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Exploiting an Imidazole-Functionalized Polyfluorene Derivative as a Chemosensory Material

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Considerable interest has been devoted to the design of new receptors for luminescent sensors capable of spying on chemical events due to their potential application in environmental monitoring and biological assays.[1] In the past decade, numerous efforts have been focused on the design and construction of π-conjugated polymer-based sensory materials containing tailored receptors to detect specific species including metal ions, small molecules, and biomolecules due to enhanced sensitivity through sensory signal amplification.[2,3] Recently, to develop new and low-cost materials is the key for metal ion-sensitive chemosensory devices.

Conjugated polymers functionalized with poly(alkyl ether) chains, crown ether, and aza crown ether moieties have been thoroughly investigated through covalently modified systems only for alkali metal ions.[4] For the sensing of other metal ions, conjugated polymers containing oligopyridyl groups exhibit metal ion-dependent ionochromic effects in their absorption and emission spectra.[5] For this type of ligand, especially for the multipyridyl segment, the strong ability to coordinate a large array of metal ions also results in the unsatisfactory selectivity of such sensory systems. Therefore, to investigate novel receptors with various degrees of affinity and selectivity toward transitional metal ions for π-conjugated sensory materials is quite intriguing.

Most recently, the imidazolium receptor has shown a different association ability for negative ions such as F^-, Cl^-, Br^-, and I^-, as well as single-stranded or double-stranded oligonucleotides.[6] In this communication, we present the synthesis and characterization of an alternating polyfluorene copolymer with imidazole ligand as the receptor in the pendent side chains. This new system takes advantage of the effective π-conjugation and strong luminescence properties of the polyfluorene and metal ion-coordinating ability of imidazoles to develop a novel class of highly effective transitional metal-sensitive chemosensors.

The facile approach to **P1**, poly[(9,9-dihexylfluorene-2,7-diyl)-*alt-co*-(9,9-bis[6′-(1-imidazole-yl)hexyl]fluorene-2,7-diyl)], and its model **5** is shown in Scheme 1. **2** was prepared from **1** by reacting with imidazole in anhydrous THF in the presence of an excess of sodium hydride. **3** and **4** were prepared according to our previous reports.[7] Finally, the Suzuki coupling polymerization with $Pd(PPh_3)_4$ as catalyst was employed to produce desired **P1** and **5**. **P1** had the molecular weight (M_n) of 15 600 with polydispersity indice (PD) of 1.63. **P1** was readily dissolved in common organic solvents, such as THF, chloroform, and toluene.

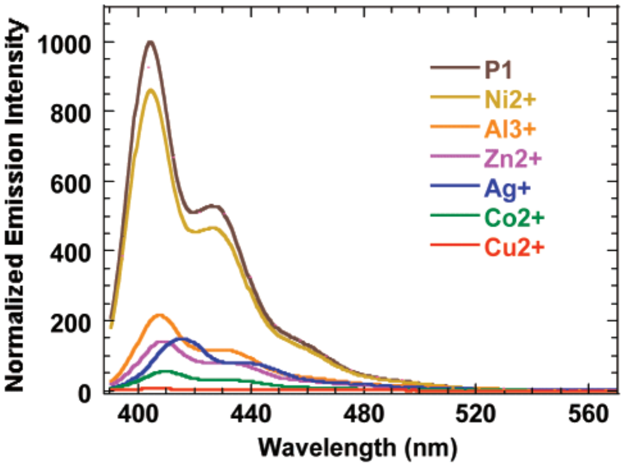

Figure 1. Emission quenching of **P1** by different metal ions. The polymer concentration is fixed at 5×10^{-6} M, corresponding to the repeating unit. The concentration of all metal ions is 1×10^{-4} M.

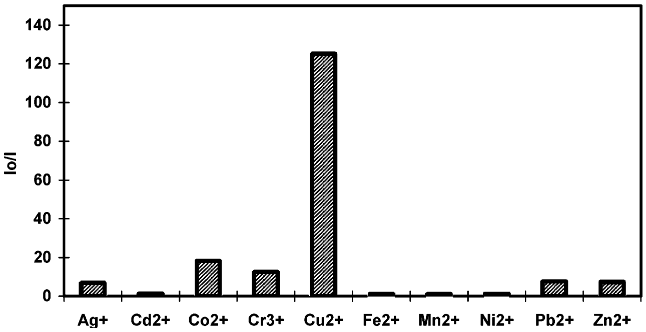

Figure 2. Fluorescence emission response profiles of **P1**.

The UV−vis absorption and photoluminescence (PL) spectra of **P1** in dilute THF solutions (ca. 5 μM) at room temperature are shown in Figure S1 of the Supporting Information. The absorption of **P1** peaked at about 390 nm, which was considerably shifted to longer wavelength in comparison with that of **5** due to addition of effective conjugation length. **P1** peaked at about 404 nm with a shoulder around 425 nm. In comparison with those of poly(9,9-dihexylfluorene), the absorption maximum of **P1** was red-shifted around 10 nm; however, the corresponding PL spectrum hardly changed at all. Such a red shift might due to the high electronic polarizability of proximal imidazole groups. The PL spectrum was obviously red-shifted although the absorption one exhibited behaviors in solid states similar to that in solutions.

P1 had no response upon addition of alkali and alkaline earth metal ions (up to 100 ppm) for either absorption and fluorescence spectra due to the poor coordination ability of the imidazole receptor with these metal ions. Therefore, **P1** exhibited almost no change in the absorption spectrum upon addition of Fe^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+}, and Al^{3+}. However, the addition of Ag^+, Pb^{2+}, Zn^{2+}, Co^{2+}, and Cu^{2+} caused a slight blue shift in absorption spectra of **P1**. For example, we observed the most obvious blue shift (about 7 nm) for Cu^{2+}. It is reasonably understood that the absorption response of **P1** upon addition of metal ions was not as apparent as that of those materials containing acceptors directly in

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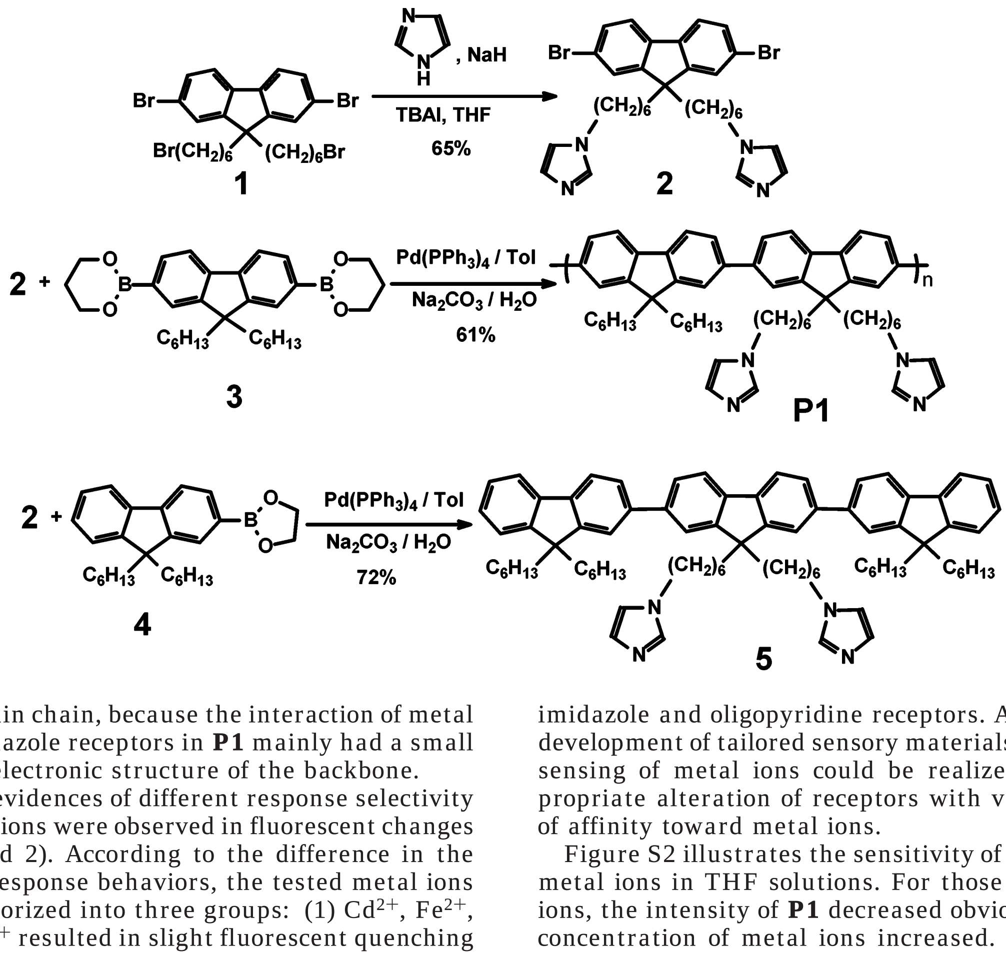
Scheme 1



conjugated main chain, because the interaction of metal ions with imidazole receptors in **P1** mainly had a small effect on the electronic structure of the backbone.

More clear evidences of different response selectivity of **P1** to metal ions were observed in fluorescent changes (Figures 1 and 2). According to the difference in the fluorescence response behaviors, the tested metal ions could be categorized into three groups: (1) Cd^{2+}, Fe^{2+}, Ni^{2+}, and Mn^{2+} resulted in slight fluorescent quenching of **P1**; (2) Al^{3+}, Zn^{2+}, Pb^{2+}, Ag^{+}, Co^{2+}, Sn^{2+}, and Cr^{3+} not only caused a minute red shift (about 3−11 nm) in the PL spectra and but also efficiently quenched fluorescence, but could not completely quench; (3) in the presence of Cu^{2+} (about 1−2 ppm) the fluorescence of **P1** was completely quenched.

Herein, for some specific ions, it was worth noting that the ion responsive property of **P1** was very different from those of traditional oligopyridyl-functionalized conjugated polymers. For example, Ni^{2+} only slightly quenched the fluorescence of **P1** even at a high concentration (100 ppm); however, for those materials with oligopyridine receptors, the fluorescence could be completely quenched by Ni^{2+} at a very low concentration.[4a−f] Such distinct ion responsive behaviors revealed the obvious difference of coordination ability of Ni^{2+} between imidazole and oligopyridine receptors. As a result, the development of tailored sensory materials for selectively sensing of metal ions could be realized through appropriate alteration of receptors with various degrees of affinity toward metal ions.

Figure S2 illustrates the sensitivity of **P1** to different metal ions in THF solutions. For those PL quenching ions, the intensity of **P1** decreased obviously when the concentration of metal ions increased. We also chose Cu^{2+} to investigate the comparison in the quenching between **P1** and its model **5**, as shown in Figure 3. The fluorescence of **P1** was quenched more strongly in the presence of Cu^{2+} than that of **5**. On the basis of the fluorescence titration of **P1** and **5** in THF solutions with Cu^{2+}, their Stern−Volmer constants (K_{sv}) were determined to be 1.2×10^7 and 1.1×10^6 M^{-1}, respectively. These results indicated that the conjugated polymer chain amplified the fluorescence quenching due to facile energy migration along the polymer backbone.

The detection of Cu^{2+} by **P1** in solid states was also studied by dipping the film into aqueous $CuCl_2$ (Figure S3) solutions. After the film was washed with methanol and dried at room temperature, spectral monitoring revealed both a slight blue shift in the absorption spectrum and efficient fluorescence quenching. More-

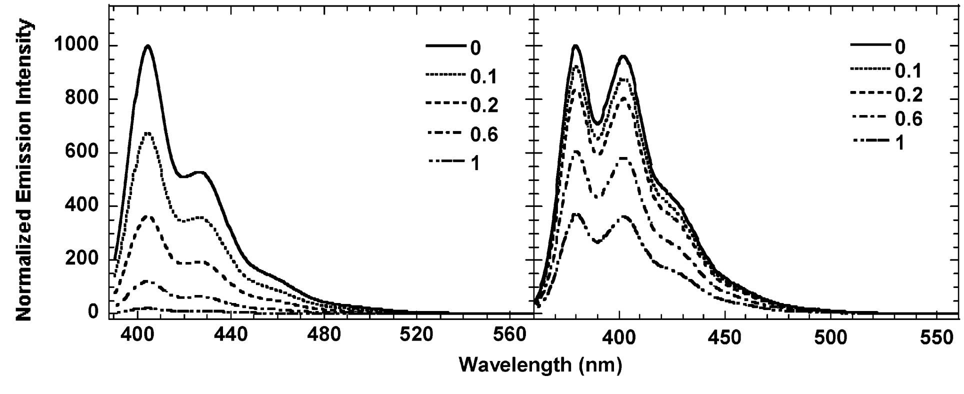


Figure 3. Emission spectra changes recorded upon addition of Cu^{2+} (ppm) to **P1** (5×10^{-6} M, left) or **5** (5×10^{-6} M, right) in THF solutions at room temperature.

over, the emission intensity recovered when the film was immersed in ammonia solutions. This reversibility is important for the practical use of metal-sensor polymers.

In conclusion, we have successfully designed and synthesized a copolymer functionalized with imidazole ligands in the side chain and also investigated its ability to sense metal ions by absorption and emission spectra. The fluorescence of **P1** was efficiently quenched upon addition of Cu^{2+}. The enhanced electronic communication properties of the backbone gave the material significant sensitivity to metal ions compared with **5**. **P1** exhibited good selectivity to transitional metal ions. Its responsive selectivity to transitional metal ions exhibits the difference in comparison with oligopyridyl-functionalized conjugated polymers reported previously. Our results demonstrated that the polymer containing imidazole groups might act as promising active materials for application as fluorescent chemosensors.

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Supporting Information Available: Synthesis and characterization of monomers and polymer and three figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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