Efficient Energy Transfer to Achieve Narrow Bandwidth Red Emission from Eu^{3+}-Grafting Conjugated Polymers

Jian Pei,*,†,‡ Xiao-Lin Liu,‡ Wang-Lin Yu,‡ Yee-Hing Lai,‡ Yu-Hua Niu,§ and Yong Cao§

Department of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China PR; Institute of Materials Research and Engineering and Department of Chemistry, National University of Singapore, Singapore 117620, Republic of Singapore; and Institute of Materials Science and Engineering, South China University of Technology, Guangzhou, Guangdong 510641, China PR

Received April 2, 2002; Revised Manuscript Received July 3, 2002

ABSTRACT: A convenient approach to novel Eu^{3+}-grafting conjugated polymers to achieve sharp red emission for polymeric light emitting diodes (PLEDs) has been developed in this contribution. The structure of polymer **1** is verified by FT-IR, ^1H, ^{13}C NMR and elemental analysis. The results indicate that efficient intramolecular Föster energy transfer depends on the overlap between the fluorescent spectrum of polymer **1** and absorption spectrum of Eu^{3+} chelates. $Eu(DBM)_3$ is obviously the best one for accepting energy from polymer **1** among three Eu^{3+} chelates to exhibit the sharp red emission. The investigation also shows that the efficiency of energy transfer relies on the content of Eu^{3+} in the complexes. The investigations on the photophysical and electrochemical properties also show that the HOMO and LUMO energy levels and the band gap of complexes have no alteration with the attachment of the Eu^{3+} chelate in comparison with those of polymer **1** due to the Eu^{3+} chelate at the side chain of the whole molecule. The pure red electroluminescence is achieved from the fabrication of PLEDs using complex **5** as the active layer with the configuration of ITO/PVK/complex **5**/Ba/Al.

Introduction

Conjugated polymers have still been attracting considerable interest since the fabrication of first polymer light-emitting diodes (LEDs).[1] As active materials applying for photonic devices, conjugated polymers exhibit their unique electrical and optical properties, the emission at wavelength spanning the entire visible spectrum, high fluorescence efficiencies, easy fabrication as uniform films, and mechanical flexibility.[2]

Most recently, it is still difficult to obtain pure emission color from conjugated polymers or small organic molecules because of their full width emission spectra at half-maximum (fwhm) of 50−200 nm due to both their inhomogeneous broadening and the presence of a vibronic progression. Especially for the efficient pure red-emitting LEDs, almost all red-emitting conjugated polymers emit little orangish red and their orange emission part has to be filtered out in order to get pure red emission light because human eyes are more sensitive to orange emission than to red. Consequently, it reduced the performance of the devices. The development of efficient pure red-emitting materials is necessary for constituting full-color, pure red−green−blue (RGB) displays, which are only a promising prospect at this time. Recently, a few studies were devoted to achieving pure red emission in LEDs by the blends of the blue-emitting conjugated polymers and red-emitting small molecular materials through energy transfer.[3] Some conjugated polymers containing porphyrins at the backbone or side chains possess effective intermolecular charge transfer to achieve red emission.[4] Moreover, the incorporation of ruthenium or rhenium polypyridine complexes into a conjugated polymer is also possible to obtain red emission electroluminescence for PLEDs through charge transport.[5] However, there are few contributions used to achieve sharper red emission from conjugated polymers.

Europium (Eu^{3+}) complexes are well-known as excellent red chromophores that exhibit intense fluorescence around 613 nm ($^5D_0$ to $^7F_2$) with a sharp spectral bandwidth (half-bandwidth ∼ 5 nm) and extremely long PL lifetime.[3a,6] Hereby, efficient and sharp red emission materials can be achieved from Eu^{3+}complexes, including not only blends of conjugated polymers and europium chelates through intermolecular energy transfer[3a] but also small molecular Eu^{3+} complexes.[7] However, for small organic molecules, their poor processability and low luminescence limited their application in OLEDs,[7] and the phenomena of concentration-quenching and phase separation existing in the blends of conjugated polymers and Eu^{3+} chelates also seriously affect the efficiency of devices fabrication since the energy transfer processes are intermolecular interactions.[3]

In this contribution, we designed and synthesized a novel conjugated polymer with a bipyridyl moiety at the side chain directly coordinating with Eu^{3+} chelates (α,β-diketone)[8] to afford new complexes. The Förster energy transfer processes[9] from the backbone of the blue-emitting conjugated polymer to the Eu^{3+} center happened within the whole molecule. As the Eu^{3+} chelates directly coordinated with the bipyridyl moiety, the phase separation, which mainly caused the self-quenching, could be avoided. Therefore, these novel materials not only inherited advantages of conjugated polymers, such as the excellent processability, the good solubility, and fluent charge transportability, but also had the inherent characteristics of europium complexes, such as high fluorescence efficiencies with sharp red emission, good stability, and long lifetime.[3a,3c] These might enable these

---

* To whom correspondence should be addressed. Telephone: (86−10) 62756866. Fax: (86−10) 62751708. E-mail: jianpei@chem.pku.edu.cn.

† Peking University.

‡ National University of Singapore.

§ South China University of Technology.

10.1021/ma020529b CCC: $22.00

materials to be used as pure red emission materials for full color RGB displays.

Experimental Section

Instrumental Measurement. ^1H and ^{13}C NMR spectra were obtained as solutions in deuterated chloroform or DMSO and recorded on a Bruker AMF300 spectrometer. TMS was used as internal reference for both monomer and polymer. Elemental analyses were obtained on a Perkin-Elmer 240C elemental analyzer in the Microanalysis Lab at the National University of Singapore. Molecular weights of the polymer were determined by gel permeation chromatography (GPC) against a polystyrene standard on a Perkin-Elmer model 200 HPLC system and THF as the eluting solvent. The UV−visible absorption spectra of the polymer were recorded on a Shimadzu UV-3101 scanning spectrophotometer. The fluorescence spectra were collected on a Perkin-Elmer LS 50B luminescence spectrometer. A pump wavelength of 371 nm was used for PL measurements because the UV spectra of polymer **1** and Eu^{3+} ligands containing complexes strongly absorbed at this wavelength. Thermogravimetric analyses (TGA) were conducted on a Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer under a heating rate of 20 °C/min from 20 to 800 °C and an air flow rate of 70 cm^3/min. DSC was run on a Du Pont DSC 2910 module in conjunction with the Du Pont Thermal Analyst system. CV experiments were conducted on an EG&G Parc model 273A potentiostat/galvanostat under argon atmosphere.

Materials. THF was dried and distilled under argon from metal sodium powder and benzophenone. All chemicals were purchased from the Aldrich Chemical Co. and used as received unless otherwise stated. 9,9-Di-*n*-hexylfluorene-2,7-bis(trimethylene boronate) was prepared using 2,7-dibromofluorene following literature procedures.[10]

Preparation of 1-Methoxy-4-[9-(5′-methyl-2,2′-bipyridyl-5-yl)nonyloxy]benzene (Compound 3). A solution of 3.45 mL of *n*-butyllithium in hexane (1.45 M, 5 mmol) was added to a solution of diisopropylamine (0.5 g, 5 mmol) in 30 mL of anhydrous THF under nitrogen at 0 °C. After being stirred for 0.5 h, the mixture was added slowly by cannula to a solution of 5,5′-dimethyl-2,2′-bipyridyl (0.92 g, 5 mmol) in 30 mL of anhydrous THF at −78 °C. The dark reddish brown mixture was stirred for more 2.5 h at −78 °C. A solution of 1-(8-bromooctyloxy)-4-methoxybenzene (3.15 g, 10 mmol) in 20 mL of anhydrous THF was added dropwise to the mixture with stirring at −78 °C. Then the reaction temperature was allowed to increase slowly to 0 °C. The mixture was stirred for 30 min more at 0 °C and was quenched by pouring it into a mixture of ethyl acetate and water. The aqueous layer was extracted by ethyl acetate. The combined extracts were washed with water and brine and dried over $MgSO_4$. Removal of the solvent under vacuum followed by flash chromatography (silica gel, ethyl acetate/hexane/acetone = 1/3/1) afforded a white solid. (Yield: 48%.) ^1H NMR ($CDCl_3$, 300 MHz, δ, ppm): 8.48 (2H, s, Py−H), 8.26−8.22 (2H, m, Py−H), 7.62−7.59 (2H, m, Py−H), 6.82 (4H, s, Ph−H), 3.91−3.86 (2H, t, $J = 6.8$ Hz, OCH_2), 3.76 (3H, s, OCH_3), 2.62−2.67 (2H, t, $J = 6.8$ Hz, CH_2), 2.38 (3H, s, CH_3), 1.61−1.32 (14H, m, CH_2). Anal. Calcd for $C_{27}H_{34}N_2O_2$: C, 77.48; H, 8.19; N, 6.69. Found: C, 76.97; H, 8.14; N, 6.73.

Preparation of 1,4-Dibromo-2-methoxy-5-[9-(5′-methyl-2,2′-bipyridyl-5-yl)nonyloxy]benzene (Compound 4). A solution of bromine (0.64 g, 4 mmol) in 50 mL of chloroform was slowly added to a solution of 1-methoxy-4-[9-(5′-methyl-2,2′-bipyridyl-5-yl)nonyloxy]benzene (0.80 g, 2 mmol) in 100 mL of chloroform at 0 °C. The mixture was stirred for 20 h more at room temperature. The mixture was neutralized by iced aqueous KOH. After washing with water, diluted hydrochloride acid solution, and brine, the organic layer was dried over $MgSO_4$. Removal of the solvent followed by recrystallization from ethanol afforded a white clumped solid. (Yield: 92%.) ^1H NMR ($CDCl_3$, 300 MHz, δ, ppm): 8.47 (2H, s, Py−H), 8.26−8.22 (2H, m, Py−H), 7.61−7.58 (2H, m, Py−H), 7.08 (2H, s, Ar−H), 3.95−3.90 (2H, t, $J = 6.4$ Hz, OCH_2), 3.82 (3H, s, OCH_3), 2.66−2.61 (2H, t, $J = 7.2$ Hz, CH_2), 2.37 (3H, s, CH_3), 1.80−1.32 (14H, m, CH_2). ^{13}C NMR ($CDCl_3$, 75.5 MHz, δ, ppm): 153.88, 153.69, 150.39, 150.07, 149.45, 149.13, 137.75, 137.30, 136.64, 132.88, 120.29, 120.22, 118.56, 116.94, 111.18, 110.31, 70.23, 56.90, 32.73, 30.97, 29.31, 29.19, 29.10, 28.99, 25.78, 18.21. Anal. Calcd for $C_{27}H_{32}Br_2N_2O_2$: C, 56.27; H, 5.60; Br, 27.73; N, 4.86. Found: C, 57.06; H, 5.73; Br, 27.70; N, 5.01.

Preparation of Eu^{3+} Chelates, $Eu(DBM)_3$, $Eu(TTA)_3$, and $Eu(NTA)_3$. DBM (dibenzoylmethyl), TTA (2-thinoyltrifluoroacetone) or NTA (2-naphathoyltrifluoreacetone) (15 mmol) was dissolved in 100 mL of ethanol in a flask at 50−60 °C. The solution was neutralized to pH = 6 with 2 M NaOH aqueous solution. The mixture was stirred at 70 °C for another 2 h. To the mixture was added 25 mL of a solution of $EuCl_3$ in ethanol (0.2 M). The mixture was stirred at 70 °C for 2 h. The resulting mixture was deposited to give a yellow solid. The solid was recrystallized from ethanol/acetone (1:1) twice to get the desired chelate.

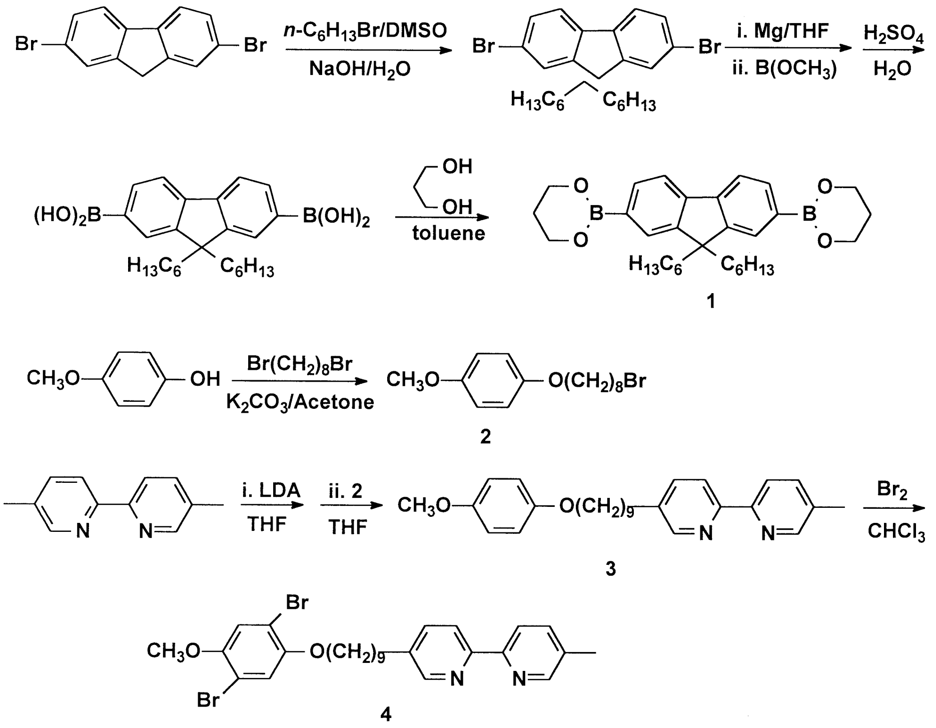
Preparation of Polymer 1. Under argon, monomer **1** (0.363 g, 0.72 mmol) and monomer **2** (0.416 g, 0.72 mmol) were added together with 1.0−1.5 mol % of $Pd(PPh_3)_4$, 5 mL of toluene, and 3 mL of 2 M aqueous potassium carbonate solution. The mixture was stirred vigorously at 80−90 °C for 48 h. The mixture was poured into stirred 100 mL of methanol to generate plenty of light-yellow precipitates. The solid was collected by filtration, washed with methanol and water. The material was washed with acetone in a Soxhlet extractor for 2 d. The light yellow solid was dried under vacuum at room temperature. (Yield: 85%.) ^1H NMR ($CDCl_3$, 300 MHz, ppm, δ): 8.47 (2H, s, Py−H), 8.26−8.22 (2H, m, Py−H), 7.81−7.66 (6H, m, Ar−H), 7.60−7.58 (2H, m, Ar−H), 7.12 (2H, s, Ar−H), 3.97 (2H, b, OCH_2), 3.84 (3H, b, OCH3), 2.65−2.61 (2H, b, CH_2), 2.37 (3H, s, CH_3), 2.03−1.02 (40H, m, OCH_2), 0.74−0.78 (6H, b, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz, δ, ppm): 151.09, 150.57, 148.66, 147.94, 139.90, 139.86, 139.07, 138.80, 138.40, 137.12, 136.86, 134.24, 131.43, 131.14, 127.95, 124.60, 124.45, 121.54, 121.42, 119.34, 116.96, 115.50, 69.99, 56.81, 55.07, 40.40, 32.84, 31.72, 31.65, 31.60, 30.95, 29.93, 50.56, 29.51, 29.35, 29.31, 29.18, 26.09, 24.06, 22.69, 18.37, 14.04. Anal. Calcd for $C_{52}H_{64}N_2O_2$: C 83.37; H 8.61; N 3.74. Found: C, 82.65; H 8.97, N 3.79.

General Procedure for Preparation of Complexes 1—7. Polymer **1** and three Eu^{3+} chelates were dissolved in a mixture of 10 mL of THF and 10 mL of ethanol, respectively. The mixture was refluxed for 2 d. After the mixture was poured into 50 mL of methanol, the precipitates were collected by filtration. The solids were washed with methanol, water, and acetone successfully. The solids were dissolved in THF and precipitated in methanol again. The desired complex was filtered, washed with acetone in a Soxhlet extractor for 2 d and dried under vacuum at room temperature.

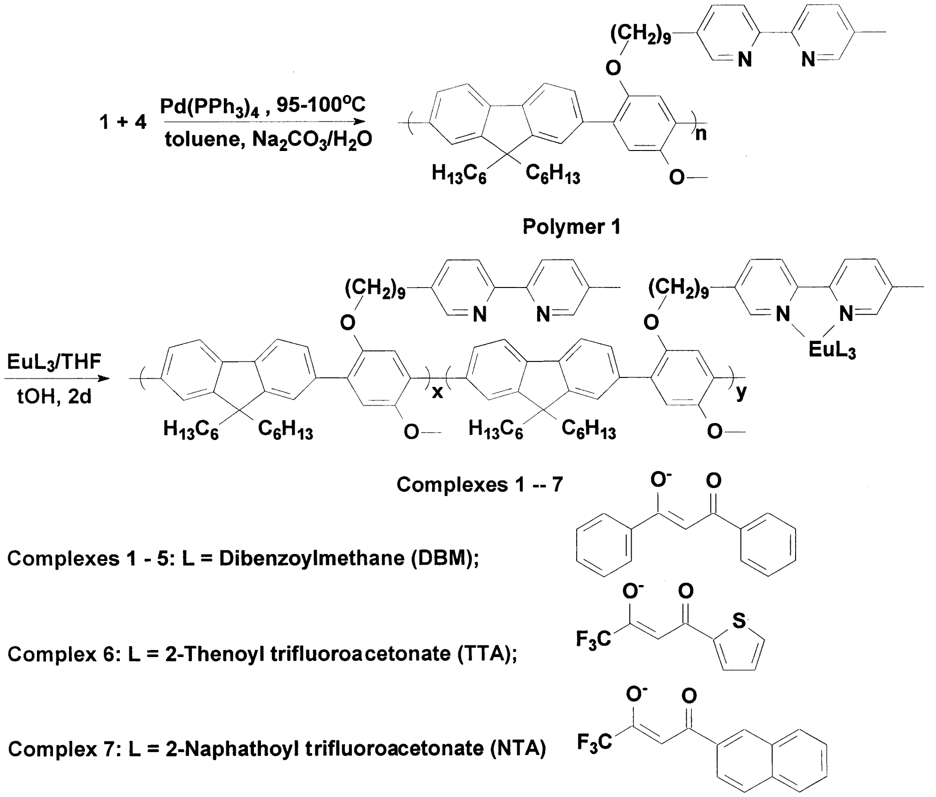
Results and Discussion

Synthesis of the Polymer and Complexes. The approach to seven complexes and their structures are sketched in Scheme 1. Monomer **1**, 9,9-di-*n*-hexylfluorene-2,7-bis(trimethylene boronate), was prepared using 2,7-dibromofluorene following literature procedures.[10] The lithiation of 5,5′-dimethyl-2,2′-bipyridiyne by 1 equiv of *n*-BuLi reacting with 1-(8-bromooctyloxy)-4-methoxybenzene afforded 1-methoxy-4-[9-(5′-methyl-2,2′-bipyridyl-5-yl)nonyloxy]benzene. The bromonation of 1-methoxy-4-[9-(5′-methyl-2,2′-bipyridyl-5-yl)nonyloxy]benzene gave monomer **4**. According to our previous contributions,[11] the Suzuki coupling polymerizations between monomers **1** and **4** with $Pd(PPh_3)_4$ as catalyst were employed to produce the desired polymer **1**, poly[(2-methoxy-5-(9-(5′-methyl-2,2′-bipyridyl)nonyloxy)-1,4-phenylene)-*alt*-*co*-(9,9-di-*n*-hexyl-9*H*-fluoren-2,7-diyl)]. After careful purification to remove ionic impurities and catalyst residues, the polymer was obtained as a pale yellow fibrous solid with a yield of over 85%. The

Scheme 1. Molecular Structures and the Synthetic Route of Complexes



Scheme 2



polymer was readily dissolved in organic solvents, such as chloroform, toluene, xylene, and THF. The chemical structure of the polymer was verified by ^{1}H NMR, ^{13}C NMR, and elemental analysis. The number molecular weight (M_n) measurement by GPC against the standard of polystyrene was about 2.3×10^4 with PD of 1.57 using THF as eluent.

Three Eu^{3+} chelates, Eu(TTA)$_3$, Eu(NTA)$_3$, and Eu(DBM)$_3$ were prepared following the typical procedures.[12] The structure of these ligands is also outlined in Scheme 2. Complexes **5**−**7** were prepared through refluxing a mixture of polymer **1** and one of three Eu^{3+} chelates [the chelate/the polymer (w/w%) = 80%] in THF and ethanol (v/*v* = 1/1) for 2d. The same procedure, refluxing a mixture of polymer **1** and Eu(DBM)$_3$ [Eu(DBM)$_3$/polymer (w/w%) = 10%, 20%, 40% and 60%] afforded complexes **1**−**4**. After precipitation, all complexes were washed with refluxing acetone in a Soxhlet

Table 1. Efficiencies of Energy Transfer Response to Eu^{3+} Contents and Ligands

compounds	% Eu (w/w)[a]	Eu (mol %)[a]	ratio of A_{Eu} and A_p[b]
complex **1**	0.58	3.01	0.17
complex **2**	1.29	6.97	0.70
complex **3**	2.53	14.7	0.98
complex **4**	3.57	22.2	2.94
complex **5**	3.89	24.8	3.84
complex **6** (with TTA)	3.58	21.1	1.07
complex **7** (with NTA)	3.67	23.9	0

[a] % Eu (w/w): the content of europium ion in complex. [b] A_{Eu}: integrating the area beneath the corrected fluorescence spectrum (from 605 to 640 nm); A_p: integrating the area beneath the corrected fluorescence spectrum (from 390 to 560 nm);

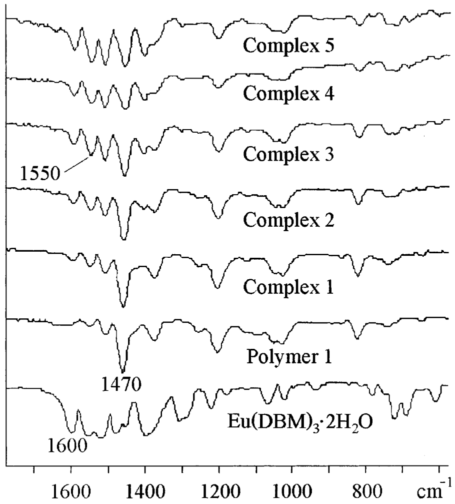


Figure 1. Comparison of infrared spectra of Eu(DBM)$_3$, polymer **1**, and complexes **1**−**5**.

extractor for 2 d to remove excess Eu(DBM)$_3$, in order to ensure no more dissociated Eu(DBM)$_3$ in the complexes, and then dried under vacuum at room temperature. The contents of Eu^{3+} in all complexes are outlined in Table 1.

Infrared Spectroscopy of Eu(DBM)$_3$, Polymer 1, and Complexes. We investigate the alteration of FT-IR spectra of polymer **1** with addition of Eu^{3+} chelates involved. The infrared spectra from 1700 to 500 cm^{-1} of polymer **1**, Eu(DBM)$_3$ and complexes **1**−**5** in KBr pellets are shown in Figure 1. In the infrared spectrum of polymer **1**, an obvious band near 1470 cm^{-1} due to the aromatic ring stretch was observed in this region. For the infrared spectrum of Eu(DBM)$_3$, it was likely that we observed the band near 1600 cm^{-1} mainly due to the C=O stretch and another band near 1550 cm^{-1} due to the C=C stretch.[13] respectively, which we did not find in the spectrum of polymer **1**. However, it was pointed out that the spectra of polymer **1** showed evident changes after Eu(DBM)$_3$ was coordinated with the bipyridyl group at the side chain of polymer **1**. For complexes **1**−**5**, these two bands were distinctly enhanced with an increase of the content of Eu(DBM)$_3$ in the complexes in comparison with the intensity of the band near 1470 cm^{-1}. In the spectrum of complex **5**, the intensity of the band near 1550 cm^{-1} was as high as that of the band near 1470 cm^{-1}, and the intensity of the band near 1600 cm^{-1} was $^{2}/_{3}$ as that of near 1470 cm^{-1}. This indicated that Eu(DBM)$_3$ successfully grafted polymer **1** after the products were carefully washed with refluxing acetone.

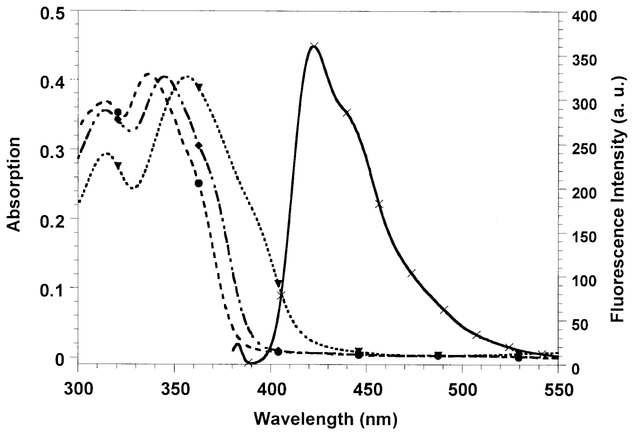


Figure 2. Absorption spectra of Eu(DBM)$_3$DMBPy (triangle), Eu(TTA)$_3$DMBPy (diamond), and Eu(NTA)$_3$DMBPy (circle) and the PL spectrum of polymer **1** (cross).

Thermal Stability. The polymer exhibited an onset of degradation up to 290 °C with no weight loss at lower temperature; however, the onset decomposition temperatures reduced to 210 or 220 °C for complexes. When the experiment was processed in air, the residue of complexes was left. Differental scanning calorimetry (DSC) also was employ to investigate the thermal behavior of the polymer and complexes. A heating rate of 20 °C/min from 20 to 250 °C and a nitrogen flow rate of 70 cm^3/min were employed. The T_g values were obtained from the onset temperatures of these transitions fro DSC. All polymers possessed T_g higher than 50 °C and were in amorphous state in room temperature. The polymer possessed lower T_g than the complexes.

Optical Properties. Figure 2 compares the absorption spectra of three Eu^{3+} chelates, Eu(DBM)$_3$DMBPy, Eu(TTA)$_3$DMBPy, and Eu(NTA)$_3$DMBPy (DMBPy for 5,5′-dimethyl-2,2′-bipyridyl) and the photoluminescent (PL) spectrum of the polymer **1** in solid states. The absorption of polymer **1** began at 420 nm and peaked at 371 nm; the PL maximum of polymer **1** peaked at about 422 nm. We observed the different spectral overlaps between the absorption of these Eu^{3+} chelates and the fluorescence of polymer **1**.

To optimize Eu^{3+} chelates for our conjugated polymer, we have to determine which one among the three Eu^{3+} ligands is suitable for accepting energy from our polymer. Three new complexes **5**−**7** with different Eu^{3+} ligands containing almost the same Eu^{3+} content without the dissociated ligand were prepared. The slight redshift in absorption spectra of complexes **5**−**7** in the solid state was observed in comparison with that of polymer **1**. Figure 3 exhibits PL spectra of complexes **5**−**7** in the solid state. All films were spin-cast from solutions of three complexes in xylene (2% w/v). As shown in Figure 3, in comparison with polymer **1**, a new obvious peak at about 612 nm, which was the typical characteristic of Eu^{3+} coming from transitions between its $^5D_0$ and $^7F_2$ levels, was observed in the PL spectrum of complex **5**; however, the emission peak intensity of polymer **1** at about 422 nm was quite low in comparison with the new peak. For complex **6**, the original emission peak of polymer **1** and the new peak at about 612 nm were observed in its PL spectrum. However for complex **7**, no peak at about 612 nm was found in its PL spectrum. It shows that among the three Eu^{3+} chelates, the obvious intramolecular energy transfer process from the

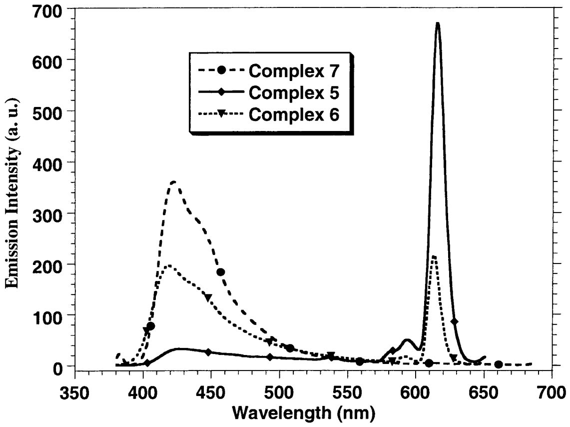


Figure 3. Comparison of the PL spectra of complexes **5** (diamond), **6** (triangle) and **7** (circle) in film states.

polymer backbone to $Eu(DBM)_3$ was involved; however, for $Eu(NTA)_3$, no transfer processes were observed. The efficiencies of energy transfer for complexes **5**−**7** are listed in Table 1.

The normal process of photoluminescence is that a conjugated polymer is photoexcited by absorption of a photon with high energy to generate an exciton. The relaxation of the exciton to the lowest ground state can be either radiative, resulting in the emission of a lower energy photo, or nonradiative with no contribution to the photoluminescence signal.[14] However, for the process of energy transfer, a molecule, as a donor, absorbs energy, undergoes intersystem crossing into a triplet state, and then transfers its energy to Eu^{3+} chelates, as an acceptor. The acceptor then may relax to its ground state by emitting a lower energy photon. This process requires a nonzero energy overlap between the absorption spectrum of Eu^{3+} chelates and the PL spectrum of polymer **1** in order to transfer energy from the donor to acceptor.[9,15,16] Our result is due to better spectral overlap between the fluorescence spectrum of polymer **1** and the absorption spectrum of $Eu(DBM)_3$-DMBPy than those between those of polymer **1** and of other two chelates. Therefore, $Eu(DBM)_3$ is the best one among these three chelates for accepting energy from the backbone of polymer **1** in our experiments.

The investigation of the optimal amount of $Eu(DBM)_3$ in the complexes to transfer the energy is also studied. Five complexes containing different Eu^{3+} contents were prepared by the same procedure. The Eu^{3+} contents in every complex are listed in Table 1. Their PL spectra in solid states are also shown in Figure 4. The maximum absorption of five complexes was about 0.22−0.32. The ratios of A_{Eu}/A_p, which excluded the possibility of the influence of the thickness of the film on the intensity of their fluorescence, are also listed in Table 2. Among these five complexes, the emission intensity of complex **5** at 612 nm containing approximately 24.8 mol % (about 3.89% w/w) content of Eu^{3+} was the highest and that of the polymer backbone at 422 nm was lowest. For complex **5**, the ratio was 3.84 while the content (w/w) of Eu^{3+}. As shown in Figure 4, at the low content of Eu^{3+}, 3.01 mol % (0.58% w/w), the ratio was only 0.17, which meant that energy transfer from the backbone to the Eu^{3+} center was incomplete. This indicates that the efficiency of energy transfer from the backbone of complexes to Eu^{3+} chelates was enhanced with the increase of the Eu^{3+} content. For our complex, since the $Eu(DBM)_3$ directly bonded with the polymer, the Eu^{3+} content could not increase limitlessly over 100 mol % (9.67% w/w). For blends, such as Eu^{3+} doped CN−PPP, the concentration of Eu^{3+} for the highest Eu^{3+} fluorescence efficiency is about 5−10% (w/w); the energy transfer efficiency was reduced by concentration quenching at the higher Eu^{3+} concentration.[3a] However, for our complex, the Eu^{3+} content of complex **5** was much higher than the maximum concentration of Eu^{3+} in the blends. From Table 1, it was observed that the Eu^{3+} characteristic light intensity was still enhanced with the increase of the Eu^{3+} contents; the concentration-quenching or self-quenching did not observed. Therefore, our desired complexes might avoid the concentration quenching or self-quenching usually existing in blends of conjugated polymers and Eu^{3+} chelates.

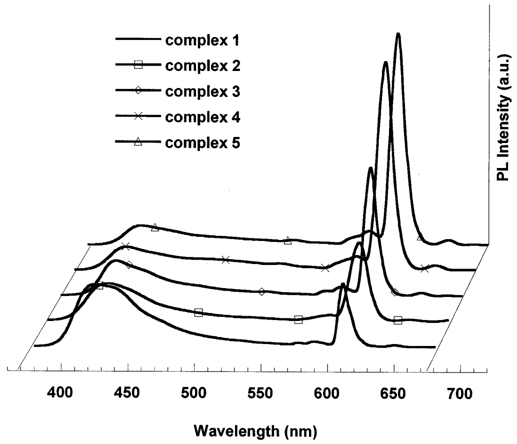


Figure 4. Comparison of the PL spectra of complexes **1** (circle), **2** (square), **3** (diamond), **4** (cross) and **5** (triangle) in film states.

Table 2. Comparison of the Decomposition Onset Temperature and Electrochemical Properties of the Polymer and Complexes

		energy levels (eV)		
compounds	dec onset (°C)	HOMO	LUMO	band gap
polymer **1**	290	5.78	2.67	3.11
complex **1**	210	5.85	2.70	3.15
complex **2**	220	5.80	2.63	3.17
complex **3**	220	5.78	2.64	3.14
complex **4**	220	5.78	2.63	3.15
complex **5**	220	5.72	2.61	3.11

Electrochemical Properties. The redox properties as well as the HOMO and LUMO energy levels of the polymer and complexes were crucial parameters for the device configuration consideration. All potentials were measured in a three-electrode cell with 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) or 0.1 M of tetrabutylammonium hexylfluorophosphate (n-Bu_4NPF_6) in acetonitrile as the electrolyte, using a Ag/Ag^+ electrode (0.1 M $AgNO_3$ in acetonitrile) as the reference electrode (0.34 V vs SCE), a platinum wire as the counter electrode, and a platinum disk (effective area 0.5−1.0 cm^2) as the working electrode. All experimental values were corrected with respect to SCE.

Observed from their cyclic voltammograms figures, the electrochemical properties of the polymer and complexes were easily compared. The oxidation and reduction reactions of the polymer and complexes are reversible. The cyclic voltammogram of polymer **1**, and complexes **3** and **5** (all complexes exhibited the same results) were displayed in Figure 5. On sweeping

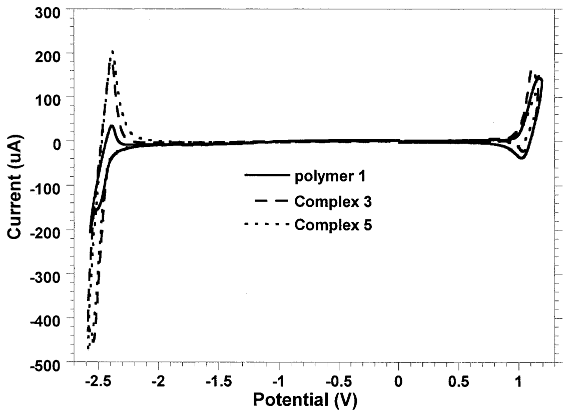


Figure 5. Cyclic voltammograms of polymer **1** and complex **3** and complex **5** films coated on platinum plate electrodes in acetonitrile containing 0.1 M Bu_4NClO_4.

polymer **1** cathodically, the onset of the n-doping occurred at about −2.08 V, above which the cathodic current quickly increased, and a cathodic peak appeared at −2.45 V. A corresponding reoxidation peak appeared at −2.40 V. For oxidation, the onset potential was about 0.98 V and an anodic peak occurred at 1.20 V with the corresponding rereduction peak at 1.02 V. We observed that complexes **1**−**5** exhibited the similar redox behavior as polymer **1**, which further indicated that the attachment of $Eu(DBM)_3$ at the side chain did not alter the backbone and conjugation length of polymer **1**.

The energies of the HOMO and LUMO levels of the polymers were calculated from the onset potential of the p-doping and n-doping, respectively.[17] Calculated HOMO and LUMO energy levels data and the band gap for the polymer and complexes from electrochemical measurement were also summary in Table 2. These results demonstrated that the energy levels of the complexes were the same as polymer **1** and had no alternation with the addition of the Eu^{3+} chelates.

Fabrication of the PLEDs. To investigate the electroluminescent properties of our new complex and to understand internal energy transfer within the whole molecule under the electronic field, complex **5**, which has the highest energy transfer efficiency among all complexes, was selected as the active material to fabricate polymer light-emitting diodes (PLEDs) with multiple layers. Their configurations were ITO/PVK/complex **5**/Ba/Al (ITO wired as the positive electrode). Indium−tin oxide (ITO) coated glass ($\sim$20 Ω/□) was used as the substrate. By spin-casting a PVK layer (about 50 nm) on the ITO substrate, complex films were spin-cast from xylene solutions onto this PVK layer. The thickness of films of complex **5** was around 100 nm. A barium layer was then deposited onto the top of the polymer films under pressures around 10^{-6} Torr at evaporating rates of 5−8 Å/s, and following by depositing a aluminum layer onto the top, the thickness of the cathode was about 200 nm. Diode area was 15 mm^2 defined by the cathode. Device characteristics were measured with a calibrated Si photodiode. All processes and measurements were carried out inside a glovebox filled with nitrogen.

In forward bias, the ITO electrode was wired as the anode. The turn-on voltage for light output was about 15 V. The EL spectrum of PLEDs using complex **5** is showed in Figure 6. The figure exhibited a striking feature in that there was no emission from the backbone of polymer **1**, but the PL spectrum of complex **5** exhibited emission from polymer **1**. This may be due to the substantial difference between the PL and EL spectra probably arising from the different ways that neutral excitations are formed.[3a] For the PL process, the complex is excited by absorption of light, and the excited states are created on polymer backbones and then transfer to the $Eu(DBM)_3$, so the emission of the polymer can also be observed; however, for the EL process, the complex is excited by injecting electrons from the anode and hole from the cathode, so the neutral excitations may be formed directly on the $Eu(DBM)_3$. The external EL efficiency was only 0.07% and the luminance was about 11 cd/m^2 at 25 V.

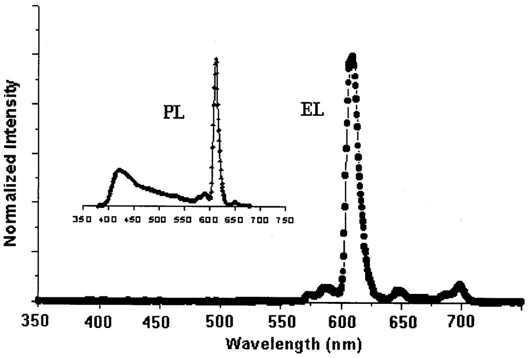


Figure 6. EL spectrum of complex **5** with the configuration of ITO/PVK/complex **5**/Ba/Al.

Conclusions

In summary, a convenient approach to the complexes consisting of a novel blue conjugated polymer coordinated with Eu^{3+} chelates for achieving narrow bandwidth red emission for PLEDs had been developed in our group. The careful purification ensured no dissociated $Eu(DBM)_3$ in the complexes. FT-IR results revealed that $Eu(DBM)_3$ successfully attached to the side chain of the polymer. Although TGA results showed that the decomposition temperature of complexes **1**−**5** decreases, the glass transition temperature (T_g) of complexes **1**−**5** improved with increase of the content of the $Eu(DBM)_3$. The films of complexes **1**−**6** exhibited the sharp red emission under UV radiation. Quantitative measurements of the fluorescent efficiencies of these complexes demonstrated that $Eu(DBM)_3$ was obviously better for energy transfer from our blue-emitting conjugated polymer than two others, $Eu(TTA)_3$ and $Eu(NTA)_3$. The reason arose from the good spectral overlap between the PL spectra of the host, polymer **1**, and the absorption of the guest, $Eu(DBM)_3$. The investigation of the optimal amount of $Eu(DBM)_3$ showed that the content of Eu^{3+} in the complex was about 20 mol % (3.5% w/w), which was enough to accept energy from the main chain of the complex. The Eu^{3+} characteristic emission light intensity quickly was enhanced, and the fluorescence intensity of polymer **1** obviously decreased with the increase in the content of Eu^{3+} in complexes **1**−**5**. No concentration quenching or self-quenching was observed in our complexes. The pure red-emission was achieved from the fabrication of PLEDs using complex **5** as the active material within the configuration ITO/PVK/complex **5**/Ba/Al. This is the first time to achieve the narrow sharp red emission from conjugated polymers through the efficient internal energy transfer from the backbone of complexes to the Eu^{3+} center at the side chain for polymeric light-emitting diodes. Further work to improve the performance of devices is still ongoing in our group.

References and Notes

(1) (a) Burroughs, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539. (b) Gustafson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477. (c) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; DosSantos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121. (d) Heeger, A. J. *Solid State Commun.* **1998**, *107*, 673.

(2) Cao, Y.; Parker, I. D.; Yu, G.; Zhang, C.; Heeger, A. J. *Nature (London)* **1998**, *397*, 414.

(3) (a) McGehee, M. D.; Bergstedt, T.; Zhang, C.; Saab, A. P.; O'Regan, M. B.; Bazan, G. C.; Srdanov, V. I.; Heeger, A. J. *Adv. Mater.* **1999**, *11*, 1349. (b) Virgili, T.; Lidzey, D. G.; Bradley, D. D. C. *Adv. Mater.* **2000**, *12*, 58. (c) Virgili, T.; Lidzey, D. G.; Bradley, D. D. C. *Synth. Met.*, **2000**, *111*, 203. (d) Cerullo, G.; Stagira, S.; Zavelani-Rossi, M.; De Silvestri, S.; Virgili, T.; Lidzey, D. G.; Bradley, D. D. C. *Chem. Phys. Lett.* **2001**, *335*, 27.

(4) (a) Jiang, B.; Jones, W. E. Jr. *Macromolecules* **1997**, *30*, 5575. (b) Burn, P. L.; Lo, S.-C. *Synth. Met.* **1999**, *102*, 1089. (c) Iqbal, R.; Yahioglu, G.; Milgrom, L.; Moratti, S. C.; Holmes, A. B.; Cacialli, F.; Morgao, J.; Friend, R. H. *Synth. Met.* **1999**, *102*, 1024.

(5) (a) Ng, P. K.; Gong, X.; Chan, S. H.; Lam, L. S. M.; Chan, W. K. *Chem. Eur. J.* **2001**, *7*, 4358. (b) Chan, W. K.; Ng, P. K.; Gong, X.; Hou, S. *J. Mater. Chem.* **1999**, *9*, 2103. (c) Yu, S. C.; Hou, S.; Chan, W. K. *Macromolecules* **1999**, *32*, 5251.

(6) Sinha, A. P. B. In *Spectroscopy in Inorganic Systems*; Rao, C. N. R., Ferraro, J. R., Eds.; Academic: New York, 1971; Vol. 2.

(7) (a) Kido, J.; Nagai, K.; Okamoto, Y.; Skotheim, T. *Chem. Lett.* **1991**, 1267. (b) Takada, N.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1994**, *33*, L863. (c) Kido, J.; Ikeda, W.; Kimura, M.; Nagai, K. *J. Appl. Phys.* **1996**, *35*, L394. (d) Kido, J.; Hayase, H.; Hongawa, K.; Nagai, K. Okuyama, K. *Appl. Phys. Lett.* **1994**, *65*, 2124. (e) Liu, L.; Li, W.; Hong, Z.; Peng, J.; Liu, X.; Liang, C.; Liu, Z.; Yu, J.; Zhao, D. *Synth. Met.* **1997**, *91*, 267.

(8) (a) Dawson, W. R.; Kropp, J. L.; Windors, M. W. *J. Chem. Phys.* **1966**, *45*, 2410. (b) Metlay, M. *J. Electrochem. Soc.* **1964**, *111*, 1253.

(9) (a) Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1. (b) Furue, M.; Yoshidzumi, T.; Kinoshita, S.; Kushida, T.; Nozakura, S.; Kamachi, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1632. (c) Gholamkhass, B.; Nozaki, K.; Ohno, T. *J. Phys. Chem. B* **1997**, *101*, 9010. (d) Foster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7.

(10) (a) Ranger, M.; Leclerc, M. *Can. J. Chem.* **1998**, *8*, 1571. (b) Ranger, M.; Leclerc, M. *Chem. Commun.* **1997**, 1597. (c) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686. (d) Wu, R.; Schumm, J. S.; Pearson, D. L. Tour, J. M. *J. Org. Chem.* **1996**, *61*, 6906. (e) Parakka, J. P.; Jeevarajan, J. A.; Jeevarajan, A. S.; Kispert, L. D.; Cava, M. P. *Adv. Mater.* **1996**, *8*, 54.

(11) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Yu, W.-L.; Pei, J.; Cao, Y.; Huang, W.; Heeger, A. J. *Chem. Commun.* **1999**, 1837. (c) Yu, W.-L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 828.

(12) Melby, L. R.; Rose, N. J.; Abramson, E.; Caris, J. C. *J. Am. Chem. Soc.* **1964**, *86*, 5117.

(13) Liang, C. Y.; Schimitschek, E. J.; Trias, J. A. *J. Inorg. Nucl. Chem.* **1970**, *32*, 811.

(14) Lakowicz, J. In *Principles of Fluorescence Spectroscopy*; Plenum: New York, 1983.

(15) Dogariu, A.; Gupta, R.; Heeger, A. J.; Wang, H. *Synth. Met.* **1999**, *100*, 95.

(16) Mattoussi, H.; Murata, H.; Merritt, C. D.; Lizumi, Y.; Kido, J.; Kafafi, Z. *J. Appl. Phys.* **1999**, *86*, 2642.

(17) (a) Li, Y.; Cao, Y.; Gao, J.; Wang, D.; Yu, G.; Heeger, A. J. *Synth. Met.* **1999**, *99*, 243. (b) De Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth. Met.* **1997**, *87*, 53. (c) Eckhardt, H.; Shacklette, L. W.; Jen, K. Y.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, *91*, 1303. (d) Cervini, R.; Li, X.-C.; Spencer, G. W. C.; Holmes, A. B.; Moratti, S. C.; Friend, R. H. *Synth. Met.* **1997**, *84*, 359.

MA020529B