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## COMMUNICATION

## Conjugated polymers containing a 2,2'-biimidazole moiety—a novel fluorescent sensing platform†

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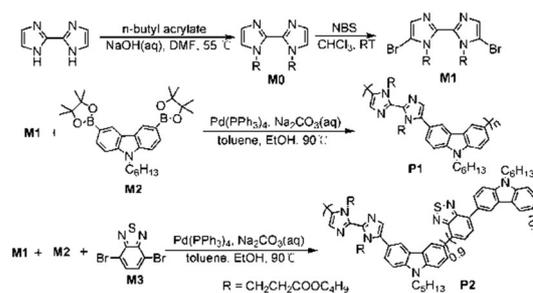
Two novel conjugated polymers containing a 2,2'-biimidazole moiety have been designed, synthesized, and demonstrated to be used as an effective fluorescent sensing platform for detection of Ag<sup>+</sup> and cysteine. This is the first example utilizing a fluorescent conjugated polymer–Ag<sup>+</sup> complex to selectively detect Cys with a nanomolar range detection limit.

Fluorescent conjugated polymers have been widely utilized as highly sensitive chemosensors for detection of many analytes in recent years due to the signal amplification effect through the “molecular wire” of the conjugated backbone.<sup>1</sup> Among these polymers, several *N*-heterocyclic aromatic structures, such as pyridine,<sup>2</sup> bipyridyl,<sup>3</sup> terpyridyl,<sup>4</sup> and phenanthroline,<sup>5</sup> have been introduced into the backbone as coordination sites for metal ions. When the interaction occurs between the coordination sites and metal ions, the conjugated polymers exhibit fluorescence quenching or emission red/blue-shift, this is generally attributed to electron density variations on the main chains or conjugation enhancement along the polymer backbone.<sup>3a,b</sup> However, the selectivity of polymer sensors based on *N*-heterocycles, especially for the bipyridyl analogue, remains unsatisfactory compared with that of the small molecule sensors.<sup>6</sup> In order to improve the properties of the polymer sensors, the design and synthesis of the conjugated polymer sensors with a new aromatic *N*-heterocycle as a receptor are still a quite important and intriguing theme.

Imidazole is an important aromatic *N*-heterocycle because of its significant role in biosystems and attractive chemical properties.<sup>7</sup> Most recently, the conjugated polymers with imidazole or imidazolium as the side groups exhibit outstanding sensing properties to metal ions, anions, nitric oxide, and amino acids.<sup>8</sup> 2,2'-Biimidazole, the dimeric analogue of imidazole, is one of the most important derivatives of imidazole and plays a particular role in crystal engineering because of the excellent coordination ability and diverse coordination modes.<sup>9</sup>

However, only very few papers have been devoted to the study of the conjugated polymers containing a biimidazole moiety. Yamamoto *et al.* prepared three 2,2'-biimidazole homopolymers by the dehalogenative polycondensation using a zerovalent nickel catalyst.<sup>10a</sup> Then MacLean *et al.* reported conjugated polymers of 2,2'-biimidazole obtained through electrochemical polymerization.<sup>10b</sup> The authors did not investigate the fluorescence properties of the polymers, they focused on the structure and chemical properties.

In order to explore and design new conjugated polymer sensors with excellent properties, we designed and prepared 2,2'-biimidazole based conjugated polymers, and studied the fluorescence sensing property of the polymers for the detection of metal ions and amino acids. Two polymers **P1** and **P2** were synthesized through Suzuki condensation and the synthetic routes are illustrated in Scheme 1. 2,2'-Biimidazole was first prepared according to the published procedure,<sup>11a</sup> and then was reacted with *n*-butyl acrylate and **P1** was conveniently prepared by the Suzuki coupling reaction between **M1** and **M2**, and **P2** was obtained in a similar approach. **P1** and **P2** were purified by precipitation from hexane and collected as slightly gray and red solids, respectively. The purified polymers were characterized by <sup>1</sup>H NMR and FTIR (see ESI†), providing conclusive evidence for the well-controlled structure as we expected by the incorporation of the monomers into the polymer backbone. Both polymers readily dissolve in common organic solvents, such as toluene, CH<sub>2</sub>Cl<sub>2</sub>, THF, and dioxane. The molecular weights (*M<sub>n</sub>*) and polydispersity index (PDI) of the polymers were determined by gel permeation chromatography (GPC) with polystyrene as the reference standard (Table S1, ESI†).



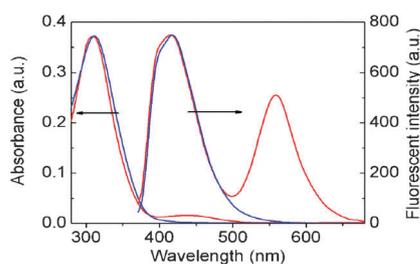
Scheme 1 Synthesis of monomers and polymers.

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**Fig. 1** UV-vis absorption and fluorescence spectra of **P1** (blue line) and **P2** (red line) in dioxane.  $[P1] = [P2] = 8.0 \mu\text{M}$ .  $\lambda_{\text{ex}} = 333 \text{ nm}$ .

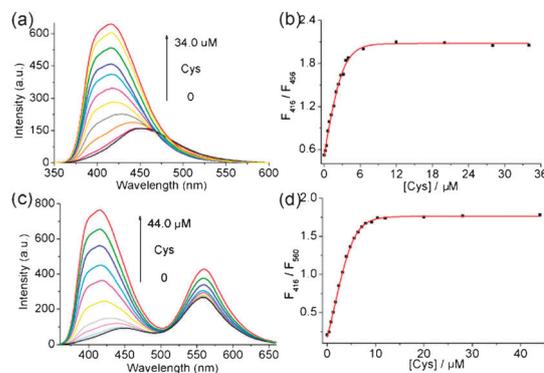
The absorption and emission spectra of the two polymers were measured in dioxane at room temperature (Fig. 1). **P1** exhibits the absorption maximum at 312 nm and its photoluminescence spectrum peaked at 416 nm. In comparison with **P1**, **P2** displays a main absorption peak at 310 nm and the other weak peak at 450 nm. Similarly in the PL spectrum, **P2** shows two peaks centred at 416 and 560 nm, which are due to the emission of carbazole–biimidazole and carbazole–benzothiazole units, respectively. Simultaneously, a Förster resonance energy transfer (FRET) process exists in **P2**, because the weak absorption peak of the carbazole–benzothiazole unit was found to overlap with the emission peak of the carbazole–biimidazole unit (Fig. 1). Both the polymers are emissive in the visible region under UV irradiation (365 nm), **P1** shows a blue-violet color whereas **P2** is a reddish orange color. The fluorescence quantum yields of **P1** and **P2** were determined to be 0.2 and 0.17, respectively.

The ion responsive properties of the polymers were studied by fluorescence emission spectroscopy in dioxane at a concentration of  $8.0 \mu\text{M}$  (Fig. S1–S4, ESI†). It was found that both of the polymers have no response to the addition of alkali as well as alkaline earth metal ions. However, upon the addition of  $\text{Ag}^+$ , the emission peaks at 416 nm exhibit a red shift of 40 nm with a decreased intensity for both of the polymers, which causes obvious changes of the fluorescence color. Besides the  $\text{Ag}^+$  ion,  $\text{Zn}^{2+}$  induces a smaller red shift, while  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Co}^{2+}$  ions can cause only fluorescence quenching in various degrees with no wavelength changes. The other metal ions examined lead to negligible changes of the fluorescence. Therefore,  $\text{Ag}^+$  can be readily distinguished from the other metal ions by the emission shift. As shown in Fig. S5 (ESI†), upon interaction with  $\text{Ag}^+$ , the emission peak of **P1** gradually red-shifts to the wavelength of 456 nm along with the concentration of  $\text{Ag}^+$ , and the fluorescence color of the solution changes from blue-violet to pale blue (Fig. S16a, ESI†). However, compared with **P1**, **P2** exhibits a notable difference during the titration experiment because of the FRET process. It was noticed that the emission peak of **P2** at 560 nm shows a weaker fluorescence quenching than that at 416 nm upon the addition of  $\text{Ag}^+$ . As a result, the intensity ratio  $F_{560}/F_{416}$  gradually increases with  $\text{Ag}^+$  concentration (Fig. S6, ESI†). Simultaneously, the fluorescence color of **P2** changes from reddish orange to yellow orange (Fig. S16b, ESI†). The coordination reaction has been confirmed by a UV-Vis titration experiment (Fig. S23 and S24, ESI†).

It is obvious that the ion responsive properties of **P1** and **P2** are quite different from those of the conjugated polymers with the oligopyridyl moieties in their backbones and also with the

imidazole moieties in their side chains, which may be due to the large M–N (metal–nitrogen) bond lengths<sup>12</sup> and different molecular rigidities of the polymer chains. It is presumed that the distinguishing responsive characteristic of the polymers to  $\text{Ag}^+$  ions is attributed to both electron density variations on the backbone and chain aggregation induced by coordination. The initial fluorescence quenching of the polymers may be attributed to the electron transfer interactions between the polymer backbone and  $\text{Ag}^+$  ions. Then the later quenching can be induced by the chain aggregation,<sup>13,14</sup> which was confirmed by the experiment of water induced aggregation (Fig. S17, ESI†). This means that the FRET effect was enhanced because of the  $\text{Ag}^+$  induced aggregation. The interesting phenomenon was not observed in the previous reports about the conjugated polymer sensor for  $\text{Ag}^+$  ions.<sup>15</sup> The possible mechanism is illustrated in Scheme S1, ESI†. The Stern–Volmer quenching constants  $K_{\text{sv}}$  of **P1**– $\text{Ag}^+$  and **P2**– $\text{Ag}^+$  systems were determined to be  $2.2 \times 10^5 \text{ M}^{-1}$  and  $4.6 \times 10^5 \text{ M}^{-1}$ , respectively.

Since cysteine (Cys) can bind  $\text{Ag}^+$  through the thiol– $\text{Ag}^+$  interaction,<sup>16</sup> this provides an approach to detect Cys by utilizing the polymer– $\text{Ag}^+$  complex as a novel sensor. There are some papers published on the study of Cys fluorescent sensors based on the  $\text{Ag}^+$  complexes of the different ligand species, such as calix[4]arene,<sup>17a</sup> amino acids,<sup>17b</sup> and DNA.<sup>17c–e</sup> Herein, we prepared the  $\text{Ag}^+$  complexes of the conjugated polymers containing 2,2′-biimidazole moieties *in situ* by mixing **P1** and **P2** with  $\text{Ag}^+$  salt, respectively, and studied their properties as Cys fluorescent sensors. We found that the emission spectra of the complexes exhibit remarkable changes upon interaction with Cys (Fig. 2 and Fig. S7 (ESI†)). As shown in Fig. 2a, the emission peak of the **P1**– $\text{Ag}^+$  complex gradually blue-shifts from 456 nm to 416 nm, accompanied by an increase in the fluorescence intensity upon increasing the concentration of Cys. Moreover, we noticed that the ratio of emission intensities ( $F_{416\text{nm}}/F_{456\text{nm}}$ ) varies from 0.52 to 2.05 and it exhibits a good linear response to a Cys concentration change from 0 to  $8.0 \mu\text{M}$  (Fig. 2b). The detection limit of Cys was determined to be as low as 90 nM by a fluorimetric assay (Fig. S8, ESI†). Similarly, the intensity ratio ( $F_{416\text{nm}}/F_{560\text{nm}}$ ) of **P2**– $\text{Ag}^+$  also varies linearly with the concentration of Cys and the detection limit was calculated to be about 150 nM by the titration experiment (Fig. S9, ESI†). These results indicate that the chemosensing complexes are excellent ratiometric fluorescent sensors for Cys



**Fig. 2** Fluorescence spectra of (a) **P1**– $\text{Ag}^+$  and (c) **P2**– $\text{Ag}^+$  upon the titration of Cys. (b) Fluorescence intensity of **P1**– $\text{Ag}^+$  and (d) **P2**– $\text{Ag}^+$  as a function of Cys concentration.  $\lambda_{\text{ex}} = 333 \text{ nm}$ .

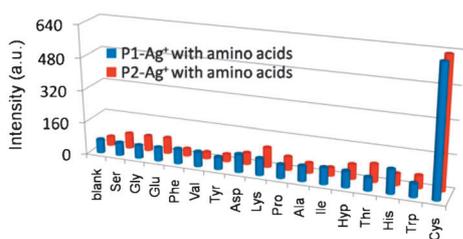


Fig. 3 Amino acid selectivity profiles of **P1**-Ag<sup>+</sup> and **P2**-Ag<sup>+</sup>.

with a high sensitivity. In addition, the fluorescence color changes under a UV lamp can be distinctly observed by the naked eye (Fig. S16, ESI†).

To determine the selectivity of the Cys-sensing systems, the fluorescence responses of **P1**-Ag<sup>+</sup> and **P2**-Ag<sup>+</sup> complexes were further examined with 15 different amino acids. The experiment results show that the other amino acids exhibit only a weak binding affinity to the Ag<sup>+</sup> ion and lead to negligible changes in the emission properties of the complexes. Therefore, Cys can be easily differentiated from other amino acids either by the fluorescence intensity or by the intensity ratio (Fig. 3 and Fig. S12–S15 (ESI†)). For comparison, the interactions of glutathione (GSH) with **P1**-Ag<sup>+</sup> and **P2**-Ag<sup>+</sup> complexes were also studied, which exhibit a similar effect compared to Cys (Fig. S18, ESI†). This phenomenon has been also observed in the previous reports.<sup>18</sup>

The reversibility of the conjugated polymer sensing systems was also examined and the results are shown, respectively, in Fig. S10b and S11b (ESI†). It can be seen that the sensing processes were reversible, and the emission intensity can be well recovered at the cyclic addition of Ag<sup>+</sup> and Cys. The attenuation of emission intensity after several cycles may be a result of the adsorption of the Ag<sup>+</sup>-Cys complex to the cuvette surface. It should be pointed out that all of the fluorescence responses do not exhibit any appreciable time-dependent effects, which makes the detection of Cys more rapid and efficient.

In summary, we have successfully designed and synthesized two novel conjugated polymers containing a 2,2'-biimidazole moiety through the Suzuki coupling reaction, which was demonstrated to be an effective fluorescent sensing platform for ratiometric detection of Ag<sup>+</sup> and cysteine. This is the first example utilizing a fluorescent conjugated polymer-Ag<sup>+</sup> complex to selectively detect Cys with a nanomolar range detection limit and this work provides a new strategy for the development of Cys sensors.

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