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A highly selective and sensitive polymer-based OFF-ON fluorescent sensor for Hg²⁺ detection incorporating salen and perylenyl moieties[†]

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A chiral conjugated polymer sensor with incorporated (R,R)-salen and perylenyl moieties in the main chain backbone could be obtained by the polymerization of 1,7-bis((3-formyl-4-hydroxyphenyl) ethynyl)perylene-3,4:9,10-tetracarboxylic tetrabutylate (**M-1**) with (R,R)-1,2-diaminocyclohexane (**M-2**) *via* a nucleophilic addition–elimination reaction. The polymer sensor can emit the fluorescence situated at 635 nm due to the introduction of a strong fluorophore perylenyl group. Compared with the other cations (including Na⁺, K⁺, Ca²⁺, Ag⁺, Ni²⁺, Cd²⁺, Pb²⁺, Cr³⁺ Al³⁺, Fe³⁺, Co²⁺, Zn²⁺), only Hg²⁺ can lead to the most pronounced response of the polymer sensor, which is as high as a 26-fold fluorescence enhancement without interference from other metal ions. More importantly, the fluorescent color of the polymer sensor displays an obvious change from red to bright yellow upon addition of Hg²⁺, which could be easily detected by the naked eye. The results indicate that the polymer sensor with incorporated (R,R)-salen and perylenyl moieties can be favorably utilized for the development of a potential sensor for Hg²⁺ detection.

Introduction

Mercury is one of the most toxic heavy metal elements due to its high affinity for thiol groups in proteins and enzymes. This leads to the dysfunction of cells and consequently causes a wide range of diseases, even in a low concentration, such as digestive, kidney and especially neurological disorders.¹ Though several techniques are currently available for Hg²⁺ detection, they require expensive instruments, well-controlled experimental conditions and complicated sample-pretreatment procedures. It is very important to develop a highly selective and sensitive sensor for mercury ions in biological and environmental samples.² Recently, fluorescent sensors for the detection of heavy and transition metal ions have been widely investigated due to their high sensitivity, selectivity, fast response, low cost and easy signal detection. Therefore, fluorescence is still of particular significance for the design of a suitable chemosensor for the rapid determination of mercury in biological and environmental samples.

In the last few decades, many fluorescent sensors for mercury ion detection have been reported, but most of them were based on small molecules, only a few were polymer-based sensors.³ An advantage of using fluorescent conjugated polymers over small molecules is that signal amplification occurs from electronic

communication along the polymer backbone. Swager et al.4 reported that the delocalizable π -electronic conjugated "molecular wire" polymer can greatly amplify the responsive fluorescence change due to facile energy migration along the polymer backbone upon light excitation. As a result, a single conjugated polymer provides an enhanced optical response relative to one of its monomer units, and conjugated polymers can be used as optical platforms in highly sensitive chemical and biological sensors. Various perylenyl derivatives are promising materials for organic solar cells,5 organic field-effect transistors,6 organic light-emitting diodes⁷ due to their excellent thermal- and photostability, strong fluorophores, high luminescence efficiency, and novel optoelectronic properties. So far, perylene-based fluorescent sensors for metal ion detection have rarely been reported.8 Wang and co-workers designed a method for the selective sensing of Hg²⁺ by utilizing a perylene fluorescence probe and a thyminerich oligonucleotides interaction with Hg²⁺ leading to a significant fluorescence enhancement.8g However, there is no report on polymer-based fluorescence sensors incorporating salen and perylenyl moieties for selective Hg²⁺ detection.

Salen, as a well-known building block, has been widely used for constructing chelation-enhanced fluorescence sensors for transition metal ion detections due to the potentially tetradentate N_2O_2 donor.⁹ Recently, our group reported a chiral fluorescence polymer sensor bearing a (*R*,*R*)-salen unit, which exhibited high selectivity and sensitivity for Zn^{2+} detection without interference from other metal ions.¹⁰ In this paper, perylene was chosen as a fluorophore dye, and (*R*,*R*)-salen acts as a chelating ligand. The polymer sensor with incorporated (*R*,*R*)-salen and perylenyl moieties in the main chain backbone can exhibit a highly selective

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and sensitive fluorescence response toward Hg^{2+} without interference from other metal ions. More importantly, the polymer sensor appears to give an obvious and characteristic color change from red to bright yellow, which indicates that the resulting polymer-based fluorescence sensor can serve as a "naked-eye" indicator for Hg^{2+} recognition.

Experimental

Metal ion titration

Each metal ion titration experiment was started using 5.0 mL of a polymer solution with a known concentration $(1.0 \times 10^{-5} \text{ mol} \text{ L}^{-1} \text{ corresponding to } (R,R)$ -salen moiety in THF). Mercury perchlorate salt $(1.0 \times 10^{-3} \text{ mol} \text{ L}^{-1} \text{ in CH}_3\text{CN})$ and other various metal salts (nitrate, $1.0 \times 10^{-2} \text{ mol} \text{ L}^{-1} \text{ in H}_2\text{O}$) were used for the titration. Polymer–metal complexes were produced by adding aliquots of a solution of the selected metal salt to the THF solution of the polymer. All types of measurements were taken 2 h after the addition of the metal salt to the polymer solution.

Results and discussion

Synthesis and characterization of the polymer-based fluorescence sensor

The synthesis procedures of the model compound 2 and polymerbased fluorescence sensor are outlined in Fig S1[†]. Compound 3, 1,7-dibromoperylene-3,4:9,10-tetracarboxylictetr-abutylate could be synthesized according to the literature.¹¹ Monomer M-1, 1,7bis((3-formyl-4-hydroxyphenyl)ethynyl)-perylene-3,4:9,10-tetracarboxylic tetrabutylate, was synthesized by a three-step reaction from the starting material 3,4:9,10-perylene-tetracarboxylic acid dianhydride.¹² The polymer sensor incorporating (R,R)-salen and perylenyl moieties in the main chain backbone could be obtained by the Schiff-base formation via a nucleophilic addition-elimination reaction between M-1 and (R,R)-1,2-diaminocyclohexane (M-2) as a dark-red powder in 59% yield. The specific rotation value ($[\alpha]_{D}^{25}$) of the model compound **2** is -0.059 (c = 0.49, THF), but $[\alpha]_{D}^{25}$ of the sensor is $-270 \ (c = 0.01, \text{THF})$. The optical rotation of the chiral polymer is much larger than its chiral monomers, which is attributed to the amplification of chiral signals of the conjugated polymer. The weight-average molecular weight (M_w) , the number-average molecular weight $(M_{\rm n})$, and polydispersity index (PDI) of the sensor were determined by gel permeation chromatography (GPC) using polystyrene standards in THF, the values of them are 12480, 7710 and 1.6, respectively. The GPC result shows the moderate molecular weight. The sensor is an air stable solid and shows that it is readily soluble in common organic solvents, such as CHCl₃, CH₂Cl₂, THF and toluene, which can be attributed to the flexible *n*-butoxy substitutents in the side chain of the polymer. In addition, the ethynyl linker can reduce steric hindrance between the perylenyl and phenyl groups which also has a beneficial influence on the stability of the resulting chiral polymer. Thermogravimetric analysis (TGA) of the polymer was carried out under a N₂ atmosphere at a heating rate of 10 °C min⁻¹ (Fig S11[†]). The result shows that the polymer sensor has a high thermal stability without loss of weight below 250 °C and tends to completely decompose at 700 °C. Therefore, the resulting

polymer can provide a desirable thermal property for the practical application as a fluorescence sensor.

Optical properties

Fig. 1 illustrates the UV-vis absorption and fluorescence spectra of the model compound 2 and polymer-based fluorescence sensor $(1.0 \times 10^{-5} \text{ mol } L^{-1} \text{ in THF})$. As can be observed in Fig. 1, the UV-vis absorption maxima λ_{max} of **2** appeared at 241 nm, and the conjugated polymer showed a strong and broad absorption in the region from 400 to 570 nm. A large red shift in the electronic absorption of the polymer can be attributed to the effective $\pi - \pi^*$ conjugated segments of the polymer main chain backbone. The polymer sensor can emit the red fluorescence situated at 635 nm under ultraviolet light (365 nm) even in low concentration $(1 \times 10^{-5} \text{ mol } \text{L}^{-1})$ due to the introduction of a strong fluorophore perylenyl group. The fluorescent emission wavelengths of **2**, **3** and the polymer sensor appear at 398 ($\lambda_{ex} =$ 310 nm), 495 (λ_{ex} = 430 nm) and 635 nm (λ_{ex} = 440 nm), respectively. Compared to 2 and 3, the conjugated polymer sensor shows a large red shift due to the extended π -electronic structure in the main chain backbone.13 The greatly enhanced fluorescence of the polymer sensor is expected to have the potential application in the polarized light-emitting materials and fluorescence chemosensor on the sensitivity in metal ions sensing.

The selective and sensitive recognition of the polymer sensor towards Hg²⁺

The effects of the fluorescence response behavior of the sensor towards Hg^{2+} have been investigated. Fig. 2 shows the fluorescence spectra of the polymer-based fluorescence sensor (1.0 × 10^{-5} mol L⁻¹ in THF) upon addition of mercury ions in anCH₃CN solution ($\lambda_{ex} = 440$ nm). The polymer sensor appears to have a weaker emission peak situated at 635 nm. However, the emission intensities of the Hg^{2+} -containing polymer complex exhibits a gradual enhancement response, as high as 26-fold, upon the addition of Hg^{2+} with a concentration molar ratio from 0.1 to 3.0 at a concentration of 1.0×10^{-3} mol L⁻¹. In addition, a large blue shift of about 85 nm for the emission spectrum peak of the Hg^{2+} -containing polymer complex can be observed, which can be attributed to an **ICT** (intramolecular-charge-transfer)



Fig. 1 UV-vis and fluorescence spectra of the model compound **2** (1×10^{-5} mol L⁻¹) and polymer-based fluorescence sensor (1×10^{-5} mol L⁻¹).



Fig. 2 Fluorescence spectra of the polymer $(1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ in THF with increasing amounts of Hg²⁺ (0, 0.1, 0.2, 0.4, 0.8, 1.0, 1.2, 1.6, 2.0, 2.4, 2.8, $3.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ ($\lambda_{\text{ex}} = 440 \text{ nm}$); Inset: fluorescence enhancement values (*F*/*F*₀) *vs.* the increasing concentration of Hg²⁺.

mechanism.¹⁴ More importantly, the Hg²⁺-polymer solution appears to undergo an obvious and characteristic color change from red to bright yellow, which can be easily detected by the naked eye (Fig. 3). The fluorescence enhancement in its response behavior of the sensor towards Hg²⁺ can be attributed to the suppressed PET (photoinduced-electron-transfer) quenching when Hg²⁺ coordinates with the tetradentate N₂O₂ donor of the (R,R)-salen moiety in the polymer main chain and oxygen atoms of the tetrabutylate groups in the side chain of polymer sensor (Fig. 3). It can also be observed that the titration curve keeps to a nearly linear correlation with the concentration molar ratio of Hg²⁺ from 0.1 to 3.0. The linear titration curve of fluorescence spectra of the polymer sensor demonstrates that chemodosimeter responds to Hg²⁺ in a 1 : 3 stoichiometry ratio. In this range of concentrations, the curve could be best described by the equation F = 4.346 - 32.241 [Hg²⁺], with R = 0.99404, N = 10 (Fig S12[†]). According to the equation and the standard deviation of the blank, the polymer sensor has a detection limit of 7.28 \times 10^{-7} mol L⁻¹ for Hg²⁺.

Compound **3** shows a strong fluorescence at 495 nm, but the model compound **2** emits a weaker fluorescence at 398 nm. Upon addition of 0.1–2.0 equiv. of Hg²⁺ ions to the solution of **2** and **3**, the compound **2-/3-Hg²⁺** complexes show nearly no changes in emission spectra (Fig S13–S14†). On the contrary, the sensor incorporating (*R*,*R*)-salen and perylenyl moieties can exhibit the most pronounced fluorescence enhancement response and a large blue shift on Hg²⁺ complexation. According to the reports of Fan

and Jones,^{15a} the polymer sensor can be thought of as a conjugated polymer PET chemosensor, in which the conjugated polymer backbone is the fluorophore and the salen or tetrabutylate groups are the receptors. In such systems, the salen and tetrabutylate receptors contain the high energy non-bonding electron pairs. In the absence of analytes, these electron pairs quench the fluorescence of the fluorophore by rapid intramolecular electron transfer from the receptor to the excited fluorophore. When these electron pairs are coordinated to Hg²⁺ (Lewis acid cations) in solution, the HOMO of the receptor is lowered. This decreases the driving force for the PET process and can turn on the fluorescence of the fluorophore. To our knowledge, most fluorescence sensors based on small organic molecules or conjugated polymers for Hg²⁺ detection exhibit a fluorescence quenching effect.15b Although few small molecule sensors work in "turn-on" mode,16 very few examples of fluorescence-based polymer sensors towards Hg²⁺ could exhibit the fluorescence enhancement effect.¹⁷ Since fluorescence quenching is not only disadvantageous for a high signal output upon complexation, but also hampers temporal separation of spectrally similar complexes with time-resolved fluorometry. The design of chemosensors with an obvious fluorescence enhancement response for the detection of mercury still remains an attractive topic.18

Further evidence for the interaction of the salen and tetrabutylate moieties with Hg²⁺ was provided by ¹H NMR titration experiments of the polymer sensor with Hg²⁺ in CD₃CN (Fig S10†). The ¹H NMR spectra of the polymer sensor demonstrates that the protons in the lateral region of the perylenyl tetrabutylate core (-COOCH₂-) shift downfield from 4.36 to 4.58 ppm upon addition of Hg²⁺ (3 equiv.) to the polymer solution in CDCl₃, which shows coordination and chelation between the ester groups and Hg²⁺. Meanwhile, obvious upfield shifts (-CH-CH-) from 3.47 to 4.23 can be also observed for the protons of (*R*,*R*)-salen, which indicates the direct interaction between (*R*,*R*)salen groups and Hg²⁺.

In this paper, we further explored the utility of the polymer sensor as an ion-selective fluorescence probe for Hg²⁺. The experiments on other various cations were also conducted under the same conditions as the Hg²⁺ determination, such as Zn²⁺, Fe³⁺, Cd²⁺, Na⁺, Ag⁺, K⁺, Al³⁺, Cr³⁺, Ca²⁺, Ni²⁺, Pb²⁺, Cu²⁺ and Co²⁺ (Fig. 4). In the experiment, the fluorescence spectra of the sensor $(1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ were determined at room temperature in the absence and presence of 3.0 equiv. of a metal ion (Fig S15†). As



Fig. 4 The selectivity of the polymer sensor toward Hg²⁺ and other metal ions. In these experiments, the fluorescence measurement was taken at $\lambda_{ex} = 440$ nm from 10 μ M of the polymer in THF at room temperature and in the absence and presence of 3.0 equiv. of a metal ion.

-2 Hg Zn Fe Cd Ni Na Ag K Al Cr Cu Ca Pb Co



Fig. 5 Fluorescence enhancement degree of the polymer sensor $(1.0 \times 10^{-5} \text{ mol } L^{-1})$ in the mixed metal ions (each $3.0 \times 10^{-5} \text{ mol } L^{-1}$).

a result, only Hg²⁺ can lead to the most pronounced fluorescence enhancement response of the polymer sensor. However, Cd²⁺, Ag⁺, Ca²⁺, Al³⁺, Cr³⁺ and Pb²⁺ can slightly enhance the fluorescence response ($I/I_0 - 1 < 0.50$), and Al³⁺ and Cr³⁺ induced a continuous blue shift of the emission peak from 635 to 550 nm. Meanwhile, Co²⁺ and Ni²⁺ can effectively quench the fluorescence of the sensor ($I/I_0 - 1 < -0.60$), and Cu²⁺ can lead to almost complete quenching of the sensor ($I/I_0 - 1 = -0.97$). Under the same conditions Zn²⁺, Na⁺ and K⁺ caused limited quenching of the fluorescence intensity. In most cases, the salen ligand has a good affinity for Zn²⁺, However, our resulting polymer sensor can exhibit a high selectivity and sensitivity towards Hg²⁺ over Zn²⁺. It is possible that the nitrogen atoms of the salen unit did not participate in binding with a Zn²⁺ ion, which induced the fluorescence of sensor quenching.¹⁹

In this paper, we further investigated the selectivity of the polymer sensor for Hg²⁺ while in the presence of a Hg-polymer treated with other metal ions (Fig. 5). The fluorescence response was measured using the metal ion solution titrations in the presence of the mercury ion, with ions such as Na⁺, K⁺, Ca²⁺, Cr3+, Pb2+ and Cd2+, the fluorescence enhancement degree $(F/F_0 - 1)$ of the polymer sensor is -0.07, 0.26, 16.94, -18.13,-13.16, -4.64 and 2.02%, respectively. Comparison of the polymers that contain both a mixture of ions (except the coexising ions Cu2+ and Co2+) and single Hg2+, the fluorescence intensities of the polymers do not appear to have any obvious changes. Herein, the fluorescence intensity of the sensor can not be influenced in the presence of mercury ions during the titration of various metal ions, which demonstrates that the polymer sensor can serve as highly selective "turn-on" fluorescent chemodosimeter for the detection of Hg²⁺.

Conclusion

In conclusion, we have designed a novel polymer-based OFF– ON fluorescence sensor incorporating perylenyl and salen moieties in the main chain backbone. The polymer sensor can exhibit a highly selective and sensitive fluorescence enhancement response for Hg^{2+} detection without interference from other metal ions. We expect that the present design strategy and the remarkable photophysical properties of this resulting polymerbased fluorescence sensor is a potential tool for the detection and quantification of mercury in environmental and biological samples.

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