

Synthesis and Characterization of Fluorescent Poly[fluorene-co-phenylene-1-(di-2-pyridylamine)] Copolymer and Its Ru(II) Complex

K. DINAKARAN, CHIA-HUNG CHOU, SO-LIN HSU, KUNG-HWA WEI

National Chiao Tung University, Department of Materials Science and Engineering, Taiwan-30049, Republic of China

Received 21 May 2004; accepted 21 May 2004

DOI: 10.1002/pola.20317

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: 2,2'-dipyridylamine substituted poly(fluorene-co-phenylene) copolymers with different concentrations of dipyrindylamine have been synthesized by Suzuki polycondensation. These polymers were found to be soluble in organic solvents such as tetrahydrofuran, chloroform, and dimethylformamide. The photoluminescence of the copolymer was slightly blueshifted as the concentration of dipyrindylamine was increased. The introduction of dipyrindylamine and the ruthenium complex into the polymer significantly improved the photoluminescence efficiency. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 4838–4846, 2004

Keywords: polyfluorene copolymers; dipyrindylamine; ruthenium complex; fluorescence; conjugated polymers

INTRODUCTION

Investigations concerning the synthesis of new blue luminous materials for light emitting diode (LED) applications have attracted a great deal of attention in recent years. Conjugated polymers with metal complexes can be used as the active material in LEDs, photovoltaic diodes, and polymer lasers.^{1–4} A large number of light emitting polymers (LEPs) have been reported during the last decade.⁵ Polymers with aromatic or heterocyclic units generally absorb light with wavelengths between 300 and 600 nm as a result of $\pi-\pi^*$ transitions in their conjugated structures.³ The introduction of substituents into the π -conjugated system can disturb the π -conjugation length along the chain, thus causing changes in the energy gap between the highest occupied mo-

lecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This enables a tuning of emission color. The emission colors of the most common π -conjugated polymers used in polymer LEPs range from blue to red.

By varying the structure of the side-chains, the photoemission properties of the polymers can be tuned. For example, the color of the emitted light and the luminescence quantum yield is strongly influenced by the steric and electronic effects of the side-chains.^{6–8} Recent reports show that the presence of *meta*-phenylene along the polyphenylenevinylene (PPV)⁹ and polyfluorene (PF)^{10,11} chain effectively interrupts π -conjugation, making the emission color tunable. There have been recent reports on PPV derivatives containing pendant carbazole¹² and triphenylamine units.¹³ For improvements in the charge-injection and charge-transport properties of polyfluorene, many moieties have been introduced, such as triarylamine, benzothiazole, quinoline, dicyanobenzene, and oxadiazole.^{14,15} However, to the best of our knowledge, there has been no report of polymers having

Correspondence to: K.-H. Wei (E-mail: khwei@cc.nctu.edu.tw)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 42, 4838–4846 (2004)
© 2004 Wiley Periodicals, Inc.

pendant di-2-pyridylamine. Dipyrindylamine has been reported as one of the best candidates for blue light-emitting materials and possesses an excellent ability to coordinate transition-metal ions.^{16,17} It has been demonstrated that di-2-pyridylamine or 7-azaindole can produce a bright blue luminescence when deprotonated and or when bound to a metal center.¹⁸ Conjugated polymers containing luminescent transition metal complexes can be used as electrophosphorescence devices because in such systems, the excited energy can be transferred from the polymer chain into the metal complex, leading to triplet excitation and high phosphorescence efficiency.¹⁹ Here, we report the synthesis of di-2-pyridylamine substituted poly(fluorene-co-phenylene), with different dipyrindylamine concentrations and its ruthenium complex. Ruthenium(II) complexes of 2,2-bipyridine in polymers are favored complexes because of their efficient and well-characterized photo-physics.^{20,21}

EXPERIMENTAL

General Considerations

Dipyrindylamine, *n*BuLi, fluorine, and 1,3,5-tribromobenzene were purchased from Aldrich and were used as received. All other solvents were distilled before use. ¹H and ¹³C NMR spectra were recorded on a Varian VXR 300 instrument. Fourier-transform infrared (FTIR) spectra were recorded on a Nicolet IR spectrometer with KBr pellets. The molecular weight was measured by gel permeation chromatography (GPC) against a polystyrene standard with tetrahydrofuran (THF) as the eluent. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on a TA Instruments 2000, at a heating rate of 10 °C/min under a nitrogen atmosphere. Ultraviolet-visible (UV-vis) and photoluminescence (PL) spectra were recorded on an ARC spectraPro-150. Polymer film thickness was measured with an α -Stepper Dektak ST surface profiler. Cyclic voltammetry analysis was carried out on a CHI600A electrochemical analyzer, with a conventional three electrode setup (0.1 M tetrabutylammonium perchlorate in THF versus Ag/AgCl, with glassy carbon as the working electrode and platinum wire as the auxiliary electrode).

1-(Di-2-pyridylamine)-3,5-dibromobenzene (DP)

Tribromobenzene (1 g, 3.1 mmol), 2,2-dipyrindylamine (544 mg, 3.1 mmol), K₂CO₃ (471 mg 3.41 mmol), and copper powder (10 mg) were refluxed in *N,N*-dimethylformamide for 48 h. The reaction mixture was cooled and poured into water. The precipitated solid product was extracted with ethylacetate, dried over anhydrous MgSO₄, and purified by column chromatography [silica gel, ethylacetate : hexane (1:1), R_f: 0.32].

Yield 950 mg (76%). MP = 122–123 °C. ¹H NMR: 8.32–8.35 (d, 2H, ArH), 7.57–7.63 (m, 2H, ArH), 7.42–7.43 (m, ¹H, ArH), 7.19–7.20 (d, 2H, ArH), 6.97–7.01 (m, 4H, ArH). ¹³C NMR: 157.26, 148.92, 147.19, 138.03, 130.45, 128.01, 123.26, 119.25, 117.41. MASS: M⁺ = 404, M⁺¹ = 405, 404, 324, 244, 166, 140, 78, 51. HRMS Calcd. for C₁₆H₁₁N₃Br₂: 403.9318 Found: 403.9252. ELEM. ANAL. Calcd. for C₁₆H₁₁N₃Br₂: C, 47.44%; H, 2.73%; N, 10.30%. Found: C, 47.85%; H, 3.04%; N, 10.38%.

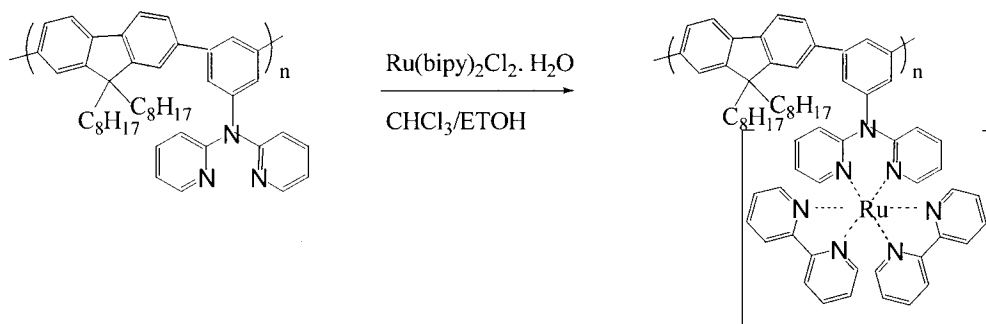
Synthesis of 9,9-Dioctylfluorene^{22(a,b)}

To a solution of 8.48 g (51.1 mmol) of fluorene (Aldrich) in THF (120 mL) at –78 °C we added, dropwise, 42.9 mL (107.3 mmol) of *n*-butyllithium (2.5 M in hexane; Aldrich). The mixture was stirred at –78 °C for 45 min and 22.70 g (117.5 mmol) of octylbromide (Aldrich) in THF (25 mL) was added, dropwise, to the mixture. The solution was allowed to warm to room temperature and was stirred for 3 h. The mixture was poured into water and extracted with ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure.

R_f: 0.85 (silica TLC in hexane). Mp: 35–37 °C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.82 (dd, 2H, J = 4.3 Hz), 7.42 (m, 6H), 2.12 (m, 4H, J = 3.8 Hz), 1.35–1.24 (m, 20H), 0.96 (t, 6H, J = 7.1 Hz), 0.79 (m, 4H, J = 3.8 Hz). HRMS Calcd. for C₂₉H₄₂: 390.6510. Found: 390.5972.

2,7-Dibromo-9,9-dioctylfluorene^{22(a,c)}

To a solution of 9,9-dioctylfluorene (15.01 g, 38.4 mmol) in CHCl₃ (58 mL) at 0 °C we added 96 mg (0.59 mmol) of ferric chloride and 4.14 mL (80.5 mmol) of bromine. It is important that the reaction proceeded in the dark to avoid any bromination of the aliphatic part of the molecule. The solution was warmed to room temperature and



Scheme 1. Synthesis of PF-DP-Ru(bipy)₂ complex.

was stirred for 3 h. The resulting slurry was poured into water and washed with sodium thiosulfate until the red color disappeared. The aqueous layer was extracted with CHCl₃ (twice), and the combined organic layers were dried over magnesium sulfate to afford 21.07 g (96%) of the title product.

R_f: 0.88 (silica TLC in hexane). Mp: 44–46 °C. ¹H NMR (300 MHz, CDCl₃): % (ppm) 7.53 (d, 2H, *J* = 7.7 Hz), 7.46 (d, 2H, *J* = 1.8 Hz), 7.44 (d, 2H, *J* = 1.1 Hz), 1.91 (m, 4H, *J* = 3.7 Hz), 1.26–1.05 (m, 20H), 0.83 (t, 6H, *J* = 3.6 Hz), 0.58 (m, 4H, *J* = 3.5 Hz). HRMS Calcd. for C₂₉H₄₀79Br₂: 546.1500. Found: 546.1496.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene^{22(a,d)}

To a solution of 2,7-dibromo-9,9-dioctylfluorene (5 g, 9.1 mmol) in THF (100 mL) at –78 °C we added, by syringe, 7.64 mL (19.1 mmol) of *n*-butyllithium (2.5 M in hexane; Aldrich). The mixture was stirred at –78 °C, warmed to –10 °C for 15 min, and cooled again at –78 °C for 15 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.00 g, 21.5 mmol; Aldrich) was added rapidly to the solution, and the resulting mixture was warmed to room temperature and stirred for 24 h. The mixture was poured into water and extracted with ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by column chromatography (silica gel, 7% ethyl acetate in hexane, *R_f*: 0.22) to provide 3.80 g (65%) of the title product.

¹H NMR (300 MHz, CDCl₃): % (ppm) 7.84 (d, 2H, *J* = 7.6 Hz), 7.78 (s, 2H), 7.75 (d, 2H, *J* = 7.6 Hz), 2.03 (m, 4H, *J* = 3.4 Hz), 1.43 (s, 24H), 1.26–1.04 (m, 20H), 0.83 (t, 6H, *J* = 6.6 Hz), 0.58

(m, 4H). HRMS Calcd. for C₄₁H₆₄O₄11B₂: 642.4990. Found: 642.4356.

Polymerization

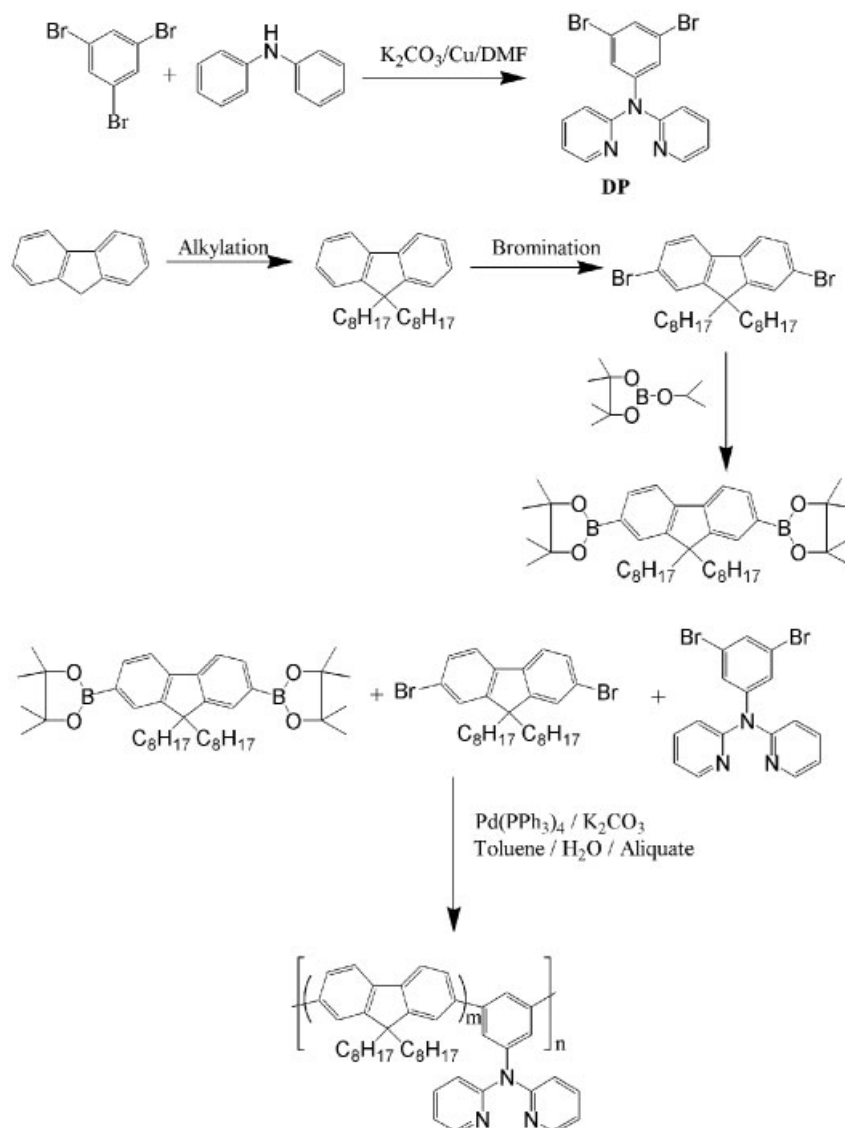
Suzuki Coupling Reaction

Carefully purified 1-(di-2-pyridylamine)-3,5-dibromobenzene, 2,7 dibromo-9,9-dioctylfluorene, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene in appropriate quantities, and (PPh₃)₄Pd(0) (1 mol %) were dissolved in a mixture of toluene and aqueous 2 M K₂CO₃ (1:1.5 toluene). The solution was placed under a nitrogen atmosphere and was refluxed with vigorous stirring for 48 h. The entire mixture was then poured into methanol (200 mL). The precipitated material was recovered by filtration through a Buchner funnel and was washed with dilute HCl. The resulting polymers were soluble in THF, CHCl₃, and dimethylformamide (DMF).

Yield: 50–60%. Poly[fluorene-co-phenylene-1-(di-2-pyridylamine)] (PFDP) = ¹H NMR(300 MHz, CDCl₃): % (ppm) 8.40–8.56 (d, 2H, ArH), 7.38–7.75(m, 8H, ArH), 7.27(s, 1H, ArH), 7.00–7.06(m, 4H, ArH), 6.82(d,2H, ArH), 1.97(m, 4H), 1.23–1.01(m, 20H), 0.83–0.85(m, 6H), 0.77(m, 4H). ELEM. ANAL. Calcd. for PFDP: C, 85.20%; H, 8.11%. Found: C, 84.49%; H, 7.84%.

Ruthenium Complexation

Ruthenium metal complexation (Scheme 1) was carried out in a chloroform/ethanol system at reflux with Ru(bipy)₂Cl₂·2H₂O with a PF-DP alternate copolymer for 5 h. After cooling, the polymer was recovered by precipitation with the addition of aqueous NH₄PF₆, and filtered and dried in a vacuum oven at 50 °C for 24 h.



Scheme 2. Synthetic route to prepare the PF-DP copolymers.

IR (KBr): 1581–1583 ($-C=N$), 1430–1465 ($-C-N$), 1259, 1168, 1141, 1091, 1021, 801. 1H NMR(300 MHz, $CDCl_3$): δ (ppm) 8.37–8.52 (d, 2H, ArH), 7.84–8.22 (m, 14H, ArH), 7.15–7.51(m, 10H, ArH), 7.21(s, 1H, ArH), 6.88–6.96(m, 4H, ArH), 6.82(d, 2H, ArH). 1.85(m, 4H), 1.22–1.00(m, 20H), 0.75–0.80(m, 6H), 0.67(m, 4H).

RESULTS AND DISCUSSION

Synthesis

The key monomer, 1-(di-2-pyridylamine)-3,5-dibromobenzene (DP), was prepared by Ulmann

condensation of di-2-pyridylamine with tribromobenzene using K_2CO_3 and Cu powder in DMF.¹² The polymer was synthesized with a Suzuki coupling reaction of aryl dioxaborolane and dibromo compound and was carried out in a mixture of toluene and aqueous potassium carbonate (2 M) containing $Pd(PPh_3)_4$. The complete procedure for the synthesis is given in Scheme 2. The comonomer feed ratios of dibromodiodoalkylfluorene and DP are 90:10, 70:30, 50:50, 45:65, 20:80, 10:90, and 00:100 and the corresponding copolymers are named PF-DP10, PF-DP30, PF-DP50, PF-DP65, PF-DP80, PF-DP90, and PF-DP. These polymers were found to be soluble in organic sol-

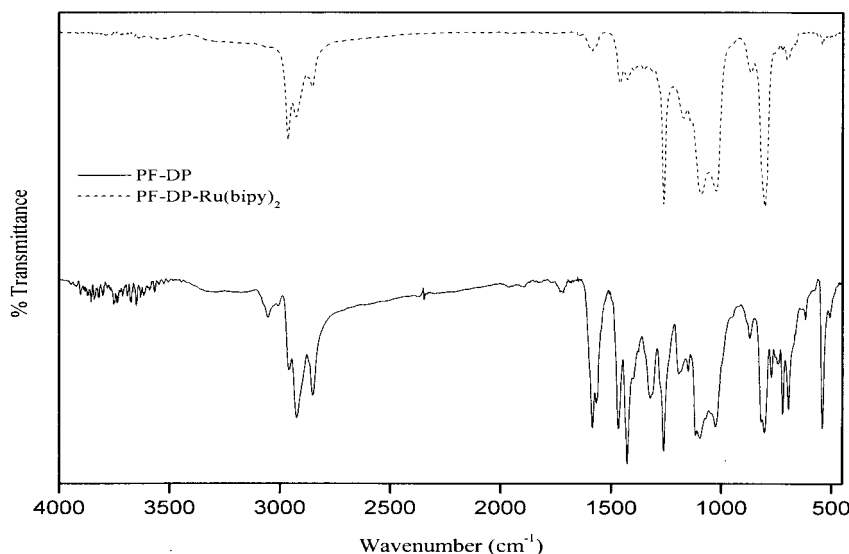


Figure 1. FTIR spectra of PF-DP and PF-DP-Ru(bipy)₂.

vents such as THF, CHCl₃, and DMF. Ruthenium metal complexation (Scheme 1) was carried out in a chloroform/ethanol system at reflux using Ru(bipy)₂Cl₂·2H₂O with PF-DP an alternate copolymer. The chemical structures of the polymers were verified by FTIR, NMR, and elemental analysis. Figure 1 shows the FTIR spectra of PF-DP and PF-DP-Ru(bipy)₂. The absorption bands that appear at 1581–1583 cm⁻¹ are characteristic of —C=N. The band at 1430–1465 cm⁻¹ for the —C—N stretch bond indicates the presence of dipyriddyamine, which is not observed in pure PF, and its intensity is substantially decreased in FTIR spectra of the Ru-bipyridine complex, as shown in Scheme 1, confirming the successful complexation of the polymer PF-DP. The elemen-

tal analysis results showed no halogen content in the polymers, indicating an absence of residual 2,7-dibromofluorene that is consistent with the FTIR data. The ¹H NMR spectrum of PF-DP shows aromatic protons of dipyriddyamine at 8.40–8.56 (d, 2H, ArH), 7.38–7.75 (m, 8H, ArH), and 7.27 (s, 1H, ArH). 7.00–7.06 (m, 4H, ArH) and 6.82(d,2H, ArH) were assigned to aromatic protons of fluorene moiety. Aliphatic protons appeared at 1.97c(m, 4H), 1.23–1.01 (m, 20H), 0.83–0.85 (m, 6H), and 0.77(m, 4H).

The molecular mass and polydispersity index (PDI) of each copolymer were measured by GPC with THF as the eluent and are given in Table 1. The number-average molecular weight (*M_n*) of the polymers was determined to be 8000–23000, with

Table 1. Molecular Weight and Thermal Properties of PF-DP Copolymers

Copolymer	Molecular Weight ^a		PDI ^b	Tg ^c (°C)	TGA, 5% Decomposition Temp. (°C)
	<i>M_n</i>	<i>M_w</i>			
PF-DP10	12,000	23,000	1.88	73.0	386
PF-DP30	23,000	42,000	1.81	77.0	387
PF-DP50	9,000	16,000	1.70	85.7	390
PF-DP65	13,000	24,000	1.81	86.5	392
PF-DP80	8,000	12,000	1.58	89.2	397
PF-DP90	8,000	11,000	1.42	91.5	397
PF-DP	13,000	19,000	1.45	91.7	403

^a Relative to polystyrene standard.

^b Polydispersity index.

^c Glass transition temperature.

polydispersities of 1.45–1.88. Figure 2 shows the UV–vis and PL spectra of the polymers in a THF solution. The absorption peak maximum was located between 334 and 367 nm. The polymer solutions show intense blue emissions with peak maximums at 416–392 nm that are slightly blue-shifted as the concentration of dipyrindylamine monomer (**DP**) is increased. The shoulder peak at 440 nm is by the excimer, as discussed elsewhere.^{23–25} Excimer formation is found to be suppressed significantly with an increase in dipyrindylamine, particularly in the case of PF–DP. Figure 3 shows the UV–vis and PL spectra of polymers in the thin film state. The absorption peak maximum is located between 334 and 369 nm in the solid state for all the polymers, with some blueshifting as the dipyrindylamine concentration is increased, whereas the PL maximum at a solid state shows similar values for all polymers. The alternate copolymer (PF–DP) shows a larger blueshift compared with the others [PF–DP(10–50)] that is consistent with the absorption spectra. The observed blueshift in the PL spectra is further evidence of reduced conjugation along the polymer backbone. The UV–vis and PL spectra of the copolymer–ruthenium complex are presented in Figure 4. It is observed from Figure 4(a) that the ruthenium complexation of the copoly-

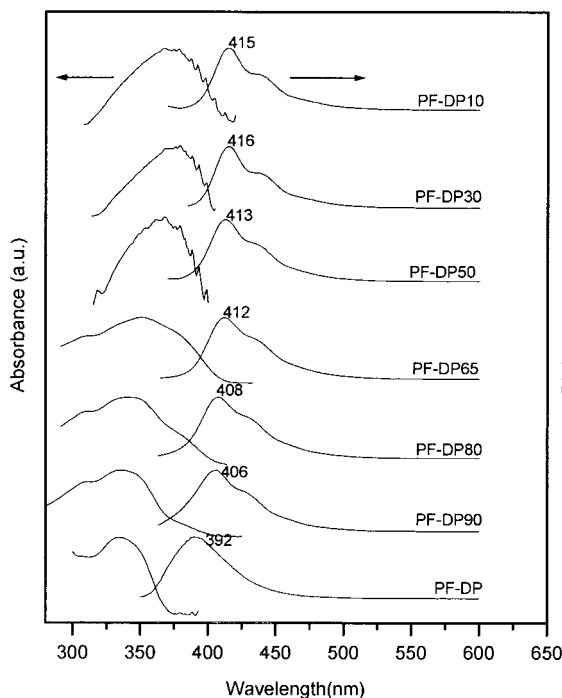


Figure 2. UV–vis and photoluminescence spectra of PF–DP copolymers in THF.

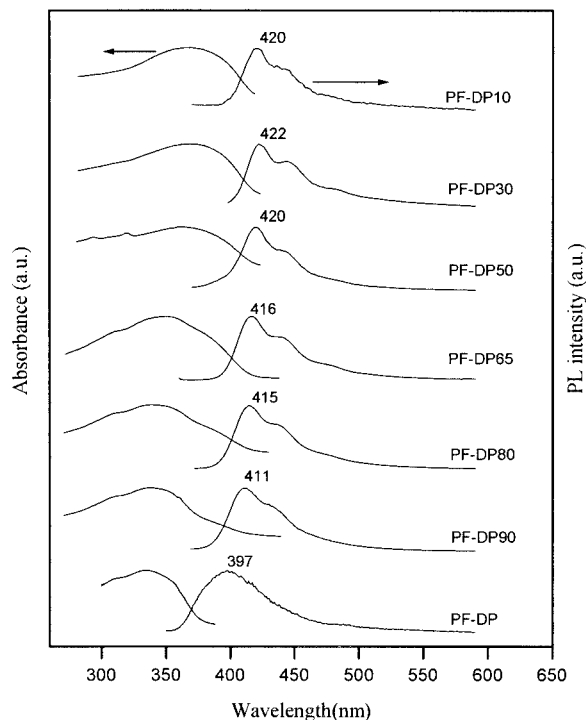


Figure 3. UV–vis and photoluminescence spectra of PF–DP in the solid state.

mer results in a redshift of PL emission of about 18 nm, and the appearance of a shoulder peak indicates excimer formation because of extended conjugation. The thin film PL spectra of the copolymer–ruthenium complex [Fig. 4(b)] also show a redshift of about 15 nm. The quantum yield of polymers in the solid state and in solution are presented in Table 2.

The decadic molar extinction coefficient (ϵ) was determined in THF with eq 1.

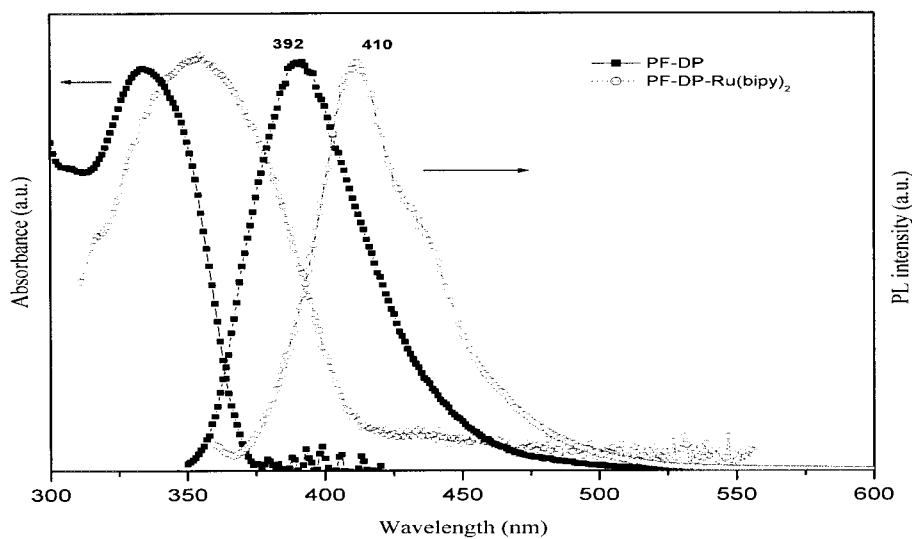
$$\epsilon = OD/cl(dm^3 \text{ mol}^{-1} \text{ cm}^{-1}) \quad (1)$$

where OD is the optical density, c is the concentration of polymer in solution, and l is the optical path length of the sample. The fluorescent chromophore concentration (M) in the thin film was determined with eq 2.

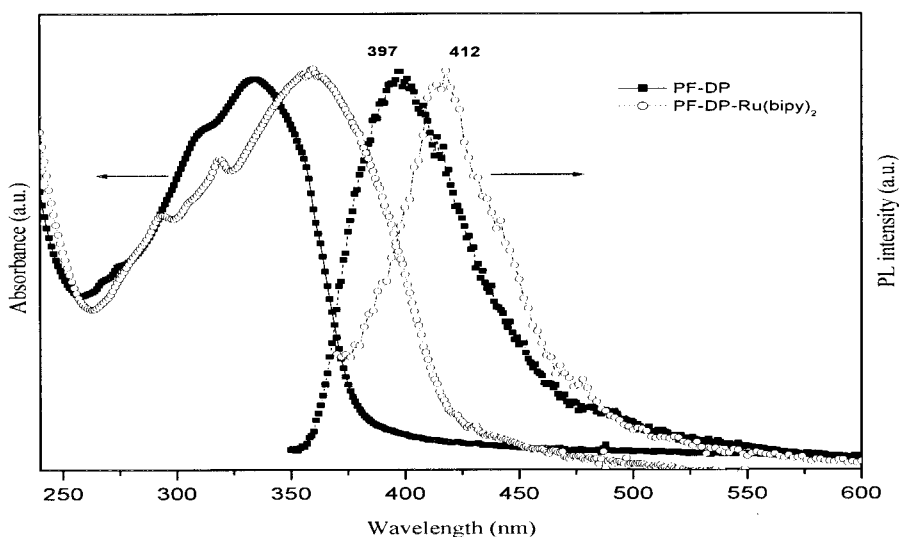
$$M = OD/\epsilon.L(\text{mol}/\text{cm}^3) \quad (2)$$

where L is the thickness of the film.

The quantum yield of the PF copolymer was found to decrease with an increase in the concentration of dipyrindylamine up to 30% because of the disturbance in π -conjugation. A slight en-



(a)



(b)

Figure 4. UV-vis and photoluminescence spectra of PF-DP and PF-DP-Ru(bipy)₂ in (a) solution and in (b) solid state.

hancement in the quantum yield with a further increase of dipyrindylamine concentration is observed and might be caused by photoemission from dipyrindylamine segments. With higher blue-

shifting, a maximum is reached for the PF-DP alternate copolymer (69%) in solution. The maximum PL efficiency displayed by the copolymer PF-DP-Ru(bipy)₂ is attributed to the influence of

Table 2. Absorption and Photoluminescence Data of PF–DP Copolymers and PF–DP–Ru(bipy)₂

Copolymer	ϵ (M ⁻¹ cm ⁻¹)	OD λ = 394 nm	L (nm)	M (mol/cm ³)	η^{tf}	η^{s}
PF-DP10	22,011	1.0664	204	2.36	0.43	0.58
PF-DP30	22,588	1.0867	203	2.36	0.34	0.36
PF-DP50	11,530	0.5597	136	3.55	0.35	0.48
PF-DP65	76,790	1.4906	120	1.61	0.38	0.46
PF-DP80	66,774	0.8754	97.8	1.34	0.47	0.55
PF-DP90	96,450	1.9868	160	1.28	0.51	0.67
PF-DP	52,571	1.54031	184	1.58	0.39	0.69
PF-DP-Ru(bipy) ₂	24,311	0.22951	22.7	4.15	0.83	0.87

ϵ = decadic molar extinction coefficient in dm³ mol⁻¹ cm⁻¹.

OD = absorbance or optical density in the solid state.

L = thickness of the thin film.

M = fluorescent chromophore concentration in the film of each composite.

η^{tf} = thin film quantum yield estimated by using poly-2,7-(9,9-dioctylfluorene) with η = 0.55 as the reference.²⁷

η^{s} = solution quantum yield estimated by using coumarin 6 in THF as the reference.

the Ru complex. The excitation spectra of the PF–DP copolymers in THF are shown in Figure 5. It is observed from Figure 5 that the excitation spectra are the same as that of the UV–vis spectra, indicating the purity of the emitting chromophores. The PL of the PF–DP alternate copolymer and the PF–DP–Ru(bipy)₂ shows that struc-

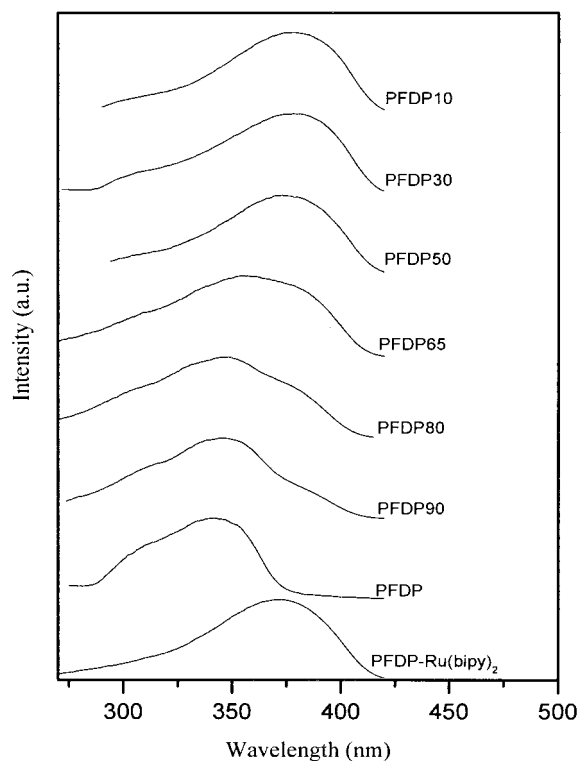


Figure 5. The solution excitation spectra of PF–DP copolymers excited at 440 nm.

tural modification by insertion of dipyriddyamine segments and subsequent metal complexation with Ru(bipy)₂ in the polyfluorene is a useful approach to increasing the quantum efficiency.

Cyclic voltammetry analysis of the polymers shows an oxidation peak potential at 0.98 V in the anodic scan. The onset of the reduction peak appears at -0.70 V in the cathodic scan. The LUMO and HOMO of the polymers were estimated according to the equations²⁶ ionization potential (IP) = -([E_{onset}]^{ox} + 4.4) eV and electron affinity (EA) = -([E_{onset}]^{red} + 4.4) eV, where [E_{onset}]^{ox} and [E_{onset}]^{red} are the onset potentials for oxidation and reduction of the polymer versus the reference electrode, respectively. The HOMO of the polymer is estimated to lie between -5.42 and -5.69 eV; the LUMO is located between -2.44 and -2.33 eV. A moderate increase of LUMO levels of copolymers with increasing dipyriddyamine content can be attributed to the increase of electron-withdrawing pyridinyl moieties in the polymer backbone. The band gap of polymers was calculated from the onset of the absorption spectra. The band gap of the polymers was determined to be between 2.98 and 3.15 eV. The increase in the band gap results in a blueshift of the emission that is undoubtedly caused by the restricted π -conjugation.

The thermal properties of the polymers were analyzed by TGA and DSC measurements. The glass-transition temperatures (T_g s) of the polymers slightly increase, from 73 to 91 °C, with respect to the dipyriddyamine content, a result of the enhanced chain rigidity imparted by the m-phenylene segments. TGA measurements reveal

good thermal stability of the polymers under nitrogen. The 5% weight loss temperature of these polymers was determined to be between 386 and 403 °C for all polymers.

CONCLUSIONS

2,2'-Dipyridylamine substituted poly(fluorene-phenylene) copolymers, with varying concentrations of dipyridylamine, have been synthesized by Suzuki polycondensation. The introduction of dipyridylamine into the polyfluorene results in a blueshift of the emission. The photoluminescence quantum yield is enhanced by the introduction of the di-2-pyridylamine and ruthenium complex, particularly in the presence of the ruthenium complex.

The authors thank the National Science Council, Taiwan for financial support through Project NSC 92-2120-M009-009.

REFERENCES AND NOTES

- Tessler, N.; Denton, G. J.; Friend, R. H. *Nature* 1996, 382, 695.
- Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackey, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* 1990, 347, 539.
- McGhee, M. D.; Heeger, A. J. *Adv Mater* 2000, 12, 1655.
- Mitschke, U.; Bauerle, P. *J Mater Chem* 2000, 10, 1471.
- Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew Chem Int Ed Engl* 1998, 37, 402.
- Braun, D.; Heeger, A. J. *J Appl Phys Lett* 1991, 58, 1982.
- Zheng, M.; Sarker, A. M.; Gurel, E. E.; Lahti, P. M.; Karasz, F. E. *Macromolecules* 2000, 33, 7426.
- Chou, C.-H.; Shu, C.-F. *Macromolecules* 2002, 35, 9673.
- Liang, L.; Yi, P.; Ding, L.; Karasz, F. E. *Macromolecules* 2001, 34, 7300–7305.
- Ling, Q. D.; Kang, E. T.; Neoh, K. G.; Wei, H. *Macromolecules* 2003, 36, 6995.
- Yang, W.; Huang, J.; Liu, C.; Hou, Q.; Yang, R.; Cao, Y. *Polymer* 2004, 45, 865.
- Kim, K.; Hong, Y.-R.; Lee, S.-W.; Jin, J.-I.; Park, Y.; Sohn, B.-H.; Kim, W.-H.; Park, J.-K. *J Mater Chem* 2001, 11, 3023.
- Pu, Y. J.; Soma, M.; Kido, J.; Nishide, H. *Chem Mater* 2001, 13, 3817.
- Yang, N. C.; Park, Y. H.; Suh, D. H. *J Polym Sci Part A: Polym Chem* 2003, 41, 674.
- Kim, J. J.; Kim, K.-S.; Baek, S.; Kim, H. C.; Ree, M. *J Polym Sci Part A: Polym Chem* 2002, 40, 1173.
- Ashenurst, J.; Wang, S. *J Am Chem Soc* 2000, 122, 2541.
- Hassan, A.; Wang, S. *Chem Commun* 1998, 211.
- Pang, J.; Tao, Y.; Frieberg, S.; Yang, X.-P.; D'Iorio, M.; Wang, S. *J Mater Chem* 2002, 12, 206.
- Zhang, M.; Lu, P.; Ma, Y.; Li, G.; Shen, J. *Synth Met* 2003, 135, 211.
- Pautzsch, T.; Blankenburg, L.; Klemm, E. *J Polym Sci Part A: Polym Chem* 2004, 42, 722.
- Smith, A. P.; Fraser, C. L. *J Polym Sci Part A: Polym Chem* 2002, 40, 4250.
- (a) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* 1997, 30, 7686. (b) Fukuda, M.; Sawada, M.; Yoshino, K. *Jpn J Appl Phys* 1989, 28, L1433. (c) Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. *J Org Chem* 1996, 61, 6906. (d) Parakka, J. P.; Jeevarajan, J. A.; Jeevarajan, A. S.; Kispert, L. D.; Cava, M. P. *Adv Mater* 1996, 8, 54.
- Cho, H.-J.; Jung, B.-J.; Cho, N. S.; Lee, J.; Shim, H.-K. *Macromolecules* 2003, 36, 6704.
- Yu, W.-L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv Mater* 2000, 12, 828.
- Zeng, G.; Yu, W.-L.; Chua, S.-J.; Huang, W. *Macromolecules* 2002, 35, 6907.
- De Leeuw, D. M.; Simenon, M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth Met* 1997, 87, 53.
- Grice, A. W.; Bradley, D. D. C.; Bernius, M. T.; Inbasekaran, M.; Wu, W. W.; Woo, E. P. *Appl Phys Lett* 1998, 75, 629.