

Metal Ionochromic Effects of Conjugated Polymers: Effects of the Rigidity of Molecular Recognition Sites on Metal Ion Sensing

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The effects of the rigidity of molecular recognition sites in fluorene-based conjugated polymers **P1** and **P2** on metal ion sensing have been investigated. The structures of polymers **P1** and **P2** have twisted 2,2'-bipyridine and planar 1,10-phenanthroline units, respectively, which alternate with one fluorene monomer unit. It is found that the absorption and emission bands of 1,10-phenanthroline-based polymer **P2** exposed to metal ions can be red-shifted up to 30 nm, and emission intensity can be quenched up to 100%, depending on metal ions present, which is very similar to that of the 2,2'-bipyridine-based analogue **P1**. However, polymer **P2** shows much higher sensitivity to metal ions than **P1**. The origins of ionochromic effects of the 2,2'-bipyridine-based conjugated polymer due to the metal ion chelation have been attributed to both conformational changes and electron density variations on the polymer chains caused by introducing positively charged metal ions (Chen et al. *J. Phys. Chem., B* 2000, 104, 1950–1960). On the basis of the comparison of **P2** with **P1**, conformational changes are not required in the ion responsive process of the phen ion-recognition unit. We demonstrate that the electron density variations play more important roles in metal ion-induced red-shifts in absorption and fluorescence quenching in photoluminescence.

Introduction

The optical properties of some conjugated polymers can be strongly modified by varying the molecular surroundings, which have been used to develop a new chemosensory system.¹ The conjugated polymers have showed significant sensitivity enhancements (amplification) over small-molecular analogues, due to the energy migration along the electronic delocalized polymer backbone. In this content, conjugated polymers containing a 2,2'-bipyridine (bpy) segment in the backbone have received considerable attention.^{2–4} For instance, bpy-substituted fluorene-based polymers (such as **P1** as shown in Chart 1) exhibit highly ionochromic effects with various transition metal ions. The structures of this kind of polymers have been studied with respect to the effect of properties such as rigidity and effective conjugated length of polymer backbone on the metal ion sensing. The origins of ionochromic effects of bpy-based conjugated polymers have been attributed to the conformational changes in the backbone, which play the most important role, although some other factors, such as electron density and the electronic structures of metal ions, also need to be considered. For the metal-free polymer, the metal ion recognition units, i.e., bpy, may take either a transoid or cisoid conformation. In solution, the rotation of two pyridyls is relatively free; however, a barrier is still present in this C–C rotation. This is why the higher backbone rigidity or solid films give lower response sensitivity. In this paper, we observed the ion-sensing properties of a conjugated polymer composed of a rigidly planar unit 1,10-phenanthroline (phen) (**P2**), which has the same or slightly stronger coordination ability with metal ions compared with 2,2'-bipyridine as molecular recognition sites. A significant improvement in the sensing sensitivity of a phen-based polymer is observed compared with that of a bpy-based polymer. On the

basis of the fact that conformational changes are not required in the ion responsive process of the phen ion-recognition unit, we demonstrate that the electron density variations play more important roles in metal ion-induced red-shifts in absorption and fluorescence quenching in photoluminescence.

Results and Discussion

P1 and **P2** have been synthesized by the Suzuki coupling reaction⁵ between monomer 5,5'-dibromo-2,2'-bipyridine⁶/3,8-dibromo-1,10-phenanthroline⁷ and 2,7-bis(4,4,5,5-tetramethyl-1,3,2,-dioxaborolane-2-yl)-9,9-dihexylfluorene.⁸ Both polymers were purified by precipitation from methanol and acetone, respectively, and obtained as slightly yellow solids. The molecular weight and the number-average molecular weights (M_n) of **P1** and **P2** were determined by gel permeation chromatography (GPC) against the polystyrene as standard to be 11 000 and 13 000 g/mol with the polydispersity index of 1.5 and 1.6, respectively. Both polymers were fully characterized by ¹H NMR and elemental analysis. **P1** and **P2** readily dissolved in aprotic solvents such as THF, chloroform, xylene, and so on. **P1** in THF solution exhibited the absorption λ_{max} at about 380 nm and the emission spectra peaking at about 414 nm with a shoulder at 450 nm. **P2** showed a slight blue-shift both in the absorption and emission spectra compared with that of **P1** (the absorption λ_{max} at about 370 nm and its PL spectra peaked at about 410 nm with a shoulder at 432 nm). The fluorescence efficiencies of both polymers in solution were determined to be over 0.6 by using quinine sulfate solution (0.1 N H₂SO₄) as standard.

Optical ion responsive properties for **P1** were first measured for comparison with the new polymer **P2**. The observed absorption shift and fluorescence quenching of **P1** in THF solution responded to the addition of metal ions and are very

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CHART 1. Structures of P1 and P2. The Molecular Recognition Site Bpy in P1, with a 20° Twist between Consecutive 2,2'-Bipyridine Units Due to *o*-Hydrogen Interactions. The Molecular Recognition Site Phen in P2, with Rigidly Planar Configurations

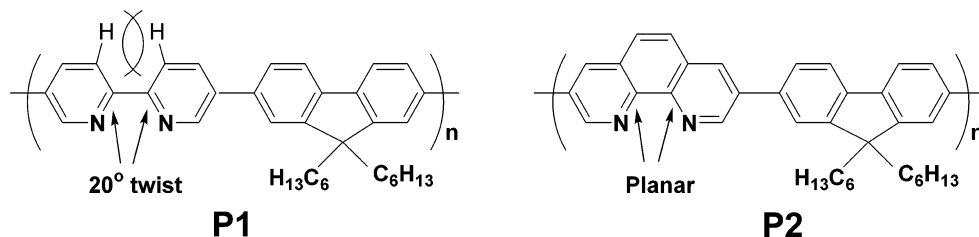


TABLE 1: Optical Responses of Polymer Chelated with Metal Ions

metal ions	P1			P2		
	absorption $\Delta\lambda_{\max}$ (nm)	$\log k_b$	$\log k_{sv}$	absorption $\Delta\lambda_{\max}$ (nm)	$\log k_b$	$\log k_{sv}$
ion-free	380			370		
Ag ⁺	25	3.53	5.75	22	4.43	6.53
Co ²⁺	34	4.85	7.27	26.5	5.46	6.25
Cr ³⁺	21	2.90	3.09	23	3.60	4.17
Cu ²⁺	30	2.89	7.08	32	3.85	6.67
Mn ²⁺	18	4.53	5.31	19	4.63	5.92
Ni ²⁺	24	4.0	8.08	25	4.35	7.02
Zn ²⁺	19	3.00	<i>a</i>	34	5.96	<i>a</i>
Bi ³⁺	≈1	1.46	1.98	8	2.7	4.58
Pb ²⁺	4	3.10	3.00	22	5.62	5.28
Sn ²⁺	≈1	2.78	3.52	36	2.67	5.39
Sr ²⁺	2	4.16	3.71	9	4.08	3.58

^a New emission band appeared.

similar to the results reported by previous authors,⁴ excepting the addition of Cu²⁺. They found that Cu²⁺ just partially quenched the fluorescence of **P1** without a noticeable absorption red-shift. To the contrary, we observe that the Cu²⁺ ion caused a large red-shift (about 30 nm) in the absorption spectrum and produced a strong fluorescence quenching. A special finding is that the anion also influenced the ion responsive properties. For example, 1 ppm CuCl₂ (0.1 M) could cause a nearly 100% fluorescence quenching, while the same amount of CuSO₄ just weakly quenched the fluorescence. This phenomenon may correspond to the different results for the same system observed by different research groups. The counteranion-assisted fluorescence quenching may be caused by the different binding ability of anion to metal cation (or metal complex), which can alter the electronic properties of metal cation (or metal complex). Extensive studies of counteranion-assisted fluorescence quenching for other metal ions and possible sensing capability for counteranions are being conducted and will be reported in a separate paper. We have further tested the coordination ability (dynamic binding coefficient k_b) of each of the metal ions to **P1** and **P2** according to methods reported by Chen et al.³ by using metal-ion concentration-dependent absorption spectra. A quantified fluorescence quenching ability (k_{sv}) of each metal ion to **P1** and **P2** is obtained from Stern–Volmer quenching curves. A more complete set of data resulted from chelation reactions between the polymers and a wide variety of metal ions and are summarized in Table 1.

From ionochromic profiles of **P2** shown in Figure 1 and the data listed in Table 1, the absorption spectra of **P2** exhibit a red-shift upon the addition of the metal ions. For the transition metal ions, the red-shifted wavelengths of **P2** ranged from 19 nm, induced by Mn²⁺, to 34 nm, induced by Zn²⁺, and are very similar to corresponding shifts of **P1** observed by our controlled experiments and by previous authors.⁴ For the heavy main group metal ions, **P2** shows significantly more red-shifted wavelengths

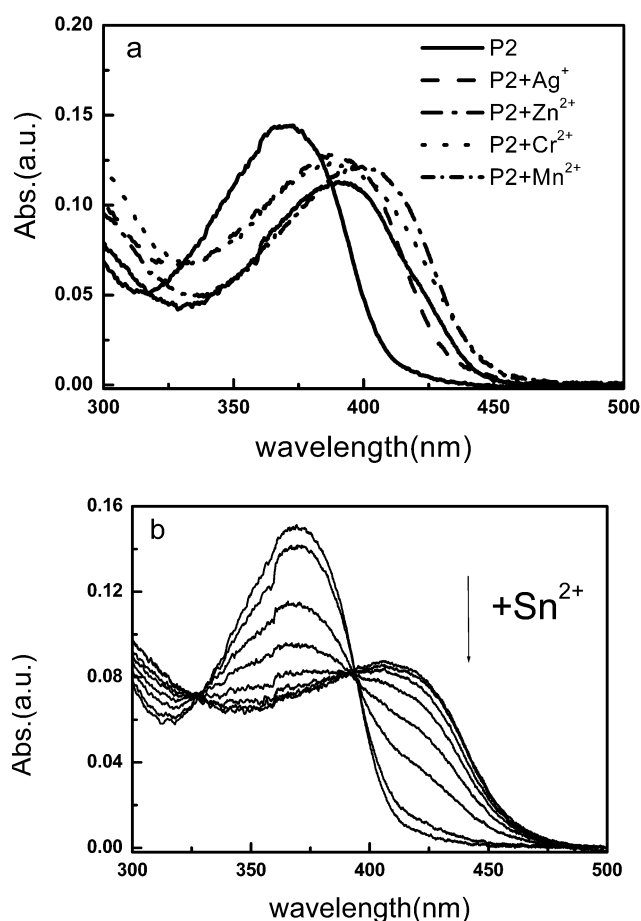


Figure 1. (top) Absorption spectra recorded in THF at room temperature for **P2** upon the addition of varied metal ions. (bottom) The Sn²⁺ ion concentration-dependent absorption spectra of **P2**.

than **P1**, for instance, the absorption maximum ($\Delta\lambda_{\max}$) of **P2** shifts 22 nm for Pb²⁺ and 9 nm for Sr²⁺, while that of **P1** shifts 4 nm for Pb²⁺ and 2 nm for Sr³⁺. On the basis of the results as above, **P2** with rigidly molecular recognition sites still shows the ion-induced red-shifted spectra, which indicates that the conformational change is not a prerequisite for ionochromic effects and also demonstrates that the often favored interpretation of the spectral red-shift of the conjugation enhancement along the polymer backbone induced by the bidentated coordination of metal ions with the 2,2'-bipyridyl units is at very least questionable. In advance, the shift of the absorption spectra for different metal ions and the coordination ability of metal ions to the bipyridyl units (stronger coordination induced a larger spectral red-shift suggested by Liu et al.⁴) have less relationship. A careful measurement of coordination ability of each metal ion to both polymers as shown in Table 1 does not support the previous conclusion, at least a direct relationship between the

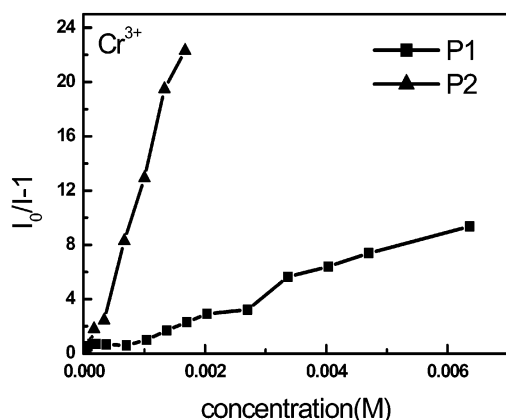


Figure 2. Titration curves of P1 and P2 with Cr^{3+} ions.

k_b and $\Delta\lambda_{\text{max}}$ is ambiguous, especially for transition metal ions. For example, $\log k_b$ of Co^{2+} , Mn^{2+} , and Cu^{2+} binding to P2 are 5.46, 4.63, and 3.85, respectively, the corresponding $\Delta\lambda_{\text{max}}$ are 26.5, 19, and 32 nm; it is clear that a large red-shift does not correspond to a strong coordination ability. For some metal ions, for example, Ag^+ , the values of $\log k_b$ of binding to P2 (4.43) are larger than those of binding to P1 (3.53), but $\Delta\lambda_{\text{max}}$ of the former (22 nm) are found to be slightly lower than those of the latter (25 nm). The observations strongly indicate that the conformational changes and coordination ability of metal ions to the polymers are not the key role of $\Delta\lambda_{\text{max}}$. In contrast, each metal ion and its complex with polymers having a solitary electronic structure and energy level are like to be determinant for ionochromic effects ($\Delta\lambda_{\text{max}}$).

Ion-responsive properties of both polymers measured by fluorescence emission spectra are also informative. The fluorescence of P2 can be completely quenched by the addition of metal ions with different concentration depending on the metal ions used, with the exception of Zn^{2+} , which induced a new emission peak. The fluorescent titration curves of P1 and P2 upon the addition of Cr^{3+} are shown in Figure 2. The fluorescent quenching coefficient k_{sv} can be calculated from the slope of the titration curve according to the Stern–Volmer equation:

$$I_0/I = 1 + k_{\text{sv}}C \quad (1)$$

where I_0 and I are the fluorescent intensity of metal-free polymer and the metal-chelated polymer and C is the metal ions concentration. More k_{sv} data for each of metal ions are summarized in Table 1. For all metal ions, we find that the fluorescence of P2 is more efficiently quenched by the additions of metal ions than that of P1. The k_{sv} of P2 is increased by two times in magnitude for main group metal ions, and one time in magnitude for transition metal ions than that of P1. The fluorescence quenching of polymers by the metal ions is most likely caused by energy or electron-transfer reactions between the polymer backbone and binding metal complexes, which is a nonradiative center and traps the excitation energy passing through them. Thus, k_{sv} can be disassembled as the following three factors:

$$k_{\text{sv}} \propto k_b k_t k_n \quad (2)$$

where k_b is the binding coefficient of metal ions to polymer, k_t is the energy or electron-transfer rate of polymer to metal complexes, and k_n is the nonradiative rate of metal complexes. Accordingly, stronger coordination ability corresponds to a larger k_{sv} . It is thus reasonable that for each metal ion, P2 shows improved quenching response compared with P1, which is due

to the stronger binding ability of metal ions to P2 than that to P1. At the same time, the k_t and k_n are also important for fluorescence quenching, contributing to the difference in quenching behaviors of different metal ions with similar binding ability. For instance, Mn^{2+} ($\log k_b = 4.63$) and Ni^{2+} ($\log k_b = 4.36$) ions show the closed binding ability to P2, but the k_{sv} of Ni^{2+} ion ($\log k_{\text{sv}} = 7.02$) is showed to be over 10 times larger than that of Mn^{2+} ion ($\log k_{\text{sv}} = 5.92$). Sometimes, metal ions with low binding ability, for example, Cu^{2+} ($\log k_b = 3.85$), still show strong fluorescence quenching ($\log k_{\text{sv}} = 6.67$). Up to now we cannot give a complete and quantitative interpretation for the specific sensing behaviors of the polymer for each metal ion, for which a direct measurement of the k_t and k_n of metal polymer complexes and corresponding small molecular metal complexes are probably required by using, for example, time-resolved spectra techniques; however, it is clear that k_t and k_n are related to the electronic structure and excited-state properties of metal complexes. In this content, metal ions with an open shell electronic structure, which generally show the strong metal–ligand orbital interaction to form low-lying metal-to-ligand (ML) or ligand-to-metal (LM) charge transfer state, may exhibit a highly quenching response as in the case of Ni^{2+} with d^8 electronic structure and Cu^{2+} with d^9 electronic structure. Metal ions with a full-occupancy outer-shell orbital or half-occupancy outer-shell orbital, which generally show the weak metal–ligand orbital interaction, may exhibit a low quenching response as in the case of Zn^{2+} (d^{10}) and Mn^{2+} (d^5). The P2 upon addition of Zn^{2+} ion still shows strong fluorescence, but the emission spectrum is red-shifted to 30 nm compared with that of metal-free P2. We attribute this newly-generated emission state to Zn^{2+} -induced intraligand $\pi-\pi^*$ transition. The Zn^{2+} –P2 complexes with emission efficiency as high as the metal-free P2 (64%) exhibit obvious potential for luminescence-based applications, for example, an electroluminescent device. From a practical viewpoint, it is interesting to develop the solid-state metal ion sensor, but most of these conjugated polymer systems have only shown the properties in solution. This is because the transduction mechanisms imply conformation modification of the polymer main chain, but the conformation changes for the polymer are generally considered not to occur as readily in the solid state as in solution. Consequently, a metal ion-responsive polymer without the conformation modification as shown in our presented polymer P2 may be useful for developing solid-state optical sensors.

In conclusion, effects of the rigidity of molecular recognition sites on metal ionochromic effects of conjugated polymers P1 and P2 are reported. P2 with rigidly molecular recognition sites phen shows higher sensing sensitivity to metal ions than P1 with twisted bipyridine as molecular recognition sites, especially for fluorescence quenching. The results suggest the use of rigid units as molecular recognition sites in the conjugated polymer chemosensors for achieving higher sensing sensitivity. On the basis of the fact that conformational changes are not required in the ion responsive process of the phen ion-recognition unit, we demonstrate that the electron density variations of polymer induced by metal ion coordination are the predomination of metal ionochromic effects. The coordination ability and fluorescence quenching ability of each metal ion to both polymers are measured by metal ion concentration-dependent spectral changes. The results suggest that coordination ability plays less important roles in metal ion-induced red-shifts in absorption bands, but more important roles in fluorescence quenching ability. The study presented herein has, to a certain degree, elucidated the nature of metal ion and polymer interactions and

demonstrated a new approach to improving the metal ion sensing properties of conjugated polymer.

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Supporting Information Available: Complete experimental details, absorption, and PL spectra of metal-free polymers and metalated polymers, and the calculated method of k_b . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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