Synthesis, Metal Complex Formation, and Electronic Properties of a Novel Conjugate Polymer with a Tridentate 2,6-Bis(benzimidazol-2-yl)pyridine Ligand

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ABSTRACT: This paper reports the synthesis and physical properties of a novel aromatic polymer which contains the tridentate 2,6-bis(benzimidazol-2-yl)pyridine moiety. It was found that the polymer exhibits different luminescence properties in solution and in the solid state because of the formation of polymer aggregates. Upon doping with iodine, the electrical conductivity of the polymer film was increased to 2.4×10^{-6} S/cm. The polymer was fabricated into a single-layer light-emitting device, and yellow light emission was observed under forward bias. Besides, it is able to form complexes with ruthenium, and the resulting polymer−metal complexes exhibit different solubilities and physical properties. The ruthenium complexes strongly enhance the absorption and photosensitivity beyond 500 nm due to the presence of the metal−ligand charge-transfer transitions. As a result, a large photocurrent response was observed when the polymer was irradiated with visible light. On the other hand, there was no electroluminescence in the metal-containing polymers because of the intrinsic nonemitting properties in ruthenium terpyridine complexes.

Introduction

The potential applications of ruthenium(II) complexes in molecular photochemical devices for energy conversion and photoinduced electron transfer have been studied extensively in the past decades.[1] Most studies were focused on molecular complexes based on bidentate and tridentate ligands such as 2,2′-bipyridine (bpy), 2,2′:6′,2″-terpyridine (tpy), and other nitrogen-containing heterocycles.[2] The chemical, electrochemical, and photochemical properties of the corresponding tris(bipyridyl)ruthenium(II), $[Ru(bpy)_3]^{2+}$, and bis(terpyridyl)ruthenium(II), $[Ru(tpy)_2]^{2+}$, type complexes are well documented. On the other hand, the use of the polymer backbone as the coordination site for metal complexation has received relatively less attention. There have been several reports of incorporating the ruthenium polypyridine complexes into polymer matrixes. Different types of polymers based on ruthenium polypyridine complexes have been prepared.[3] In our continuous efforts of developing metal-containing polymers for optoelectronic applications, we have synthesized several types of conjugated polymers which contain ruthenium bipyridine or terpyridine complexes.[4] It has been shown that the ruthenium complexes can play different roles in certain electronic and photonic processes. They are efficient photosensitizers in photoconduction processes because they exhibit a characteristic spin allowed $d-\pi^*$ metal-to-ligand charge transfer (MLCT) transitions in the vicinity of 500−600 nm. As a result, the absorptive region of the polymer is extended beyond the main chain absorption. In addition, the metal complexes are also potentially charge carriers in the charge transport process as they usually exhibit a reversible $Ru^{II,III}$ oxidation process and a number of reversible reductive ligand-centered processes.[5] Recently, we have synthesized a series of thermally stable heterocyclic poly(benzobisoxazole)s and poly(benzobisthiazole)s based on 2,2′-bipyridine[6] which can form complexes with ruthenium. The resulting polymer−metal complexes exhibit good thermal stabilities and can be processed into thin films for various optical and electronic characterizations.

In this paper, we report the synthesis of a novel conjugate polymer based on the tridentate 2,6-bis(benzimidazol-2-yl)pyridine ligand by the polymerization reaction between pyridine-2,6-dicarboxylic acid and 3,3′-diaminobenzidine tetrahydrochloride in the presence of polyphosphoric acid. Different kinds of chiral or achiral bis(oxazolinyl)pyridine derivatives have been reported in the literature.[7] When coordinated to transition metals such as ruthenium,[8] rhodium,[9] or copper,[10] the resulting complexes exhibit specific catalytic activities, and they are potentially useful in asymmetric synthesis. Our new polymer can act as the precursor for various types of polymer−metal complexes with potential applications in catalysis, photonics, and electronics. In this work, the polymer formed complexes with ruthenium and the photoconductivity, luminescent, and light-emitting properties of the polymers and polymer−metal complexes have been studied.

Experimental Section

Materials. *N*-Methyl-2-pyrrolidinone (NMP) and *N*,*N*-dimethylformamide (DMF) were distilled over calcium hydride under reduced pressure. Phosphorus pentoxide, phosphoric acid, pyridine-2,6-dicarboxylic acid (**1**), *o*-phenylenediamine (**2a**), 2-aminothiophenol (**2b**), and ruthenium trichloride trihydrate ($RuCl_3{\cdot}3H_2O$) were purchased from Lancaster Synthesis Ltd. and were used as received. 3,3′-Diaminobenzidine tetrahydrochloride dihydrate was purchased from Aldrich Chemical Co. and was recrystallized from 4 N hydrochloric acid. 2,6-Bis(2-benzimidazol-2-yl)pyridine (**4a**)[7a] and 2,6-bis(2-benzothiazolyl)pyridine (**4b**)[7b−c] were prepared according to the literature procedures by the reaction between **1** and **2a** or **2b** in the presence of polyphosphoric acid.

Instruments. ^1H and ^{13}C NMR spectra were collected on a Bruker 300 DPX NMR spectrometer. FTIR spectra (KBr pellet) were collected on a Bio-Rad FTS-7 FTIR spectrometer. Mass spectrometry was performed on a high-resolution Finnigan MAT-95 mass spectrometer. UV−vis spectra were collected on a HP 8452 spectrometer. Thermal analyses were performed

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on a Perkin-Elmer DSC7 and a TGA7 thermal analyzer with heating rates of 10 and 15 °C/min, respectively. The viscosity measurements were performed in a constant-temperature bath (30 °C) using an Ubbelohde viscometer, with a solution concentration of 0.5 g/dL in NMP.

2,6-Bis(2-benzimidazol-2-yl)pyridine Ruthenium Trichloride (5a). A solution of $RuCl_3{\cdot}3H_2O$ (0.21 g, 1.0 mmol) in ethanol (20 mL) was added to a hot solution of **4a** (0.31 g, 1.0 mmol) in ethanol (30 mL). The resulting brown solution was heated under reflux for 3 h and then cooled to room temperature. The brown solid was filtered, washed with ethanol and ether, and dried in a vacuum for 1 day (76% yield). FTIR (KBr pellet): $\nu = 3300-2800$ (N−H stretching), 1655 (imidazole C═N stretching), 1606 cm^{-1} (pyridine C═N stretching). FABMS: *m*/*e* 483 ($M^+ - Cl$); $C_{19}H_{13}N_5RuCl_2$ requires *m*/*e* 483.3.

2,6-Bis(2-benzothiazolyl)pyridine Ruthenium Trichloride 5b. It was prepared according to the same procedure as in **5a** except that dioxane was used as the solvent. The product was isolated as a dark brown solid (77% yield). FTIR (KBr pellet): $\nu = 1655$ (imidazole C═N stretching), 1605 cm^{-1} (pyridine C═N stretching). FABMS: *m*/*e* 518 ($M^+ - Cl$); $C_{19}H_{11}N_3S_2RuCl_2$ requires *m*/*e*: 517.4.

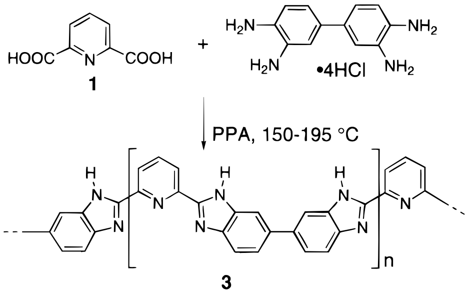
Complex 6a. A solution of **4a** (0.31 g, 1.0 mmol) in DMF (15 mL) was added to a hot solution of **5a** (0.52 g, 1.0 mmol) in DMF (5 mL). The solution was heated at 100 °C for 1 day under a nitrogen atmosphere. After the solution cooled to room temperature, diethyl ether (100 mL) was added to the reaction mixture, and the dark brown precipitate was collected by suction filtration. The product was purified by dissolving the solid in acetonitrile and reprecipitated in diethyl ether. The metal complex was dried under vacuum at 50 °C for 1 day (67% yield). ^{1}H NMR (DMSO-d_6): $\delta = 13.08$ (s, 4 H), 8.97 (d, $J = 8.1$ Hz, 4 H), 8.85 (t, $J = 7.8$ Hz, 1 H), 7.64 (d, $J = 8.2$ Hz, 4 H), 7.29 (t, $J = 7.7$ Hz, 4 H), 7.08 (t, $J = 7.7$ Hz, 4 H), 6.11 (d, $J = 8.2$ Hz, 4 H). ^{13}C NMR (DMSO-d_6): $\delta = 152.0$, 150.0, 141.0, 137.2, 133.9, 125.8, 124.9, 122.9, 115.0. FABMS: *m*/*e* 723 ($M^+ - 2Cl$); $C_{38}H_{26}N_{10}Ru$ requires *m*/*e* 723.8.

Complex 6b. It was synthesized by the reaction between complex **5b** and **4a** in DMF using the same procedure as in complex **6a** (63% yield). ^{1}H NMR (DMSO-d_6): $\delta = 9.36$ (d, $J = 7.7$ Hz, 2 H), 8.93 (d, $J = 7.9$ Hz, 2 H), 8.67 (m, 3 H), 8.57 (d, $J = 8.3$ Hz, 2 H), 8.30 (d, $J = 8.1$ Hz, 2 H), 8.05 (m, 3 H), 7.90 (t, $J = 7.7$ Hz, 2 H), 7.54 (t, $J = 7.5$ Hz, 2 H), 7.40 (t, $J = 7.8$ Hz, 2 H). ^{13}C NMR (DMSO-d_6): $\delta = 165.7$, 164.4, 154.2, 151.8, 151.4, 150.3, 142.3, 141.3, 133.8, 133.3, 129.7, 128.9, 127.1, 126.3, 125.6, 125.2, 124.7, 124.4, 121.7, 113.2. FTIR (KBr pellet): $\nu = 1638$ (imidazole C═N stretching), 1603 (pyridine C═N stretching) cm^{-1}. FABMS: *m*/*e* 757 ($M^+ - 2Cl$); $C_{38}H_{24}N_8S_2Ru$ requires *m*/*e* 757.9.

Synthesis of Polymer 3. 3,3′-Diaminobenzidine tetrahydrochloride dihydrate (1.85 g, 5.0 mmol) was added to a freshly prepared polyphosphoric acid solution (10 g, 75% P_2O_5 content) at 80 °C. The mixture was stirred at 80 °C for 24 h under nitrogen atmosphere and then for 24 h under reduced pressure until no more gas bubbles were evolved. Pyridine-2,6-dicarboxylic acid (**1**) (0.84 g, 5.0 mmol) and phosphorus pentoxide (14.5 g) were then added to the reaction mixture. The resulting slurry (83% in P_2O_5 content with 6 wt % of polymer) was heated at 150 °C for 24 h, 160 °C for 24 h, 185 °C for 24 h, and finally 195 °C for 24 h. The viscous polymer solution was poured into hot water, and the mixture was stirred vigorously for 1 h. The solid was filtered and washed with aqueous sodium hydroxide solution (5%). It was finally purified by washing with water in a Soxhlet extractor for 2 days (81% yield).

Polymer−Metal Complex Ru3a,b. The preparation of polymer−metal complex **Ru3a** is described as the general procedure. Under a nitrogen atmosphere, a mixture of **5a** (0.17 g, 0.32 mmol) and polymer **3** (0.1 g, 0.32 mmol, calculated from the molecular weight of the repeating unit) was added to DMF (25 mL), and the solution was heated at 100 °C for 24 h. All of the polymer dissolved, and the solution became homogeneous during the course of the reaction. The reaction mixture was cooled to room temperature and poured into excess diethyl ether (150 mL). The product was washed thoroughly with methanol and was collected as a dark brown solid.

Scheme 1. Synthesis of Polymer 3



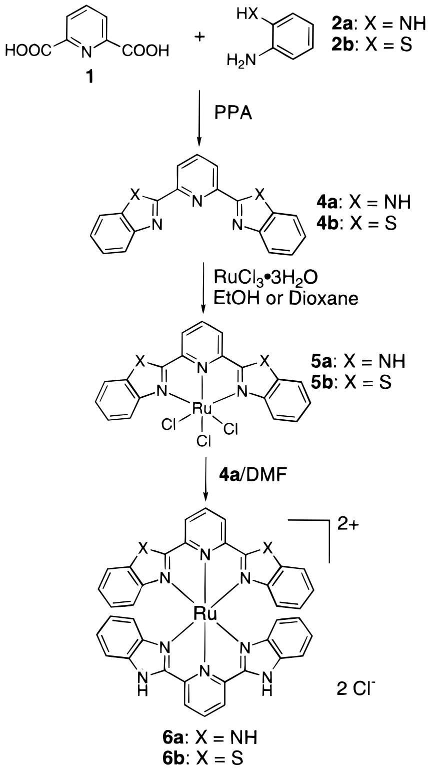
Physical Characterizations. The polymer film for photocurrent measurement was prepared by casting a polymer solution (10 mg/mL) onto an indium−tin−oxide (ITO) glass, and the solvent was evaporated slowly. The typical thickness of the polymer film was approximately 1 μm. The polymer film surface was coated with a thin layer of semitransparent gold electrode (120 Å) by vacuum deposition. The photocurrent was determined by measuring the voltage drop across a resistor resulting from the photocurrent passing through the polymer film.[11] A Laser Physics Reliant 300M argon ion laser (488 nm) was used as the light source. For the fabrication of the light-emitting devices, the polymer thin film was prepared by spin coating onto ITO glass slide with a typical thickness of 80−100 nm. A layer of aluminum electrode (thickness = 100 nm) was coated on the polymer film surface by vacuum deposition. A forward bias was applied to the light-emitting diode with a dc power supply, and the current−voltage characteristics were studied by a Keithley 2400 sourcemeter. The electrical conductivity of the polymer film was measured by using the standard four-point probe technique. The photoluminescence (PL) and electroluminescence (EL) spectra of the polymers were collected on a ORIEL MS-257 monochromator equipped with a photomultiplier and ANDOR DV420−BV charge-coupled device (CCD) detector. The external quantum efficiencies of the devices were estimated by calibrating the detectors with a standard tungsten lamp (Optronic Laboratories, Inc. OL740−20).

Results and Discussion

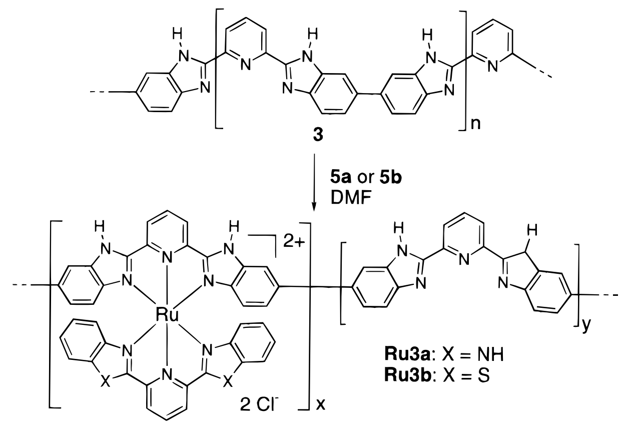
Syntheses of Polymers, Model Compounds, and Polymer−Metal Complexes. Polymer **3** was synthesized by the condensation reaction between pyridine-2,6-dicarboxylic acid in the presence of polyphosphoric acid (PPA) as the reaction medium (Scheme 1). In this reaction, PPA serves as the solvent, catalyst, and dehydrating agent. This method is widely used in the syntheses of different rigid poly(benzobisoxazole)s and poly(benzobisthiazole)s in good yield.[12] The resulting polymer **3** is soluble in organic acids such as methanesulfonic acid, formic acid, trifluoroacetic acid, and nitromethane/$AlCl_3$. In addition, it is also soluble in NMP because of the less rigid structure compared to other *para*-ordered polybenzimidazoles. Optical quality films can be obtained by spin coating or solution casting on different substrates.

It has been reported that complex **6a** was synthesized by the reaction between $RuCl_3$ with 2 equiv of ligand **4a** in a one-step process.[8a,13] However, to study the optimum condition for the synthesis of polymer−metal complexes, the intermediate ruthenium complexes **5a** and **5b** were prepared by an equimolar reaction between the ligands and $RuCl_3$ (Scheme 2) in ethanol or dioxane. Complexes **5a** and **5b** then reacted with equimolar amounts of ligand **4a** to give the resulting complexes **6a** and **6b**. The overall yields of these two-step reactions

Scheme 2. Synthesis of Ruthenium Complexes 6a and 6b



Scheme 3. Synthesis of Polymer–Metal Complexes Ru3a and Ru3b



are comparable to the one-step process reported in the literature. DMF was chosen as the solvent because polymer **3** has poor solubility in ethanol.

The polymer–metal complexes **Ru3a** and **Ru3b** were synthesized by heating a mixture of **5a** or **5b** with polymer **3** in DMF at 100 °C (Scheme 3). The polymer–metal complexes were obtained in high yield and have much higher solubility in DMF than polymer **3**. This indicates the polymer backbone is attached with positively charged ruthenium complexes. The enhancement in solubility in these polymer–metal complexes in polar aprotic solvents provides the flexibility of processing the polymers into thin films or fibers. This was also observed in our previously reported conjugated polymers with ruthenium bipyridine complexes. From the elemental analysis results, the C, H, and N contents in **Ru3a** and **Ru3b** differ from the proposed structure by less than 1%, and the percentage of complexation was estimated to be > 90%.

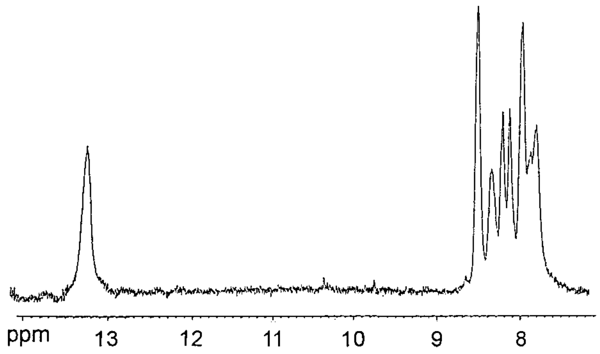


Figure 1. ^{1}H NMR spectra of polymer **3** in DMSO-d_6.

Table 1. Properties of Polymer 3 and Model Compounds[a]

compound	$\lambda_{max,abs}$ (nm)	T_d (°C)[b]	ϵ_{max} (L mol^{-1} cm^{-1})	σ[d] (S cm^{-1})
polymer **3**	266	565	7738[c]	10^{-11} [e]
	358		20110	2.4×10^{-6} [f]
				4.5×10^{-5} [g]
6a	336		31400	
	358		32850	
	578		3700	
6b	306		31400	
	358		34750	
	370		31450	
	518		4750	
Ru3a	335, 365, 565	357		5.0×10^{-10}
Ru3b	310, 356, 372, 492	363		5.6×10^{-10}

[a] All spectra were collected in NMP solution. [b] Decomposition determined by TGA under N_2. [c] The unit of the absorption coefficient for polymer **3** is L g^{-1} cm^{-1}. [d] Electrical conductivity at 25 °C. [e] Undoped. [f] Doped with iodine. [g] Doped with $NaPh_2CO$.

Structural Characterization. Polymer **3** exhibits an inherent viscosity of 1.8 dL/g at 30 °C (c = 0.5 g/dL in NMP) and is able to form an optical quality film by solution casting or spin coating. Figure 1 shows the proton NMR spectrum of polymer **3** in DMSO-d_6. The broad peak observed at $\delta = 13.2$ ppm is assigned to the imino protons of the benzimidazole unit,[7a] while the peak at 8.5 ppm corresponds to the two pyridine protons at the 3 and 5 positions. In the FTIR spectrum, a very broad absorption band is observed at 3300–2750 cm^{-1} due to the imino N–H stretching, while the transition bands at 1656 and 1603 cm^{-1} correspond to the C=N stretching in the imidazole and pyridine ring, respectively.

The electronic transition data for the polymers and model compounds in NMP are summarized in Table 1. For polymer **3**, only one broad absorption band is observed at 358 nm owing to the π–π^* transitions of the polymer main chain (Figure 2). The transition energy is higher than that for other conjugated polymers because of the less extended conjugation in the polymer main chain. After the formation of the polymer–metal complexes, new absorption bands are observed at ca. 550 (**Ru3a**) or 500 nm (**Ru3b**). These are assigned to the metal–ligand charge transfer [MLCT, d(Ru) → π^*-(pyridine)] transitions, which form a characteristic transition band in ruthenium polypyridine complexes. The main chain transitions at ca. 360 nm are preserved, and the vibronic structures are resolved in **Ru3b**. The model complexes **6a,b** exhibit spectral features similar to those of **Ru3a,b**. However, it is interesting to note that the peak position of model complex **6a** shows a significant red-shift compared to the same peak for the same compound reported in the literature (measured

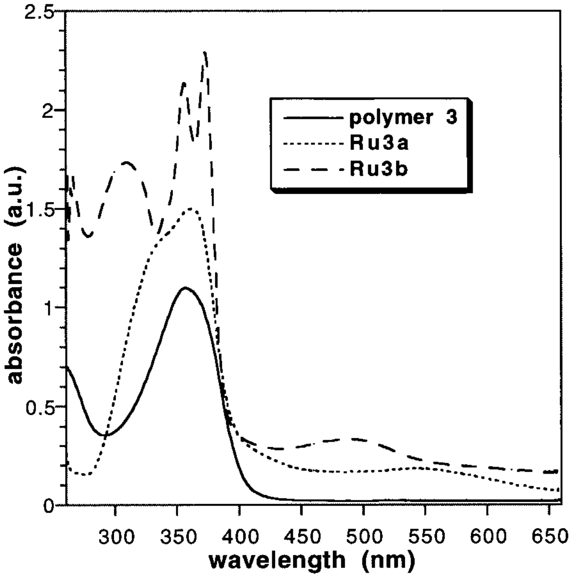


Figure 2. Electronic spectra of polymer **3**, **Ru3a**, and **Ru3b** in NMP solution.

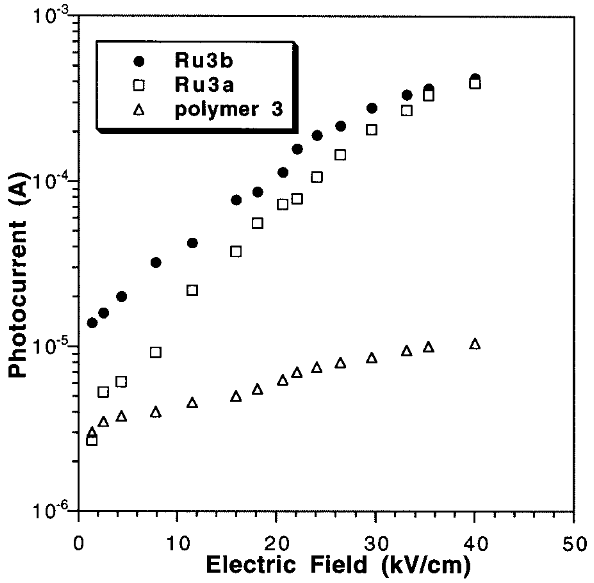


Figure 3. Photocurrent response of polymer **3**, **Ru3a**, and **Ru3b** at 488 nm under different applied field strength.

in CH_3CN).[8a] This clearly shows the effect of solvents on the electronic transition energies.

Thermal analysis results reveal that polymer **3** exhibits glass transition and decomposition processes at 183 and 565 °C, respectively. After the incorporation of ruthenium complexes, no glass transition process was observed and the decomposition temperature of the resulting polymer–metal complexes decreased to ca. 360 °C, indicating that the metal complexes decompose first upon heating.

The HOMO and LUMO levels of polymer **3** were estimated by the electrochemical method. From the cyclic voltammogram of polymer **3**, a cathodic process was observed at −1.2 V (vs ferrocene/ferrocenium internal standard) which is quasi-reversible. This is assigned to the reduction of the pyridine moieties, and the reduction potential is similar to those of other polypyridine ligands. On the other hand, no anodic peak was found up to 2 V. From these results, the LUMO level is estimated to be −3.3 eV with respect to the vacuum level. With reference to the optical band gap obtained from the electronic absorption spectrum, the HOMO level is estimated to be −6.3 eV. The low LUMO level suggests that this polymer could be a potential candidate as an electron transport material.

Electrical Conductivities and Photoconductivities. A solution of polymer **3** in NMP was cast on a glass slide for the conductivity measurement. The polymer film was exposed to iodine vapor at room temperature for 12 h. The resulting polymer film was dark brown in color, and the conductivity was studied by the four-point probe technique. It was found that, after doping with iodine, the electrical conductivity of polymer **3** increased by more than 4 orders of magnitude (from 10^{-11} up to 2.4×10^{-6} S/cm). When the polymer film was n-doped with sodium benzophenone ketal, the electrical conductivity increased up to 4.5×10^{-5} S/cm. Compared to the electrical conductivity of *trans*-poly(benzobisoxazole) and its derivatives,[14] the lower conductivity exhibited by polymer **3** may be due to a lower crystallinity and less extended conjugated π-system in its backbone. For polymer–metal complexes **Ru3a,b**, they have similar conductivities, on the order of 10^{-10} S/cm (Table 1).

Photoconductivity is a typical phenomenon for many organic semiconductors. When a photoconductor is illuminated by light that it is able to absorb, charge carriers are produced, and consequently the conductivity of the material increases. Generally speaking, photoconduction process involves three steps: (1) charge excitation by absorbing a photon; (2) charge separation under the influence of an externally applied electric field; (3) migration of charge in the forms of either hole or electron.[15] It has been shown previously that in some conjugated polymers the tris(2,2′-bipyridyl)ruthenium complexes are able to act as hopping sites, and they enhance the charge carrier mobilities.[5] Figure 3 shows the photocurrent response of different polymers at 488 nm under different applied electric fields. At this wavelength, **Ru3a** and **Ru3b** absorb strongly due to the presence of the ruthenium terpyridine complex, while polymer **3** has very little absorption. As a result, under the same electric field, **Ru3a** and **Ru3b** show higher photocurrent responses than the metal-free polymer **3** because the photosensitivity is enhanced by the ruthenium terpyridine complexes. These results show that the ruthenium complexes play a very important role in enhancing the conductivity of the polymers under the action of light.

Luminescent Properties. The luminescent properties of polymer **3** are different in solution and in the solid state (Figure 4). The fluorescence efficiency in NMP solution was measured to be 0.3 using 9,10-diphenylanthracene as the reference standard. For pure polymer, the quantum efficiency is estimated to be less than 4%. The emission wavelength in the solid state is approximately 50 nm longer than that in NMP solution. We suggest the formation of polymer aggregates in the solid state, which leads to the formation of excimer when excited by light. It was proposed that the luminescence of some rigid-rod conjugated polymers originates from the excimer formation. π-Conjugated polymers usually possess a rigid and stiff polymer main chain, and the strong intermolecular interaction leads to the formation of polymer aggregates.[16,17] Typical excimer emission exhibits featureless, strongly Stokes-shifted emission compared to dilution solution. To test this hypothesis, we prepared different polymer blend samples by mixing

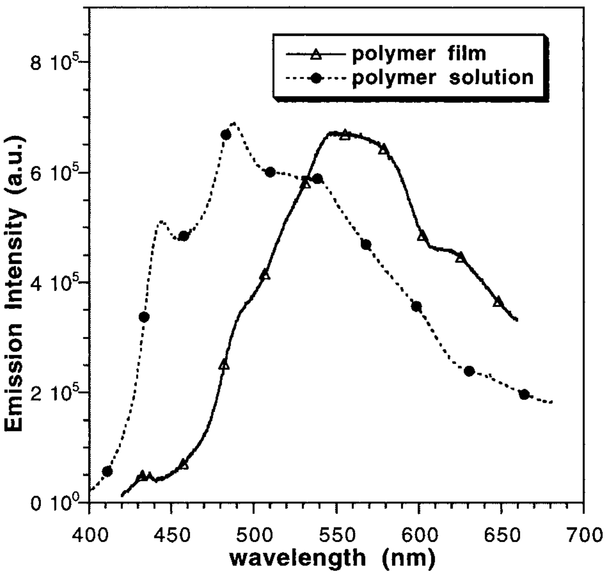


Figure 4. Emission spectra of polymer **3** in solid state and in NMP solution.

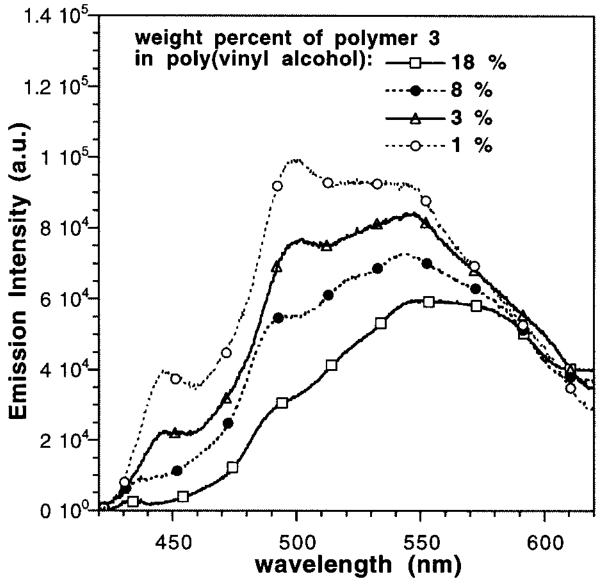


Figure 5. Emission spectra of polymer **3** blended with different amounts of poly(vinyl alcohol).

polymer **3** with poly(vinyl alcohol) (PVOH) in different proportions. Thin films of these polymer blends were obtained by casting the NMP solution on glass slides, and their emission spectra are shown in Figure 5. At high dilution (1% in PVOH), no aggregates can form and the emission spectrum of polymer **3** resembles its solution spectrum. When the concentration of polymer **3** is gradually increased, the effect of aggregate formation becomes dominant. The emission spectral features of the polymer blend are almost identical to the solid state spectra when the concentration reaches 18%. This clearly shows the effect of interchain interaction to the emission properties.

Model complexes **6a,b** and polymer−metal complexes **Ru3a,b** are not luminescent at room temperature. The lack of luminescence in this kind of tridentate ruthenium complex is also observed in other bis(terpyridyl)-ruthenium (II) complexes.[18] This is attributed to the weakly bound terminal benzimidazole rings which are subject to photodissociation.[19] The low lying d−d metal-centered (MC) states are able to quench the neighboring MLCT emission.[20]

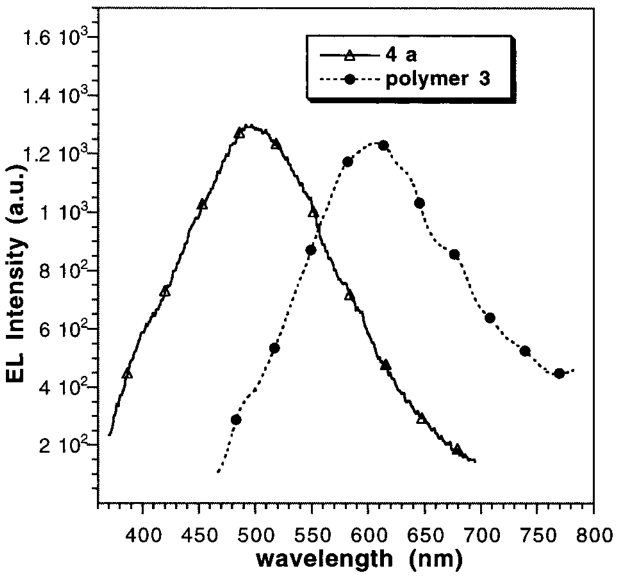


Figure 6. Electroluminescence spectra of polymer **3** and compound **4** under a forward bias of 20 V.

Table 2. Emission Properties of the Light-Emitting Devices

device	turn-on voltage (V)	emission peak (nm)	external quantum efficiency (%)	maximum luminance (cd/m^2)
ITO/polymer **3**/Ca	7	610	0.19	140
ITO/polymer **3**/Al	9	608	0.10	120
ITO/**4a**/Al	16	504	0.09	90

Fabrication of Light-Emitting Devices. The light-emitting properties of compound **4a** and polymer **3** were studied by fabricating the materials into simple single-layered light-emitting devices. A thin film of polymer **3** was obtained by spin coating on an ITO glass slide, while **4a** was evaporated onto the ITO surface under high vacuum (10^{-6} mbar). Three light-emitting devices ITO/polymer **3**/Al, ITO/polymer **3**/Ca, and ITO/**4a**/Al and were prepared. A typical thickness of the thin film was approximately 100 nm. Table 2 summarizes the emission properties of these two devices. The current−voltage characteristics were measured by applying a dc voltage across the devices with the ITO electrode being positive and the aluminum electrode being negative. Under this forward bias condition, the device fabricated from polymer **3** with calcium and aluminum electrode exhibit turn-on voltages at 7 and 9 V, respectively. Yellow light emission was observed, and the EL spectrum is shown in Figure 6. On the other hand, the turn-on voltage for the device ITO/**4a**/Al is 16 V, and it emits blue light. It can be seen clearly that the use of a calcium electrode can improve the device performance by facilitating the electron injection from the cathode to the polymer. We suggest that the emission originates from the $\pi^* \rightarrow \pi$ transitions resulting from the recombination of hole and electrons along the polymer main chain. Compared to the corresponding PL spectra, the EL spectrum of polymer **3** shows an emission band at lower energy, indicating the EL processes may undergo a different mechanism. The formation of aggregates may also play an important role in these processes. The external quantum efficiencies of the devices are estimated to be on the order of 0.1%, and the maximum luminance was in the range of 90−140 cd/m^2 at 24 V with a current density of approximately 5×10^{-3} A/cm^2. Devices fabricated from polymer−metal complexes **Ru3a,b** do not show electroluminescent behavior due to the same reasons as observed in their photoluminescent properties.

Conclusions

An aromatic polymer based on 2,6-bis(benzimidazol-2-yl)pyridine was synthesized. The doped polymer exhibits modest electrical conductivity when treated with iodine. It can be fabricated into a simple light-emitting device, and yellow light emission was observed. After formation of a coordination complex with ruthenium, the photosensitivity in the visible region was enhanced, as can be seen from the photocurrent measurements. It is envisaged that the photophysical and electronic properties can be modified easily by changing the transition metal complexes attached to the polymer main chain. A great variety of metal-containing polymers can be obtained from this approach, and they have potential applications in optoelectronics and catalysis.

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