

Zinc(II)-Induced Color-Tunable Fluorescence Emission in the π -Conjugated Polymers Composed of the Bipyridine Unit: A Way to Get White-Light Emission

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A series of fluorene and bipyridine (bpy) copolymers were synthesized, and their optical properties were investigated in the presence of zinc(II). By adjusting the bpy content in the polymer backbone, the emitting color of the polymer solution could be tuned from initial blue to green to white and violet when it interacted with zinc(II) ions. The counteranions of zinc(II) ions were also found to influence the optical properties of copolymers greatly.

π -conjugated polymers composed of chelating ligands in the backbones have attracted much attention recently because they provide an easy way to tune the optical and electronic properties of the conjugated polymers through metal ion chelation.^{1–5} Studies of metal ions' interactions with poly(phenylenevinylene) (PPV)- and polyfluorene (PF)-type copolymers that contain metal ion binding sites, such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen), showed a strong ionochromic effect and demonstrated a new approach to sensitive, selective, and highly reversible ion-responsive polymers for metal ion sensors.^{6–8} Most metal ions would quench the fluorescence of polymers; however, closed-shell metal ions, such as the zinc(II) ion, were found to increase the photoluminescence quantum yields⁹ and change the emission colors.¹⁰ Recently, Yamamoto's group reported a soluble blue-light-emitting polymer composed of alternating 1,10-phenanthroline and 2,5-didodecyloxybenzene, and its optical properties could be tuned by metal complexes.^{11,12} The colors of the emitting light from these polymers could be tuned from blue to green and red by using different metal ions such as Zn^{2+} (green), Li^+ (green), Al^{3+} (yellow), and Eu^{3+} (red). Though current studies of metal ions' interactions with π -conjugated polymers are usually performed in solution, they show potential application as color-tunable electroluminescence materials because both conjugated polymers and the metal complexes are expected to be good materials for organic light-emitting devices (OLEDs). For the application of these hybrid materials composed of organic compounds and metal complexes, the controlled binding fashion and number of binding metal ions in polymer backbones are very important, and in principle, the number of binding metal ions depends on the number of binding sites in polymer backbones because the metal ions are in excess in solution. Aimed at revealing the effect of the number of binding metal ions on the optical properties of conjugated polymers, a series of fluorene-based copolymers that contain different numbers of bpy units in backbones were synthesized, and their optical properties, such as zinc(II) binding in solution,

were studied. Interestingly, we investigated white-light emission as zinc(II) binding to the polymer with low bpy content. This spectrum contained the emission band from the polymer backbone, and zinc(II) induced a new energy level due to incomplete energy transfer. Counteranions such as NO_3^- and OAc^- were also found to influence the optical properties of zinc(II) binding polymers. Herein we reported the results.

In this letter, $(\text{P})(\text{bpy})_x$ ($x = 0.1, 0.2$, and 0.5) is used as the representation of the series of fluorene and 2,2'-bipyridine copolymers, in which the x is the molar ratio of 2,2'-bipyridine to the corresponding copolymer. The structures of $(\text{P})(\text{bpy})_x$ ($x = 0.1, 0.2$, and 0.5) are shown in Figure 1, and the synthetic procedures and characterizations have been reported previously.¹³ The polymers were obtained in high yields as a slightly yellow solid exhibiting intense luminescence and could be well dissolved in common organic solvents at room temperature. The number-average molecular weight (M_n) and M_w/M_n of $(\text{P})(\text{bpy})_x$ were 9400–14000 and 1.5–1.6, respectively, as determined by GPC using polystyrene (PS) as a standard. In tetrahydrofuran (THF) solution, this series of polymers had similar optical properties and only a small blue shift in the PL and UV spectra (see Supporting Information) with increasing amounts of bpy. The absorption λ_{max} was at about 382 nm, and the emission spectral peak was at about 417 nm with a shoulder at 440 nm. They all emitted bright blue light and had similar fluorescence efficiencies of about 0.6, determined by using quinine sulfate solution (0.1 M H_2SO_4) as a standard in THF solution.

In the experiment, when $\text{Zn}(\text{NO}_3)_2$ was gradually adding to the polymer solution, the apparent color of the solution changed from nearly colorless to light yellow. From zinc(II) titration curves presented in Figure 1, the obvious ionochromic effects were observed. The binding of zinc(II) caused red shifts of the absorption spectra relative to those of the metal-free polymers. In contrast to no obvious change in the absorption spectra of zinc(II) mixing with PF (without bpy binding sites) solution, the absorption spectra of $(\text{P})(\text{bpy})_x$ regularly varied after zinc(II) addition, indicating the occurrence of a chelating reaction between zinc(II) and the bpy unit. All of the absorption spectra

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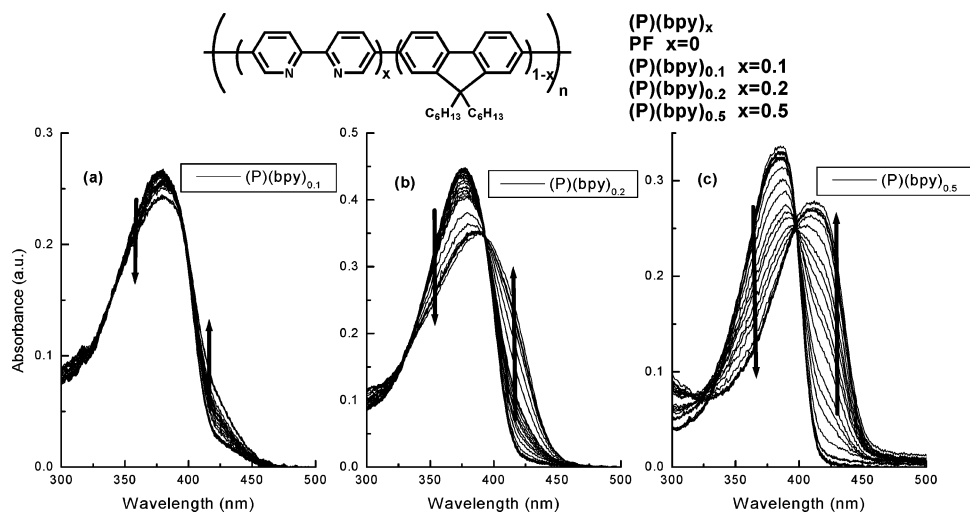


Figure 1. Structural formula and titration curves of polymers.

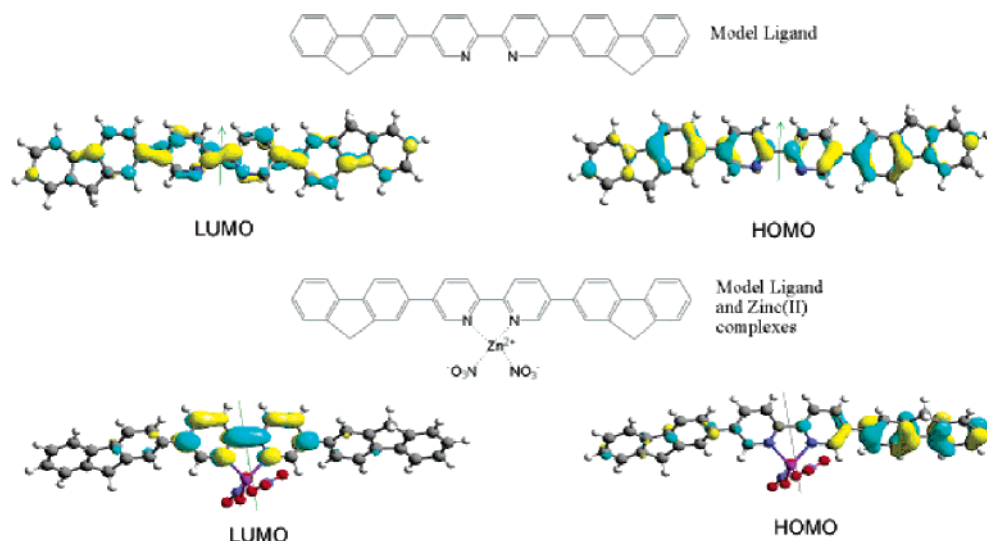


Figure 2. Contour plots of calculated HOMO and LUMO orbitals of the model compound and its zinc(II) complex, with the corresponding molecular formulas shown above.

had only one isosbestic point, which suggested that there existed only one binding state and most likely a bidentate binding structure, viz., zinc(II) chelation with both nitrogen atoms of a bpy group.^{7,11–12}

To reveal the nature of the red shift in the absorption spectra caused by zinc(II) chelation, a quantum chemical calculation was performed on the simplified model compound, difluorene-substituted bipyridine, before and after zinc(II) chelation⁹ (see Supporting Information). From electron clouds of HOMO and LUMO shown in Figure 2, we found that zinc(II) did not participate in the formation of frontier molecular orbitals (MOs) but induced a redistribution of the electron cloud density of the frontier MOs. The electron clouds of the HOMO and LUMO extended mostly across the whole fragment for the metal-free compound, but for the zinc(II) chelation compound, the electron clouds of HOMO and LUMO were found to localize on fluorene and bpy units, respectively, indicating a charge-transfer (CT) excited-state characteristic in the zinc(II) chelating compound. The calculation for energy gap ΔE ($E_{\text{LUMO}} - E_{\text{HOMO}}$) demonstrated that the energy levels of the entire set of MOs dropped greatly because of zinc(II) chelation, and a simultaneous reduction in energy gap ΔE ($E_{\text{LUMO}} - E_{\text{HOMO}}$) happened. Thus, the lower-energy gaps ΔE for the lowest-energy transition (HOMO \rightarrow LUMO) resulted in the red shift of absorption peak,

and the computed red-shift value of about 30 nm was in good agreement with the experimental investigation.

Figure 3 shows the PL spectra of (P)(bpy)_x and (P)(bpy)_x in the presence of an excess of Zn(NO₃)₂ in THF solution. (P)(bpy)_x showed a strong blue emission that was assigned to the π - π^* transitions of the copolymer backbone. After zinc(II) ion chelation, a significant decrease in the blue emission combined with an increase in a new emission at about 500 nm was observed. The intensity of the new emission depended on the bpy content of the polymer backbone (i.e., more bpy units in the polymer backbone), with the stronger the emission at 500 nm. Meanwhile, the wavelength (λ_{em}) of the new emitting band was also dependent on the bpy content in the polymer backbone (i.e. $\lambda_{\text{em}} = 531$ nm for (P)(bpy)_{0.1}, $\lambda_{\text{em}} = 521$ nm for (P)(bpy)_{0.2}, and $\lambda_{\text{em}} = 493$ nm for (P)(bpy)_{0.5}, with a tendency toward a blue shift in wavelength as the bpy content increases in the polymer backbone). The new emission band could be assigned to a newly induced energy level by zinc(II) chelation. The shift of this new emitting band along with the variation in the amount of bpy is reasonable if the bpy unit is considered to be a ligand in the zinc(II)-polymer complex. It may exhibit more extending π -conjugation when a bpy unit is linked with more fluorene units; consequently, a lower emission energy (red shift) of the resultant complex in the case of Zn-(P)(bpy)_{0.1} was observed.

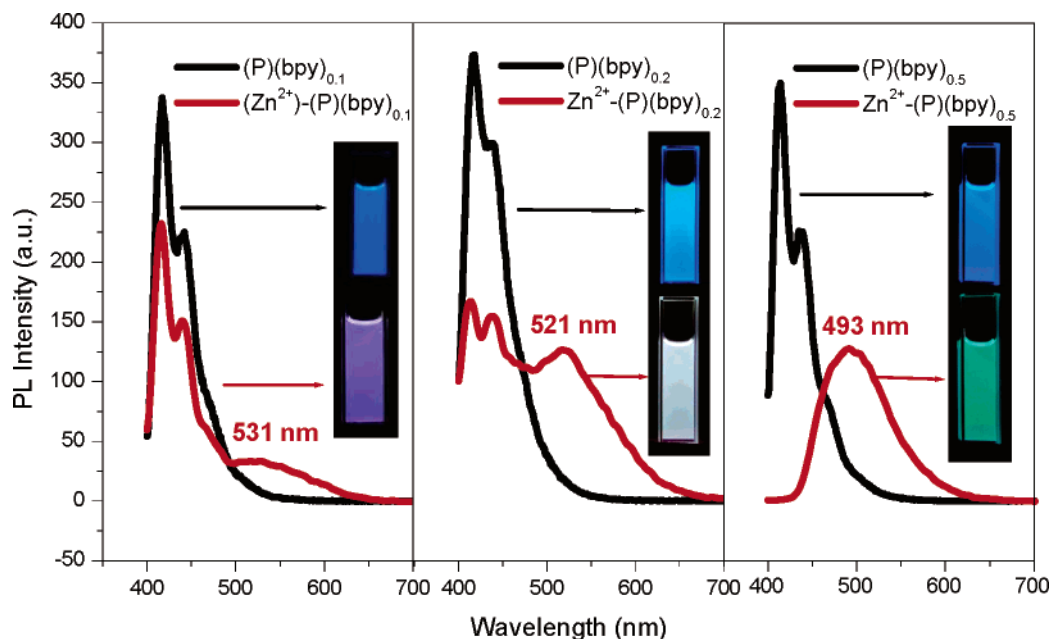


Figure 3. Photoluminescence spectra of $(P)(bpy)_x$ and zinc(II)- $(P)(bpy)_x$ (excess zinc(II)) in THF solution were excited at 380 nm and the spectra were normalized. The colors of light emission from the polymers before and after $Zn(NO_3)_2$ chelation were recorded by photographs under UV light irradiation.

This good tuning of λ_{em} from the metal binding site may operate with the observed color-tunable characteristics more or less. For polymer $(P)(bpy)_{0.5}$ with the highest bpy content in the backbone, green-light emission was observed with zinc ion chelation, and the original blue-light emission band had completely disappeared. For polymers $(P)(bpy)_{0.1}$ and $(P)(bpy)_{0.2}$ with relatively low bpy content, emission bands from both polymer backbone and zinc(II) that induced a new energy level could be observed, and interestingly, $(P)(bpy)_{0.2}$ emitted a bright white light with a PL yield of about 0.3 as zinc(II) chelation. Apparently, this was due to the incomplete energy transfer from polymer backbone to zinc(II), which induced new emission, and a matching of both intensities and wavelengths (a blue $\lambda_{max} = 417$ nm and a yellow $\lambda_{max} = 521$ nm) of emission bands produced white-light emission. To our knowledge, there are very few materials that can emit white light by themselves.^{14,15} This metal-conjugated polymer complex provides an easy way to get white-light emission. It may have the advantage of stability, especially in color purity, because the optical properties of a molecule or polymer should be more stable than those of the mixture of two or three types of molecules.^{16–18}

Upon further investigation, we found that the counteranions also dramatically impact the resultant emission colors, and this anion effect is shown in Figure 4. In the experiment, excess $Zn(NO_3)_2$, $ZnCl_2$, $ZnSO_4$, and $Zn(OAc)_2$ were added to the solution of $(P)(bpy)_{0.5}$, and the spectra were normalized at the new emission peaks. From the spectra, completely energy transfer from the polymer backbone to the zinc(II) induced a new energy level that can be observed for all kinds of zinc salts, with the original emission peaks disappearing and only the new emission peaks existing. However, counteranions of zinc salts made a difference in the wavelengths of the new emission peaks; they were at 493, 490, 473, and 468 nm for $Zn(NO_3)_2$, $ZnSO_4$, $ZnCl_2$, and $Zn(OAc)_2$ in turn. The maximal shift was up to 20 nm between $Zn(NO_3)_2$ and $Zn(OAc)_2$, which could induce dramatic variation in the emitting colors. In Figure 5, the emission spectra of $Zn(NO_3)_2$ and $Zn(OAc)_2$ occupied copolymers as well as the resulting different emitting colors were contrasted. In the case of $Zn(OAc)_2$, the red-light element in

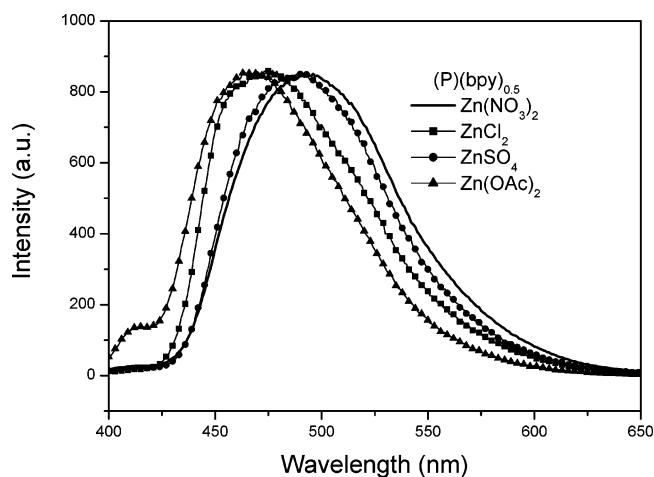


Figure 4. Photoluminescence spectra of $(P)(bpy)_{0.5}$ in THF solution in the presence of excess zinc salts $Zn(NO_3)_2$, $ZnCl_2$, $ZnSO_4$, and $Zn(OAc)_2$. The spectra were excited at 380 nm and were normalized.

the new rising peaks was relatively lacking and could not compete with the original color, so $Zn(NO_3)_2$ and $Zn(OAc)_2$ could induce completely different emitting colors in all three copolymers in solution. For example, in $(P)(bpy)_{0.5}$ a pure green-light emission could be observed in the case of $Zn(NO_3)_2$ chelation, but only light-blue emission could be observed in the case of $Zn(OAc)_2$. The effect of different counteranions on luminescent properties can be ascribed to the different coordinating abilities between the counteranion and zinc(II). Generally, the cations and anions are not uniformly distributed in solution because of the electrostatic interaction between oppositely charged ions. The net charge quantities of zinc cations depend on the average distance between zinc cations and counterions, which is determined by the ionization equilibrium coefficient of zinc salt in solution. Accordingly, zinc(II) may possess more net charge in the case of NO_3^- as the counterion because of the larger ionization equilibrium coefficient of $Zn(NO_3)_2$ in solution, and it is reversed when OAc^- is the counterion because of the more covalent bond property of the zinc acetate bond. The theoretical investigation of the zinc(II) chelating compound

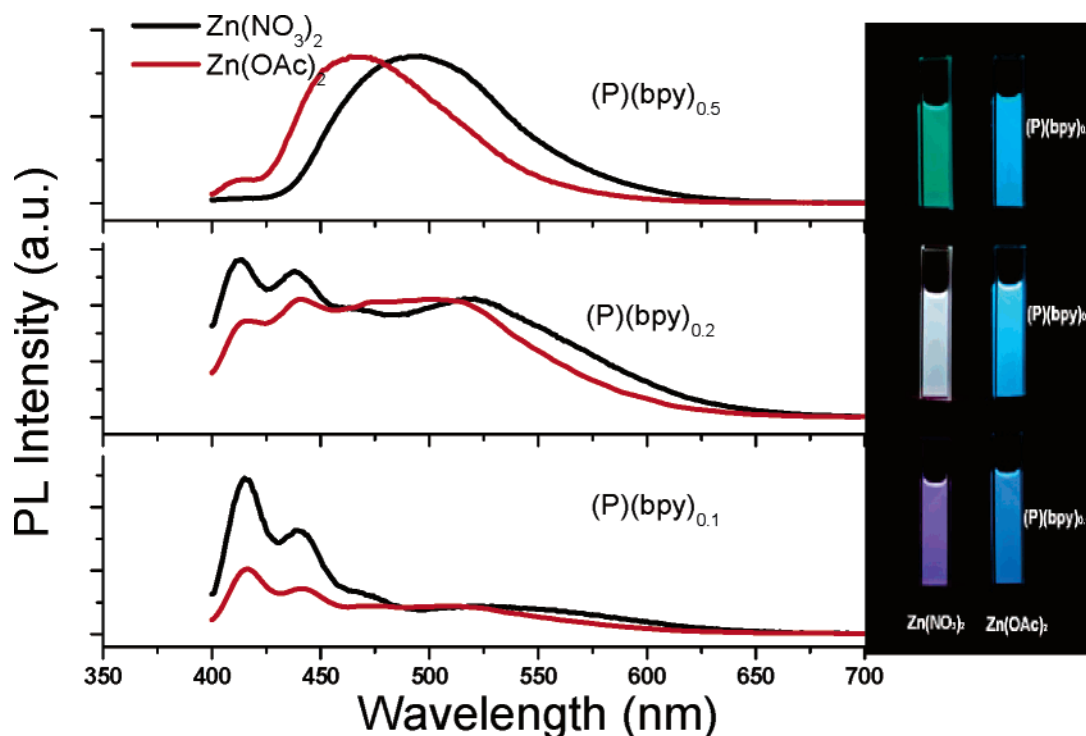


Figure 5. (Left) emission spectra of $\text{Zn}(\text{NO}_3)_2$ - and $\text{Zn}(\text{OAc})_2$ -occupied $(\text{P})(\text{bpy})_x$, which were all normalized at the new induced peaks. (Right) photographs of emission colors from polymers interacting with different zinc salts.

(Supporting Information) suggested that, when using a point charge instead of the zinc(II) ion, increasing the charge of zinc(II) lowered the HOMO–LUMO band gaps, which was in agreement with experimental results. The positive charges of zinc(II) are counteracted by anions to a different degree and, they exhibit different net charges, which may be the nature of the anion effect.

In conclusion, the color modulation effect over a wide range was observed in the conjugated polymers interacting with the zinc(II) ion. The resultant emission colors were found to depend on the number of chelating units in the polymer backbone and also on the counteranions. Because both conjugated polymers and the metal complexes were expected to serve as good materials for OLEDs, the combination of these two kinds of materials should show potential application as color-tunable and white-light-emitting electroluminescence materials. We demonstrate that the counteranion effect may be a very important factor in adjusting the coordination stability between zinc(II)- and bpy-containing copolymers.

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Supporting Information Available: General experimental procedure, metal ion titration method, PL and UV spectra of polymers without zinc(II) chelation, optical properties summarization, molecular simulation method, simulation of absorption spectra, and theoretical investigation of the counteranion effect. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (18) The mixture of two or three types of molecules is a more frequently used method to get white light, but the change in intermolecular interaction and phase separation can result in a variety of optical properties.