of excimer, or even distorted excimer.

The stability of pyrene on the slide surface was examined by monitoring the fluorescence emission of the system and the medium, in which the slide had been immersed, as functions of time at 376 nm with 346 nm as the excitation wavelength. It was demonstrated that the emission intensity of the slide was hardly changed with time, and the final emission intensity of the medium was less than 1% of that of the slide after 2 days immersing of the film in water, indicating that the sensing molecules had been successfully coupled on the substrate surface.

3.2. Selective response to organic copper(II) salts

Fig. 3 depicts the plots of I_0/I against the concentrations of various copper(II) salts, where I_0 and I stand for the fluorescence intensity of the film analyzed at 376 nm in the absence and presence of the copper(II) salts, respectively. Similar to our previous studies [25–27], the present film also showed highest sensitivity towards $Cu(Ac)_2$ among the copper(II) salts tested. The emission intensity decreased dramatically with the addition of $Cu(Ac)_2$. Titration with cupric tartrate and cupric citrate could also induce a significant quenching to the emission of the film even though the quenching efficiencies were less than that observed with $Cu(Ac)_2$. Presence of $Cu(NO_3)_2$, $CuCl_2$ or $CuSO_4$ quenched, however, the fluorescence emission of the film moderately. With reference to the figure, it can be found that with the whole concentration range of the quenchers, the quenching efficiency of $Cu(Ac)_2$ is more than two times greater than those of inorganic copper(II) salts. Considering the fact that Cu(II) is the real quenching species rather than the anions [2–4], the difference may be explained by "counter ion effect", which was schematically shown in Scheme 2.

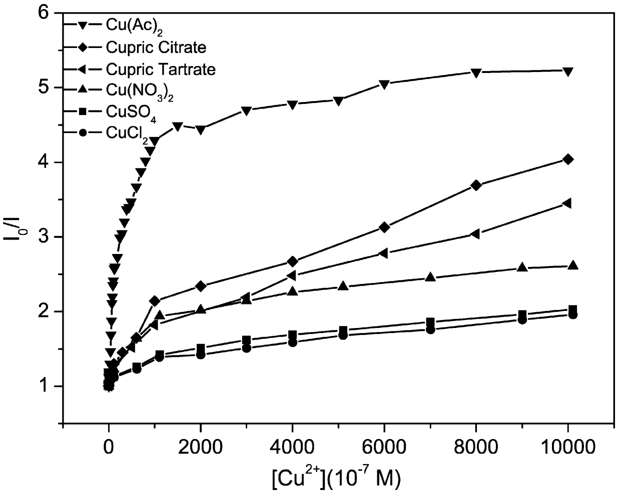
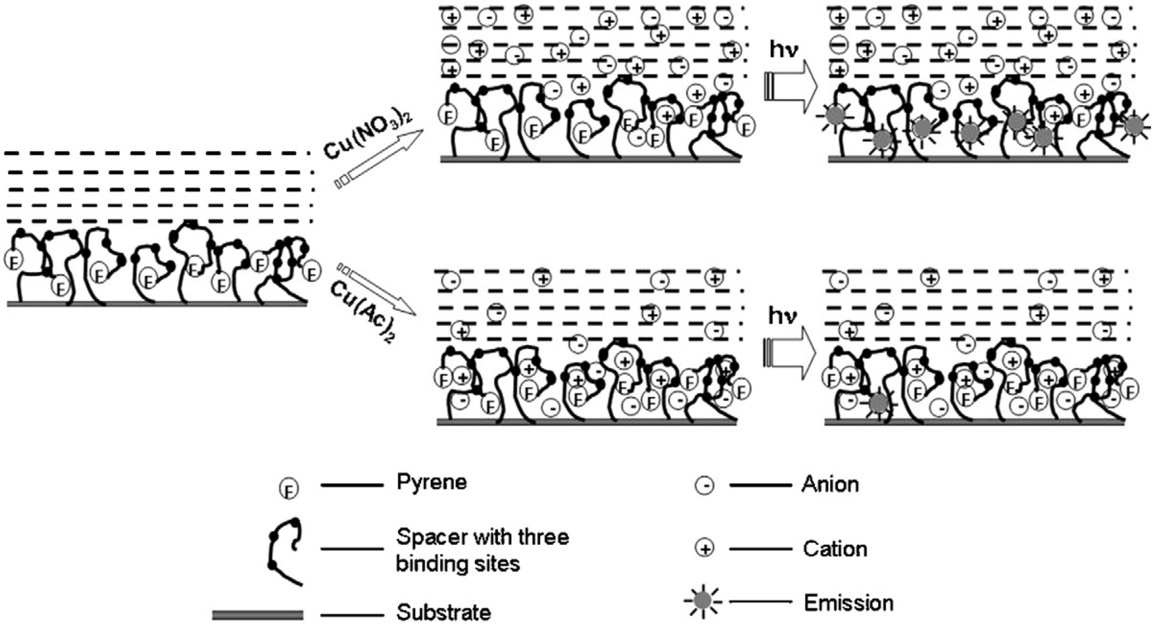


Fig. 3. Quenching effect to the pyrene-functionalized film induced by different copper salts of various concentrations.



Scheme 2. Schematic demonstration of the distribution of pyrene on the glass plate surface.

With reference to the scheme, it can be seen that the spacers are relatively long, flexible and hydrophobic, and it should adopt coiled conformations, and form hydrophobic "domains" if the film was put in an incompatible polar solvent. In this way, the sensing molecule, pyrene, would stay inside the "domain", avoiding contact with quencher, Cu(II), and resulted lower quenching efficiency. For the copper(II) salts with organic counter anions, however, the anions should have more chances to enter the "domain", and bring the quencher, Cu(II), into it due to charge balance. Higher local concentration of Cu(II) must result in greater quenching efficiency. Further reference to the figure, it can be found that the sensitivity of the film towards cupric tartrate and cupric citrate was much lower than that of copper acetate. It can be explained by steric effect and polarity effect. Compared with acetate, citrate and tartrate anions have relatively large sizes which made them enter the "domains" not as easily as acetate. Besides the steric effect, the presence of hydroxy groups enhanced the polarity of the citrate and tartrate which may be also one of the reasons to explain why the quenching efficiencies by cupric citrate and cupric tartrate were less than that of copper acetate.

It is worth well to mention that the emission of the present film is more sensitive to the presence of $Cu(Ac)_2$ than that of the film reported earlier where 1,3-diaminopropane was employed as the subunit in the spacer [25]. The detection limit of the present film to $Cu(Ac)_2$ is 2.6×10^{-7} M, a value two orders lower than that reported before [25]. The great improvement implies other factors, which favor enrichment of the quencher in the spacer layer, might exist. Considering the difference in the structure of the spacer employed in the present film and that in the previous film, it can be found that the diethylenetriamine subunit in the spacer of the present film is an obvious chelating structure for copper(II). Presence of the structure must further enhance the enrichment of the quencher ion in the nearby of the fluorophore, and results in increase in the sensitivity of the film to the copper(II) salts. This is to say that the higher sensitivity of the present film towards organic copper(II) salts was a combined result of "counter ion effect" and chelating effect.

To gain further insights into the effect of counter anions on the sensing behavior of the film for organic copper(II) salts, a titration experiment was conducted in which NaAc was intentionally introduced into a system containing $Cu(NO_3)_2$. The results are shown in Fig. 4. As reported earlier, presence of $Cu(NO_3)_2$ has limited effect upon the emission of the film. Addition of NaAc increased the quenching efficiency remarkably, in support of the statement that the nature of counter anions plays crucial role for the quenching efficiency of copper(II) salts to the emission of the fluorescent film. This statement is further supported by the result from titration of the same system with sodium trifluoroacetate. As expected, trifluoroacetate, a special organic anion which behaves more like an inorganic anion rather than organic anion, shows very limited enhancing effect for the quenching of the system (c.f. Fig. 4).

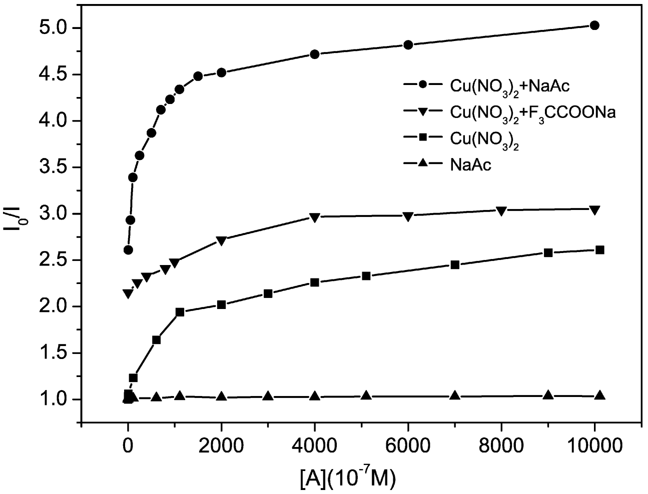


Fig. 4. Effects of organic anions upon the sensing film to $Cu(NO_3)_2$ ($\lambda_{ex}/\lambda_{em}$ = 346/376 nm).

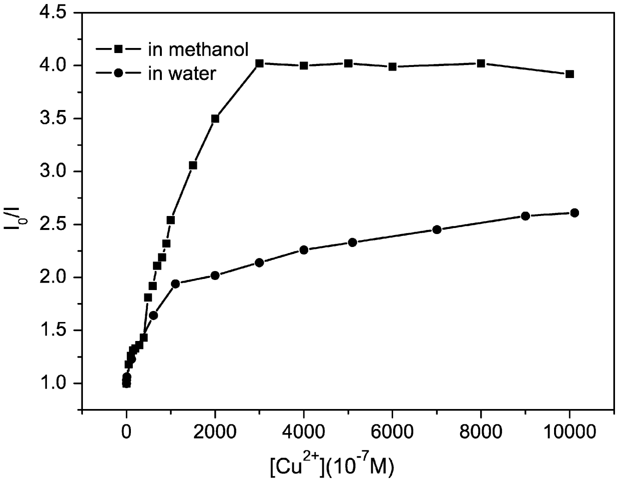


Fig. 5. Plots of I_0/I vs. the concentration of $Cu(NO_3)_2$ in methanol and water ($\lambda_{ex}/\lambda_{em}$ = 346/376 nm).

Fig. 5 shows the solvent effect upon the quenching efficiency of $Cu(NO_3)_2$ to the emission of the film. Inspection of the data shown in the figure indicates that the inorganic copper(II) salt quenches the emission of the film more efficiently in methanol than that in aqueous phase. This result can only be explained by supposing that the spacers connecting the fluorophore moieties and the substrate might have adopted more extended conformations in organic medium, and thereby made the fluorophores have more chances to be quenched by the Cu(II), a strong evidence for the hypothesis that the spacers take different conformations in different solvents.

3.3. Selectivity studies

To test the sensing specificity, the ability to only sense the target metal ion [32], titration experiments with other divalent metal acetates, including $Ni(Ac)_2$, $Zn(Ac)_2$, $Pd(Ac)_2$ and $Co(Ac)_2$ were also conducted (c.f. Fig. 6). It was found that the quenching efficiencies of these metal acetates are much lower than that of $Cu(Ac)_2$. This is not a very surprising result because Cu(II) is a well known efficient fluorescence quencher [2–4]. To investi-

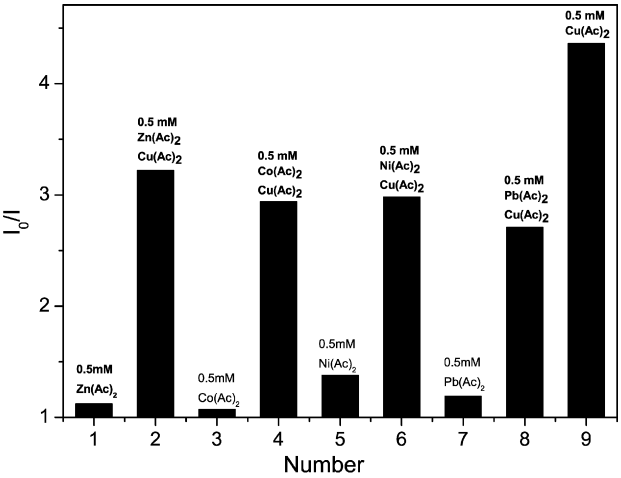


Fig. 6. Interference of other metal acetates to the sensing of copper acetate.

gate the selectivity, which is the ability to sense target metal ion in the presence of interferes [32], 1 mM of $Cu(Ac)_2$ was added into the systems containing 1 mM of one of the tested metal acetates, including $Ni(Ac)_2$, $Zn(Ac)_2$, $Pd(Ac)_2$ and $Co(Ac)_2$, respectively. And the fluorescence intensity was measured in a way as that described before (c.f. Fig. 6). As shown in the figure, presence of the salts except $Ni(Ac)_2$ had little effect upon the emission of the film if compared with that of $Cu(Ac)_2$. For $Ni(Ac)_2$, its quenching efficiency to the film is about one third of that of $Cu(Ac)_2$. Reference to the figure further, it can be seen that presence of any of the interfere salts reduced the quenching efficiency of $Cu(Ac)_2$ significantly. The interfere effect of the salts to the sensing of the film to $Cu(Ac)_2$ can be only attributed to the competition of the chelating sites in the spacer. Clearly, occupation of the sites by other metal ions must reduce the local concentration of Cu(II) near the film, and thereby decreasing the quenching efficiency of the salt. This is a strong evidence to support the statement that chelating effect is crucial for the high quenching efficiency of the copper(II) salt to the emission of the film.

3.4. Comparison of different sensing films

The detection limit of the present film to $Cu(Ac)_2$ is 2.6×10^{-7} M, which is at least 60 times lower than that of the previous film reported earlier [25]. Considering the special structures of the film, the better performance of the present film may be originated from the following factors. Firstly, the long, flexible and hydrophobic spacer may adopt a coiled conformation to form a hydrophobic "micro-domain" if it is compared with the bulk aqueous phase. Pyrene moieties immobilized on the substrate surface might be buried in the domain to avoid contacting the polar solvent, water. No doubt, it is the organic anions rather than the inorganic anions that are more compatible to the domain, and thereby the organic anions have more chance to stay near or inside the "micro-domains", resulting in greater Cu(II) concentration near the domain due to charge balance. This increase must also enhance the quenching efficiency of Cu(II) to the emission of the film. Secondly, spacers containing diethylenetriamine subunit have provided more chelating sites for Cu(II), which can increase the association constant of the binding event. This is why the new film is more sensitive than the previous one in which 1,3-diaminopropane is the main component of the spacers. Thirdly, a sulfonyl structure connecting the spacer and the sensing fluorophore, pyrene, was replaced by a methylene structure, which may make the spacer more hydrophobic and the sensing fluorophore, pyrene having stronger tendency to stay in hydrophobic "micro-domain". It is these factors that make the new film have stronger binding ability to copper(II), consume less quencher molecules and show great sensitivity to the organic salts of the ion.

3.5. Quenching mechanism

To explore the nature of the quenching process, the average lifetimes of the immobilized pyrene moieties were determined in the presence of different concentrations of $Cu(Ac)_2$, and the results are shown in Fig. 7 by plotting τ_0/τ against the concentration of the salt, where τ_0 and τ represent the fluorescence lifetimes of the film in the absence and presence of the salt, respectively. As a comparison, the result from steady-state measurement was also shown in the figure. Examination of the plots, it is obvious that the lifetime of the sensing molecules did not change very much along with increasing concentration of the salt, a sharp contrast to that of the emission intensity, indicating that the quenching is static in nature. Clearly, both the chelating effect and the counter ion effects are responsible for the formation of the non-fluorescent species.

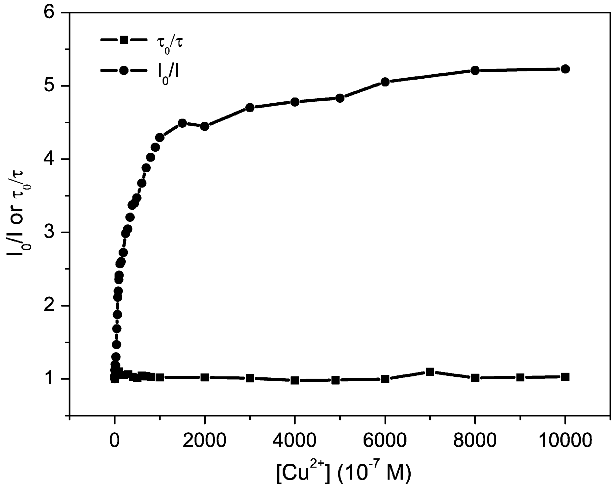


Fig. 7. Quenching plots of the fluorescence intensity and fluorescence lifetime ($\lambda_{ex}/\lambda_{em}$ = 346/376 nm).

3.6. Reversibility of the quenching process

The reversible sensing ability of this functional film was investigated by alternatively exposing the film to an aqueous solution of copper acetate of 0.01 mM and pure water, and the corresponding fluorescence intensity at 376 nm was measured. The intensity ratio, I_0/I, was calculated and reported in Fig. 8. After each measurement of the salt solution, the film was washed with EDTA solution and pure water for several times. The emis-

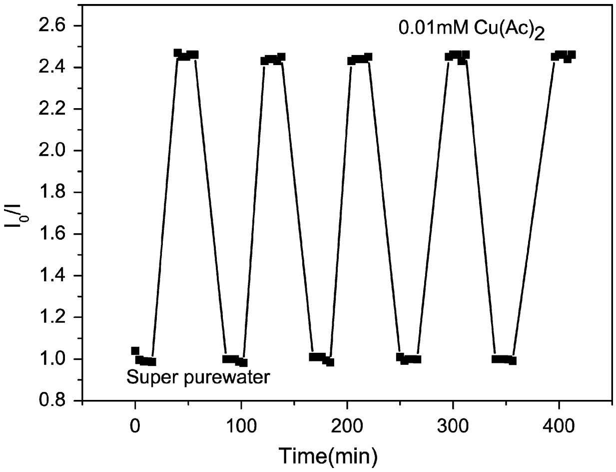


Fig. 8. Reversibility of the sensing film to $Cu(Ac)_2$ ($\lambda_{ex}/\lambda_{em}$ = 346/376 nm).

sion could not be restored when the film was washed with just pure water even if the washing was repeated for more than 10 times, in supporting of the statement that the quencher, Cu(II), was not simply dissolved in the layer, but complexed by the spacer. It was found that the response of the film to the salt is fast and fully reversible. Compared with molecular sensors, the reversible response of the film to analyte may open up a way for the development of sensor devices.

4. Conclusions

We have described the preparation and optical properties of a novel fluorescence film, a sensing film for organic copper(II) salts with higher sensitivity. The chemical attachment of the fluorophore, pyrene, via a spacer containing diethylenetriamine subunit to glass slide surfaces modified with an epoxy-terminated SAM not only ensures the stability of the sensor, but also increases the sensitivity of the film towards organic copper(II) salts. The improvement in the sensing performance of the film has been attributed to the increase in the binding sites of the spacer to copper(II) ions, and to the increase in the hydrophobicity of the spacer due to substitution of the sulfonyl structure in the spacer with methylene. It is to be noted that the sensing performance of the present film to organic copper(II) salts could be affected by the presence of other transition metal ions due to competition of the binding sites. In addition, the sensing process is static in nature and fully reversible.

Acknowledgements

We thank the Natural Science Foundation of China (NNSFC, 20543002, 20674048), the Ministry of Education of China (306015, 20040718001) for financial support.

References

[1] Y.J. Zheng, J. Orbulescu, X.J. Ji, F.M. Andreopoulos, S.M. Pham, R.M. Leblanc, J. Am. Chem. Soc. 125 (2003) 2680–2686.

[2] Q.Y. Wu, E.V. Anslyn, J. Am. Chem. Soc. 126 (2004) 14682–14683.

[3] T. Gunnlaugsson, J.P. Leonard, N.S. Murray, Org. Lett. 6 (2004) 1557–1560.

[4] H.H. Zeng, R.B. Thompson, B.P. Maliwal, G.R. Fones, J.W. Moffett, C.A. Fierke, Anal. Chem. 75 (2003) 6807–6812.

[5] R. Krämer, Angew. Chem., Int. Ed. 37 (1998) 772–773.

[6] Y. Xiang, A.J. Tong, P.Y. Jin, Y. Ju, Org. Lett. 8 (2006) 2863–2866.

[7] S.H. Kim, J.S. Kim, S.M. Park, S.-K. Chang, Org. Lett. 8 (2006) 371–374.

[8] M. Arduini, S. Marcuz, M. Montolli, E. Rampazzo, F. Mancin, S. Gross, L. Armelao, P. Tecilla, U. Tonellato, Langmuir 21 (2005) 9314–9321.

[9] A. Mokhir, A. Kiel, D. Herten, R. Krämer, Inorg. Chem. 44 (2005) 5661–5666.

[10] M. Royzen, Z.H. Dai, J.W. Canary, J. Am. Chem. Soc. 127 (2005) 1612–1613.

[11] N. Shao, Y. Zhang, S.M. Cheung, R.H. Yang, W.H. Chan, T. Mo, K.A. Li, F. Liu, Anal. Chem. 77 (2005) 7294–7303.

[12] M. Crego-Calama, D.N. Reinhoudt, Adv. Mater. 13 (2001) 1171–1174.

[13] N.J. van der Veen, S. Flink, M.A. Deij, R.J.M. Egberink, F.C.J.M. van Veggel, D.N. Reinhoudt, J. Am. Chem. Soc. 122 (2000) 6112–6113.

[14] S. Flink, F.C.J.M. van Veggel, D.N. Reinhoudt, Chem. Commun. (1999) 2229–2230.

[15] L. Basabe-Desmonts, J. Beld, R.S. Zimmerman, J. Hernando, P. Mela, M.F.G. Parajó, N.F. van Hulst, A. van den Berg, D.N. Reinhoudt, M. Crego-Calama, J. Am. Chem. Soc. 126 (2004) 7293–7299.

[16] M.A. Fox, Acc. Chem. Res. 32 (1999) 201–207.

[17] H.M. Schessler, D.S. Karpovich, G.J. Blanchard, J. Am. Chem. Soc. 118 (1996) 9645–9651.

[18] J.P. Rasimas, K.A. Berglund, G.J. Blanchard, J. Phys. Chem. 100 (1996) 17034–17040.

[19] Y. Fang, G.H. Ning, D.D. Hu, J.R. Lü, J. Photochem. Photobiol. A 135 (2000) 141–145.

[20] H. Wang, Y. Fang, L.P. Ding, L.N. Gao, D.D. Hu, Thin Solid Films 440 (2003) 255–260.

[21] L.N. Gao, Y. Fang, X.P. Wen, Y.G. Li, D.D. Hu, J. Phys. Chem. B 108 (2004) 1207–1213.

[22] L.P. Ding, Y. Fang, L.L. Jiang, L.N. Gao, X. Yin, Thin Solid Films 478 (2005) 318–325.

[23] L.N. Gao, Y. Fang, F.T. Lü, L.P. Ding, Sci. China Ser. B 47 (2004) 240–250.

[24] L.N. Gao, Y. Fang, F.T. Lü, M.W. Cao, L.P. Ding, Appl. Surf. Sci. 252 (2006) 3884–3893.

[25] F.T. Lü, L.N. Gao, L.P. Ding, L.L. Jiang, Y. Fang, Langmuir 22 (2006) 841–845.

[26] L.P. Ding, X.A. Cui, Y.N. Han, F.T. Lü, Y. Fang, J. Photochem. Photobiol. A 186 (2007) 143–150.

[27] F.T. Lü, L.N. Gao, H.H. Li, L.P. Ding, Y. Fang, Appl. Surf. Sci. 253 (2007) 4123–4131.

[28] A.W. Czarnik, Fluorescent chemosensors for ion and molecular recognition, in: ACS Symposium Series, American Chemistry Society, Washington, DC, 1993, p. 538.

[29] Q. Zhou, T.M. Swager, J. Am. Chem. Soc. 117 (1995) 7017–7018.

[30] P.H. Fliger, N. Agorastos, B. Spingler, O. Georgiev, G. Viola, R. Alberto, ChemBioChem 6 (2005) 414–421.

[31] S. Onclin, B.J. Ravoo, D.N. Reinhoudt, Angew. Chem., Int. Ed. 39 (2005) 6282–6304.

[32] M. Beltramello, M. Gatos, F. Mancin, P. Tecillab, U. Tonellato, Tetrahedron Lett. 42 (2001) 9143–9146.