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New Conjugated Polymers with Donor−Acceptor Architectures: Synthesis and Photophysics of Carbazole−Quinoline and Phenothiazine−Quinoline Copolymers and Oligomers Exhibiting Large Intramolecular Charge Transfer

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ABSTRACT: Alternating carbazole−quinoline and phenothiazine−quinoline donor−acceptor conjugated copolymers and a corresponding oligomer were synthesized, and their solution and solid-state photophysics were investigated. The new copolymers, poly(2,2′-9-methyl-3,6-carbazolylene-6,6′-bis(4-phenylquinoline)) and poly(2,2′-10-methyl-3,7-phenothiazylene-6,6′-bis(4-phenylquinoline)), had intrinsic viscosities of 11.2−22.0 dL/g, indicating very high molecular weights. The optical band gaps of the new copolymers were 2.35−2.64 eV, which are significantly smaller than the corresponding homopolymers. The absorption and emission spectra of the related donor−acceptor oligomers, 3,6-[bis(4-phenyl-2-quinolyl)]-9-methylcarbazole and 3,7-[bis(4-phenyl-2-quinolyl)]-10-methylphenothiazine, in solvents of varying polarity showed positive solvatochromism. An unusual dual fluorescence, with a blue emission band at 454 nm and an orange emission band at 584 nm, was observed in solid films of the carbazole-linked oligomer and related to intramolecular excitons and intermolecular excimers. Solid-state emission from the phenothiazine oligomer and copolymer was from intramolecular excitons with strong charge-transfer character. The red solid-state emission from the carbazole copolymer originated from intermolecular excimers with dominant fluorescence lifetimes of 2−10 ns. The observed intramolecular charge-transfer effects on photophysics and properties were larger in the phenothiazine-containing oligomer and copolymer than the corresponding carbazole-containing materials, reflecting the fact that phenothiazine is a stronger electron-donating unit. Preliminary results suggest that the oligomers and copolymers are useful for light-emitting and photovoltaic devices.

Introduction

π-Conjugated polymers with donor−acceptor architectures are currently of interest because the built-in intramolecular charge transfer can facilitate ready manipulation of the electronic structure (HOMO/LUMO levels), leading to small band gap semiconducting polymers[1−5] or materials with enhanced third-order nonlinear optical properties.[3b,6] Through design and synthesis of new architectures, donor−acceptor conjugated polymers can extend to systems with efficient photoinduced charge transfer and separation for photovoltaic devices[7] and to bipolar charge transport materials for light-emitting diodes,[8,9] lasers,[10] and other applications.[11] Whereas several *electron-accepting* moieties have been explored, thiophene, oligothiophenes, and derivatives have mostly been the *electron-donating* moieties used in constructing donor−acceptor conjugated copolymers.[1−4] We have previously synthesized and investigated many thiophene−quinoline, bithiophene−quinoline, thiophene−anthrazoline, bithiophene−anthrazoline, thiophene−quinoxaline, and related donor−acceptor conjugated polymers (Chart 1).[1] Such alternating donor−acceptor chain structures have allowed the optical,[1,12] nonlinear optical,[6] redox,[1e] and electroluminescent[9] properties to be tuned over a wide range; for example, light-emitting devices with colors spanning the visible were obtained.[9] However, those series of conjugated polyquinolines were shown to be excellent electron acceptors and electron-transport materials, but they had poor hole injection and transport (electron-donating) properties.[9] Herein we explore new donor−acceptor conjugated copolymers based on *N*-alkylcarbazole and *N*-alkylphenothiazine as the electron-donating moieties.

Poly(*N*-vinylcarbazole) (PVK) is a well-known electron donor and hole transport material which has been used in photocopiers[13a] and more recently in light-emitting diodes.[13b,c] Since PVK is not a conjugated polymer, charge transport is via radical cation hopping among the discrete carbazole units.[13a] π-Conjugated polycarbazoles and polyphenothiazines (Chart 1) were first investigated many years ago by one of us.[14] They were shown to be p-type (hole transport) conducting polymers with dc conductivities as high as the 10−50 S/cm range when doped with iodine; hence, they can be expected to have significantly improved hole mobilities compared to that of PVK. The polyquinolines, exemplified by those shown in Chart 1, have excellent electron-accepting and transport properties.[9,15] Recent studies of single crystals of many phenylquinoline−aromatic ring−phenylquinoline oligomers in our group have shown that small aromatic ring donors such as thiophene and bithiophene formed relatively coplanar π-electron delocalized systems with adjacent quinoline rings.[16] Although this feature maximized intramolecular charge transfer (ICT) and produced the smallest HOMO−LUMO gaps, it enhanced electron-accepting properties much more than

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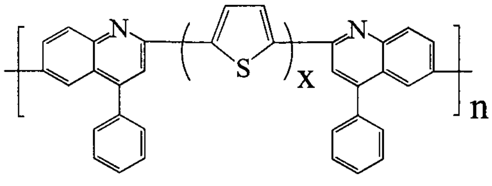
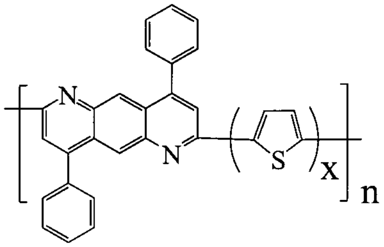
Chart 1



1a. x = 1 (PTPQ)
1b. x = 2 (PBTPQ)



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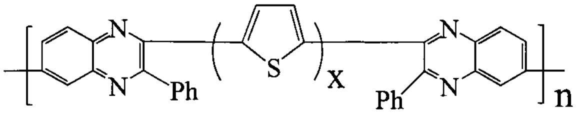
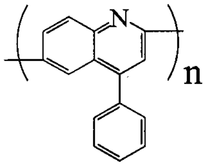
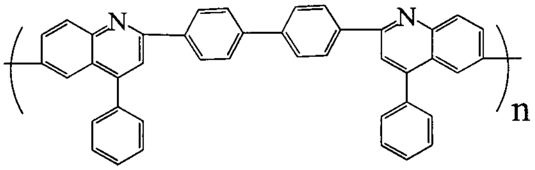


3a. x = 1 (PTQX)
3b. x = 2 (PBTQX)



4. PPQ



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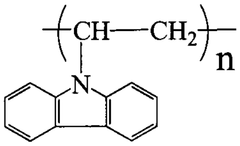
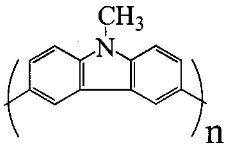


6. PVK



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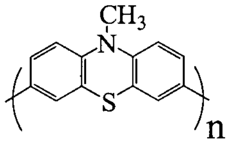
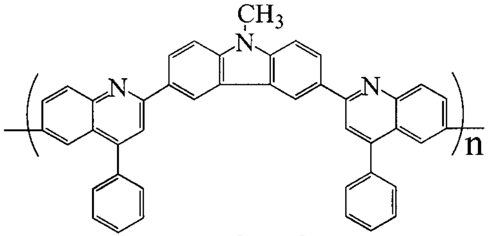
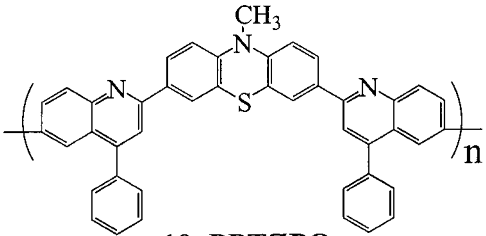


8. PMPTZ

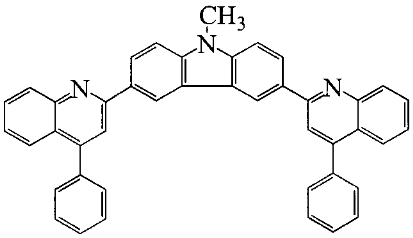
Chart 2



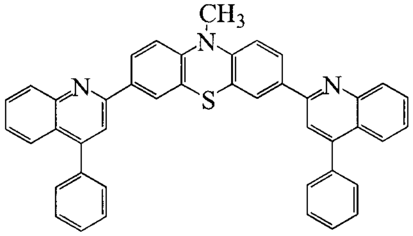
9. PCZPQ



10. PPTZPQ



11. BPQ-MCZ



12. BPQ-PTZ

electron-donating ones.[1e,9] Here, we propose to incorporate carbazole[4,14] and phenothiazine[14] rings into donor–acceptor π-conjugated polymers with the goal of influencing the molecular packing, photophysics, and charge transport properties. The specific new conjugated polymers we have synthesized and investigated are shown in Chart 2: poly(2,2′-(9-methylcarbazole-3,6-diyl-6,6′-bis(4-phenylquinoline)) (PCZPQ) and poly(2,2′-(10-methylphenothiazine-3,7-diyl-6,6′-bis(4-phenylquinoline)) (PPTZPQ). Two related donor–acceptor oligomer model compounds were also investigated (Chart 2): 3,6-[bis(4-phenyl-2-quinolyl)]-9-methylcarbazole (BPQ–MCZ) and 3,7-[bis(4-phenyl-2-quinolyl)]-10-methylphenothiazine (BPQ–PTZ).

Experimental Section

Materials. 9-Methylcarbazole, 10-methylphenothiazine, 2-aminobenzophenone, diphenyl phosphate, aluminum chloride, acetyl chloride, carbon disulfide, *m*-cresol, chloroform, and formic acid were reagent grade or better and were used as received. 3,3′-Dibenzoylbenzidene was prepared according to the methods described in the literature.[1,16,17]

3,6-Diacetyl-9-methylcarbazole. 9-Methylcarbazole (2.0 g, 11 mmol), 25 mL of CH_2Cl_2 (freshly distilled over calcium hydride), and $AlCl_3$ (4.5 g, 33.8 mmol) were added to a three-neck flask under nitrogen atmosphere. Acetyl chloride (2.5 mL, 35.4 mmol) was added dropwise to make the reaction mixture reflux gently. Thereafter, it was stirred at room temperature for another 5 h. The reaction mixture was taken up with 200 mL of CH_2Cl_2 and 100 mL of water. The organic layer was washed with H_2O (2 × 300 mL), dried with $MgSO_4$, and evaporated under vacuum to yield 4.5 g of off-white solid. The crude product was decolorized with carbon black with Celite 545. Mp: 198−201 °C. ^1H NMR (400 MHz/$CDCl_3$): δ 8.79 (s, 2H), 8.19(d, J = 10.8 Hz, 2H), 7.46 (d, J = 10.8 Hz, 2H), 3.94 (s, 3H), 2.76 (s, 6H).

2,7-Diacetyl-10-methylphenothiazine. The Friedel−Crafts reaction of 10-methylphenothiazine with acetyl chloride was reported by Gipstein et al.[18] The procedure was followed starting with 10-methylphenothiazine (12 g, 56.1 mmol), 100 mL of anhydrous CS_2, and $AlCl_3$ (20 g, 0.15 mmol) with addition of acetyl chloride (2.5 mL, 35.4 mmol). 5 g of greenish crude solid product was obtained. 2.5 g of greenish powder was obtained after recrystallizing the crude product in 120 mL of 1:1 ethanol/acetic acid three times. Mp: 206−208 °C (lit.[18] mp 205−206 °C). ^1H NMR (400 MHz/$CDCl_3$): δ 7.820 (d, J = 10.6 Hz, 2H), 7.72 (s, 2H), 6.85 (d, J = 10.6 Hz, 2H), 3.48 (s, 3H), 2.56 (s, 6H).

Oligomer Synthesis: **BPQ−MCZ.** 2-Aminobenzophenone (2.0 g, 10.1 mmol) and 3,6-diacetyl-9-methylcarbazole (0.83 g, 3.13 mmol) were added along with 16 g of diphenyl phosphate (DPP) and 6 g of *m*-cresol in a glass reactor fitted with mechanical stirrer, two glass inlets, and a sidearm. The reaction mixture was purged with argon for 20 min, and then the temperature was gradually raised to 90 °C under argon atmosphere for 1 h and then to 140 °C for 6 h. After cooling, the product was precipitated in a solution of 150 mL of ethanol/15 mL of triethylamine (TEA). The oligomer was purified by continuously extracting it with 10% TEA/methanol solution for 2 days and was dried in a vacuum at 40 °C. Mp: 312−314 °C. UV/vis, λ_{max} (nm) ($CHCl_3$): 359 (log ϵ = 4.49), 373 (4.47). ^1H NMR (400 MHz, $CDCl_3$): δ 9.09 (s, 2H), 8.49 (d, J = 10.71 Hz, 2H), 7.94 (d, J = 5.79 Hz, 2H), 7.77 (s, 2H), 7.66 (d, J = 9.74 Hz, 2 H), 7.49 (m, 16H), 4.00 (s, 3H). FT-IR (KBr pellet, cm^{-1}): 3061, 2932, 1594, 1552, 1490, 1376, 1127, 816, 775. MS (FAB): m/e 588.2 ($M^+ + 1$). Anal. Calcd for $C_{43}H_{29}N_3$: C, 87.88; H, 4.97; N, 7.15. Found: C, 86.13; H, 4.83; N, 6.75.

BPQ−PTZ Oligomer. The synthesis and electrochemiluminescence (ECL) of the phenothiazine−phenylquinoline oligomer was recently described elsewhere.[19]

Copolymer Synthesis. The two new copolymers, PCZPQ and PPTZPQ, were synthesized according to the general literature procedures for the polyquinolines.[1,17]

PCZPQ. Equimolar amounts of 3,3′-dibenzoylbenzidine (1.500 g, 3.82 mmol) and 3,6-diacetyl-*N*-methylcarbazole (1.014 g, 3.82 mmol) were added along with 10 g of diphenyl phosphate (DPP) and 5 g of *m*-cresol in a glass reactor fitted with mechanical stirrer, two glass inlets, and a sidearm. The reaction mixture was purged with argon for 20 min, and then the temperature was raised to 90 °C under positive pressure of argon for 2.5 h and then to 140 °C for 48 h, during which time 5 mL of *m*-cresol was added twice to facilitate efficient stirring of the reaction mixture whenever it became highly viscous. After cooling, the semisolid polymerization mixture was taken out into a solution of 300 mL of ethanol/30 mL of triethylamine (TEA). The polymer was then chopped in a blender and collected by suction filtration. The polymer was purified by continuously extracting it with 20% TEA/ethanol solution for 6 days and was dried in a vacuum at 40 °C. $[\eta]$ = 22.0 dL/g (30 °C, formic acid). ^1H NMR (400 MHz, CD_3NO_2/$GaCl_3$):[20] δ 9.29 (s, 2H), 8.71 (s, 2H), 8.69 (d, J = 8.7 Hz, 2H), 8.65 (s, 2H), 8.56 (d, J = 9.2 Hz, 2H), 8.52 (d, J = 8.9 Hz, 2H), 8.08 (d, J = 8.8 Hz, 2H), 7.79 (m, 10H), 4.28 (s, 3H). FT-IR (free-standing film, cm^{-1}): 3061, 2932, 1594, 1547, 1490, 1376 1289 1252, 1132, 883, 826. Anal. Calcd for $C_{43}H_{27}N_3$: C, 88.21; H, 4.61; N, 7.18. Found: C, 85.44; H, 4.78; N, 7.18.

PPTZPQ. Equimolar amounts of 3,3′-dibenzoylbenzidine (0.9870 g, 2.52 mmol) and 2,7-diacetyl-*N*-methylphenothiazine (0.7479 g, 2.52 mmol) were added along with 15 g of diphenyl phosphate (DPP) and 10 g of *m*-cresol in a glass reactor fitted with mechanical stirrer, two glass inlets, and a sidearm. The reaction mixture was purged with argon for 20 min, and then the temperature was raised to 90 °C under argon atmosphere for 2.5 h and then to 140 °C for 24 h. After cooling, the semisolid polymerization mixture was taken out into a solution of 10% triethylamine/ethanol (300 mL). The polymer was then chopped in a blender and collected by suction filtration. The polymer was purified by continuously extracting it with 20% TEA/ethanol solution for 5 days and was dried in a vacuum at 40 °C. $[\eta]$ = 11.2 dL/g (30 °C, formic acid). FT-IR (free-standing film, cm^{-1}): 3067, 2932, 1593, 1546, 1481, 1450. 1345, 1162, 1132, 885, 837. Anal. Calcd for $C_{43}H_{27}N_3S$: C, 83.63; H, 4.38; N, 6.81; S, 5.18. Found: C, 81.51; H, 4.66; N, 6.99; S, 4.61.

Characterizations. Optical absorption spectra were obtained on a Perkin-Elmer Lamda 900 spectrophotometer. Steady-state photoluminescence studies were done by using a Spex Fluorolog-2 spectrofluorometer with a Spex DM3000f spectroscopy computer. Thin films on silica substrates were positioned such that the emission was detected at 22.5° from the incident radiation beam. Fluorescence quantum yields of the solutions were determined by comparison with a standard quinine sulfate (10^{-6} M in 1 N H_2SO_4)(Φ_f = 0.55).[21] Fluorescence quantum yields of the thin films were determined by comparison with a thin film of $\sim 10^{-3}$ M 9,10-diphenylanthracene in poly(methyl methacrylate) (Φ_f = 0.83).[9d,21]

Time-correlated single photon counting experiments for the measurement of fluorescence lifetimes were carried out on an instrument consisting of mode-locked Nd:YLF laser (Quantronix) operating at 76 MHz as the primary laser source.[21b] The second harmonic (KTP crystal) of the Nd:YLF laser was used to synchronously pump a dye laser (Coherent 700). The pulse width of the dye laser was typically 8 ps and was cavity-dumped at a rate of 1.9 MHz. The dye laser was tuned to the desired excitation wavelength. Measurements were made on air-saturated samples at room temperature.

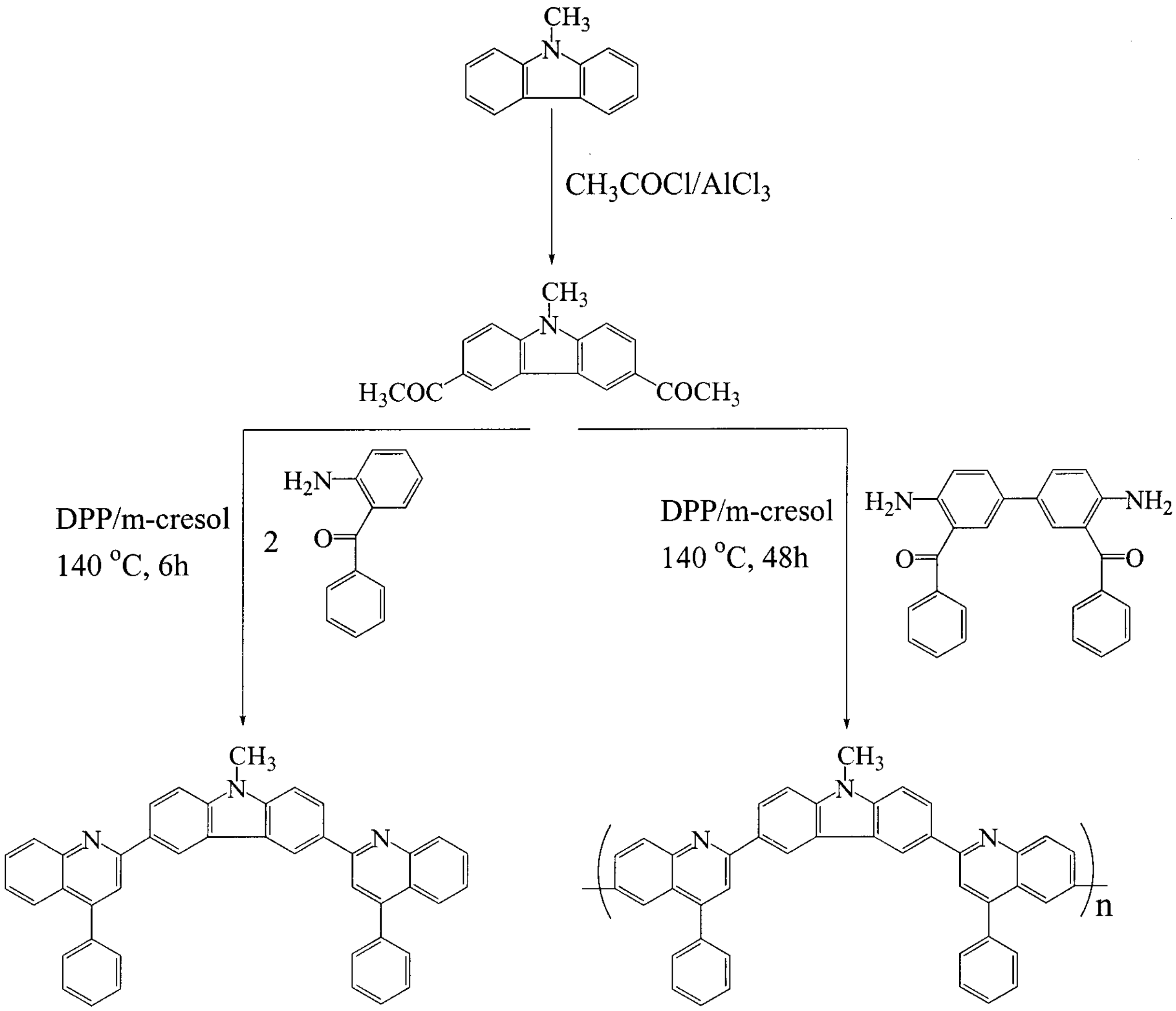
The intrinsic viscosity $[\eta]$ of the copolymers was measured by using dilute formic acid solutions in the range 0.05−0.10 g/dL at 30 °C on a Cannon Ubbelohde capillary viscometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and melting points were done by using a TA instruments model 3000 thermal analyst based on IBM PS/253 model 60 computer and equipped with a model 2050 TGA unit and a model 2920 DSC unit. The TGA data and DSC thermograms were obtained in flowing nitrogen at a heating rate of 10 °C/min. The FT-IR spectra were taken on thin films of the polymers on NaCl substrate or free-standing films and KBr pellet of the oligomers using a Nicolet model 20SWC Fourier transform infrared spectrometer under nitrogen. ^1H NMR spectra were taken at 400 MHz on a Bruker Avance-400 instrument.

Results and Discussion

Synthesis and Characterization. Scheme 1 describes the synthesis of the 9-methylcarbazole−phenylquinoline donor−acceptor oligomer BPQ−MCZ and the corresponding alternating copolymer PCZPQ. The synthesis of the 10-methylphenothiazine−phenylquinoline copolymer PPTZPQ followed a similar scheme.

The very high intrinsic viscosities of the new copolymers, 22.0 dL/g for PCZPQ and 11.2 dL/g for PPTZPQ, shows that they are very high molecular weight materi-

Scheme 1



11. BPQ-MCZ **9. PCZPQ**

als and that the starting monomers were very pure.[1,15,17] For comparison purposes, we note that prior studies of the absolute molecular weight of the related polyquinoline PBPQ (Chart 1) with an intrinsic viscosity of 20 dL/g gave a weight-average molecular weight (M_w) of 370 000 by a light scattering measurement.[17] These new copolymers were only slightly soluble in common organic solvents such as chloroform and tetrahydrofuran. However, they were very soluble in formic acid and nitromethane/$GaCl_3$.[20] Polymer solutions in the latter solvent system were used to characterize the polymers by ^1H NMR spectroscopy in addition to the ^1H NMR spectra of the oligomers in common organic solvents. Formic acid solutions of the copolymers were used to prepare thin films for all spectroscopic studies in the solid state and for devices.

Molecular structures of the new copolymers and oligomer (BPQ–MCZ) were confirmed by FT-IR, ^1H NMR, elemental analysis, and comparisons with previously reported related materials.[1,16,19] The strong peak due to the carbonyl group of the monomers was completely absent in the FT-IR spectra (not shown) of PCZPQ, PPTZPQ, and the oligomers. Instead, new strong bands between 1600 and 1400 cm^{-1} due to the imine (C=N) group and characteristic of the quinoline ring[1,16] were observed. This is usually an excellent confirmation of the completion of cyclization reaction forming quinoline rings.[1a–c] The ^1H NMR spectra of oligomer BPQ–MCZ in $CDCl_3$ and PCZPQ in $GaCl_3$/nitromethane-d_3, which are summarized in the Experimental Section, confirmed their molecular structures. For better comparison with the polymer, the ^1H NMR spectrum of oligomer BPQ–MCZ was also taken in $GaCl_3$/nitromethane-d_3. The structure of the oligomer BPQ–PTZ was previously established using its ^1H NMR and ^{13}C NMR spectra and other characterization results.[19] In $GaCl_3$/nitromethane-d_3 (0.5–1.0 wt %) both BPQ–PTZ and PPTZPQ gave similar, relatively broad, ^1H NMR spectra with merged peaks that were not distinct enough to be assigned. This appears to be due to long relaxation time caused by strong intermolecular interactions in the complexes.[20]

The elemental analysis data, which were included in the Experimental Section, were in good agreement with the proposed structures. The UV–vis and photoluminescence spectra of the two copolymers and both oligomers, to be presented and discussed later, also provided additional evidence confirming their molecular structures. The thermal behavior of PCZPQ and PPTZPQ was measured by TGA and DSC. The initial decomposition temperature of PCZPQ and PPTZPQ under nitrogen was about 600 and 400 °C, respectively, where over 95% of their mass was retained. No clear phase transition was observed in DSC scans up to 350 °C, suggesting

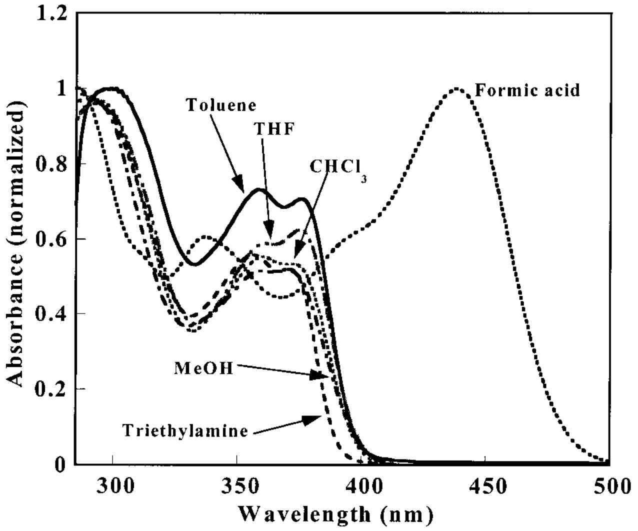


Figure 1. UV−vis absorption spectra of BPQ−MCZ oligomer in solvents of varying polarity.

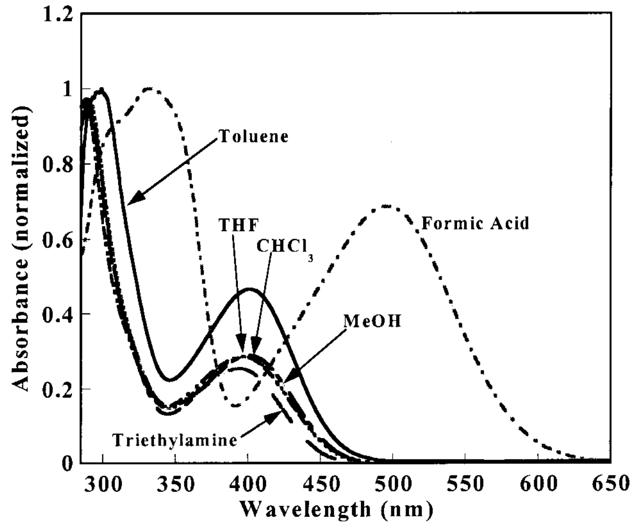


Figure 2. UV−vis absorption spectra of BPQ−PTZ oligomer in solvents of varying polarity.

that the glass transition temperatures of the copolymers are very high.

Photophysics of Donor−Acceptor Oligomers. a. Solutions. A unique feature of these oligomer model compounds is that they are identical to the repeating units of the corresponding alternating donor−acceptor conjugated copolymers. Therefore, the essential π-electronic structure in the ground and excited states and ICT effects expected in the copolymers due to the donor−acceptor architecture should be captured in the oligomers. The photophysics of the donor−acceptor oligomers in solution is expected to depend on the polarity of the solvent. We have thus examined the absorption and emission properties of both BPQ−MCZ and BPQ−PTZ in different solvents.

The UV−vis absorption spectra of BPQ−MCZ and BPQ−PTZ in different solvents are shown in Figures 1 and 2, respectively. The absorption maxima, which are collected in Table 1, are correlated well with an empirical solvent polarity measures such as the Kamlet−Taft π^* parameter.[22] As the solvent polarity increases from nonpolar triethylamine, to moderately polar chloroform, and to very polar and protic formic acid, the lowest energy absorption maxima of both oligomers undergo a significant red shift accompanied by spectral shape changes. *Positive solvatochromism*, i.e., a bathochromic shift of the absorption band with increasing solvent polarity, was observed in both oligomers, indicating the charge-transfer nature of the absorption band and that the excited state of each oligomer is more stabilized than the ground state.[22c]

The absorption spectra of each oligomer in the different solvents are characterized by two bands, one near 290−300 nm and the other at around 360−400 nm. The former band can be assigned to $\pi-\pi^*$ transition whereas the lowest-energy band, which is less intense, is largely of charge transfer character. It is this lowest-energy absorption band that is most sensitive to the solvent polarity and to the donor moiety (phenothiazine vs carbazole). In all the solvents, the lowest-energy absorption maximum of BPQ−PTZ is consistently red-shifted from that of BPQ−MCZ; this red shift of the phenothiazine oligomer ranges from 25 nm in toluene or THF and 39 nm in triethylamine to 57 nm in formic acid. This confirms the fact that the phenothiazine ring which contains an extra sulfur heteroatom is a much stronger electron-donating moiety than carbazole. Consequently, ICT effects in the phenothiazine-containing oligomer are expected to be much stronger than in the one containing carbazole. The experimental observations from all the absorption spectra (Figures 1 and 2, Table 1) are in accord with this expectation.

The absorption spectra of both oligomers in formic acid (Figures 1 and 2) are dramatically different in line shape and absorption maxima compared to the spectra in aprotic organic solvents. For example, the absorption maxima of BPQ−MCZ and BPQ−PTZ in this solvent are 439 and 496 nm, respectively. Here, protonation of the quinoline moieties in the oligomers results in a much stronger electron-accepting group, thereby enhancing charge separation of π-electrons in the conjugated donor−acceptor structure.[1] The net effect of the protonation is thus an enhanced ICT in formic acid compared to the aprotic organic solvents such as chloroform and toluene.

Another evidence of the ICT effects in these new donor−acceptor oligomers comes from a direct comparison of the absorption spectra of BPQ−MCZ and BPQ−PTZ with the previously reported results for the related oligomer: 2,2′-bis(4-phenylquinoline)−4,4′-biphenylene (BPQ−BP).[16] The lowest-energy absorption maximum of BPQ−BP in chloroform was only 348 nm compared to 360 nm for BPQ−MCZ and 398 nm for BPQ−PTZ in the same solvent even though the number of π-electrons is the same in the biphenylene, carbazole, and phenothiazine linkages. The greater extent of π-electron delocalization in the phenothiazine- and carbazole-containing oligomers clearly comes from the greater charge separation and ICT character of their electronic ground states.

The emission spectra of both oligomers in different solvents also exhibited positive solvatochromism as shown in the photoluminescence (PL) spectra of BPQ−MCZ and BPQ−PTZ in Figures 3 and 4, respectively. The emission maxima increased dramatically as the medium undergo change from apolar to very polar. The solvatochromic shifts of the emission spectra are much larger than those of absorption spectra, implying that the excited-state energy levels are influenced more than those in the electronic ground state.[22] This confirms the

Table 1. Absorption and Emission Properties of Oligomers and Copolymers in Solvents of Varying Polarity

material	solvent	$\lambda_{\max}^{\mathrm{UV}}$, nm	log ϵ	$\lambda_{\max}^{\mathrm{PL}}$, nm	Stokes shift, cm^{-1} (eV)
BPQ−MCZ	triethylamine	290, 356	5.15, 4.92	401	3153 (0.39)
	toluene	299, 376	4.59, 4.44	414	2441 (0.30)
	THF	289, 375	4.99, 4.80	429	3356 (0.42)
	$CHCl_3$	293, 360	4.89, 4.66	430	4522 (0.56)
	MeOH	293, 370	4.92, 4.67	469	5705 (0.71)
	formic acid	286, 439	4.94, 4.94	546	4464 (0.55)
BPQ−PTZ	triethylamine	289, 395	5.07, 4.52	506	5553 (0.69)
	toluene	299, 401	4.57, 4.24	524	5854 (0.73)
	THF	290, 400	4.91, 4.42	531	6168 (0.76)
	$CHCl_3$	290, 398	4.83, 4.33	531	6293 (0.78)
	MeOH	288, 397	4.92, 4.42	562	7395 (0.92)
	formic acid	333, 496	4.92, 4.76	*a*	*a*
PCZPQ	formic acid	300, 474	4.69, 4.60	579	3826 (0.47)
PPTZPQ	formic acid	299, 566	4.88, 4.71	*a*	*a*

[a] Too low to measure.

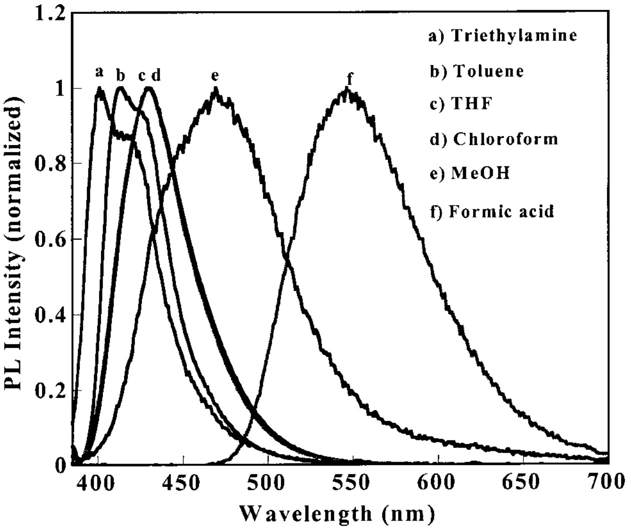


Figure 3. Normalized emission spectra of BPQ−MCZ oligomer ($\lambda_{\mathrm{ex}} = 370$ nm, except formic acid at 439 nm) in solvents of varying polarity.

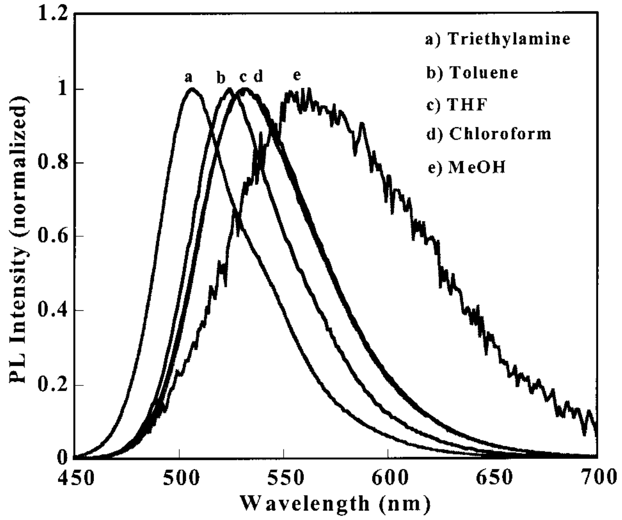


Figure 4. Normalized emission spectra ($\lambda_{\mathrm{ex}} = 400$ nm) of BPQ−PTZ oligomer in solvents of varying polarity.

earlier finding in connection with the absorption results that both BPQ−MCZ and BPQ−PTZ are more charge-separated in the excited state than in the ground state.

The progressive red shift of the PL spectra of BPQ−MCZ with increasing solvent polarity are accompanied by significant broadening of the emission band, particularly in methanol and formic acid (Figure 3). The full width at half-maximum (fwhm) of the emission spectrum of BPQ−MCZ increases from 45 nm in triethylamine to 86 nm in methanol to 88 nm in formic acid. In the case of BPQ−PTZ, fwhm increases from 54 nm in triethylamine to 107 nm in methanol. The emission maximum increased from 401 nm in triethylamine to 469 nm in methanol and 546 nm in formic acid. The large emission maximum in methanol can be understood from its protic nature.[23] Protons from methanol molecules can form hydrogen bonding to the nitrogen heteroatoms of quinoline rings, and such hydrogen bonding usually enhances charge separation. As a result, intramolecular charge-transfer interaction becomes important even in the moderate polar solvent methanol.[23] In the extreme case of formic acid, protonation of the quinoline rings is more complete, resulting in a red-shifted emission band due to dominant intramolecular charge transfer. Similar emission spectra results were obtained for BPQ−PTZ except that fluorescence was completely quenched in formic acid (Figure 4). Another important difference with the BPQ−MCZ is that the emission maxima of the phenothiazine-containing oligomer are even larger, varying from 506 nm in triethylamine to 562 nm in methanol.

The Stokes shift of oligomer emission in solution was found to increase with the polarity of solvent and to be unusually large. In the case of BPQ−MCZ, the Stokes shift increased from 2400 cm^{-1} (0.3 eV) in toluene to 5705 cm^{-1} (0.71 eV) in methanol. The Stokes shift in BPQ−PTZ was even larger, varying from 5553 cm^{-1} (0.69 eV) in triethylamine to 7395 cm^{-1} (0.92 eV) in methanol (Table 1). These huge Stokes shifts further support the view that intramolecular charge-transfer interactions in these donor−acceptor oligomers are large. The exceptionally large case is again in methanol where hydrogen-bonding interaction between methanol and the oligomers enhances the charge separation. As a result, there is a big change in geometry of BPQ−MCZ or BPQ−PTZ in methanol from the ground state to the excited state.[23b] Each oligomer in methanol shows the largest Stokes shift among all solvents tested.

The fluorescence quantum yield (Φ) of both oligomers was measured in chloroform and found to be 0.29 for BPQ−MCZ and 0.37 for BPQ−PTZ. These values are less than the 54% fluorescence efficiency ($\Phi = 0.54$) found for BPQ−BP, the biphenylene-linked oligomer.[16] The fairly high (37%) fluorescence quantum efficiency of BPQ−PTZ in aprotic solvents is consistent with the recent observation of efficient electrochemiluminescence (ECL) in it by Bard and co-workers.[19] Although the

Table 2. PL Decay Lifetime of Oligomers and Copolymers in Solution and Thin Films

material	τ_1, ns	τ_2, ns	τ_3, ns	amplitude, % $\tau_1/\tau_2/\tau_3$	χ^2
BPQ−MCZ ($CHCl_3$)	1.99			100	2.0
BPQ−MCZ (DMSO)	4.01			100	1.9
BPQ−MCZ (film, 450 nm)	0.85	0.12	0.024	5.3/44.0/50.8	1.08
BPQ−MCZ (film, 580 nm)	21.1	4.09	0.62	54.2/36.6/9.3	2.1
BPQ−PTZ (film)	3.15	1.04	0.20	30.0/51.4/18.6	1.49
PCZPQ (film)	9.61	2.07	0.33	30.9/46.1/23.0	1.84
PPTZPQ (film)	1.58	0.29	0.071	9.7/30.6/59.7	1.2

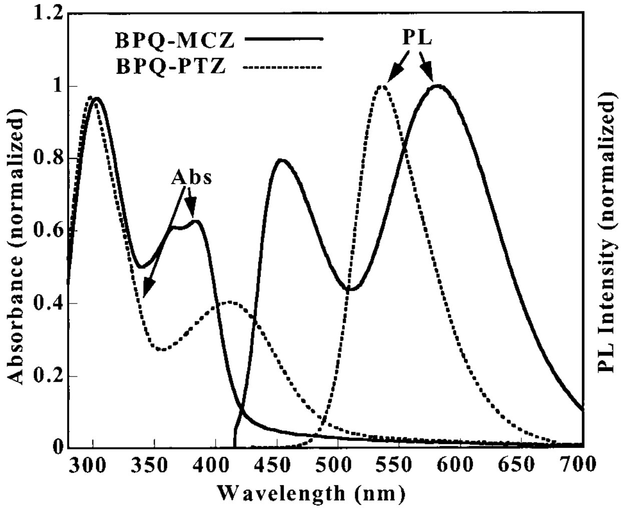


Figure 5. UV−vis absorption and PL emission spectra of thin films of donor−acceptor oligomers (λ_{ex} = 384 nm for BPQ−MCZ and 411 nm for BPQ−PTZ).

fluorescence quantum yield was not measured in all the different solvents, it was found that the fluorescence intensity of both oligomers decreased by orders of magnitude with increasing solvent polarity. In the extreme case of BPQ−PTZ in formic acid, the fluorescence was completely quenched. These results are consistent with the expected effects of ICT on fluorescence quantum yield; i.e., fluorescence efficiency should decrease with increasing strength of intramolecular charge transfer.

The PL decay dynamics of BPQ−MCZ in dilute solution (ca. 10^{-6} M) was examined in two solvents, chloroform and dimethyl sulfoxide (DMSO). In both solvents the picosecond time-resolved PL decay dynamics was well fitted (100% amplitude) by a single exponential, giving fluorescence lifetimes of 1.99 and 4.01 ns in chloroform and DMSO, respectively (Table 2). The interesting suggestion from these results is that the fluorescence lifetime of this donor−acceptor oligomer increased with increasing solvent polarity. Additional studies of PL decay dynamics in other solvents of varying polarity in conjuction with computational modeling are needed to establish the general validity of this suggestion.

b. Thin Films. The solid-state photophysical properties of the two donor−acceptor oligomers, BPQ−MCZ and BPQ−PTZ, were investigated in thin films prepared by spin-coating from chloroform, formic acid, or toluene solutions. Figure 5 shows the optical absorption spectra of thin films of both oligomers. The main features of these spectra are similar to those observed in aprotic solvents: two characteristic bands near 300 and 385−410 nm. The absorption maxima in the carbazole-linked oligomer are at 303 and 385 nm while the optical band gap (absorption edge) is 2.90 eV. The absorption of the phenothiazine-linked oligomer has peaks at 298 and 410 nm while showing a band gap of 2.54 eV (Table 3). For comparison, the high molecular weight conjugated polycarbazole (PMCZ) and polyphenothiazine (PMPTZ) (Chart 1) have optical band gaps of 3 eV or greater. The high molecular weight conjugated polyquinolines (PPQ and PBPQ, Chart 1) have band gaps of 2.65 and 2.81 eV, respectively. Thus, even at the repeat unit (oligomer) level the present phenothiazine−quinoline donor−acceptor architecture has already resulted in smaller band gaps than the parent homopolymers. Clearly, the basic ICT structure of the oligomers is preserved in the solid state.

Table 3. Absorption and Emission Properties of Thin Films of Oligomers and Copolymers

material	λ_{max}^{UV}, nm	E_g, eV	λ_{max}^{PL}, nm	Stokes shift, cm^{-1} (eV)
BPQ−MCZ	300, 384	2.90	454, 584	4016 (0.50), 8918 (1.11)
BPQ−PTZ	298, 411	2.44	540	5813 (0.72)
PCZPQ	312, 410	2.64	640	8765 (1.09)
PPTZPQ	304, 437	2.35	577	5552 (0.69)

The PL emission spectra of thin films of the oligomers are also shown in Figure 5. The phenothiazine-containing oligomer (BPQ−PTZ) has a featureless emission band centered at 540 nm, resulting in a Stokes shift of 5813 cm^{-1} (0.72 eV). Thin films of the carbazole-linked oligomer (BPQ−MCZ) exhibit dual fluorescence with emission maxima at 454 and 584 nm (Table 3). The blue emission band corresponds to a Stokes shift of 4016 cm^{-1} (0.50 eV) while the orange emission band has a Stokes shift of 8918 cm^{-1} (1.11 eV). The blue emission band is very similar to the dilute solution emission band of the oligomer in chloroform or THF. On the basis of this similarity, we assign the blue emission band to singlet emission from BPQ−MCZ molecules. The broad featureless orange emission band of BPQ−MCZ solid films can be assigned to an intermolecular excimer,[24,25] requiring favorable molecular packing with intermolecular distances on the order of 0.35 nm as found by single-crystal X-ray diffraction of related oligomers.[16] The intriguing question is why the two different emitting species coexist in the solid state of BPQ−MCZ. A possible reason is that the spin-coated thin films of this oligomer are semicrystalline, allowing highly ordered regions to coexist with amorphous regions with consequent different molecular packing and different emitting species. Supporting this view is the fact that attempts to grow single crystals of either of the two oligomers from different solvents were unsuccessful unlike over one dozen other oligomers we have been able to obtain single crystals for X-ray crystallography.[16] Furthermore, we have found that solid films of BPQ−MCZ spin-coated from either chloroform or formic acid exhibit the dual fluorescence shown in Figure 5. However, solid films spin-coated from toluene had only the blue band with an emission maximum of 459 nm. The dual fluorescence of BPQ−MCZ oligomer is thus related to the morphology of solid films. In contrast, only one emission band was observed from BPQ−PTZ solid films spin-coated from different solvents. The solid-state emission from the phenothiazine-linked oligomer appears to be from an intramolecular exciton with strong charge-transfer character. Preliminary molecular mechanics examination of the minimum-energy geometries of these oligomers

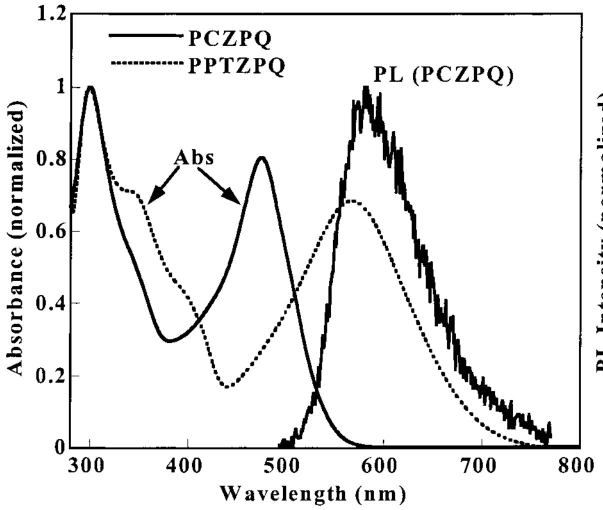


Figure 6. UV−vis absorption spectra of formic acid solutions of PCZPQ (5.6×10^{-5} M) and PPTZPQ (2.7×10^{-5} M). The PL emission spectrum (λ_{ex} = 474 nm) of PCZPQ in formic acid is also shown.

showed that whereas the phenothiazine-linked oligomer was highly bent, which would prevent efficient intermolecular packing, the carbazole-containing oligomer was relatively coplanar.

A rough estimate of fluorescence quantum yield of thin films of the oligomers, i.e., without using an integrating sphere, showed that it was significantly lower than in solution. For both BPQ−MCZ and BPQ−PTZ solid films, the flourescence quantum yield was less than 0.1. The PL decay dynamics of oligomer solid films was examined by monitoring their PL emission maxima. As discussed previously, the solution PL decay dynamics of BPQ−MCZ in two different solvents was well described by a single exponential and one fluorescence lifetime. However, in solid films the PL decay dynamics of both oligomers was not monoexponential, requiring three exponentials to achieve best fits of the data (Table 2). The decay dynamics of each of the dual fluorescence emission bands of BPQ−MCZ solid film was monitored at 450 and 580 nm, respectively. The blue monomer-like emission was characterized by extremely short dominant fluorescence lifetimes of 24−120 ps. The orange emission band in contrast gave dominant lifetimes of 4−21 ns. These PL decay data are consistent with the previous assignment of the orange band to intermolecular excimers.[24,25] The dominant fluorescence lifetimes of the phenothiazine-linked oligomer were in the 1−3 ns range and in line with an intramolecular exciton with strong charge-transfer character.[26]

Photophysics of Donor−Acceptor Copolymers. a. Solutions. Because the high molecular weight copolymers were only partially soluble in aprotic organic solvents without the aid of complexation, they were investigated in formic acid solutions. The UV−vis absorption spectra of both copolymers in solution are shown in Figure 6. These copolymer absorption spectra are red-shifted from those of the corresponding oligomers; PCZPQ and PPTZPQ have absorption maxima of 474 and 566 nm, respectively (Table 1). That the absorption maximum increases with increasing chain length due to electronic delocalization increase is a general feature of conjugated polymers.[27] However, considering that the present donor−acceptor oligomers are actually identical to the alternating copolymer repeat units (Chart 2), one sees that the increase in absorption maximum beyond one repeat unit is only modest. The reason for this unusual feature in these conjugated copolymers is the dominant role of intramolecular charge transfer on their electronic structures. The large red shift of the absorption maximum of the phenothiazine copolymer relative to the carbazole can be understood from its stronger ICT since phenothiazine is a stronger electron-donating ring.

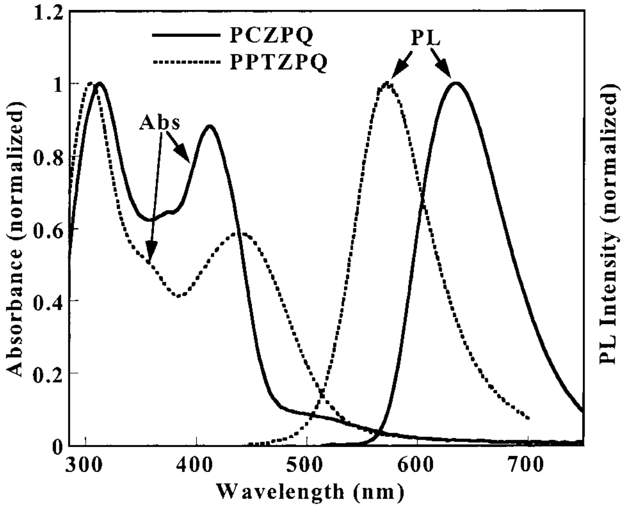


Figure 7. UV−vis absorption and emission spectra of thin films of donor−acceptor copolymers (λ_{ex} = 410 nm for PCZPQ and 437 nm for PPTZPQ).

In formic acid solutions, PCZPQ has a weak PL emission with a low fluorescence efficiency (~3%) and maximum at 579 nm. The phenothiazine copolymer, PPTZPQ, has no detectable emission in formic acid solutions, indicating that the very strong ICT state when the quinoline rings are protonated is nonflourescent. Similar observations of fluorescence quenching in alternating donor−acceptor copolymers have been reported.[2]

b. Thin Films. The UV−vis absorption spectra of thin films of the copolymers, spin-coated from formic acids, are shown in Figure 7. Lowest energy absoption maxima of 410 and 437 nm were observed for the carbazole and phenothiazine copolymers, respectively. The corresponding optical band gap (E_g), measured from the absorption edge, are 2.64 and 2.35 eV, respectively (Table 3). The smaller optical band gap in the phenothiazine copolymer shows that its greater ICT seen in solution is preserved in the solid state. The observed band gaps of both copolymers are significantly less than the parent homopolymers or related polyquinolines linked by *p*-phenylene and *p*-biphenylene. However, these band gaps are somewhat larger than those of thiophene- and bithiophene-linked polyquinolines.[1b] This latter comparison demonstrates that if lowering of the band gap is the primary aim, coplanarity between the donor and acceptor units in a copolymer, and consequent efficient π-electron delocalization is a very important design criterion. By choice of the 3,6-carbazolylene and 3,7-phenothiazylene linkages in the present copolymers, our aim was not to achieve the smallest possible optical band gaps but of understanding the influence of the donor strength and geometry of the electron-donating moieties in donor−acceptor copolymer architectures on photophysics and charge transport properties.

The PL emission spectra of the copolymer thin fims are also shown in Figure 7. Here, the featureless and broader emission band of the carbazole copolymer, with maximum at 640 nm and a Stokes shift of 1.1 eV, is actually red-shifted from the phenothiazine copolymer by 63 nm. The solid-state fluorescence efficiency of both copolymers is reduced compared to the oligomers in solution. In the case of the carbazole copolymer, its solid-state PL emission spectrum has all the features of intermolecular excimers[24,25] and, in comparison with the oligomer thin-film results, can be readily assigned as such. We point out that the absorption edge feature at ∼470−550 nm in the UV−vis spectrum of PCZPQ was confirmed to be real by a PL excitation scan of the 640 nm emission band. Such an absorption edge feature has been interpreted in some conjugated polymer films to imply existence of ground-state aggregates and the luminescence as arising from "aggregate emission."[28] However, existence of ground-state aggregates does not preclude excimer emission since often such "aggregate" species are preform excimer sites in a material.[24,25,28c] The nature of the emission from the phenothiazine copolymer seems more intriguing since its formic acid does not fluoresce. However, the PL emission blue shift of this copolymer relative to the carbazole copolymer, which is the opposite of the absorption spectra relationship of the two materials, strongly rules out intermolecular excimer emission. Insights provided by the previously discussed emission features of the phenothiazine oligomer allow us to assign the phenothiazine copolymer emission to intramolecular excitons with strong charge-transfer character,[26] in accord with the dominant role of ICT in the lowest excited states of this copolymer.

The solid-state PL decay dynamics of the two copolymers are also shown in Table 2. Similar to the oligomer thin films, three exponentials were required to adequately fit the data. The PCZPQ solid films have rather long-lived excited-state species with dominant fluorescence lifetimes in the 2.0−9.6 ns range. This is consistent with the intermolecular excimer assignment of the emission. In contrast, the dominant lifetimes of the phenothiazine copolymer (PPTZPQ) thin films are only in the range 70−290 ps, which are rather short compared to excimer-forming conjugated polymers.[9d] The PL decay dynamics support the view that the emission from the phenothiazine copolymer is from intramolecular excitons with a strong charge-transfer character. In the limit of very strong intramolecular charge transfer as observed in PPTZPQ solutions in formic acid, the fluorescence is quenched. In solid films of the phenothiazine copolymer, ICT is sufficiently strong to dramatically reduce the fluorescence lifetime along with the quantum yield.

Light-Emitting and Photovoltaic Devices. Compared to our previous studies of electroluminescent polyquinolines,[9] the present donor−acceptor copolymers have lower fluorescence efficiencies. However, because these new copolymers contain both electron-donating and electron-accepting moieties, it is reasonable to expect that charge injection and transport could be more balanced in light-emitting diodes (LEDs). In preliminary studies, single-layer devices of the configuration ITO/PCZPQ/Al and ITO/PPTZPQ/Al were fabricated and tested in ambient laboratory conditions by using previously reported procedures and methods.[9,29] Red electroluminescence (EL), with emission maximum at 630−640 nm and luminance levels less than 10 cd/m^2, was observed in the carbazole copolymer. EL emission was not observed from the single-layer phenothiazine copolymer devices. Given these single-layer results, it appears that use of these copolymers in bilayer or blend LEDs is more promising for preparing tunable multicolor devices or white light LEDs.[29] Also, because of their higher fluorescence efficiencies, the two oligomers which can be vapor-deposited are promising for LEDs. Detailed device studies along these lines are in progress and will be reported in the future.[29]

Photovoltaic cells of the Schottky barrier type, ITO/copolymer (50−100 nm)/Al, were also fabricated and evaluated by using methods previously reported.[7a,30] Initial results showed that the donor−acceptor copolymers exhibit a photovoltaic effect with photocurrents of ca. 10−20 μA/cm^2 and photovoltages of 0.8−1.1 V at simulated sunlight intensities (up to 100 mW/cm^2). The photovoltaic power conversion efficiencies were only about 0.1−0.2%, which are comparable but not better than many single-layer conjugated polymer solar cells.[7a,30] Here again, it appears that a multicomponent system would be essential to enhance device performance as found in other semiconducting polymers.[7]

Conclusions

We have described the synthesis and characterization of new high molecular weight conjugated donor−acceptor copolymers containing electron-donating carbazole and phenothiazine units and electron-accepting phenylquinoline unit. The copolymers have significantly reduced optical band gaps compared to the parent homopolymers. Two oligomers were also investigated, providing unique insights into the intramolecular charge transfer and photophysics of the donor−acceptor copolymers. Large *positive solvatochromism* was observed in the absorption and emission spectra of the oligomers in solution due to strong intramolecular charge transfer between the donor and acceptor moieties. ICT effects were enhanced in the phenothiazine-linked oligomer and copolymer compared to the carbazole-based materials. The solid-state emission from the phenothiazine-containing materials was from charge-transfer excitons whereas the carbazole-linked oligomer and copolymer were dominated by excimers. A detailed investigation of electroluminescent and photovoltaic devices fabricated from these copolymers and oligomers is in progress and will be reported in a future paper.

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References and Notes

(1) (a) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1991**, *24*, 6806. (b) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 895. (c) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1993**, *5*, 633. (d) Cui, Y.; Zhang, X.; Jenekhe, S. A. *Macromolecules* **1999**, *32*, 3824. (e) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1996**, *8*, 579.

(2) (a) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 5355. (b) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 5065. (c) Devasagayaraj, A. Tour, J. M. *Macromolecules* **1999**, *32*, 6425.

(3) (a) Lee, B.-L.; Yamamoto, T. *Macromolecules* **1999**, *32*, 1375. (b) Yamamoto, T.; Zhou, Z. H.; Kanbara, T.; Shimura, M.; Kizu, K.; Maruyama, T.; Nakamura, Y.; Fukuda, T.; Lee, B. L.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota,

K.; Sasaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 10389. (c) Hay, C.; Vilain, D. L.; Deborde, V.; Toupet, L.; Reau, R. *Chem. Commun.* **1999**, *4*, 345. (d) Ferraris, J. P.; Bravo, A.; Kim, W.; Hrncir, D. C. *J. Chem. Soc., Chem. Commun.* **1994**, 991.

(4) After our work and manuscript were completed we found that Siove and co-workers have recently prepared a donor−acceptor copolymer alternating bicarbazolyl units with phenylenebis(cyanovinylene) moieties [these authors did not cite our prior work on the poly(*N*-alkyl-3,6-carbazolylene)s]: Boucard, V.; Ades, D.; Siove, A.; Romero, D.; Schaer, M.; Zuppiroli, L. *Macromolecules* **1999**, *32*, 4729.

(5) For an alternative strategy to small band gap conducting polymers, see: (a) Jenekhe, S. A. *Nature* **1986**, *322*, 345. (b) Chen, W. C.; Jenekhe, S. A. *Macromolecules* **1995**, *28*, 465.

(6) (a) Agrawal, A. K.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *J. Phys. Chem.* **1992**, *96*, 2837. (b) Agrawal, A. K.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *Chem. Mater.* **1991**, *3*, 765. (b) Yang, C.-J.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *Ind. Eng. Chem. Res.* **1999**, *38*, 1759.

(7) (a) Jenekhe, S. A.; Yi, S. *Appl. Phys. Lett.* **2000**, *77*, 2635. (b) Jenekhe, S. A.; Yi, S. *Adv. Mater.* **2000**, *12*, 1274. (c) Kohler, A.; dos Santos, D. A.; Beljonne, D.; Shuai, Z.; Bredas, J. L.; Holmes, A. B.; Kraus, A.; Mullen, K.; Friend, R. H. *Nature* **1998**, *392*, 903. (d) Alam, M. M.; Jenekhe, S. A. *J. Phys. Chem. B* **2001**, *105*, 2479.

(8) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (b) Sokolik, I.; Yang, Z.; Karasz, F. E.; Morton, D. C. *J. Appl. Phys.* **1993**, *74*, 3584.

(9) (a) Tarkka, R. M.; Zhang, X.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1996**, *118*, 9438. (b) Jenekhe, S. A.; Zhang, X.; Chen, X. L.; Choong, V.-E.; Gao, Y.; Hsieh, B. R. *Chem. Mater.* **1997**, *9*, 409. (c) Zhang, X.; Shetty, A. S.; Jenekhe, S. A. *Acta Polym.* **1998**, *49*, 52. (d) Zhang, X.; Shetty, A. S.; Jenekhe, S. A. *Macromolecules* **1999**, *32*, 7422. (e) Zhang, X.; Jenekhe, S. A. *Macromolecules* **2000**, *33*, 2069.

(10) Schon, J. H.; Kloc, C.; Dodabalapur, A.; Batlogg, B. *Science* **2000**, *289*, 599.

(11) (a) Chen, X. L.; Jenekhe, S. A. *Macromolecules* **1997**, *30*, 1728. (b) Jenekhe, S. A.; de Paor, L. R.; Chen, X. L.; Tarkka, R. M. *Chem. Mater.* **1996**, *8*, 2401.

(12) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1992**, *4*, 95.

(13) (a) Borsenberger, P. M.; Weiss, D. S. *Organic Photoreceptors for Imaging Systems*; Marcel Dekker: New York, 1993. (b) Hu, B.; Yang, Z.; Karasz, F. E. *J. Appl. Phys.* **1994**, *76*, 2419. (c) Gebler, D. D.; Wang, Y. Z.; Fu, D.-K.; Swager, T. M.; Epstern, A. J. *J. Chem. Phys.* **1998**, *108*, 7842.

(14) (a) Jenekhe, S. A.; Wellinghoff, S. T.; Reed, J. F. *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 175. (b) Jenekhe, S. A.; Wellinghoff, S. T.; Deng, Z. *Synth. Met.* **1985**, *10*, 281. (c) Racchini, J. R.; Wellinghoff, S. T.; Jenekhe, S. A. *Synth. Met.* **1988**, *22*, 291. (d) Racchini, J. R.; Wellinghoff, S. T.; Schwab, S. T.; Herrera, C. D.; Jenekhe, S. A. *Synth. Met.* **1988**, *22*, 273.

(15) Tunney, S. E.; Suenaga, J.; Stille, J. K. *Macromolecules* **1987**, *20*, 258.

(16) Shetty, A. S.; Liu, E. B.; Lachicotte, R. J.; Jenekhe, S. A. *Chem. Mater.* **1999**, *11*, 2295 and manuscript in preparation.

(17) (a) Sybert, P. D.; Beever, W. H.; Stille, J. K. *Macromolecules* **1981**, *14*, 493. (b) Stille, J. K. *Macromolecules* **1981**, *14*, 870.

(18) Gipstein, E.; Hewett, W. A.; Need, O. U. *J. Polym. Sci., Part A-1* **1970**, *8*, 3285.

(19) Lai, R. Y.; Fabrizio, E. F.; Lu, L.; Jenekhe, S. A.; Bard, A. J. *J. Am. Chem. Soc.*, in press.

(20) (a) Jenekhe, S. A.; Johnson, P. O.; Agrawal, A. K. *Macromolecules* **1989**, *22*, 3216. (b) Jenekhe, S. A.; Johnson, P. O. *Macromolecules* **1990**, *23*, 4419. (c) Yang, C. J.; Jenekhe, S. A. *Chem. Mater.* **1991**, *3*, 878.

(21) (a) Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1107. (b) Osaheni, J. A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1995**, *117*, 7389.

(22) (a) Reichardt, C. *Solvents and Solvent Effect in Organic Chemistry*; Verlag Chemie: New York, 1988; Chapter 6. (b) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027. (c) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.

(23) (a) Kessler, M. A.; Wolfbeis, O. S. *Spectrochim. Acta, Part A* **1991**, *47*, 187. (b) Srividya, N.; Ramamurthy, P.; Ramkrishnan, V. T. *Spectrochim. Acta, Part A* **1997**, *53*, 1743.

(24) (a) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765. (b) Osaheni, J. A.; Jenekhe, S. A. *Macromolecules* **1994**, *27*, 739.

(25) (a) Reynders, P.; Kuhnle, W.; Zachariasse, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 3940. (b) Winnik, F. M. *Chem. Rev.* **1993**, *93*, 587.

(26) Dubovsky, O.; Mukamel, S. *J. Chem. Phys.* **1992**, *96*, 9201.

(27) Bredas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 6555.

(28) (a) Lemmer, U.; Heun, S.; Mahrt, R. F.; Scherf, U.; Hopmeier, M.; Siegner, U.; Gobel, E. O.; Mullen, K.; Bassler, H. *Chem. Phys. Lett.* **1995**, *240*, 373. (b) Blatchford, J. W.; Jessen, S. W.; Lin, L. B.; Gustafson, T. L.; Fu, D. K.; Wang, H. L.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1996**, *54*, 9180. (c) Jenekhe, S. A.; Chen, X. L. *J. Phys. Chem. B* **2000**, *104*, 6332.

(29) (a) Meeker, K.; Jenekhe, S. A. Unpublished results. (b) Yi, S.; Jenekhe, S. A. Unpublished results.

(30) Antoniadis, H.; Hsieh, B. R.; Abkowitz, M. A.; Jenekhe, S. A.; Stolka, M. *Synth. Met.* **1994**, *62*, 265.

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