

Electronic and Light-Emitting Properties of Some Polyimides Based on Bis(2,2':6',2''-terpyridine) Ruthenium(II) Complex

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A series of novel aromatic polyimides that contain bis(2,2':6',2''-terpyridine) ruthenium(II) complex was synthesized, and their optoelectronic properties were studied. The absorption of the polymers at 500 nm was strongly enhanced by the ruthenium complex. As a result, the photosensitivity of the polymers in the visible region is increased, as can be seen from the increase in photoconductivity. The glass transition temperature of the polymers is approximately 220 °C and they also exhibit modest thermal stabilities. The electron and hole carrier mobilities of polyimides are on the order of 10^{-4} cm² V⁻¹ s⁻¹, which suggests that the electron-withdrawing diimide moieties play a role in the charge transport process. Emission from the metal complexes and charge transfer states were observed in these polymers. The polyimides also exhibited electroluminescent behavior when the polymer films were fabricated into single-layered light-emitting diodes. The external quantum efficiency and maximum luminance of the devices were found to be 0.1% and 120 cd/m², respectively.

Introduction

Polyimides constitute an important class of materials because of their desirable properties for a variety of applications in a number of widely different technologies. The applications of polyimides range from aerospace to microelectronics to medical, largely due to the fact that they offer certain desirable properties such as high mechanical strength, chemical resistance, thermal stability, and low dielectric constant.¹ Several potential applications have been demonstrated by synthesizing polyimides for advanced technology such as intermetal dielectric, photoresist, separation membrane, photoconductor,² light-emitting,³ and nonlinear optical materials.^{4,5}

The chemistry, electrochemical properties, and photo-physics of bis(2,2':6',2''-terpyridine) ruthenium(II) {[Ru(tpy)₂]²⁺} complex and its derivatives have been studied extensively.⁶ The [Ru(tpy)₂]²⁺-type complexes exhibit a characteristic spin-allowed d- π^* metal-to-ligand charge transfer (MLCT) transitions and are well-known photo-

sensitizers. They are widely used as the key components in the studies of photoinduced electron-transfer processes. In addition, the use of ruthenium bipyridyl containing polymers for electroluminescence devices was also reported.⁷ Our research group has been exploring the feasibility of incorporating different ruthenium bipyridyl or terpyridyl complexes into conjugated polymer mainchain. One of our main objectives is to study the effect of transition metal complexes on the optoelectronic properties of polymers. We have found that in some conjugated polymers, the charge transport and other photonic properties were found to be dependent on the content of metal complex in the polymer.⁸ It is envisaged that by incorporating the [Ru(tpy)₂]²⁺ into the photoconducting polyimide backbone, the photosensitivity can be extended to the longer wavelength region. We have also synthesized a series of conjugated poly(*p*-phenylenevinylene)s which contain the [Ru(tpy)₂]²⁺ complexes.⁹ These polymers exhibit modest photoconductivity and charge carrier mobility which are comparable to some organic photoconductors. In this paper, we describe the results of the synthesis and properties of a new series of polyimides functionalized with the [Ru(tpy)₂]²⁺ complex. Different physical properties such as thermal stability, photoconductivity, luminescence, and charge transport properties were investigated. The polymers were fabricated into single-layered light-emitting devices, and the properties of the light-emitting diode were studied.

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Experimental Section

Materials. *N*-Methyl-2-pyrrolidinone (NMP) was distilled over CaH₂ under reduced pressure. Pyridine was distilled over CaH₂ and stored under N₂ before used. Ruthenium trichloride trihydrate, pyromellitic dianhydride (PMDA, **4a**), and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, **4b**) were purchased from Lancaster Synthesis Ltd. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA, **4c**) was purchased from Aldrich Chemical Co. Inc. 4,4'-Oxydiphthalic anhydride (OPDA, **4d**), biphenyl tetracarboxylic dianhydride (BPDA, **4e**), and 3,3',4,4'-diphenyl sulfone tetracarboxylic dianhydride (DSDA, **4f**) were purchased from Chriskev Co. Inc. All of the dianhydride monomers were purified by sublimation under vacuum before use. Other chemicals were used as received unless otherwise specified.

Instruments. ¹H and ¹³C NMR spectra were collected on a Bruker 300 DPX NMR spectrometer. FTIR spectra were collected on a Bio-Rad FTS-7 FTIR spectrometer. Mass spectrometry was performed on a high-resolution Finnigan MAT-95 mass spectrometer. Thermal analyses were performed on a Perkin-Elmer DSC7 and TGA7 thermal analyzer with a heating rate of 10 and 15 °C/min, respectively. The viscosity measurements were performed in a constant-temperature bath (30 °C) using an Ubbelohde viscometer, with the solution concentration of 0.5 g/dL in NMP.

4'-(4-Aminophenyl)-2,2':6',2''-terpyridine (2). A mixture of 4'-(4-nitrophenyl)-2,2':6',2''-terpyridine **1**¹⁰ (5.0 g, 14.2 mmol) and tin(II) chloride dihydrate (12.8 g, 56.7 mmol) in concentrated hydrochloric acid (75 mL) was heated at 60 °C for 6 h. The solid was collected by filtration and stirred in a sodium hydroxide solution (10%, 30 mL) for 1 h. The product was filtered and recrystallized with a mixture of MeOH/CHCl₃. Yield: 3.7 g (80%). Mp: 250 °C. FTIR (KBr): $\nu = 3389, 1584$ cm⁻¹. ¹H NMR (DMSO-*d*₆) δ : 8.75 (d, *J* = 3.9 Hz, 2H), 8.63–8.66 (m, 4H), 8.00–8.05 (m, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.49–7.54 (m, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 5.62 (s, 2H). ¹³C NMR (DMSO-*d*₆) δ : 155.2, 150.4, 149.5, 149.2, 137.3, 127.5, 124.2, 123.6, 120.7, 116.0, 114.1. MS (EI, *m/e*, relative intensity %): 324 (M⁺, 100), 246 (15.7).

Bis[4'-(4-aminophenyl)-2,2':6',2''-terpyridyl]ruthenium(II) Hexafluorophosphate (3). Ruthenium trichloride trihydrate (1.0 g, 4.82 mmol) and **2** (3.2 g, 10.1 mmol) were heated under reflux in ethanol (150 mL) under a nitrogen atmosphere for 24 h. After filtration, the filtrate was concentrated and added to an aqueous solution of KPF₆ (2.0 g in 10 mL water). The brick-red precipitate was washed with water (20 mL) and the solid was recrystallized two times with a mixture of acetonitrile and diethyl ether. Yield: 3.0 g (60%). ¹H NMR (CD₃CN) δ : 8.91 (s, 4H), 8.61 (d, *J* = 8.0 Hz, 4H), 7.89–8.02 (m, 8H), 7.42 (d, *J* = 5.2 Hz, 4H), 7.15 (t, *J* = 6.8 Hz, 4H), 6.96 (d, *J* = 8.6 Hz, 4H), 4.77 (s, 4H). ¹³C NMR (DMSO-*d*₆) δ : 159.6, 156.3, 153.4, 151.8, 149.5, 138.9, 129.9, 128.3, 125.4, 125.3, 120.9. IR (KBr): $\nu = 1600, 838$ cm⁻¹. FABMS: *m/e* 895 (M – PF₆)⁺, C₄₂H₃₂N₈PF₆Ru requires: 894.8.

Polymerization. The synthesis of polymer **5a** is described as the general procedure. Under a nitrogen atmosphere, **4a** (0.02 g, 0.99 mmol) and monomer **3** (0.10 g, 0.99 mmol) were dissolved in NMP (5 mL), and the reaction mixture was stirred at 50 °C for 24 h. The imidization was achieved by adding a mixture of pyridine (4 mL) and acetic anhydride (8 mL), and the solution was stirred for another 24 h at 90 °C. The polymer solution was added to diethyl ether (50 mL) and the polymer was redissolved in NMP (15 mL) followed by precipitation in diethyl ether (50 mL). It was then purified by washing with methanol in a Soxhlet extractor for 2 days. The polymer was collected as dark red solid (0.11 g, 94% yield).

Physical Characterizations. The polymer film for photocurrent and charge transport mobility measurements was prepared by casting a polymer solution (6 mg/mL in NMP) onto an ITO glass, and the solvent was evaporated slowly. The typical thickness of the polymer film was approximately 1 μ m.

The photocurrent was determined by measuring the voltage drop across a resistor resulting from the photocurrent passing through the polymer film.¹¹ A 150 W xenon lamp with different band-pass filters was used as the light source. The charge carrier mobilities were determined by the conventional time-of-flight experiment.¹² A thin layer of gold electrode (120 Å) was coated on the polymer film surface by sputtering. A Laser Science VSL-337 nitrogen laser was used to generate a pulsed laser source [wavelength = 337.1 nm, pulse energy = 120 μ J, and pulse width (full width at half-maximum, fwhm) = 3 ns]. For the fabrication of the light-emitting devices, the polymer thin film (typical thickness = 70–80 nm) was prepared by spin coating the polymer solution onto an ITO glass slide. 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 and the current–voltage characteristics were studied by a Keithley 2400 source meter. 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.

Results and Discussion

Polymerization. The synthesis of the ruthenium-containing monomer [Ru(NH₂Phtpy)₂][PF₆]₂ (**3**) is shown in Scheme 1. It was synthesized by the direct complexation of ruthenium trichloride trihydrate with 2 equiv of 4'-(*p*-aminophenyl)-2,2':6',2''-terpyridine **2**, which was prepared by the reduction of the corresponding nitro-substituted compound **1** with tin(II) chloride. Polyimides **5a–f** were synthesized by polymerizing monomer **3** with different dianhydride monomers **4a–f**. The first step of the polymerization involves the ring-opening addition of the amino group to the acid anhydride in NMP to give the corresponding polyamic acid. The synthesis of polyamic acid between the diamine and dianhydride was usually carried out in polar aprotic solvents at room temperature or below. However, we found that higher reaction temperature would slightly increase the yield and viscosities of the resulting polyimides compared to the low-temperature polymerization (see Table 1). This is probably due to the lower reactivity of the amino group in metal complex **3**. The second imidization process was completed by heating the polyamic acid solution with a mixture of pyridine and acetic anhydride. All the resulting polyimides are soluble in polar solvents such as DMF, NMP, and DMSO because the polymer main chain includes the positively charged bisterpyridyl ruthenium(II) moiety.

Structural Characterization. From the FTIR spectra, all polyimides show absorption bands at 1776 and 1723 cm⁻¹ that are the characteristic peaks of the imide C=O stretching. No absorption peak due to the carboxylic acid C=O stretching was found at 1670 cm⁻¹, indicating that the imidization process was completed. In addition, the peaks found at 1600 and 842 cm⁻¹ are assignable to the pyridine ring C=N stretching and the counteranion P–F stretching, respectively.

The UV–vis spectra of some polyimides are shown in Figure 1. All polyimides show very similar absorption features, which are dominated by the electronic transitions due to the ruthenium terpyridine complexes. The

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Scheme 1. Syntheses of Monomers and the Metal-Containing Polyimides

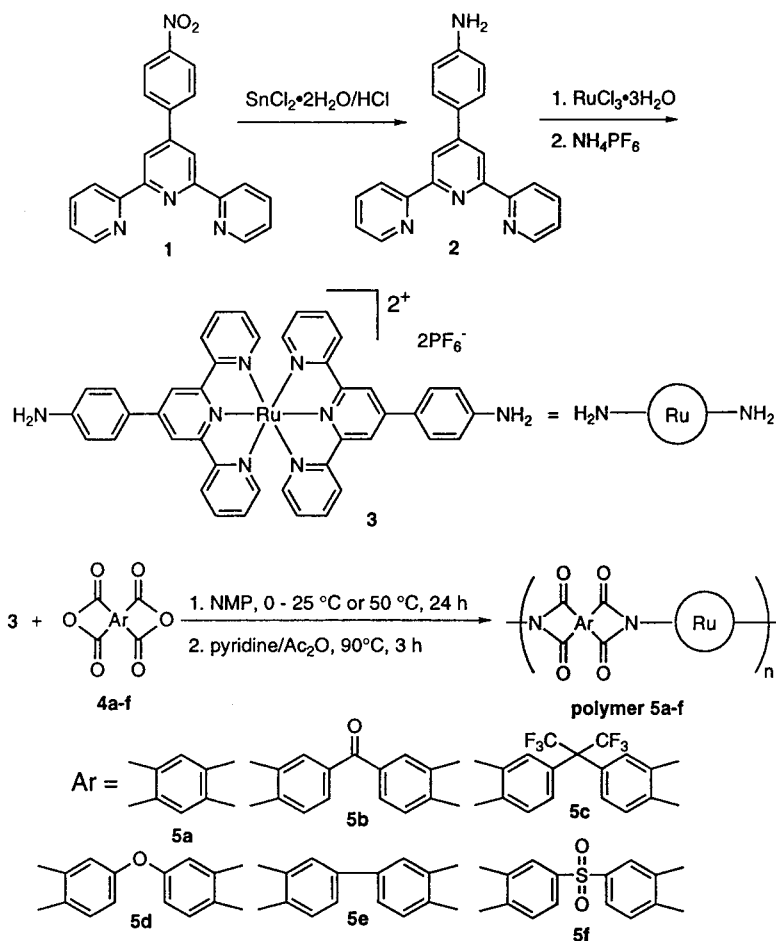
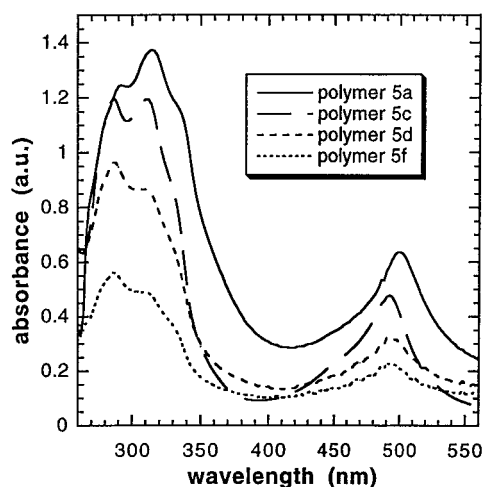


Table 1. Synthesis and Thermal Properties of Polymers 5a-f

polymer	dianhydride	yield (%) ^a		η_{inh} (dL/g) ^b		T_g (°C)	T_d (°C) ^c	
		RT	50 °C	RT	50 °C		N ₂	air
5a	PMDA	71	94	0.22	0.41	231	358	345
5b	BTDA	78	88	0.15	0.21	218	361	352
5c	6FDA	76	80	0.16	0.62	214	350	340
5d	ODPA	84	94	0.34	0.34	^d	351	344
5e	BPDA	79	83	0.15	0.29	228	358	343
5f	DSDA	81	92	0.24	0.28	224	348	339

^a Yield of polymerization reaction carried out at 25 and 50 °C.^b Inherent viscosity measured at 30 °C in NMP with $c = 0.5$ g/dL.^c Decomposition temperature measured under N₂ atmosphere and in air. ^d Not observed.

absorption spectra of the polyimides are characterized by intense bands in the UV and visible region (see Table 2). The bands centered at ca. 286 and 310 nm correspond to the ligand-centered (LC, $\pi-\pi^*$) transitions of the terpyridine moieties. Another absorption at approximately 500 nm is ascribed to the metal-to-ligand charge transfer (MLCT, $Ru^{2+} \rightarrow tpy$) transitions, which is described as the promotion of an electron from the metal-centered d orbitals to an unfilled ligand-centered π^* orbitals.¹³ When the polyimide films were irradiated with an excitation source (argon ion laser, 488 nm), they all exhibit two major emission bands at the vicinities

Figure 1. UV-vis spectra of some polyimides in CH₃CN.

of 650 and 750–800 nm (Table 2). On the other hand, solution PL spectra only gave rise to one emission band at ca. 600–650 nm. The photoluminescence spectra of some polyimide films are shown in Figure 2. The higher energy emission bands originate from the emission of the MLCT states. These spectral features are interesting because most of the $[Ru(tpy)_2]^{2+}$ -type complexes are not luminescent or have very short lifetime at room temperature.¹⁴ The weak emission is attributed to the weakly bound terminal pyridines because of the unfavorable bite angles. This results in a weak ligand field such that the low-lying d–d metal centered (MC) states

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Table 2. Electronic Absorption, Emission, and Charge Carrier Mobilities Data for Polymers 5a–f

polymer	$\lambda_{\max}(\text{abs}), \text{nm}$ ($a, \text{L g}^{-1} \text{cm}^{-1}$) ^a	$\lambda_{\max}(\text{em}), \text{nm}$ ^b	$\mu_{\text{h}}, 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ^c	$\mu_{\text{e}}, 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ^d
5a	496 (3 700), 312 (7 500), 286 (7 200)	652, 766, 810	1.1	3.6
5b	494 (5 900), 310 (16 000), 286 (16 800)	660, 765	0.22	0.28
5c	492 (24 000), 310 (59 000), 286 (60 000)	666, 760, 785	1.1	3.5
5d	494 (12 000), 312 (31 600), 286 (35 300)	668, 750	0.63	0.27
5e	492 (9 800), 312 (21 000), 288 (24 200)	675, 752	0.64	0.83
5f	494 (10 200), 310 (30 500), 286 (32 800)	652, 752, 800	2.5	1.6

^a Absorptivity measured in CH_3CN solution. ^b Emission spectra measured with polymer film. ^c Hole drift mobility measured at $E = 40$ kV/cm. ^d Electron drift mobility measured at $E = 40$ kV/cm.

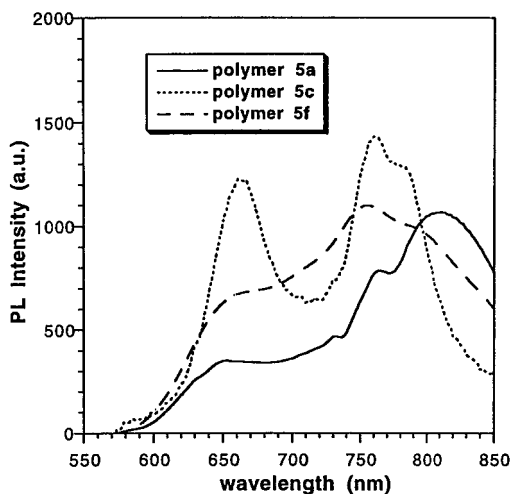


Figure 2. Photoluminescence spectra of some polyimide films measured by using argon ion laser (488 nm) as the excitation source.

are able to quench the MLCT emission.^{15,16} The presence of PL in our polyimides indicates that the lifetime of the MLCT states is affected by the polymer matrixes. It is also well-known that some aromatic polyimides exhibit charge transfer (CT) transitions between the electron-donating aminophenyl fragment and the electron-accepting diimide fragment.¹⁷ The CT theory was used to explain a number of properties such as photo-degradation¹⁸ and photoconductivity.¹⁹ In our polyimides, we assign the lower energy emission near-IR region to be the emission from the charge transfer states. The intensity ratio of the MLCT and CT emission bands vary with different polymers, probably due to the structural differences in the diimide unit.

Thermal Properties. The thermal analyses data of the polyimides are summarized in Table 1. From the DSC results, it was found that polymers with more rigid diimide unit (**5a**, **5e**) exhibited higher glass transition temperature (T_g) than those with flexible linkage (**5b**, **5c**). The T_g of all polyimides are in the range of 214–230 °C, which is similar to other functionalized poly-

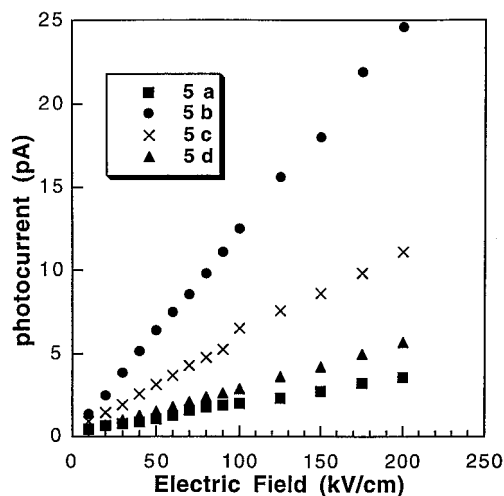


Figure 3. Photocurrent response as a function of applied field strength for different polyimides. The irradiation wavelength was 520 nm.

imides.⁵ The decomposition temperatures (T_d) of the polyimides are approximately 350–360 °C (under N_2). When measured in air, they are 10–15 °C lower than that measured in nitrogen. The independence of the T_d on the diimide structure indicates that the weight loss at T_d is caused by the decomposition of the ruthenium complex. No significant weight loss was observed when the polymers were heated at 250 °C for a period of 24 h.

Photoconducting Properties. 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, and (3) migration of charge in the forms of either hole or electron. Previous work has attributed the photoconduction in polyimides to the formation of CT species in which a virtual one-electron transfer occurs from the donor to the acceptor. It was proposed that the imide radical anions and aminophenyl donor cations are possible charge carriers.² In our polymer systems, the ruthenium terpyridine moiety in the polyimides can function as the photosensitizer, which was demonstrated by measuring the photoconductivity of the polymers at 520 nm, where the $[\text{Ru}(\text{tpy})_2]^{2+}$ strongly absorbs. The polymers have very small dark conductivity of the order of $10^{-15} \Omega^{-1} \text{cm}^{-1}$. When the polymers were exposed to visible light irradiation, the conductivity increased by 2 orders of magnitude. The photocurrent response was found to be dependent on both applied electric field strength and irradiated light intensity (Figures 3 and 4). Figure 5 shows the normalized photocurrent response of polymer **5b** measured at different wavelengths. It was found that the photocurrent spectra of the polyimides resemble their absorp-

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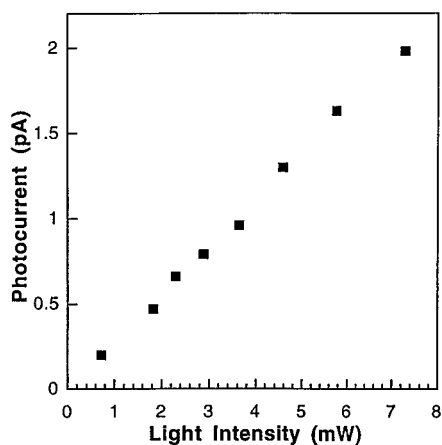


Figure 4. Photocurrent response of polymer **5b** at different irradiated light intensity.

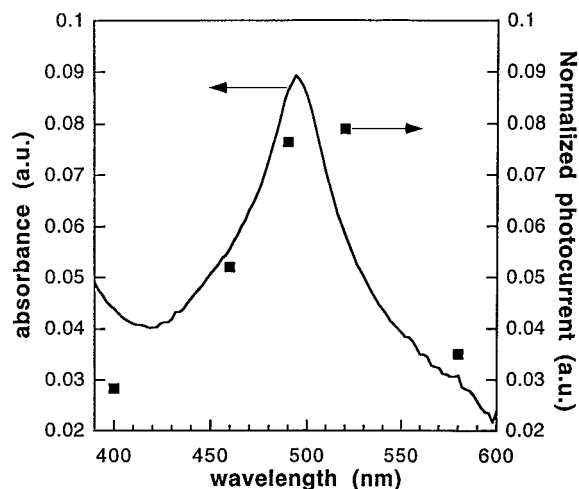


Figure 5. Normalized photocurrent and absorption spectrum of polymer **5b** in the visible region.

tion spectra due to the $[Ru(tpy)_2]^{2+}$ moiety. This clearly shows the enhancement of the photoconductivity by the ruthenium complex in the photoconduction process.

After the photocharge generation process, it is followed by charge transport between the charge carriers under the influence of applied electric field. The charge mobility reveals how fast the charge carriers (electron or hole) are transported in the material. To design materials for optoelectronic applications, it is of fundamental importance to understand the nature of charge transport process. The drift carrier mobilities of the polyimides were determined by a conventional time-of-flight experiment, and the results are summarized in Table 2. All polyimides show similar values of hole and electron carrier mobilities on the order of 10^{-5} – 10^{-4} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ (at 298 K), which are both electric field and temperature dependent. In some polyimides, the electron carrier mobilities are slightly higher than that of the hole carrier. Compared to our terpyridine-containing poly(phenylenevinylene)s,^{8b} the polyimides exhibit similar hole carrier mobilities and higher electron mobilities. We suggest that the charge transport process results from the migration of hole carriers (mainly confined on the metal ion) and electron carriers (diimide units). Both the ruthenium terpyridine complexes and the electron-withdrawing diimide are playing important roles in the charge transport process in both polymer systems.

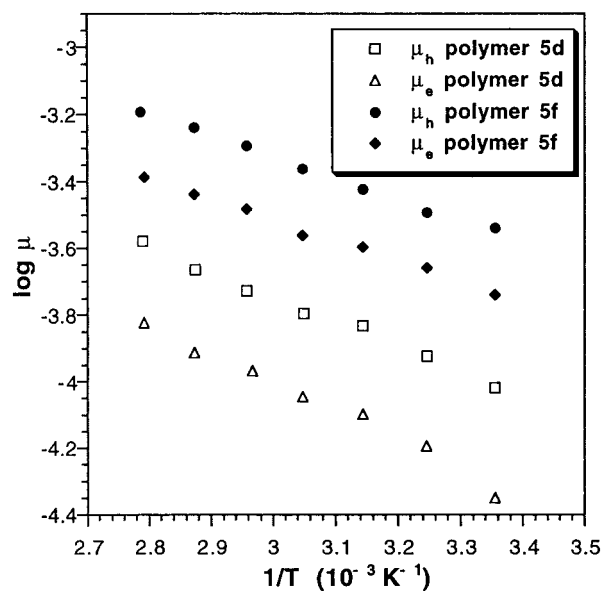


Figure 6. Temperature dependence of the electron mobility at $E = 26$ kV/cm for polymers **5d** and **5f**.

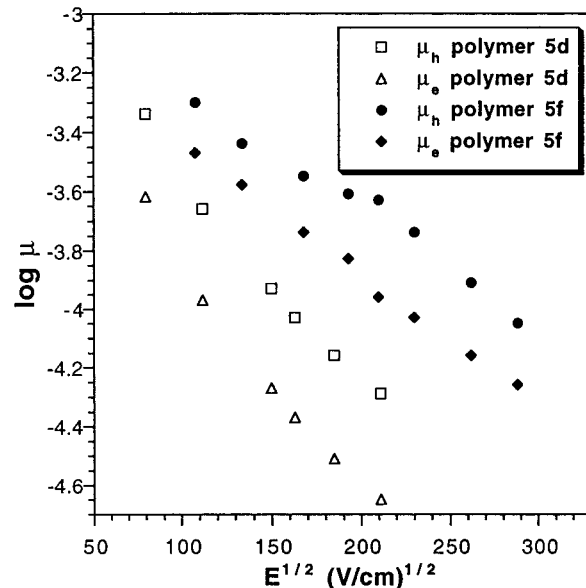


Figure 7. Field dependence of the electron and hole mobilities at 298 K for polymers **5d** and **5f**.

Figure 6 shows the electron carrier mobilities of polymers **5d** and **5f** at different temperatures. The Arrhenius plot reveals a thermally activated charge transport process with activation energy of 0.15 eV at $E = 26$ kV/cm for both polymers. Figure 7 shows the plot of $\log \mu$ vs $E^{1/2}$ for different polyimides. As the electric field was increased, the carrier mobilities decreased. This interesting phenomenon was explained by the presence of off-diagonal disorder in the polymers. Due to the fluctuations of the overlap between different hopping sites, the charge may take some indirect paths which contain steps against the direction of the applied field.²⁰

Light-Emitting Properties of the Polymers. The polyimides were fabricated into single-layered light-emitting devices: ITO/polyimide/Al. The current–volt-

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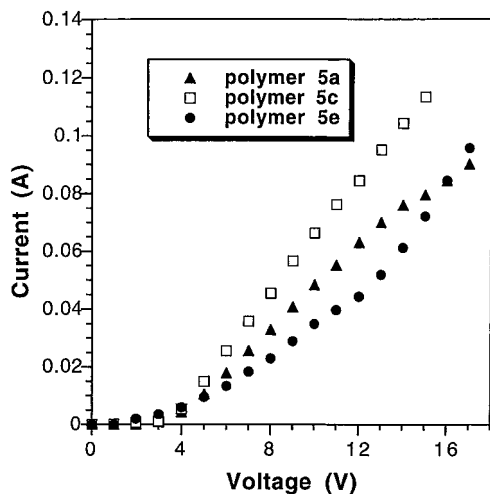


Figure 8. Current–voltage characteristic of the light-emitting devices fabricated from different polyimides.

age characteristic of the device was measured by applying a dc voltage across the device with the ITO electrode being positive and the aluminum electrode being negative (forward bias; see Figure 8). The threshold of electroluminescence emission in this device is approximately 5 V. Red light emission from the diode was observed instantaneously upon applying voltage. For some ruthenium-containing polymers reported in the literature, it was proposed that the electrochemically generated Ru(III)/Ru(I) species could also give light emission by electrochemical process.²¹ Such electrochemical light emission processes are characterized by a long “charging time”, which represents the accumulation of Ru(I) and Ru(III) species at each side of the electrodes. In our devices, the light instantaneous emission indicates that the light emission processes are electronic in nature, although the possibility of light emission contributed from the electrochemical processes cannot be completely excluded. Figure 9 shows the EL spectra of the polyimides under an applied voltage of 15 V. Compared to the corresponding PL spectra, the EL spectra are dominated by the emission from the metal complexes at ca. 650 nm, while the relative intensities of the charge transfer emission at 750–800 nm decrease. We suggest that the red light emission originates from the $\pi^*(\text{tpy}) \rightarrow d\pi$ (Ru) transitions resulting from the recombination of hole and electrons along the polymer main chain. The external quantum

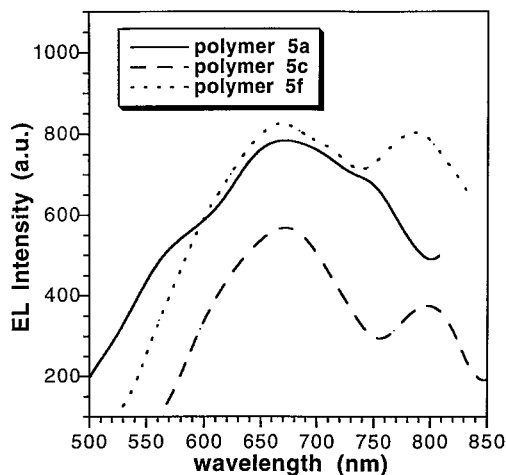


Figure 9. Electroluminescence spectra of the ITO/polyimide/Al devices under a forward bias of 15 V.

efficiency of the device is estimated to be on the order of 0.1%. At 20 V, the maximum luminance of the light-emitting diode was measured to be 120 cd/m².

Conclusions

In summary, we have developed novel types of aromatic polyimides which contain the bis(2,2':6',2''-terpyridine) ruthenium(II) complex. The polymerization condition and the optoelectronic properties of the resulting polyimides have been studied in detail. Charge mobility measurements suggest the involvement of the electron-withdrawing diimide moieties in the charge transport process. The polyimides were fabricated into light-emitting diodes, and their electroluminescent behavior was studied. It is of interest to further study in detail the light-emitting mechanisms of the metal complexes and the charge transfer states. By using different metal complex monomers, it is able to prepare metal-containing polymers with different emission colors and charge transport properties.

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