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Polymer-based fluorescent sensor incorporating 2,2'-bipyridyl and benzo[2,1,3]thiadiazole moieties for Cu²⁺ detection

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ABSTRACT

The polymer was synthesized by the polymerization of $4,4'-((4-iodophenoxy)methyl)-2,2'-bipyridine (M-1) with 4,7-diethynylbenzo[2,1,3]-thiadiazole (M-2) via Pd-catalyzed Sonogashira reaction. The fluorescence responses of the polymer towards various transition metal ions were investigated by fluorescence spectra and UV–Vis spectra. The polymer shows green fluorescence under ultraviolet lamp, which can be quenched by <math>Cu^{2+}$ completely due to the heavy metal effect. The results suggested that the polymer can be used as a Cu^{2+} -selective sensor via a naked eyes detecting mode.

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 Cu^{2+} ranks the third in abundance among the essential heavy metals and is a vital trace element in human bodies. It plays a crucial role in various fundamental physiologic processes ranging from haemopoiesis to enzyme-catalyzed reactions and redox processes [1]. Disorders of Copper metabolism could lead to an increasing risk of various neurodegenerative diseases, such as Alzheimer's, Parkinson's, Menke's and Wilson's diseases [2]. On the other hand, Cu^{2+} is known as one of the most important ecological pollutions around the world [3]. Therefore, an intense effort has been placed on design and synthesis of highly sensitive chemosensors for Cu^{2+} [4], such as laser ablation inductively coupled plasma mass spectrometry [4d], UV Spectroscopy [4f], Atomic Emission Spectroscopy [4g], potentiometry [4h,i], and so on. Of these sensors, fluorescent chemosensors have distinct advantages over other types due to their simplicity, high sensitivity and fast response time [5].

Due to the electron-withdrawing properties and high fluorescence quantum yield both in solution and in the solid state, benzo[2,1,3] thiadiazole (BTD) has been used for developing optoelectronic materials during the past few years [6], such as constructing $D-\pi-A-\pi-D$ -type fluorescent dyes, developing liquid crystal displays (LCDs) and light-emitting diodes [7]. More recently, molecules incorporating BTD moieties have found their applications in the field of fluorescence probing and imaging due to their attractive and tunable fluorescence properties [8], and several BTD-based polymers were designed and applied as metal-ion sensor and biosensor [9]. Pyridyl and bipyridyl ligands have been extensively used as an excellent metal chelating ligand in a variety of

approaches dealing with structural coordination chemistry or functional systems based on bipyridine containing metal complexes because of their redox active behavior, luminescent properties, and supramolecule forming reactivity [10]. Dennis [11a] and Zhang [11b] recently reported two 2,2'-bipyridine based fluorescence sensors for Zn²⁺ detection. Some fluorescent sensors have limitation of distinguishing Cu²⁺ from Hg²⁺ under no external stimuli [4k]. To our best knowledge, very few polymer-based fluorescence sensor incorporating bipyridyl moieties as binding site was reported [10c, d].

An advantage of fluorescent polymers over small molecules is that signal amplification occurs from electronic communication along the polymer backbone [12]. As a result, a single polymer provides enhanced optical response relative to one of its monomer units. During the last few years, our interest has been focused on the designing of fluorescence polymer sensors and their applications in metal ions detection and chiral molecule recognition [13]. In this paper, we described the synthesis of a non-conjugated fluorescence polymer incorporating 2,2'-bipyridyl and benzo [2,1,3] thiadiazole moieties in the polymer main chain backbone by Pd-catalyzed Sonogashira coupling reaction. The responsive optical properties of the polymer sensor on various metal ions were investigated by fluorescence and UV-Vis spectra. The results show that the polymer exhibits bright green under ultraviolet lamp, which could be quenched completely by Cu^{2+} , rather than other cations (Na⁺, K⁺, Mg²⁺, Ca²⁺, Cr³⁺, Fe³⁺, Zn²⁺, Ag⁺, Cd²⁺, Hg²⁺, and Pb²⁺). More importantly, the color changing process could be easily detected by naked eyes under UV lamp. The results also indicate that this kind of non-conjugated polymer incorporating 2,2'-bipyridyl moiety as a recognition site could exhibit high sensitivity and selectivity for Cu²⁺ detection.

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4,4'-((4-iodophenoxy)methyl)-2,2'-bipyridine (**M-1**) was synthesized from the starting material 4,4'-methyl-2,2'-bipyridine by a twostep reaction according to reported literatures [14]. 4,7-bis(ethynyl)-2,1,3-benzothiadiazole (M-2) was prepared through a two-step reaction from the starting material 5-bromosalicylaldehyde according to a reported method [15]. The non-conjugated polymer incorporating 2,2'-bipyridyl and benzo[2,1,3]thiadiazole Moieties was obtained by a typical Sonogashira reaction between M-1 and M-2 as a brown powder in 63.0% yield (Scheme 1). Relative molecular weight of polymer was determined by GPC with Waters-244 HPLC pump and THF was used as solvent and polystyrene as standards. Mw, Mn and PDI of the polymer are 6710, 5590 and 1.20, respectively. The nonconjugated polymer is an air stable powder with yellow color and shows good solubility in common organic solvents, such as toluene, acetone, ethyl acetate, THF, CHCl₃ and CH₂Cl₂, which facilitates its application in the sensory system. Meanwhile, the 2,2'-bipyridyl moieties can form stable complexes with various metal ions due to the potentially non-hindering bidentate N₂ donor.

According to thermal analysis of the polymer (Fig. 1), it has a high thermal stability with 5% loss of weight from 20 to 325 °C. An accelerated degradation was observed at the temperature ranging from 325 °C to 570 °C, and then the polymer tends to complete decomposition at 680 °C with a total loss of about 48%. Therefore, the chiral polymer is stable enough and can provide desirable thermal property for practical application as a fluorescence sensor.

Fig. 2 illustrates the absorption spectra (a) and emission spectra (b) of polymer, model compounds **1** and **2**, respectively. UV spectrum of model compound **1** shows a maximum absorption at 280 nm, and UV spectrum of model compound **2** exhibits two absorptions at 311 nm and 440 nm; compared to model compound **2**, the two absorption peaks of polymer are blue shifted to 294 nm and 430 nm



Fig. 1. TGA of the polymer sensor.

due to the electric drawing character of bipyridine group. The emission spectrum of polymer (515 nm) also shows a blue shift compared with model compound **2** (534 nm).

As shown in Fig. 3, the UV spectrum of polymer shows a maximal absorption at 294 nm and a broad band centered at 430 nm before titrations in THF. With the increasing amount of Cu^{2+} , UV–Vis spectra at 430 nm remain unchanged, but new peaks arise at 311 nm. This phenomenon may be attributed to 2,2'-bipyridyl moiety in the backbone of the non-conjugated polymer, where the binding event with Cu^{2+} happens. To make it more clearly, the UV-titration experiment of model



Scheme 1. Synthesis procedures of model compounds 1, 2 and chiral polymer sensor.



Fig. 2. (a): UV spectra of polymer, model compounds 1 and 2; (b): emission spectra of polymer and model compound 2 (10 μ M in THF).



compounds **1** and **2** was conducted (SI, Figs. S1 and S2). Almost no change is observed in UV spectra in the absence and presence Cu^{2+} for model compound **2**, which is in accordance with Fig. 3; UV titration of model

Fig. 3. UV–Vis spectra of the chiral polymer (1.0×10^{-5} mol/L) with increasing amounts of Cu²⁺ (0.05–0.70 equiv.).



Fig. 4. Fluorescence quenching efficiencies of the polymer in the presence of various transition metal ions (2:1).

compound **1** shows a similar increase as Fig. 3 at 310 nm due to the coordination between 2,2'-bipyridyl moiety and Cu²⁺.

The fluorescence titration of the polymer with various metal ions was conducted to check its selectivity. Fig. 4 shows the quenching efficiencies of various metal ions for the polymer sensor. Addition of 1.0 eq Na⁺, Mg²⁺, K⁺, Ca²⁺, Cr³⁺, Fe³⁺, Ag²⁺, Hg²⁺, Cd²⁺, and Pb²⁺ causes fluorescence quenching less than 0.2 $(1 - F/F_0)$, Zn²⁺ leads to a fluorescence quenching efficiency of 0.23. However, in the presence of 0.5 eq Cu²⁺, a completely quenching is observed. Fluorescence titration of model compound **2** was also conducted under the same condition (SI, Fig. S3), and no obvious fluorescence response can be observed from the titration spectra of model compound **2**, which also proves that benzo[2,1,3]thiadiazole unit does not bind Cu²⁺ in this experiment. In addition, water has a quenching effect on the fluorescence of this polymer sensor (10 μ M in THF), along with a red shift from 516 to 539 nm due to the hydrogen bond formation between water and the polymer (SI, Fig. S4).

We further studied the fluorescence response of polymer to an increasing amount of Cu^{2+} . The polymer shows a strong fluorescence emission centered at 515 nm. With the addition of Cu^{2+} from 0.05 to 0.50 molar ratio, the fluorescence intensity was quenched steadily with almost no wavelength changed due to the heavy metal effect (Fig. 5). The result indicates that binding ratio between ligand unit



Fig. 5. Fluorescence spectra of the polymer $(1.0 \times 10^{-5} \text{ mol/L})$ with increasing amounts of Cu²⁺ (0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, $7.0 \times 10^{-6} \text{ mol/L})$ (λ_{ex} = 449 nm); *Inset*: visible emission changes observed: 10 µM polymer solution in THF, left; in the presence of Cu²⁺, right.



Fig. 6. Plot of the concentration of $Cu^{2+}vs.1 - F/F_0$, where F: the fluorescence intensity of the polymer $(1.0 \times 10^{-5} \text{ mol/L})$ with addition of Cu^{2+} at $\lambda_{em} = 521 \text{ nm}$ and F_0 : the fluorescence intensity of the polymer without Cu^{2+} at $\lambda_{em} = 515 \text{ nm}$.

and Cu^{2+} is 2:1, which is also justified by the UV spectra (Fig. 3). It can also be found that the addition curve keeps nearly linear correlation with the concentration molar ratio from 0 to 0.35 (Fig. 6). On the other hand, the non-conjugated polymer emits green fluorescence under UV lamp (365 nm), which can be detected by naked eyes (Fig. 5, inset). However, when 0.5 eq Cu^{2+} is added in, the fluorescence is turned off instantly. This distinct change provides us a real-time and easy way to monitor Cu^{2+} in aqueous solution. The competition experiment was conducted which reveal that the quenching efficiency of Cu^{2+} would not be influenced by addition of other cations (SI, Fig. S5).

In conclusion, a novel non-conjugated polymer sensor incorporating bipyridyl moiety as receptors was synthesized by a typical Sonogashira reaction. Compared with other cations, such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Cr³⁺, Fe³⁺, Pb²⁺, Ag⁺, Cd²⁺, Hg²⁺ and Zn²⁺, Cu²⁺ produce the most fluorescence quenching effect of the polymer. The polymer can be used as sensitive fluorescent sensor for Cu²⁺ detection, even under a UV lamp. The solution color of this polymer changes from bright green to dark with addition of Cu²⁺, which can be witnessed by naked eyes.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.inoche.2011.07.014.

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