Photoluminescent and Electrochemical Properties of Novel Poly(aryl ether)s with Isolated Hole-Transporting Carbazole and Electron-Transporting 1,3,4-Oxadiazole Fluorophores

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ABSTRACT: Four novel poly(aryl ether)s consisting of alternate isolated hole-transporting carbazole and electron-transporting 1,3,4-oxadiazole segments were synthesized from the nucleophilic displacement reaction of bis(fluoride) monomers with bis(phenol) monomers. These poly(aryl ether)s are soluble in common organic solvents and exhibit good thermal stability with 5% weight loss temperature above 400 °C under a nitrogen atmosphere. The photoluminescent (PL) spectra and quantum yields of these polymers are dependent on the composition of the two isolated fluorophores. The formation of exciplex in **P3** was observed in the film and solution state and resulted in the lower quantum yield. The quantum yields of **P4** in solutions can increase from 0.04 of **P3** to 0.36, due to the dilute effect, by introducing the inert bisphenol A segments. However, the PL spectra of **P4** only showed a little blue shift in the film state. This means the interchain exciplex still dominated the emission of polymeric films. The HOMO and LUMO energy levels of these polymers have been measured from cyclic voltammetry. All the observations directly proved that the oxidation in polymers started at the hole-transporting segments. Both the electron and hole affinities of these polymers could be enhanced simultaneously due to the introduction of isolated hole-transporting carbazole and electron-transporting 1,3,4-oxadiazole segments.

Introduction

π-Conjugated polymers with donor−acceptor architectures are currently of interest because the electron or hole affinities can be enhanced,[1] and the intramolecular charge transfer can lead to small band gap semiconducting polymers for red emission.[2] These polymers can extend to systems with efficient photoinduced charge transfer and separation for photovoltaic devices and to bipolar charge transport materials for light-emitting diodes,[3,4] lasers,[5] and other applications.[6] The isolated polymers consisting of defined hole-transporting (donor) or electron-transporting (acceptor) segments are also interesting because the electron and hole affinities can be enhanced simultaneously,[7] and the nonconjugated spacers can conduce to big band gap for blue emission.[8−11] 1,3,4-Oxadiazole derivatives, such as 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), are commonly used as electron-transporting layer in the organic light-emitting diodes (OLEDs). But the efficiency can be limited due to their crystallization during the operation of LED. This problem was mitigated by incorporating the electron-transporting units into the main chain or as pendants attached to the backbone of a polymer.[12−14] Carbazole derivatives or correlative polymers have also been paid increasing attention because of their unique optical properties and strong hole-transporting ability in optoelectronic devices.[15−17]

In this paper, four novel poly(aryl ether)s consisting of alternate isolated carbazole and 1,3,4-oxadiazole segments were synthesized and characterized. The optical and electrochemical properties of these poly(aryl ether)s have been investigated in detail. Both the electron and hole affinities of these polymers could be enhanced due to the isolated hole-transporting carbazole and electron-transporting 1,3,4-oxadiazole segments. Interestingly, the photoluminescent (PL) spectra and quantum yields of these polymers are dependent on the composition of the two isolated fluorophores. This research attempts to seek the possibility that the polymers could emit white light by copolymerizing R, G, and B fluorophores.

Experimental Section

Materials. The synthetic procedures of the monomers **1**−**4** and model compounds were analogous to that provided elsewhere.[7,9,18,19] *N*-Methyl-2-pyrrolidone (NMP, Riedel-Dehaen Co.), *N*-cyclohexylpyrrolidone (CHP, Janssen Chimica Co.), chloroform ($CHCl_3$, Tedia Co.), tetrahydrofuran (THF, Tedia Co.), and other solvents were HPLC grade reagents. All reagents were used without any further purification.

Instrumentations. All new compounds were identified by ^1H NMR, FT-IR, and elemental analysis (EA). The ^1H NMR spectra were recorded on a Bruker AMX-400 MHz FT-NMR, and chemical shifts are reported in ppm using tetramethylsilane (TMS) as an internal standard. The FT-IR spectra were measured as KBr disk on a Fourier transform infrared spectrometer, model Valor III from Jasco. The elemental analysis was carried out on a Heraus CHN-Rapid elemental analyzer. The thermogravimetric analysis (TGA) of the polymers was performed under a nitrogen atmosphere at a heating rate of 20 °C/min using a Perkin-Elmer TGA-7 thermal analyzer. UV/vis spectra were measured on Jasco V-550 spectrophotometer. The photoluminescence (PL) spectra were obtained using a Hitachi F-4500 fluorescence spectrophotometer. The diagrammatic curves of cyclic voltammetry were measured on BAS CV-50W at room temperature under a nitrogen atmosphere using ITO glass as working electrode, Ag/AgCl electrode as reference electrode, and platinum wire electrode as auxiliary electrode supporting in 0.1 M (n-Bu)$_4$N-ClO$_4$ in acetonitrile. The energy levels were calculated using the ferrocence (FOC) value of -4.8 eV with respect to vacuum level, which is defined as zero.[20]

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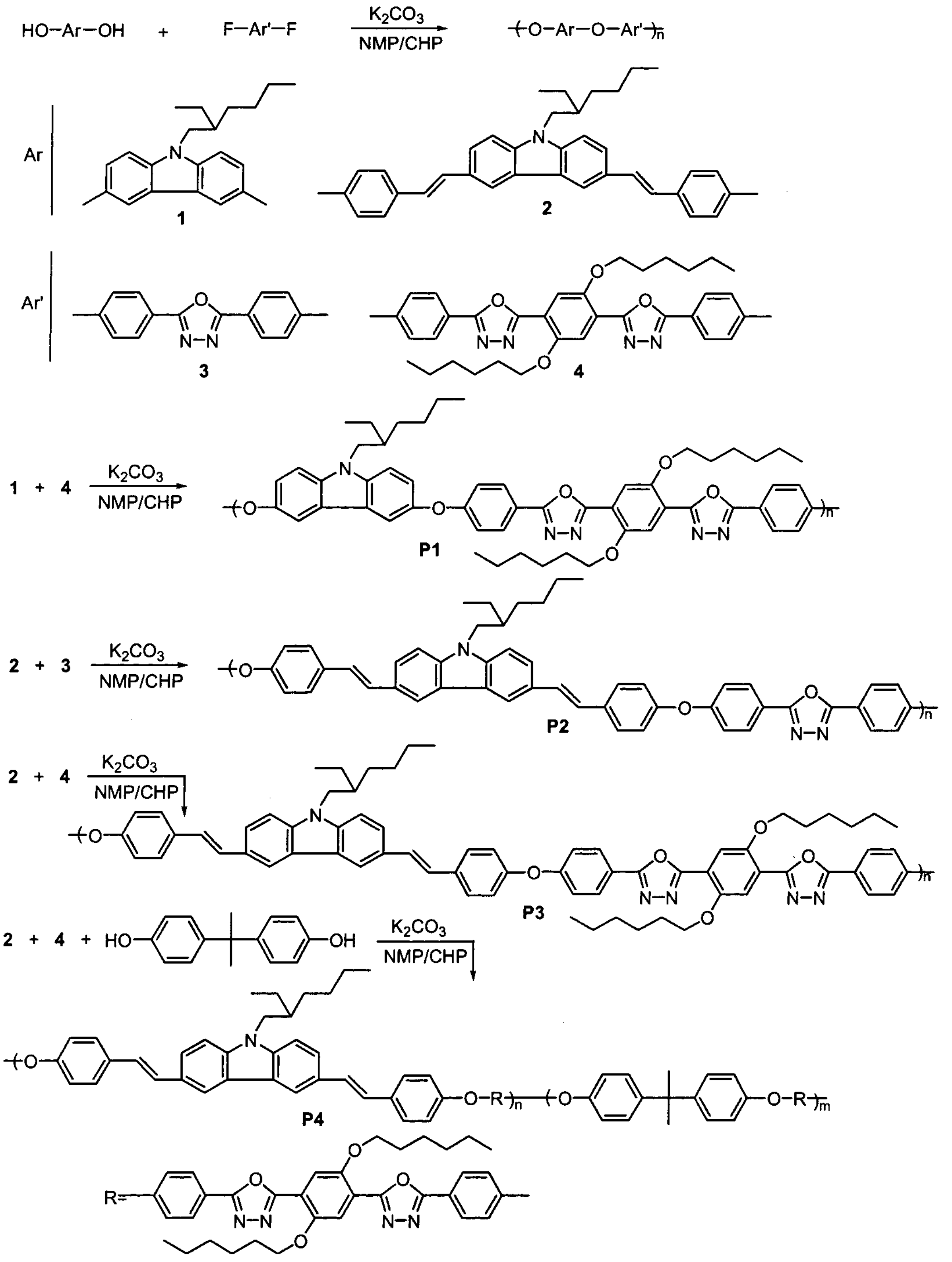
Scheme 1



Synthesis of the Polymers (Scheme 1). P1. To a two-necked 10 mL glass reactor was charged with compound **1** (0.156 g, 0.50 mmol), compound **4** (0.301 g, 0.50 mmol), and 10 mL of toluene, 5 mL of solvent mixture of NMP/CHP (v/v = 1/1), and an excess of K_2CO_3 (0.166 g, 1.20 mmol). The reaction mixture was then heated to 170 °C and reacted for 24 h. The toluene was removed by condensing in the Dean−Stark trap. The reaction mixture was diluted with 2 mL of NMP and then dropped into 250 mL of methanol/distilled water (v/v = 2/1) solvent mixture. The appearing precipitates were collected by filtration and further purified by Soxhlet extractor for 24 h using isopropyl alcohol as solvent. The polymer yield was 0.403 g (92.2%). $\eta_{\mathrm{red}} = 0.48$ dL/g. ^{1}H NMR ($C_2D_2Cl_4$, ppm): δ 8.01 and 7.99 (d, 4H, Ar H), 7.72 and 7.71 (s, 4H, Ar H), 7.41 and 7.39 (d, 2H, Ar H), 7.32 (d, 2H, Ar H), 7.08 and 7.05 (d, 4H, Ar H), 4.14 (d, 2H, NCH_2-), 4.09 (t, 4H, OCH_2-), 2.03 (m, 1H, $-CH-$), 1.82 (m, 4H, $-CH_2-$), 1.47−1.24 (m, 20H, $-CH_2-$), 0.92−0.68 (m, 12H, $-CH_3$). FT-IR (film, cm^{-1}): 3031, 2955, 2930, 2871, 1613, 1482, 1418, 1290, 1240 (C−O−C), 1174, 1145, 1077, 1015, 944, 873, 840, 750. Anal. Calcd (%) for $C_{54}H_{59}N_5O_6$: C, 74.20; H, 6.80; N, 8.01. Found: C, 73.16; H, 6.86; N, 7.71.

P2. To a two-necked 10 mL glass reactor was charged with compound **2** (0.258 g, 0.50 mmol), compound **3** (0.129 g, 0.50 mmol), and 10 mL of toluene, 5 mL of solvent mixture of NMP/CHP (v/v = 1/1), and an excess of K_2CO_3 (0.166 g, 1.20 mmol). The reaction mixture was then heated to 170 °C and reacted for 12 h. The following synthetic procedures were performed in analogy to that given for **P1**. The polymer yield was 0.252 g (68.7%); $\eta_{\mathrm{red}} = 0.23$ dL/g. ^{1}H NMR ($C_2D_2Cl_4$, ppm): δ 8.20 (s, 2H, Ar H), 8.05 and 8.03 (d, 4H, Ar H), 7.65and 7.63 (d, 2H, Ar H), 7.56 and 7.55 (d, 4H, Ar H), 7.34 and 7.33 (d, 2H, Ar H), 7.26 and 7.22 (d, 2H, vinyl H), 7.13−7.09 (m, 10H, vinyl H and Ar H), 4.10 (d, 2H, NCH_2-), 2.00 (m, 1H, $-CH-$), 1.32−

Table 1. Polymerization Results and Characterization of P1∼P4

no.	$M_n{}^a \times 10^4$	$M_w{}^a \times 10^4$	PDI^a	$T_d{}^b$ (°C)	UV−vis $\lambda_{max}{}^c$ solution (nm)	UV−vis λ_{max} film (nm)	PL λ_{max} film (nm)	$\Phi_{PL}{}^d$
P1	3.51	8.20	2.34	424	316, 374	319, 381, 404_s	450	0.36
P2	1.99	4.40	2.21	445	322, 366_s	324, 376_s	440	0.14
P3				426	328, 368	328, 371	500	0.04
P4				417	320, 372	325, 381	490	0.36

[a] M_n, M_w, and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards. **P3** and **P4** are part solute in THF. [b] The 5% weight loss temperatures. [c] 1×10^{-5} M in $CHCl_3$. Subscript s means the wavelength of the shoulder. [d] These values were measured by the right-angle geometry using quinine sulfate (dissolved in 1 N H_2SO_4(aq) with a concentration of 10^{-5} M, assuming Φ_{PL} of 0.55) as a standard at 24−25 °C. The excitation wavelength is 350 nm for these solutions, which had an absorbance of less than 0.05.

1.11 (m, 8H, $-CH_2-$), 0.87−0.83 (m, 6H, $-CH_3$). FT-IR (film on KBr disk, cm^{-1}): 3030, 2957, 2928, 2871, 1600, 1505, 1488, 1418, 1243 (C−O−C), 1200, 1167, 1067, 1012, 960 (trans −C═C−), 876, 745. Anal. Calcd (%) for $C_{50}H_{43}N_3O_3$: C, 81.83; H, 5.91; N, 5.73. Found: C, 79.79; H, 5.95; N, 5.58.

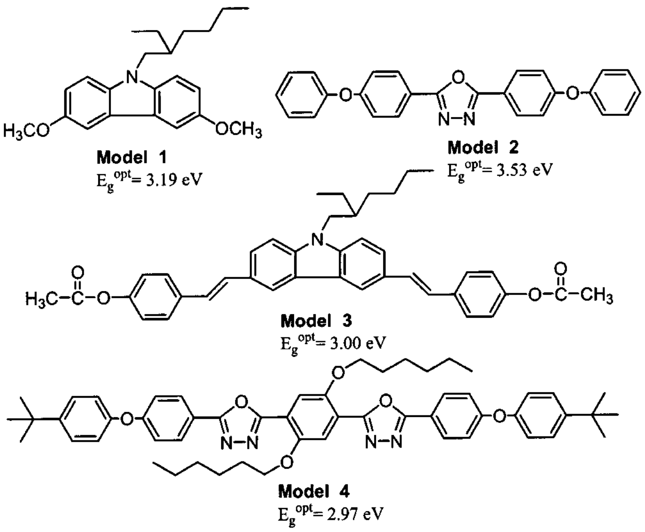
P3. To a two-necked 10 mL glass reactor was charged with compound **2** (0.258 g, 0.50 mmol), compound **4** (0.301 g, 0.50 mmol), and 10 mL of toluene, 5 mL of solvent mixture of NMP/CHP (v/v = 1/1), and an excess of K_2CO_3 (0.166 g, 1.20 mmol). The reaction mixture was then heated to 170 °C and reacted for 23 h. The following synthetic procedures were performed in analogy to that given for **P1**. The polymer yield was 0.402 g (74.6%); η_{red} = 0.32 dL/g. ^{1}H NMR ($C_2D_2Cl_4$, ppm): δ 8.20 (s, 2H, Ar H), 8.06 and 8.04 (d, 4H, Ar H), 7.74 (s, 2H, Ar H), 7.65 and 7.64 (d, 2H, Ar H), 7.57 and 7.55 (d, 4H, Ar H), 7.35 and 7.33 (d, 2H, Ar H), 7.26 and 7.22 (d, 2H, vinyl H), 7.22−7.07 (m, 10H, vinyl H and Ar H), 4.12 (m, 6H, NCH_2- and OCH_2-), 2.00 (m, 1H, −CH−), 1.85 (d, 4H, $-CH_2-$), 1.50 (d, 6H, $-CH_2-$), 1.28 (m, 14H, $-CH_2-$), 0.88−0.81 (m, 12H, $-CH_3$). FT-IR (film on KBr disk, cm^{-1}): 3031, 2954, 2927, 2856, 1600, 1505, 1490, 1464, 1243 (C−O−C), 1168, 1014, 958 (trans −C═C−), 874, 751. Anal. Calcd (%) for $C_{70}H_{71}N_5O_6$: C, 77.97; H, 6.64; N, 6.49. Found: C 75.83; H, 6.63; N, 6.29.

P4. To a two-necked 10 mL glass reactor was charged with compound **2** (0.052 g, 0.10 mmol), compound **4** (0.301 g, 0.50 mmol), bisphenol A (0.091 g, 0.40 mmol), and 10 mL of toluene, 5 mL of solvent mixture of NMP/CHP (v/v = 1/1), and an excess of K_2CO_3 (0.166 g, 1.20 mmol). The reaction mixture was then heated to 170 °C and reacted for 24 h. The following synthetic procedures were performed in analogy to that given for **P1**. The polymer yield was 0.392 g (92.5%); η_{red} = 0.44 dL/g. ^{1}H NMR ($C_2D_2Cl_4$, ppm): δ 8.21 (Ar H on carbazole segments), 8.04 and 8.02 (d, 4H, Ar H), 7.73 (s, 2H, Ar H), 7.69−7.34 (Ar H on carbazole segments), 7.58 and 7.55 (Ar H on carbazole segments), 7.36 and 7.34 (Ar H on carbazole segments), 7.25and 7.23 (d, 4H, Ar H), 7.12−7.09 (d, 4H, Ar H), 6.99−6.97 (d, 4H, Ar H), 4.12 (m, 4H, OCH_2- and NCH_2-), 2.00 (m, −CH− on carbazole segments), 1.84 (m, 4H, $-CH_2-$), 1.68 (s, 6H, $-CH_3$ on bisphenol A segments), 1.50 (m, 4H, $-CH_2-$), 1.27−1.13 (m, 8H, $-CH_2-$), 0.90−0.71 (m, 6H, $-CH_3$). FT-IR (film on KBr disk, cm^{-1}): 3035, 2930, 2870, 1600, 1552, 1491, 1289, 1242 (C−O−C), 1170, 1080, 1014, 966 (trans −C═C−), 875, 749.

Results and Discussion

Synthesis and Characterization. Four novel poly(aryl ether)s (**P1**−**P4**) consisting of alternate isolated hole-transporting carbazole and electron-transporting 1,3,4-oxadiazole segments were synthesized from the nucleophilic displacement reaction of bis(phenol) monomers (**1**, **2**) with bis(fluoride) monomers (**3**, **4**). The molecular weights of these polymers are commonly higher than the analogous poly(aryl ether)s obtained by the Wittig reaction.[21,22] The number-average molecular weights (M_n) and the weight-average molecular weights (M_w) of the polymers, determined by gel permeation chromatography using polystyrene as standard, were 3.51×10^4, 8.20×10^4 and 1.99×10^4, 4.40×10^4 with dispersity indexes of 2.34 and 2.21 for **P1** and **P2**, respectively. All the synthesized polymers were soluble in common organic solvents such as chloroform and 1,1,2,2-tetrachloroethane. For **P4** the feed ratio n/m is 1/4, and the incorporation ratio n/m determined via ^{1}H NMR is about 3/7. Monomer 2 exhibited better nucleophilic ability, which resulted from the electron-donating nitrogen atom of carbazole, than bisphenol A. Thermal properties of the synthesized polymers were evaluated by the TGA under a nitrogen atmosphere. The weight losses were less than 5% on heating to 400 °C for each polymer. The thermogravimetric analysis of the polymers exhibited that the weight percentages of these polymers remain 30−40% even at 800 °C. The inaccuracy of elemental analyses for carbon may be due to the carbonization of these polymers. The polymerization results and characterization of these polymers are tabulated in Table 1.

Scheme 2



Optical Properties. For isolated polymers, it is reasonable that the emission of polymer is originated from the isolated fluorophores. The steady-state absorption and PL spectra of model compounds (as shown in Scheme 2), which simulated the isolated fluorophores in our polymers, in chloroform solutions are shown in Figure 1. Model **1** and model **2** show the maximum PL peaks at 390 and 360 nm, respectively. Because of the longer conjugated length, the maximum PL peaks of model **3** and model **4** red shift to the wavelength of about 410 nm. However, as shown in Figure 2a, the PL spectra of these poly(aryl ether)s in chloroform solutions are dominated by the fluorophores with longer emissive wavelength; i.e., their PL maximum peaks are all at 410 nm. In Figure 1 the emission spectra of donor segments (model **1** and model **2**) cover partly with the absorption

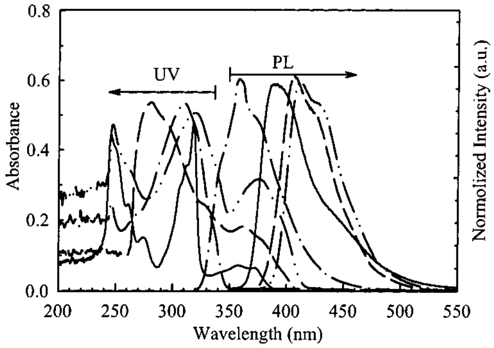


Figure 1. Photoluminescence (excitation at 320 nm) and UV−vis absorption spectra of model compounds **1** (—), **2** (-·-), **3** (- -), and **4** (-··-) in $CHCl_3$ solutions of 1×10^{-5} M.

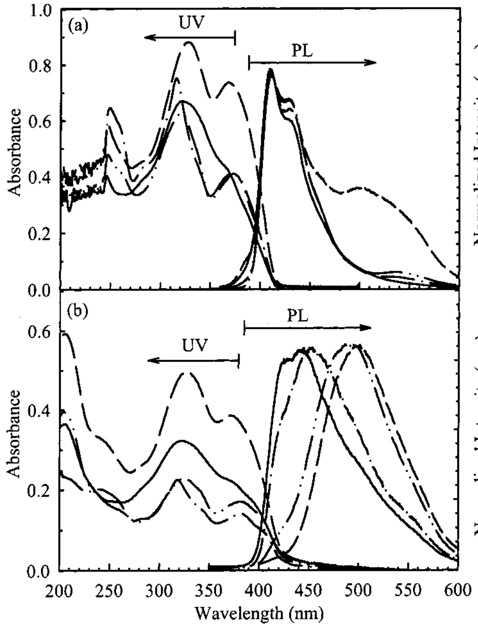


Figure 2. Photoluminescence (excitation at 320 nm) and UV−vis absorption spectra of **P1** (-·-), **P2** (—), **P3** (- -), and **P4** (-··-) in $CHCl_3$ solutions of 1×10^{-5} M (a) and films coated on quartz plate (b).

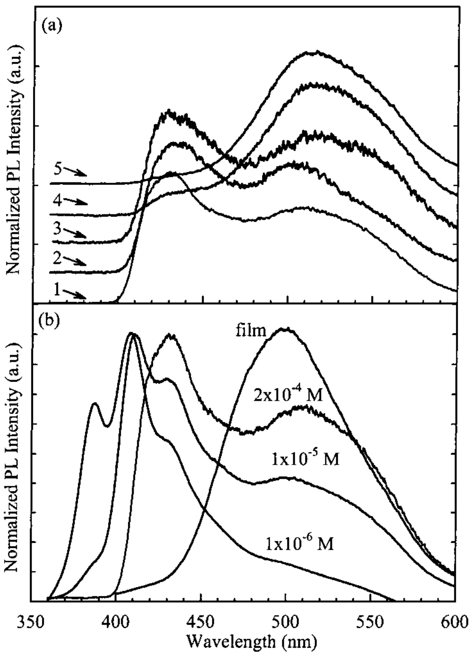


Figure 3. (a) Photoluminescence (excitation at 320 nm) spectra of **P3** in $CHCl_3$ (1), MeOH/NMP v/v = 0 (2), 0.2 (3), 0.5 (4), and 1 (5) solutions of 1×10^{-4} M. (b) Photoluminescence (excitation at 320 nm) spectra of **P3** in $CHCl_3$ solutions of 1×10^{-6}, 1×10^{-5}, and 2×10^{-4} M.

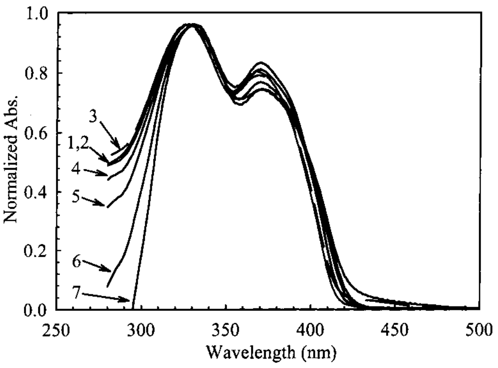


Figure 4. UV−vis absorption spectra of **P3** in film (1), $CHCl_3$ solutions of 1×10^{-5} (2), 1×10^{-6} M (3), and MeOH/NMP v/v = 0 (4), 0.2 (5), 0.5 (6), and 1 (7) solutions of 1×10^{-4} M.

of acceptor segments (model **3** and model **4**), and therefore reabsorption could dominate the emission of **P1** and **P2** in solution states due to larger interchain distance. In **P3** and **P4**, the excitation spectra (not shown here) exhibit that the two fluorophores, which have almost the same PL λ_{max}, contribute to the emissions of polymers. Interestingly, the **P3** presents a further broad peak at 500 nm, but the **P4** introduced bisphenol A segments to dilute the 3,6-bis(styryl)-carbazole segments do not have. It is clear that there is another emissive species related to the hole- and electron-transporting fluorophores in **P3**.

Figure 2b exhibits the PL spectra of these polymeric films coated on quartz plate. The PL maximum peaks locate at 450, 440, 500, and 490 nm for **P1**, **P2**, **P3**, and **P4**, respectively. The PL spectra of the polymers in films are still dominated by the fluorophores with longer emissive wavelength. Nevertheless, we are not sure which mechanism, reabsorption or energy transfer, dominated the emission of **P1** and **P2** in film state. Comparing the long wavelength bands of absorption in solutions (Figure 2a) with those in films (Figure 2b), the absorption maximum wavelength in the films of **P1**, **P2**, and **P4** red shift about 10 nm. The broad emissive band of **P1** and **P2** may be due to the aggregate or the disorder of polymeric chains. What is the emissive species in the **P3** and **P4**? In Figure 3a, the emissive bands of **P3** do not red shift with the increase of solvent polarity, so there is not an intrachain or interchain charge transfer in these polymers.[2,23] The disappearance of the peak at 430 nm, by increasing the ratio of methanol (poor solvent), was due to the aggregation or shrinkage of polymeric chains, which enhanced the local concentration of fluorophores and the formation of new emissive species.[24,25] Figure 3b shows that the relative intensity of the peak at 500 nm increases with the concentration of solution, and Figure 4 reveals the absorption spectra of **P3** are almost independent of the concentration of solution or the polarity of solvent.[26,27] It was concluded that the interchain emissive species is an emissive excited-state complex, which is delocalized over two isolated segments, and cannot be directly excited optically.[28] Therefore, we presume the interchain emissive species is the exciplex.

The optical properties and the relative quantum yields (Φ_{PL}) of these poly(aryl ether)s in chloroform

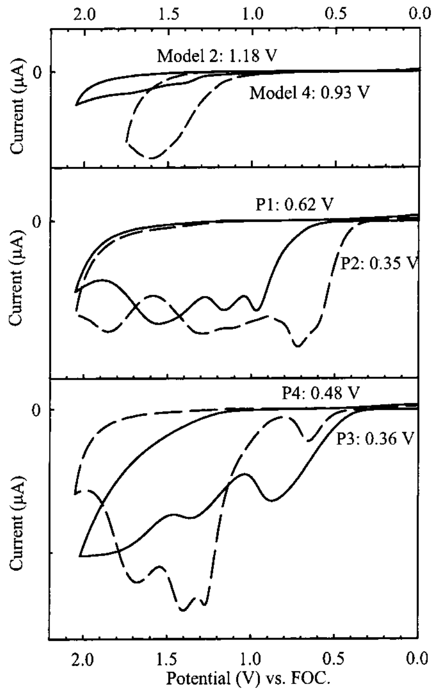


Figure 5. Cyclic voltammograms of (a) model **2** (—) and **4** (- -) (50 mV/s), (b) **P1** (—) and **P2** (- -) (100 mV/s), and (c) **P3** (—) and **P4** (- -) (100 mV/s) in film coated on ITO glass electrode in CH_3CN solution of Bu_4NClO_4 (0.1 M).

solutions are summarized in Table 1. The relative quantum yields (Φ_{PL}), which were calculated from the corrected PL spectra, of **P1**, **P2**, **P3**, and **P4** in solution are 0.36, 0.14, 0.04, and 0.36, respectively. The formation of less radiative exciplex explained why the **P3** has the lowest quantum yields. The introduction of the inert bisphenol A segments in **P4** resulted in the lower exciplex formation and the higher quantum yield than **P3** in solution due to the dilute effect. According to our previous work and above discussion,[7,9,11] the photoluminescence of poly(aryl ether)s containing two or more fluorophores could exhibit three type of results: (1) the emission of polymers contributed from each fluorophore; (2) the emission of polymers was dominated by the fluorophores with longer emissive wavelength via reabsorption or energy transfer; (3) the emissive wavelengths of polymers were longer than each fluorophore due to the interchain interaction (such as excimer or exciplex). If we extend the synthetic tactic to obtain the white light by copolymerizing the R, G, and B fluorophores, the problem of reabsorption, energy transfer, or interchain exciton, which leads to unexpected wavelength shift, will need to be overcome.

Electrochemical Properties. The typical p-doping cyclic voltammograms (CV) of model **2**, model **4**, and four poly(aryl ether)s are shown in Figure 5. The onset potentials of oxidation of **P1** and **P3**, which have the same electron-transporting segments, were determined at 0.62 and 0.36 V vs FOC. However, the oxidative onset potential of model **4** (0.93 V), which simulated the electron-transporting segments in **P1** and **P3**, was much larger than that of **P1** and **P3**. The same trend was also present to the model **2** and **P2**. In **P4**, which has lower ratio of the hole-transporting segments, the relative intensity of first oxidative peak at 0.66 V was reduced compared with **P3**. All the observations directly proved that the oxidation in polymers started at the hole-transporting segments. Identically, we could presume that the reduction would also started at the electron-transporting segments. Thus, the **P2** and **P3** reveal almost the same onset because of the same hole-transporting segments. So the band gap of isolated poly(aryl ether)s measured directly from the CV would be underestimated.[7]

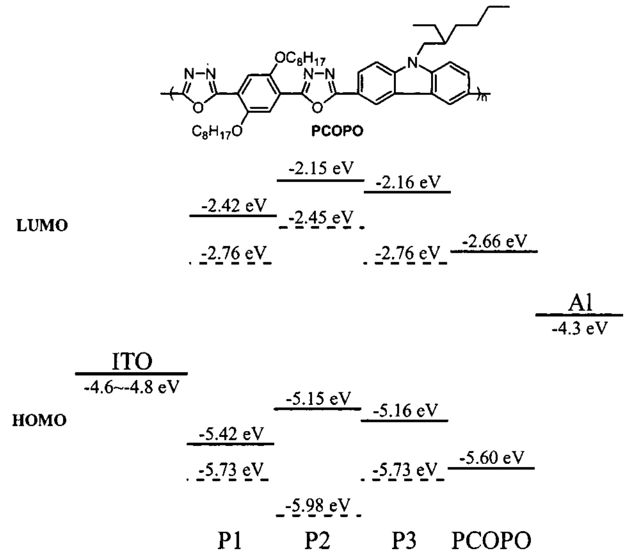


Figure 6. Energy band diagram of **P1**−**P3** (hole-transporting segments, —; electron-transporting segments, - - -) and **PCOPO**.

The HOMO levels of the electron- and hole-transporting segments can be calculated by comparing with the ferrocence value of 4.8 eV below the vacuum level.[20] Furthermore, the LUMO levels of each segments were obtained by adding the optical band gaps (E_g^{opt}) of model compounds, which were calculated from the onset of the UV−vis absorption spectra and list in Scheme 2. The unabridged energy band diagram of the polymers is proposed in Figure 6. In **P3** the hole-injection barrier was reduced because of the introduction of electron-rich styryl group into the carbazole, and the electron affinity was enhanced by more electron-withdrawing 1,3,4-oxadiazole rings. Compared with the conjugated **PCOPO**, the isolated **P1** exhibited lower barriers of electron and hole injection from the opposite electrodes.[29] So the hole and electron affinities of the isolated polymers can be promoted simultaneously by the introduction of hole- and electron-transporting segments. However, the isolated hole- and electron-transporting fluorophores in these poly(aryl ether)s function as hole and electron trap centers. The hole and electron cannot recombine via intrachain migration. Thus, we can imagine that the carrier-hopping barrier between the hole- and electron-transporting fluorophores may be a factor to influence the exciton formation.[30]

Finally, the single-layer devices, ITO/P1 (or P2, P3)/Al, have been fabricated. The electroluminescent spectra are shown in Figure 7 and consistent with the PL spectra.

4. Conclusion

Four novel poly(aryl ether)s (**P1**−**P4**) consisting of alternate isolated fluorophores have been synthesized, and their photoluminescent and electrochemical properties have also been studied in detail. These poly(aryl ether)s have high molecular weight and good thermal stability and are soluble in common organic solvents.

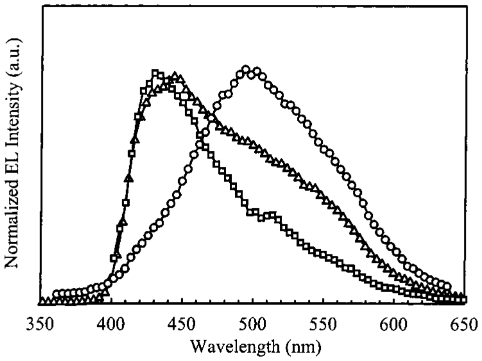


Figure 7. Electroluminescence spectra of the devices ITO/**P1**/Al (△), ITO/**P2**/Al (□), and ITO/**P3**/Al (○).

For this kind of synthetical tactic, the hole and electron affinities of the isolated polymers can be promoted simultaneously by the introduction of hole- and electron-transporting segments. Unfortunately, the reabsorption or exciplex, which would reduce the quantum yield, could occur depending on the composition of the two isolated fluorophores. The introduction of inert segments (bisphenol A) can reduce the formation of exciplex and enhance the quantum yield in solution due to the dilute effect, but not in film because the PL spectrum of **P4** did not change conspicuously.

Acknowledgment. We thank the National Science Council of the Republic of China for financial aid through Project NSC 90-2216-E-006-034.

Supporting Information Available: ^{1}H NMR spectra for polymers **P1**−**P4**. The material is available free of charge via the Internet at http://pubs.acs.org.

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