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Synthesis and Electrochemical and Optical Properties of Novel Poly(aryl ether)s with Isolated Carbazole and *p*-Quaterphenyl Chromophores

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ABSTRACT: Two novel poly(aryl ether)s consisting of alternate isolated chromophores, poly[oxy-[9-(2-ethylhexyl)carbazole-3,6-oxy]-3,3‴-dicyano-*p*-quaterphenyl-4,4‴-ylene] (**PCNCA**) and poly[oxy-[9-(2-ethylhexyl)carbazole-3,6-oxy]-3,3‴-bis(trifluoromethyl)*p*-quaterphenyl-4,4‴-ylene] (**PCFCA**), have been synthesized and characterized. The synthesized polymers are completely soluble in common organic solvents such as tetrahydrofuran (THF) and chloroform. The two poly(aryl ether)s exhibit good thermal stability with 5% weight loss temperature above 400 °C in nitrogen. The UV/vis and photoluminescent spectra of the two polymers show maximum peaks at around 318−319 and 407−413 nm in the film state, respectively. The HOMO and LUMO energy levels of these polymers, which have been measured by cyclic voltammetry, are −5.23, −3.25 eV for **PCNCA** and −5.41, −3.32 eV for **PCFCA**. The *p*-quaterphenyl segments are regarded as electron transporting units because the electron withdrawing substitutes (cyano and trifluoromethyl) enhance the electron affinity. On the contrary, the carbazole segments act as hole transporting units. The two units could decrease the barriers of charge injection from opposite electrodes. Furthermore, all of the two units are emissive chromophores so the photoluminescence (PL) of polymers resulted from the two units. The relative quantum yields of the two polymers are respectively 0.02, 0.40 in film state, and 0.04, 0.19 in THF for **PCNCA**, **PCFCA**.

Introduction

In the past decade, electroluminescence (EL) from low molecular weight, oligomeric, and polymeric materials has been extensively investigated.[1,2] The EL of polymers could be promisingly applied to organic light emitting diodes (OLEDs) or display technics because of their unique processability, lower cost, band gap tunability, and mechanical flexibility. In 1990, Holmes et al. first reported electroluminescence of full conjugated poly(*p*-phenylenevinylene) (PPV) sandwiched between an anode and a cathode of appropriate work functions.[3] The EL arises from the recombination of electrons and holes, which are injected from the two opposite electrodes, to become excitons in an emissive polymer layer. To achieve high EL efficiency, it is necessary to balance the injection rates of opposite charges and decrease the barriers of charge injection from the opposite contacts.[4] In general, most of the conjugated polymers, such as PPV, polythiophene (PT), and other derivatives, have excess π electrons to own better hole affinity than the electron.[5] Other polymers, such as poly(*p*-phenylene)s (PPPs), are blocking materials of the hole and need a hole injecting or transporting layer to enhance the EL efficiency.[6,7] To balance the electron or hole affinity of these polymers, the common tactic is to incorporate electron or hole transporting segments into the side chain or backbone of the conjugated polymers.[4,8−9]

So as to overcome several drawbacks of established compounds, a new class of materials for EL devices has been developed. Defined charge transporting and/or emissive chromophores have been alternatively introduced to a nonconjugated polymer. The nonconjugated spacers could be ether,[10,11] ester,[12] amide,[13] hexafluoropropylidene,[14] and silane groups.[15] Phenylenevinylene,[16] oligophenylene,[17,18] quinoline,[19] oxadiazole,[10,11] and triphenylamine,[10,19] for example, are representative of chromophores in these polymers. This approach ensures control of the conjugated length as well as emissive color. Moreover, recrystallization process of low molecular weight materials, such as triarylamines and oxadiazoles, can be suppressed, and the covalent bond to a polymeric network impedes phase separation.

In this work, new poly(aryl ether)s (**PCNCA** and **PCFCA**) consisting of alternate isolated 3,3‴-dicyano-*p*-quaterphenyl (or 3,3‴-bis(trifluoromethyl)*p*-quaterphenyl) and carbazole chromophores have been synthesized and characterized. The electron-withdrawing cyano or trifluoromethyl substitutes were introduced to the *p*-quaterphenyl in order to enhance the electron affinity and reduce the band gap.[20] Moreover, the carbazole unit is known as hole transporting and electroluminescent material.[21] The carbazole chromophores were expected to compensate for the obstruction of holes by the *p*-quaterphenyl segments. We attempted to balance the electron and hole affinities in these polymers, and decrease the both barriers of electron and hole injection from the opposite electrodes. The synthetic route is given in Scheme 1. The optical and electrochemical properties of these poly(aryl ether)s have also been investigated in detail.

Experimental Section

Materials. 4,4′-Dimethoxydiphenylamine, potassium *tert*-butoxide (*t*-BuOK), 5-bromo-2-fluorobenzonitrile, 4,4′-biphenyldiboronic acid bis(neopentyl glycol) cyclic ester, 5-bromo-2-fluorobenzotrifluoride, and tetrakis(triphenylphosphine)palladium [Pd(Ph$_3$)$_4$] were purchased from Lancaster Co. Palladium diacetate, triethylene glycol, and 2-ethylhexyl bromide were procured from Acros Organics Co. *N*,*N*-Dimethylformamide (DMF, Tedia Co.), *N*-methyl-2-pyrrolidone (NMP, Riedel-Dehaen Co.), ethylene glycol diacetate (Janssen Chimica Co.), *N*-cyclohexyl-pyrrolidone (CHP, Janssen Chimica Co.), and all reagents were used without any further purification.

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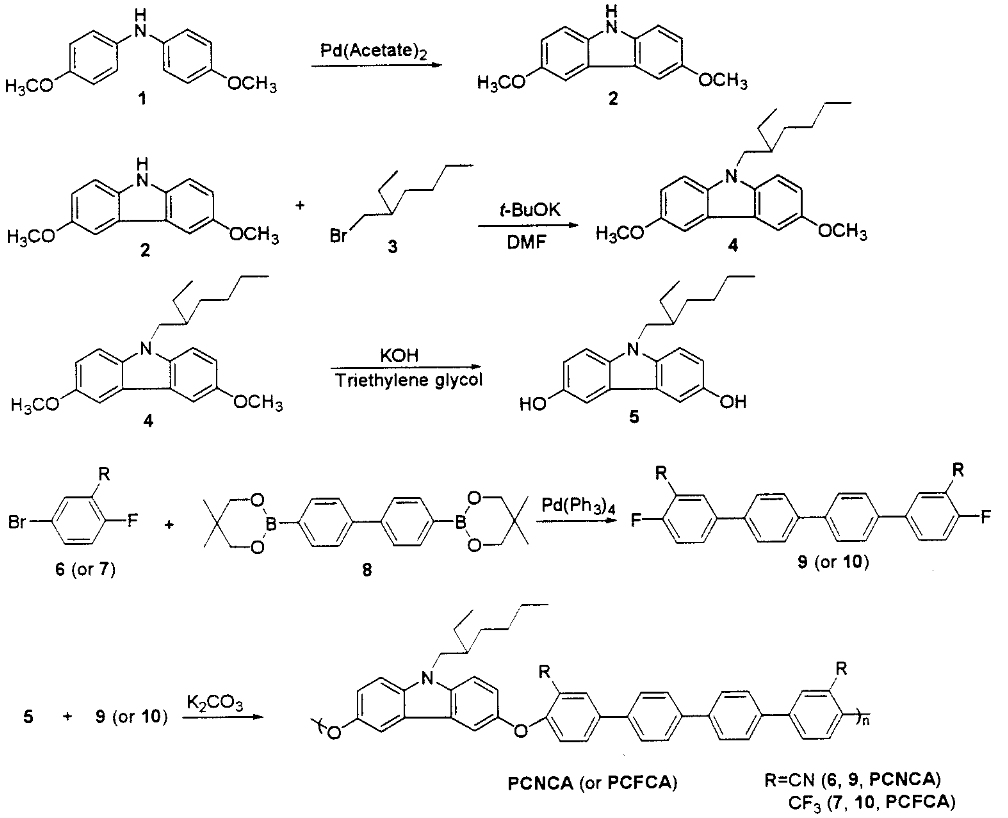
Scheme 1. Synthetic Routes to the Monomers and the Polymers



Instrumentations. All new compounds were identified by ^{1}H NMR, FT-IR, and elemental analysis (EA). The ^{1}H 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 pellets 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 nitrogen atmosphere at a heating rate of 20 °C/min using a Perkin-Elmer TGA-7 thermal analyzer. UV/Visible 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 at room temperature under 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)$_4$NClO$_4$ 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.[22]

3,6-Dimethoxy-9*H*-carbazole (2). A mixture of 4,4′-dimethoxydiphenylamine (**1**) (2.29 g, 10.0 mmol) and palladium diacetate (2.25 g, 10.0 mmol) was dissolved in 10 mL of acetic acid plus 40 mL of ethylene glycol diacetate. The mixture was stirred at 110 °C for 5 h in a nitrogen atmosphere. The solution was cooled to room temperature, poured into water, and extracted with ethyl acetate. The extract was filtered through Celite, dried with anhydrous magnesium sulfate, and then concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel using n-hexane/ethyl acetate (v/v = 8/3) and n-hexane/isopropyl alcohol (v/v = 9/1) as eluent in sequence. Evaporation of the eluent afforded orange powders of **2** (0.886 g, 39.0%); mp 131−133 °C. ^{1}H NMR (acetone-d_6, ppm): δ 7.63 (s, 2H, Ar H), 7.37 and 7.35 (d, 2H, Ar H), 7.00 and 6.98 (d, 2H, Ar H), 3.86 (s, 6H, $-CH_3$). FT-IR (KBr pellet, cm^{-1}): 3358 (N−H), 2933, 2830, 1612, 1575, 1497, 1473, 1435, 1208, 1157, 1028. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C 73.98; H, 5.83; N, 6.09.

9-(2-Ethylhexyl)-3,6-dimethoxycarbazole (4). Compound **2** (2.27 g, 10 mmol), t-BuOK (1.68 g, 15 mmol), and 10 mL of DMF were added to a two-necked flask. The mixture was stirred in an ice bath under nitrogen atmosphere. After 30 min, 2-ethylhexyl bromide (3.86 g, 20 mmol) dissolved in 10 mL of DMF was added, and the mixture was allowed to react at 80 °C for 24 h. After reaction was completely promoted, the reaction mixture was poured into distilled water and extracted with chloroform. The extract was washed with distilled water, dried with anhydrous magnesium sulfate, and then concentrated under reduced pressure. A yellow liquid was obtained by column chromatography on silica gel using n-hexane/ethyl acetate (v/v = 8/3) as eluent (2.72 g, 80.0%). ^{1}H NMR (acetone-d_6, ppm): δ 7.67 (s, 2H, Ar H), 7.40 and 7.37 (d, 2H, Ar H), 7.06 and 7.03 (d, 2H, Ar H), 4.21 and 4.19 (d, 2H, $-NCH_2-$), 3.87 (s, 6H, $-CH_3$), 2.04 (m, 1H, −CH−), 1.38−1.20 (m, 8H, $-CH_2-$), 0.91−0.79 (m, 6H, $-CH_3$). FT-IR (KBr pellet, cm^{-1}): 2931, 2872, 1578, 1492, 1437, 1200, 1160, 1066, 1039. Anal. Calcd for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13. Found: C 77.95; H, 8.63; N, 4.02.

9-(2-Ethylhexyl)-3,6-dihydroxycarbazole (5). The mixture of compound **4** (2.14 g, 6.30 mmol) and KOH (10.7 g, quintuple of weight of compound **4**) was dissolved in 31.5 mL of triethylene glycol. The reaction mixture was stirred at 200 °C for 12 h in a nitrogen atmosphere. The reaction mixture was poured into distilled water, and then neutralized by adding 6 N HCl(aq). The mixture was extracted with chloroform, and the extract was washed by distilled water. The organic layer was dried with magnesium sulfate, filtered, and concentrated to give crude products of **5**. The crude products were purified by column chromatography on silica gel using ethyl acetate/n-hexane (v/v = 1/1) as eluent. Evaporation of the eluent and then recrystallization in n-hexane/isopropyl alcohol (v/v = 9/1) afforded pink flaky crystal of **5** (1.37 g, 69.8%); mp 149−151 °C. ^{1}H NMR (DMSO-d_6, ppm): δ 8.88 (s, 2H, −OH), 7.29 (s, 2H, Ar H), 7.24 and 7.21 (d, 2H, Ar H), 6.88 and 6.86 (d, 2H, Ar H), 4.07 and 4.05 (d, 2H, $-NCH_2-$), 1.89 (m, 1H, −CH−), 1.26−1.16 (m, 8H, $-CH_2-$), 0.84−0.75 (m, 6H, $-CH_3$). FT-IR (KBr pellet, cm^{-1}): 3287 (OH), 2957, 2925, 2857, 1490, 1475, 1358, 1319, 1197, 1154, 936. Anal.

Calcd for $C_{20}H_{25}NO_2$: C, 77.14; H, 8.09; N, 4.50. Found: C 77.17; H, 7.99; N, 4.52.

4,4‴-Difluoro-3,3‴-dicyano-*p*-quaterphenyl (9). To a round-bottom flask were added with 5-bromo-2-fluorobenzonitrile (**6**) (2.64 g, 13.2 mmol), $Pd(Ph_3)_4$ (0.458 g, 0.396 mmol), 30 mL of toluene, and 12 mL of 2 M Na_2CO_3(aq) under nitrogen atmosphere. After complete mixing, the mixture was then added with 4,4′-biphenyldiboronic acid bis(neopentyl glycol) cyclic ester (**8**) (2.27 g, 6.00 mmol) and 6 mL ethanol (99%). It was allowed to react at 80 °C for 12 h. After reaction was completely promoted the product was precipitated from methanol. The crude product was filtered and then washing with distilled water. The product of **9** was obtained by recrystallizing in DMSO (1.73 g, 73.5%); mp 278−279 °C. ^{1}H NMR ($C_2D_2Cl_4$, ppm): δ 7.77−7.80 (m, 4H, Ar H), 7.68 and 7.66 (d, 4H, Ar H), 7.56 and 7.53 (d, 4H, Ar H), 7.27−7.23 (t, 2H, Ar H). FT-IR (KBr pellet, cm^{-1}): 3066, 2237 (C≡N), 1486, 1276, 1242, 1116, 804. Anal. Calcd for $C_{26}H_{14}F_2N_2$: C, 79.58; H, 3.60; N, 7.14. Found: C 79.55; H, 3.73; N, 7.16.

4,4‴-Difluoro-3,3‴-bis-trifluoromethyl-*p*-quaterphenyl (10). To a round-bottom flask were added with 5-bromo-2-fluorobenzotrifluoride (**7**) (3.21 g, 13.2 mmol), $Pd(Ph_3)_4$ (0.458 g, 0.396 mmol), 30 mL of toluene, and 12 mL of 2 M Na_2CO_3(aq) under nitrogen atmosphere. After complete mixing, the mixture was then added with compound **8** (2.27 g, 6.00 mmol) and 6 mL of ethanol (99%). It was allowed to react at 80 °C for 6 h and then poured into a large amount of methanol to precipitate the products. The crude products were filtered and then washed with distilled water. The product of **10** was obtained by recrystallizing in ethanol/benzene (v/v = 1/1) (2.20 g, 76.8%); mp 224−226 °C. ^{1}H NMR (acetone-d_6, ppm): δ 8.10−8.03 (m, 4H, Ar H), 7.89−7.79 (m, 8H, Ar H), 7.56−7.50 (t, 2H, Ar H). FT-IR (KBr pellet, cm^{-1}): 3036, 1621, 1490, 1429, 1332, 1239, 1130 (CF_3), 1055, 820. Anal. Calcd for $C_{26}H_{14}F_8$: C, 65.28; H, 2.95. Found: C 65.33; H, 3.00.

Synthesis of PCNCA and PCFCA. Poly[oxy[9-(2-ethylhexyl)carbazole-3,6-oxy]-3,3‴-dicyano-*p*-quaterphenyl-4,4‴-ylene] (PCNCA). A two-necked 10 mL glass reactor was charged with compound **5** (0.156 g, 0.50 mmol), compound **9** (0.196 g, 0.50 mmol), and 5 mL of toluene, 2.5 mL of solvent mixture of NMP/CHP, and an excess of K_2CO_3 (0.166 g, 1.20 mmol). The reaction mixture was then heated to 150 °C for 0.5 h until the toluene was all condensed in the Dean−Stark trap. The reaction temperature was then rose to 170 °C and reacted for extra 24 h. The reaction mixture was diluted with 2 mL of NMP and then dropped into 150 mL of methanol/distilled water (v/v = 1/1) solvent mixture. The precipitates were collected by filtration and further purified by Soxhlet extractor for 48 h using isopropyl alcohol as solvent. The polymer yield was 0.266 g (80.1%); η_{red} = 0.17 dL/g. ^{1}H NMR ($C_2D_2Cl_4$, ppm): δ 7.87 (s, 2H, Ar H), 7.78 (s, 2H, Ar H), 7.67 (m, 6H, Ar H), 7.56 (d, 4H, Ar H), 7.45 (d, 2H, Ar H), 7.30 (d, 2H, Ar H), 6.90 (d, 2H, Ar H), 4.18 (d, 2H, $-NCH_2-$), 2.04 (m, 1H, $-CH-$), 1.37−1.12 (m, 8H, $-CH_2-$), 0.94−0.83 (m, 6H, $-CH_3$). FT-IR (KBr pellet, cm^{-1}): 3031, 2955, 2869, 2228 (C≡N), 1604, 1579, 1477, 1269, 1243, 1171, 1145, 813. Anal. Calcd for $C_{46}H_{37}N_3O_2$: C, 83.23; H, 5.62; N, 6.33. Found: C 79.27; H, 5.86; N, 4.52.

Poly[oxy[9-(2-ethylhexyl)carbazole-3,6-oxy]-3,3‴-bis-(trifluoromethyl)-*p*-quaterphenyl-4,4‴-ylene] (PCFCA). A two-necked 25 mL glass reactor was charged with compound **5** (0.311 g, 1.00 mmol), compound **10** (0.478 g, 1.00 mmol), and 10 mL tof oluene, 5 mL of solvent mixture of NMP/CHP, and an excess of K_2CO_3 (0.332 g, 2.40 mmol). The reaction mixture was then heated to 150 °C for 0.5 h until the toluene was all condensed in the Dean−Stark trap. The reaction temperature was then rose to 170 °C and reacted for extra 22 h. The following synthetic procedures were performed in analogy to those given for **PCNCA**. The polymer yield was 0.707 g (94.3%); η_{red} = 0.43 dL/g. ^{1}H NMR ($C_2D_2Cl_4$, ppm): δ 7.79 (s, 2H, Ar H), 7.74−7.61 (m, 12H, Ar H), 7.40 (d, 2H, Ar H), 7.27 (d, 2H, Ar H), 6.94 (d, 2H, Ar H), 4.16 (d, 2H, $-NCH_2-$), 2.03 (m, 1H, $-CH-$), 1.36−1.26 (m, 8H, $-CH_2-$), 0.91−0.84 (m, 6H, $-CH_3$). FT-IR (thin film, cm^{-1}): 3032, 2931, 2873, 1617, 1481, 1332, 1250, 1140 (CF_3), 1053, 816. Anal. Calcd for $C_{46}H_{37}F_6NO_2$: C, 73.69; H, 4.97; N, 1.87. Found: C 72.64; H, 5.03; N, 1.92.

Table 1. Polymerization Results and Characterization of PCNCA and PCFCA

polymers	yield (%)	η_{red} (dL/g)[a]	M_n[b]	M_w[b]	PDI[b]	T_d[c] (°C)
PCNCA	80.1	0.17	11 524	22 720	1.97	435
PCFCA	94.3	0.43	37 500	81 234	2.17	505

[a] Measured in 0.3 g/dL in chloroform at 30 °C. [b] M_n, M_w, and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards. [c] The 5% weight loss temperatures.

Results and Discussion

Synthesis and Characterization. The carbazole derivative **2** was synthesized by palladium-promoted intramolecular cyclization of 4,4′-dimethoxydiphenylamine.[23] Although the rate of cyclization can be promoted in acetic acid, it also facilitated the side-reaction. The ethylene glycol diacetate of the cosolvent played an important role in the intramolecular coupling, and prevented formation of oxidation byproducts.[24] The *p*-quaterphenyl derivatives were synthesized by the Suzuki biaryl coupling reaction.[25] To decrease the distortion of adjacent rings, we designed that the substituents are at the position *meta* to the adjacent rings. The syntheses of poly(aryl ether)s were obtained from nucleophilic displacement reaction of bis(fluoride) monomers (**9** or **10**) with bis(phenol) monomers (**5**). Another function of the electron-withdrawing cyano and trifluoromethyl substitutes is to activate the bis(fluoride) monomers and enhance the polymerization.[11] All the synthesized polymers were highly soluble in common organic solvents such as tertrahydrofuran, chloroform, 1,1,2,2-tetrachloroethane, and so on. 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 11 524, 22 720 and 37 500, 81 234 with dispersity indexes of 1.97 and 2.17 for **PCNCA** and **PCFCA**, respectively. The polymerization results and characterization of **PCNCA** and **PCFCA** are summarized in Table 1. Compared with **PCFCA**, the smaller molecular weight and bigger inaccuracy in elemental analysis may result from the extra side-reaction. However, **PCNCA** was well identified by ^{1}H NMR and FT-IR. Thus, the other reason may be the carbonization of **PCNCA** during elemental analysis. Figure 1 shows the ^{1}H NMR spectra of **PCNCA** and **PCFCA**, respectively. Thermal properties of the synthesized polymers were evaluated by the TGA under nitrogen atmosphere. Figure 2 shows that both **PCNCA** and **PCFCA** exhibited good thermal stability. The weight losses of the polymers were less than 5% on heating to 435 °C for **PCNCA** and 505 °C for **PCFCA**.

Optical and Photoluminescent Properties. Figure 3 exhibits the photoluminescent (PL) maxima of powders for monomer **5**, **9**, and **10**, which are 420, 420, and 408 nm, respectively. The carbazole and 3,3‴-substituted *p*-quaterphenyl units both are emissive chromophores so the PL of polymers resulted from the two segments. Figure 4 shows the UV/vis absorption spectra of **PCNCA** and **PCFCA** in film coated onto the quartz plate. As shown in the absorption spectra, the absorption peaks are at 319, 225 nm and 318, 210 nm for **PCNCA** and **PCFCA**, respectively. The PL spectra (Figure 4) reveal the emission maxima at 413 nm for

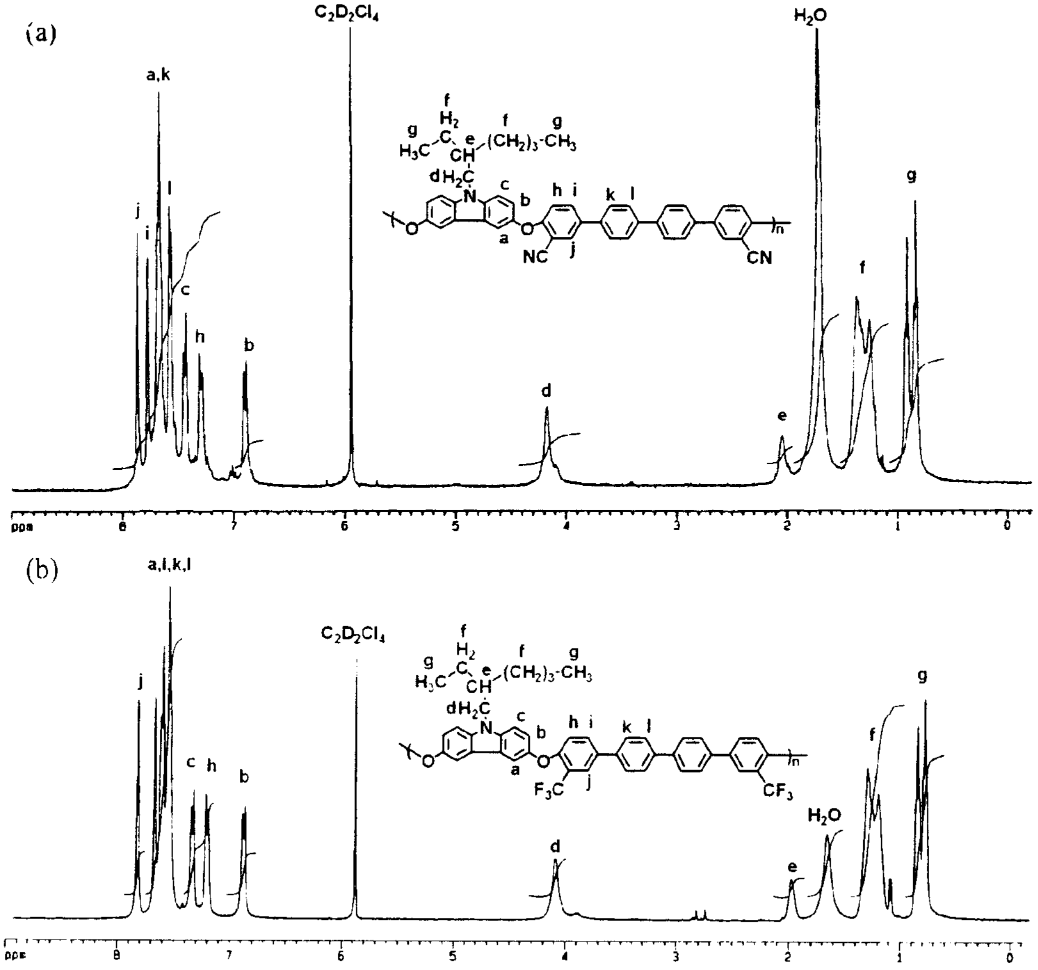


Figure 1. ^{1}H NMR spectra of (a) **PCNCA** and (b) **PCFCA** in $C_2D_2Cl_4$.

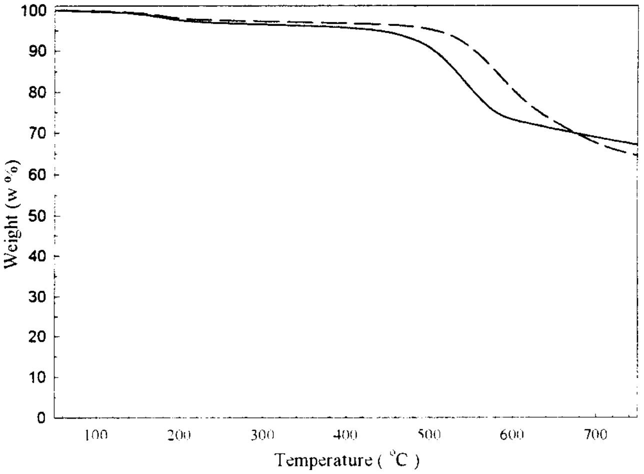


Figure 2. TGA thermograms of **PCNCA** (-) and **PCFCA** (- - -) at a heating rate of 20 °C/min in nitrogen.

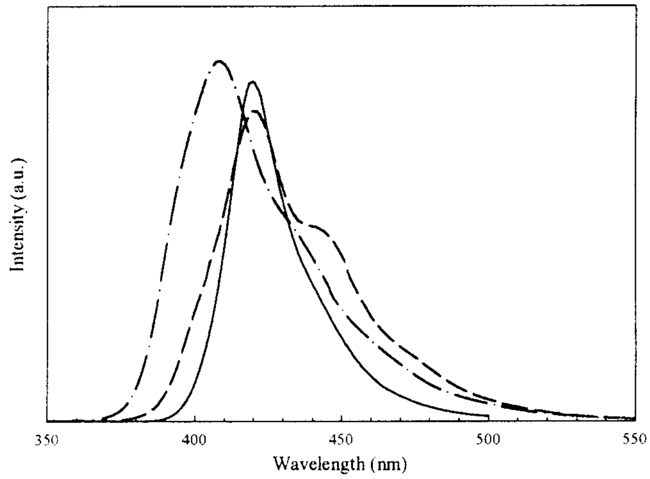


Figure 3. Photoluminescent spectra of compound **5** (-), **9**(- - -), and **10** (-—-) in powder state.

PCNCA and 407 nm for **PCFCA**. Unlike the structureless PL spectrum of **PCNCA**, **PCFCA** shows a shoulder peak at 392 nm. The emissive maxima of **PCNCA** and **PCFCA** were respectively red-shifted about 17 and 11 nm as compared with the 3,3‴-unsubstituted *p*-quaterphenyl containing copolymer (PL λ_{max} at 396 nm).[17] This proves that the substituents at the *meta* position to the adjacent rings could prevent the distorted extent of adjacent rings from being enlarged.

The relative quantum yields (Φ_{PL}) of **PCFCA** in film and THF, which are measured from the corrected PL spectra, are 0.40 and 0.19.[26−28] However, the Φ_{PL} values of **PCNCA**, which are respectively 0.02 and 0.04 in film and THF, showed a drastic decrease. This may be due to the more bulky trifluoromethyl groups which prevent self-quenching processes via exciplexes or polaron pairs, induced by closely packed emissive segment.[26,29] The another reason may be that there are more quenching sites, which result from a side-reaction during polymerization, in **PCNCA**. The Φ_{PL} of **PCFCA** in dilute solution is lower than that in film. This is abnormal and requires further investigation. The optical and photo-

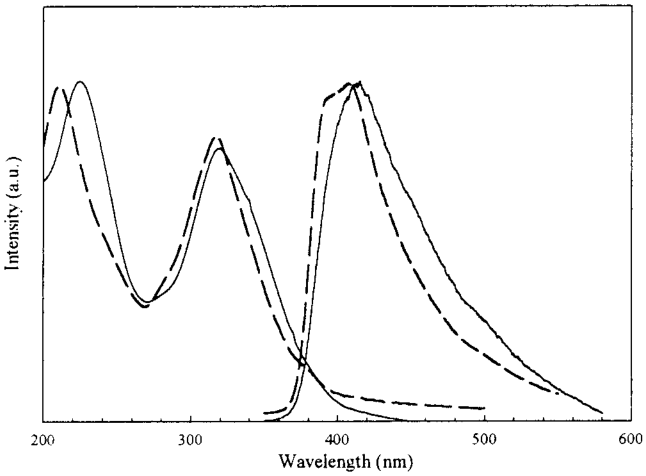


Figure 4. Photoluminescence and UV/vis absorption spectra of **PCNCA** (-) and **PCFCA** (- - -) thin films coated on a quartz plate.

Table 2. Optical and Photoluminescent Properties of PCNCA and PCFCA

polymers	UV/vis λ_{max} (nm)	PL λ_{max} (nm)	E_g^{opt} (eV)	$\Phi_{PL}{}^a$ in film	$\Phi_{PL}{}^b$ in THF
PCNCA	319 (225)	413	3.17	0.02	0.04
PCFCA	318 (210)	407	3.25	0.40	0.19

[a] These values were measured by the front-surface geometry using 9,10-diphenylanthracene (dispersed in PMMA film with a concentration less than 10^{-4} M, assuming Φ_{PL} of 0.83) as a standard at 24−25 °C. The excitation wavelength is 360 nm for the standard and 320 nm for the polymers. The optical densities of polymeric films are 0.155 and 0.163 for **PCNCA** and **PCFCA**. [b] These values were measured by the right-angle geometry using quinine sulfate (dissolved in 1 N H_2SO_4(aq) with a concentration less than 10^{-4} M, assuming Φ_{PL} of 0.55) as a standard at 24−25 °C. The excitation wavelength is 320 nm for the standard and the polymers.

luminescent properties of the polymers are summarized in Table 2.

Electrochemical Properties. The typical cyclic voltammorgams (CV) of **PCNCA** and **PCFCA** are showed in Figure 5. For **PCNCA**, the reductive peak potentials (n-doping) are located at −1.36 and −1.85 V, while reoxidative peak potentials are at −2.17 V vs Ag/AgCl. The oxidative peak potentials (p-doping) of **PCNCA** are revealed at 1.55 and 2.39 V vs Ag/AgCl. **PCFCA** shows similar redox trend to **PCNCA**, i.e., reductive peak potentials at −1.28, −1.69 V and oxidative peak potentials at 1.49, 2.21 V. The energy values of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) for the synthesized polymers were calculated using the ferrocence (FOC) value of −4.8 eV below the vacuum level.[22] The onset potentials of reduction and oxidation of **PCNCA** were determined at −1.07 and 0.91 V vs Ag/AgCl, corresponding to −1.55 and 0.43 V vs FOC (E_{FOC} = 0.48 V vs Ag/AgCl). Thus, the LUMO and HOMO levels and the electrochemical band gap (E_g^{el}) should be −3.25, −5.23, and +1.98 eV, respectively [$E_{LUMO} = -e(E_{re,onset,FOC} + 4.8)$, $E_{HOMO} = -e(E_{ox,onset,FOC} + 4.8)$]. From the same calculation, the LUMO and HOMO levels and the E_g^{el} of **PCFCA** are −3.32, −5.41, and +2.09 eV, respectively.

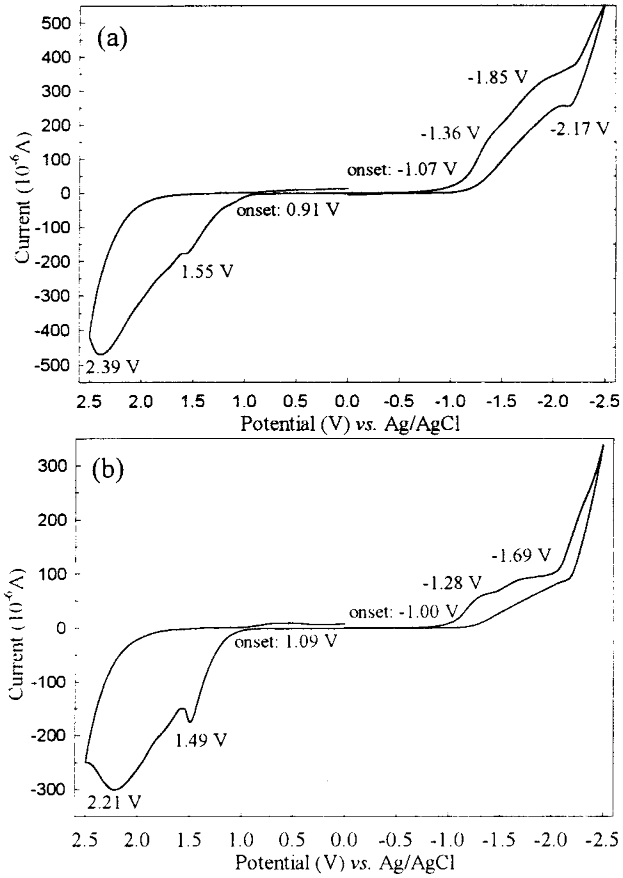


Figure 5. Cyclic voltammograms of (a) **PCNCA** and (b) **PCFCA** in film on ITO glass electrode in CH_3CN solution of Bu_4NClO_4 (0.1 M) at a scan rate of 100 mV/s.

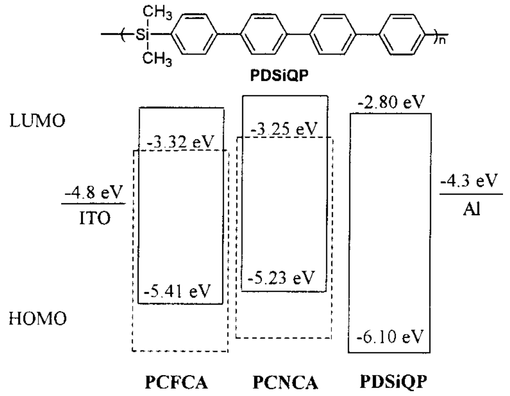


Figure 6. Energy band diagram of **PCNCA**, **PCFCA** (hole transporting segments, —; electron transporting segments, − −), and **PDSiQP**.

The optical band gap (E_g^{opt}) calculated from the onset of the UV/vis absorption spectra was 3.17 eV for **PCNCA** and 3.25 eV for **PCFCA**. There is a large difference between the E_g^{el} and E_g^{opt}. A sensible reason is that the reduction and oxidation progressed in isolated electron and hole transporting units and not in a full conjugated system. The E_g^{el} is the difference in energy level between the LUMO of electron transporting units and the HOMO of the hole transporting units. The energy band diagram of the polymers is proposed in Figure 6. Compared with **PDSiQP**,[18] the barriers of electron and hole injection from the opposite electrodes have been diminished successfully. The electron affinities (EA) of these polymers are even larger than CN−PPV (3.02 eV) or other poly(oxadiazole)s (2.8−2.9 eV).[30] The ionization potential (IP) of **PCNCA** is lower than that of PPV, and that of **PCFCA** is almost the same as that of PPV (5.40 eV).[30]

Conclusions

Two novel soluble alternating poly(aryl ether)s, which contain isolated electron-transporting/emissive segments (3,3‴-dicyano-*p*-quaterphenyl or 3,3‴-bis(trifluoromethyl)*p*-quaterphenyl) and hole-transporting/emissive segments (carbazole), were synthesized and characterized. The polymers can be dissolved in general organic solvents such as THF and chloroform and show good thermal stability. In the film state, the photoluminescence of the polymers locate in the blue emission region. The relative quantum yields of the two polymers are respectively 0.02, 0.40 in the film state and 0.04, 0.19 in THF for **PCNCA**, **PCFCA**. Moreover, from cyclic voltammetric observation the reduction and oxidation progressed first in isolated electron and hole transporting segments, respectively. Both the electron and hole affinities of these polymers have been enhanced, and the barriers of charge injection from the Al and ITO electrodes have been diminished successfully.

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