Phenothiazine-Based Conjugated Polymers: Synthesis, Electrochemistry, and Light-Emitting Properties

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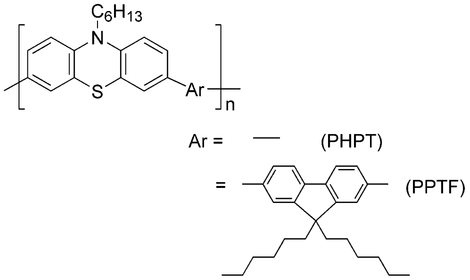
Received July 27, 2003; Revised Manuscript Received September 29, 2003

ABSTRACT: Two new phenothiazine-containing conjugated polymers, poly(10-hexylphenothiazine-3,7-diyl) (PHPT) and poly(10-hexylphenothiazine-3,7-diyl-*alt*-9,9-dihexyl-2,7-fluorene) (PPTF), were synthesized and characterized, and their photophysical, electrochemical, and electroluminescent properties were investigated. The optical band gaps of PHPT and PPTF were 2.69 and 2.76 eV, respectively. Both polymers showed greenish-blue photoluminescence (490 nm) in dilute solutions with a fluorescence quantum yield of 0.40. Identical solid-state and dilute solution absorption and emission spectra were observed, showing that excimers were not formed in PHPT or PPTF thin films. Ionization potentials (HOMO levels) estimated from cyclic voltammetry were 5.0−5.1 eV for the phenothiazine-based polymers, making them good candidates for hole transport materials in devices. Spectroelectrochemistry revealed that the observed multiple oxidation peaks in the cyclic voltammetry of PHPT have associated multiple absorption peaks due to the formation of radical cations (polarons) and dications (bipolarons). Greenish-blue electroluminescence with luminance of up to 320 cd/m^2 was observed for the PPTF organic light-emitting diodes. These results show that the phenothiazine ring is an excellent building block for lowering the ionization potential and for impeding π-stacking aggregation and excimer formation in conjugated polymers.

Conjugated polymer semiconductors are finding growing applications in electronics and optoelectronics,[1−7] including light-emitting diodes,[1−3] photovoltaic cells,[4,5] thin film transistors,[6] and electrochromic cells.[7] Synthesis and investigation of new conjugated polymers are essential to improving the electronic and optoelectronic properties of these materials and in turn improvement of the performance of the devices. One general challenge in the field is achievement of high electron affinity (n-type) conjugated polymers [2d−h,8] for improving electron injection/transport and low ionization potential (p-type) conjugated polymers[9] for better hole injection/transport in polymer electronic devices. Of particular interest are polymers that combine high fluorescence quantum yields with low ionization potential or high electron affinity.

In this paper, we report the synthesis, photophysics, electrochemistry, and electroluminescence of two new soluble phenothiazine-based conjugated polymers: poly(10-hexylphenothiazine-3,7-diyl) (PHPT) and poly(10-hexylphenothiazine-3,7-diyl-*alt*-9,9-dihexyl-2,7-fluorene) (PPTF). We show that the electron-rich phenothiazine ring is an excellent molecular building block for achieving low ionization potential conjugated polymer semiconductors. We also demonstrate that the presence of the highly nonplanar phenothiazine ring in the homopolymer PHPT and alternating copolymer PPTF impedes π-stacking aggregation and intermolecular excimer formation, resulting in identical dilute solution and solid-state photophysics.



Carbazole-based π-conjugated polymers were shown to be good p-type (hole transport) conducting polymers many years ago.[10] Recent interest in the polycarbazoles has focused on their potential as semiconductors for light-emitting diodes (LEDs)[10c,11a] and photovoltaic cells.[11a] Unlike carbazole, however, the related phenothiazine ring has not been fully explored as a building block for the synthesis of conjugated polymers even though it is clearly a stronger electron donor by virtue of the extra sulfur heteroatom.[11] Efficient electrogenerated chemiluminescence (ECL) was recently observed in co-oligomers of 10-methylphenothiazine,[12a,b] and interesting redox properties were observed in other co-oligophenothiazines.[12c,d] One particularly striking difference between the carbazole and phenothiazine rings is that the former is planar whereas the latter is highly nonplanar.[12a,d] The possible consequences of the nonplanarity of the phenothiazine ring for the photophysics, light-emitting properties, molecular aggregation, and charge transport of π-conjugated polymers containing this ring are very intriguing to us and thus motivated our studies.

Results and Discussion

Synthesis and Characterization. The general synthetic routes to the monomers and polymers are outlined in Scheme 1. The monomer 3,7-dibromo-10-hexylphenothiazine was synthesized in two steps from the starting phenothiazine. 9,9-Dihexylfluorene-2,7-bis(trimethylene boronate) was synthesized from 9,9-dihexylfluorene-2,7-diboronic acid. PHPT was synthesized in 77% yield by Ni(0)-mediated coupling polymerization of dibromophenothiazine in a toluene/DMF mixture solvent. The alternating copolymer of fluorene and phenothiazine,

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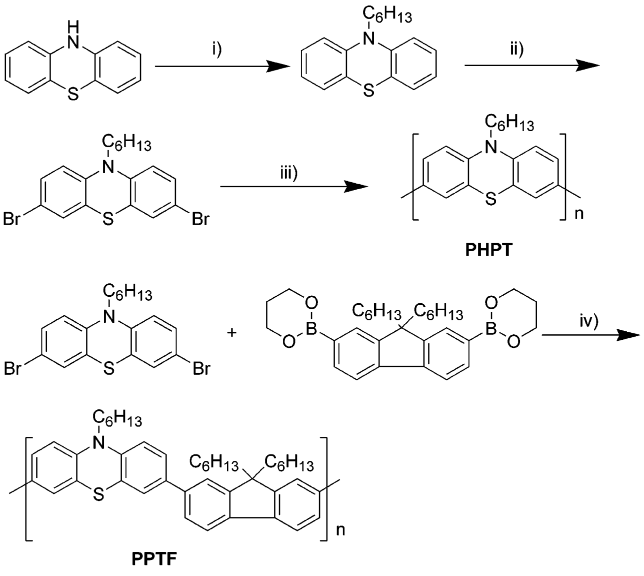
10.1021/ma035087y CCC: $25.00

Scheme 1[a]



[a] Reaction conditions: (i) NaH, THF, 1-bromohexane; (ii) Br_2, NaAc/HAc, 5−10 °C; (iii) $Ni(COD)_2$, COD, bpy, DMF, 60 °C; (iv) $Pd(PPh_3)_4$, toluene/2 M Na_2CO_3, Aliquat 336.

PPTF, was synthesized in 86% yield by Suzuki coupling in a mixture of toluene and aqueous sodium carbonate solution (2 M) containing 1 mol % $Pd(PPh_3)_4$ and a phase transfer reagent (Aliquat 336) under vigorous stirring at 100 °C for 3 days.

NMR spectra analyses clearly indicate that well-defined PHPT and PPTF have indeed been obtained. The ^1H NMR and ^{13}C NMR spectra of PHPT and PPTF and their assignment shown in Figure 1 are consistent with the proposed structures. In addition to the peaks seen in PHPT, the ^{13}C NMR spectra of PPTF showed additional peaks corresponding to the 9,9-dihexyl-2,7-fluorenyl units.

Both polymers are readily soluble in common organic solvents such as chloroform, THF, and toluene. The weight-average molecular weights of PHPT and PPTF were found to be 1.53×10^4 and 1.83×10^5, with polydispersity indexes of 3.00 and 6.45 by gel permeation chromatography (GPC) based on polystyrene standards, respectively. The much larger polydispersity in the molecular weight of PPTF may be a result of the precipitation of polymer from the reaction solution during polymerization. The polymers possess excellent thermal stability with onset decomposition temperatures (T_d) of 320−324 °C (Table 1). PHPT showed a glass transition at 166 °C and PPTF at 167 °C (Figure 2). The similarity of the T_g of both polymers may seem surprising given the extra 9-hexyl side chain in PPTF compared to PHPT. However, the 2,7-fluorene linkage in PPTF makes the chain stiffer than the 3,6-phenothiazine linkage of PHPT and thus balances the effect of the 9,9-dihexyl side chains on the T_g. No melting transition was observed in the DSC thermograms up to 300 °C, indicating that both PPTF and PHPT are amorphous polymers. The relatively high glass transition temperature of these polymers is important and desirable for many applications such as light-emitting diodes.

Photophysical Properties. The optical absorption and photoluminescence (PL) emission properties of PHPT and PPTF in dilute THF solution (1×10^{-5} M) and as thin films are shown in Figure 3. In dilute solution, PHPT has a rather broad absorption with no clear peak in the 320−400 nm region and an absorption maximum (λ_{max}) at 287 nm. The thin film absorption spectrum of PHPT is identical to the dilute solution spectrum. In the case of the phenothiazine-fluorene alternating copolymer, PPTF, it has a strong absorption in the 300−400 nm range with absorption maxima at 384 and 328 nm in solution and as a thin film. The related polyfluorene homopolymer has an intense structureless absorption centered at 380 nm.[13] The ground-state electronic structure of the alternating copolymer PPTF is thus completely different from those of the related homopolymers.

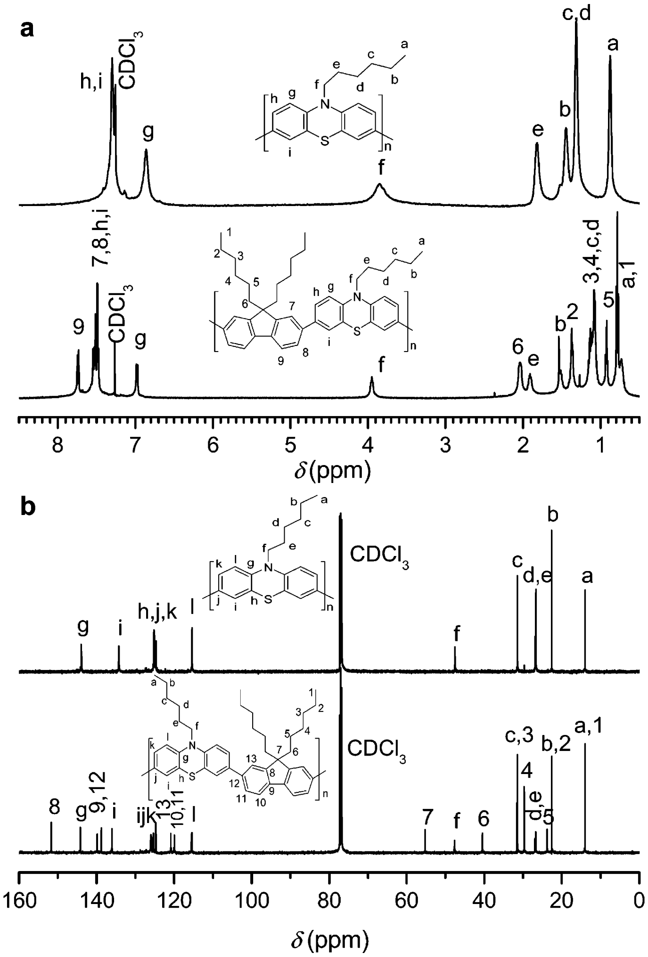


Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectra of PHPT and PPTF in chloroform-*d*.

Table 1. Molecular Weights and Thermal Properties of PPTF and PHPT

polymer	yield (%)	M_w[a] ($\times 10^4$)	M_w/M_n[a]	T_g (°C)	T_d (°C)[b]
PHPT	77	1.53	3.00	166	320
PPTF	86	18.3	6.45	167	324

[a] Determined by GPC in THF based on polystyrene standards. [b] Onset decomposition temperature measured by TGA under nitrogen.

The dilute solution PL emission spectra of PHPT and PPTF shown in Figure 3 reveal that they are nearly identical; the slight difference is that PHPT has a peak at 490 nm whereas that of PPTF is at 485 nm. The PL quantum yield in solution was 0.43 for PHPT and 0.39 for PPTF. Interestingly, the thin film PL spectra of both polymers are identical to those in dilute solution (Figure 3). This exact correspondence of the PL spectra of PHPT or PPTF in dilute solution and solid state clearly rules out intermolecular aggregates or excimers[14] as the

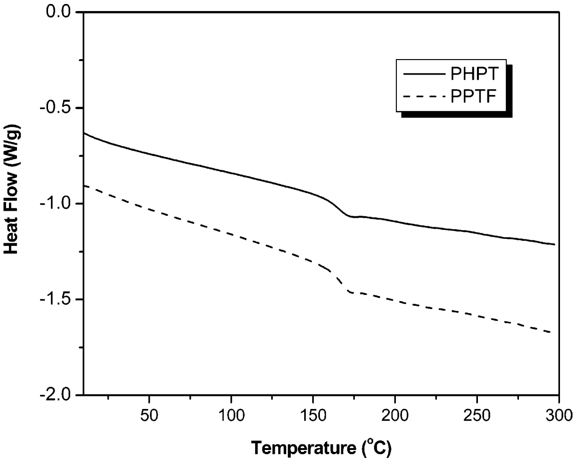


Figure 2. Second heating DSC curves of PHPT and PPTF with a heating rate of 10 °C/min in N_2.

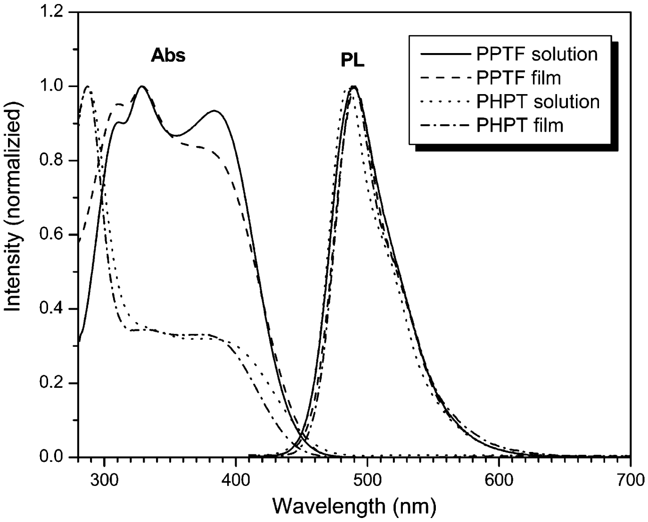


Figure 3. Optical absorption and PL emission spectra of PHPT and PPTF in THF solution (1×10^{-5} M) and as thin films.

origin of emission in both polymers. The rather large Stokes shift of 0.7 eV observed in the PL spectra of these polymers must thus be explained by an alternative mechanism. Toward this end we note that the phenothiazine ring is highly nonplanar in the ground state,[12a,d] precluding sufficiently close intermolecular interactions essential to forming aggregates or excimers.[14] We propose that in dilute solution or thin film the phenothiazine ring in excited PHPT or PPTF molecule is more planar than in the ground state. Consequently, the relaxed singlet excited state from which emission occurs is lower lying than if photoinduced planarization were absent. Additional studies such as time-resolved PL spectroscopy will be necessary to confirm this picture of the origin of the Stokes shift in the photophysics of these polymers. The most interesting insight from these photophysics results is that the phenothiazine ring is an excellent building block for impeding π-stacking aggregation and intermolecular excimer formation.

Photochemical Reaction of PHPT in Chloroform Solutions. An interesting photochemical phenomenon was observed in chloroform solutions of PHPT. The brownish color of freshly prepared PHPT solutions in chloroform was noticed to change to dark blue, with formation of some blue-black precipitate in the bottom of the vial, upon storing the solutions several days in ambient light conditions. The original greenish-blue emission of PHPT in chloroform was dramatically decreased in intensity in the blue-black aged solutions. In other solvents such as THF, benzene, and toluene, the color and emission properties of the PHPT solutions remained unchanged even after being stored under ambient room light for several weeks. The origin of this phenomenon is likely due to the reaction between photogenerated phenothiazine radical cation and the halogenated solvent as known for phenothiazine compounds in halogenated solvents.[15] The photochemical reaction between PHPT and chloroform is a good indication of the facile generation of radical cations (holes) in PHPT. We note that the phenothiazine–fluorene copolymer PPTF does not exhibit such a photochemical reaction in chloroform.

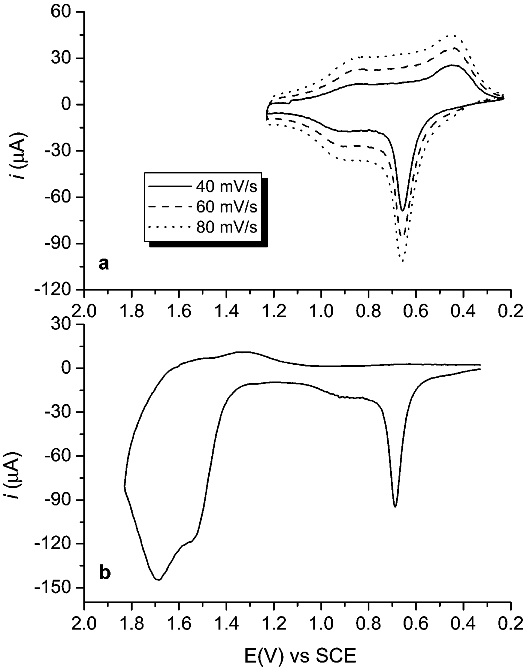


Figure 4. CV curves of PHPT film on Pt electrode in 0.1 M Bu_4NPF_6 solution in acetonitrile: (a) CV curves in the 0.2–1.3 V scaning range; (b) CV curve in the 0.3–1.8 V scanning range with a scan rate of 40 mV/s.

Electrochemical Properties. Charge injection processes and associated electronic states (HOMO/LUMO levels) of conjugated polymer thin films, which are important for understanding EL devices, can be investigated by cyclic voltammetry (CV).[8b,16] No reduction wave for either polymer was observed in the range from 0 to −2.5 V vs SCE, suggesting that both polymers are intrinsic p-type semiconductors. We thus concentrate the following discussion on the electrochemical oxidation of the polymers.

Figure 4 shows the electrooxidation CVs of PHPT. The anodic oxidation peak of PHPT in the first CV scan was observed at 0.80 V (vs SCE) (not shown). However, all subsequent scans shifted to a less positive potential and stabilized at an anodic oxidation peak of 0.66 V, indicating that the PHPT film was swelled with electrolyte during the first electrooxidation scan. The corresponding cathodic peak at 0.46 V means that the oxidation of PHPT is only quasi-reversible (Figure 4a). In addition to the main peak at 0.66 V, a second anodic shoulder peak at 0.9–1.0 V was observed. From the onset oxidation potential ($E_{\mathrm{ox}}^{\mathrm{onset}} = 0.58$ V) the ionization potential (IP, HOMO level) of PHPT is estimated to be

Table 2. Photophysical and Redox Properties of PPTF and PHPT

	λ_{max}^{Abs} (nm)[a]				λ_{max}^{em} (nm)[a]					
polymer	soln	log ϵ_{max}	film	E_g^{opt} (eV)[b]	soln	film	Φ_f soln	E_{ox}^{onset} (V)[c]	E_{ox}^{peak} (V)	IP (eV)[d]
PHPT	287	4.38	287	2.76	486	490	0.43	0.58	0.66	5.0
PPTF	328	4.82	328	2.69	489	490	0.39	0.69	0.74	5.1
MPT	310				441		0.014		0.80	

[a] Measured in solution (THF, 10^{-5} M) and as a thin film on silica substrate. [b] Optical band gap. [c] Onset oxidation potentials vs SCE. [d] Ionization potential was obtained based on IP = E_{ox}^{onset} + 4.4 eV.

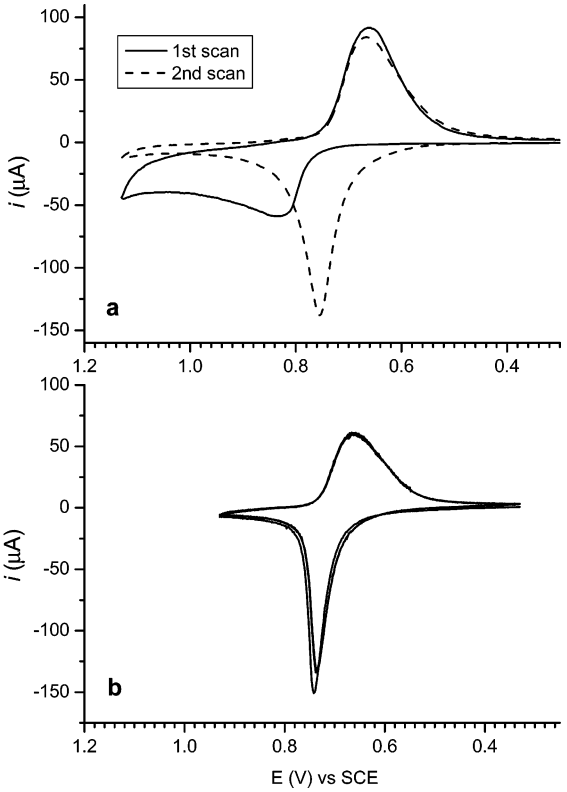


Figure 5. CV curves of PPTF film on Pt electrode in 0.1 M Bu_4NPF_6 solution in acetonitrile at a scan rate of 40 mV/s: (a) first scan and second scan; (b) three-cycle consecutive scans.

5.0 eV based on IP = E_{ox}^{onset} +4.4 eV, where the SCE energy level of −4.4 eV below the vacuum level is used.[8b,16]

Shown in Figure 4b is a CV of PHPT film upon scanning up to 1.8 V. A third oxidation with onset at 1.4 V and peak at 1.7 V is observed to follow that at 0.66 V. Both the first and second oxidations are completely irreversible when the scanning goes up to 1.4−1.8 V. This is an indication that the trication of this polymer is unstable.

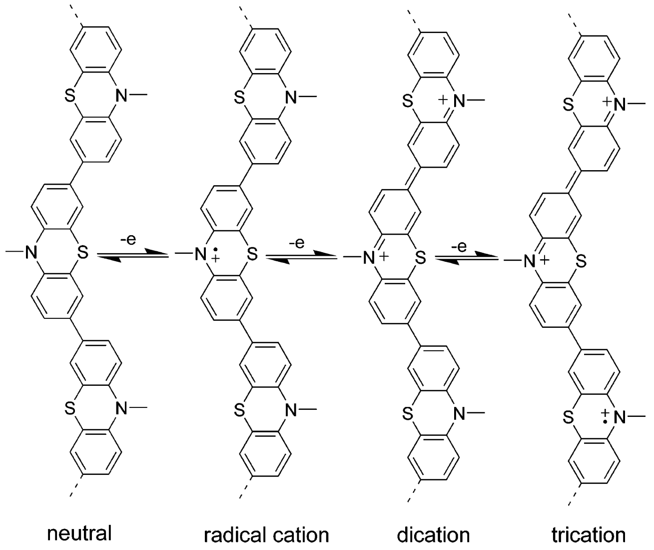
Figure 5 shows the CV scans of PPTF films. The anodic peak of the second scan at 0.76 V is shifted from 0.84 V observed in the first scan. All subsequent scans were the same, showing an anodic peak at 0.74 V and a cathodic peak at 0.66 V (Figure 5b). The one-electron oxidation of PPTF is thus quite reversible. We note that only one oxidation wave is observed in the CV of this polymer. Scanning above 1.2 V leads to an irreversible second oxidation due to the formation of an unstable dication of PPTF. From the onset oxidation potential of PPTF (0.69 V vs SCE) we similarly estimated the IP or HOMO level to be 5.1 eV. Given that the HOMO level of poly(9,9-dihexylfluorene) (PF6) or poly(9,9-dioctylfluorene) (PFO) is 5.8 eV based on a similar (−4.4 eV SCE level relative to vacuum) estimation from electrochemistry,[16a] it is clear that the HOMO level of the phenothiazine−fluorene copolymer is dominated by contribution from the phenothiazine moiety. Therefore, one can expect the phenothiazine ring to be an excellent building block for lowering the IP of conjugated copolymers.

The observed electrochemical redox behavior of PHPT and PPTF can be related to known redox properties of 10-methylphenothizine (MPT) (Table 2) and oligophenothiazines.[12c,d] As expected, the conjugated homopolymer PHPT has a lower oxidation potential (E_{ap} = 0.66 V) than MPT (E_{ap} = 0.80 V vs SCE) due to the electron delocalization in the polymer. However, the observed 0.14 V difference between the monomer and PHPT is rather small compared to other monomer/polymer systems such as thiophene/polythiophene and pyrrole/polypyrrole. The main reason is that electronic delocalization is limited by the nonplanar geometry of the phenothiazine ring. Interestingly, there is only a small shift of the oxidation potential of PPTF (E_{ap} = 0.74 V), containing alternating phenothiazine and fluorene, compared to MPT. This means that there is even less electronic coupling between two phenothiazine rings separated by the 2,7-fluorene moiety.

The observed multiple oxidation peaks in the CV of PHPT (Figure 4a) are analogous to similar observations in oligomers of phenothiazine[12c,d] and carbazole.[17] Three reversible oxidations at 0.61, 0.715, and 0.837 V (vs Ag/AgCl) were observed in the trimer of phenothiazine and interpreted as due respectively to the formation of the radical cation, dication, and trication.[12d] In 3,3′-dicarbazole, electrochemical oxidation revealed two peaks that were assigned to the successive formation of the radical cation and dication.[17] We propose that the oxidation of PHPT can be similarly described as shown in Scheme 2. We further explored the nature of the electrooxidation of PHPT by spectroelectrochemistry as shown in Figure 6. The CV curve from the first scan from 0.1 to 1.3 V is shown in the inset of Figure 6 for a PHPT film on ITO glass. After the first complete CV scan, the optical absorption was identical to the original neutral polymer as expected. However, at a potential of 0.63 V (vs SCE) a new broad absorption band at 560 nm and another in the infrared (>1000 nm) were observed. The 560 nm peak increased to a maximum when a potential of 0.83 V was applied. These absorption characteristics at 0.63−0.83 V potential can be assigned to the radical cation (polaron) of PHPT. Further increase of the potential to 0.93−1.03 V resulted in the decrease of the 560 nm band and appearance of another band at ~500 nm while the infrared peak also increased. We can also attribute these absorption spectra changes at higher potentials to the dication of PHPT.

Electroluminescence. To evaluate the potential of the two phenothiazine-based polymers as emissive and/or hole transport materials for light-emitting diodes, a preliminary investigation of simple device structures was made. Figure 7 shows the device characteristics of

Scheme 2



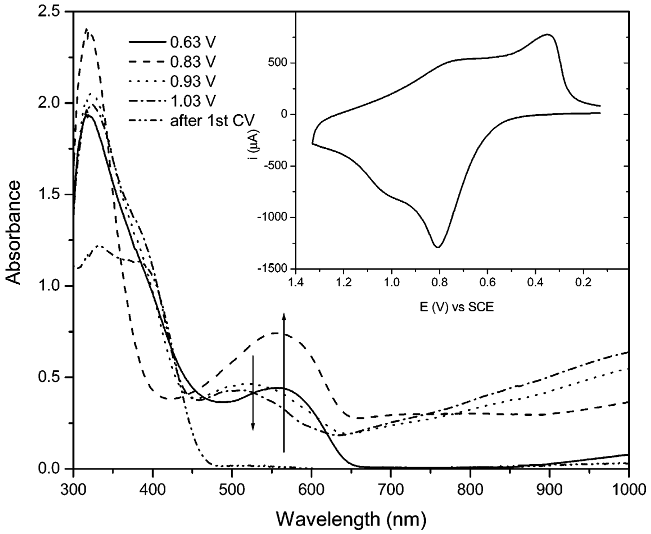


Figure 6. Spectroelectrochemistry of PHPT film on ITO glass in 0.1 M Bu_4NPF_6 in acetonitrile at different potentials (vs SCE). Inset is the CV curve of PHPT film on ITO glass with a scan rate of 40 mV/s in 0.1 M Bu_4NPF_6/acetonitrile.

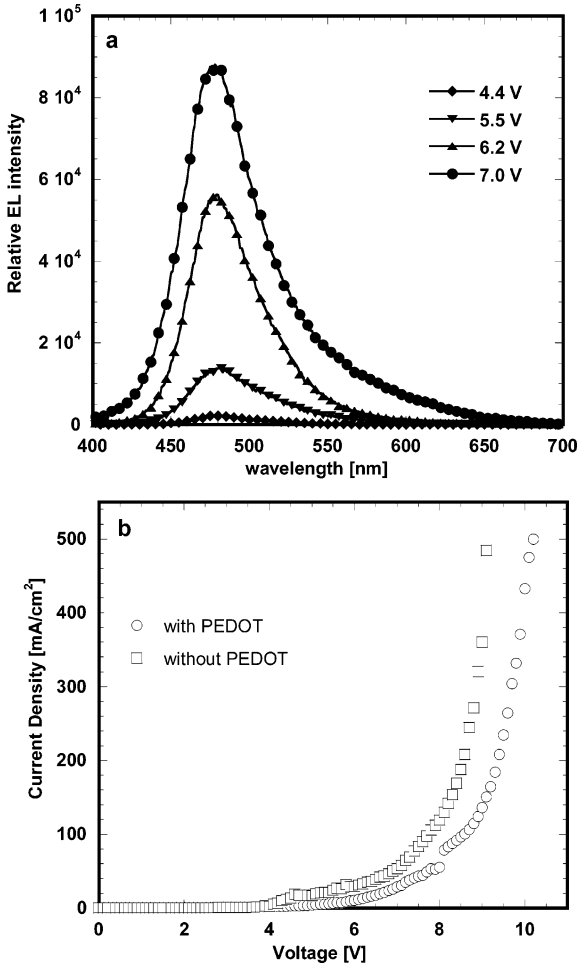


Figure 7. (a) EL spectra of single-layer LED from PHPT. (b) Current density–voltage characteristics of the corresponding diodes with and without PEDOT.

a single-layer LED fabricated from PHPT both with and without a PEDOT layer, i.e., ITO/PHPT/Al and ITO/PEDOT/PHPT/Al. Electroluminescence (EL) of very low brightness levels was observed although the EL spectra with a maximum at 480 nm (Figure 7a) could be recorded. The EL spectra are nearly identical to the previously discussed PL emission spectra. Figure 7b shows the current–voltage characteristics of 40 nm thick PHPT diodes with and without PEDOT. The turn-on voltage for EL was quite low at 4 V in both cases, and good rectifying diode-like behavior was observed, indicating good hole injection and transport in PHPT thin films. The identical turn-on voltage (4 V) of these diodes with and without PEDOT suggests that holes can be as efficiently injected into PHPT from ITO as from PEDOT. The low brightness level of the PHPT single-layer diodes is likely due to p-type doping near the ITO electrode, the excessive holes in the diodes, and poor electron injection and transport. The ITO/PEDOT/PPTF(60 nm)/Al single-layer devices with the phenothiazine–fluorene copolymer showed brightness levels up to 25 cd/m^2, as shown in Figure 8. An EL maximum at ~490 nm is seen for all applied voltages (Figure 8a), with the emission intensity progressively increasing with increase in applied bias. The EL maximum matches with the PL emission maximum of PPTF thin film, suggesting that the same excited-state species is responsible for both the PL and EL emission. The relatively higher brightness in PPTF than PHPT could be due to the higher fluorescence quantum yield of PPTF thin films containing fluorene units along the backbone. Although the LED brightness and efficiencies using these new polymers as emissive materials are modest, we think they could be significantly improved by optimizing the device architecture.

Bilayer devices were made with an electron transport (n-type) polyquinoline, poly(2,2′-biphenyl-6,6′-bis-(4-phenylquinoline)) (PBPQ),[8a] and PPTF as the hole transport and emissive polymer. The EL spectra of the ITO/PEDOT/PPTF/PBPQ/Al diodes are shown in Figure 9a. At lower voltages (8.5 V or less), there is a small contribution from PBPQ in the EL with emission at ~550–600 nm from PBPQ in addition to the main peak at 490 nm from PPTF. As the voltage increases, the emission originates solely from PPTF with a peak at 490 nm at 12.5 V. This means that the recombination zone is located in the PPTF layer at higher electric fields. Depending on the film thickness of the electron transport PBPQ layer, one could get emission exclusively from PPTF. The current density–voltage–luminance characteristics corresponding to the EL

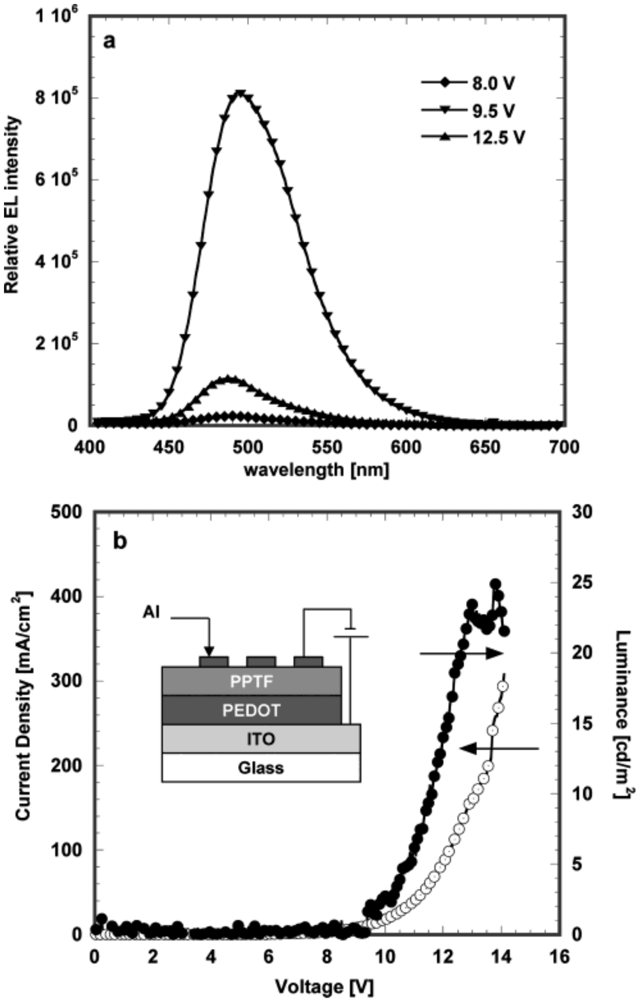


Figure 8. (a) EL spectra of LED from PPTF. (b) Current density−voltage−luminance characteristics of corresponding diode. The inset shows the device schematic.

spectra of Figure 9a are shown in Figure 9b. The turn-on voltage of the diode is 5 V with a maximum brightness of 320 cd/m^2 and a maximum external quantum efficiency of 0.10% at 12.5 V. This represents a factor of 13 enhancement in performance compared to the single-layer PPTF LED. The use of an electron transport polymer to improve the performance of blue-green PPTF electroluminescence confirms the fact that this polymer is a poor electron acceptor (EA ∼ 2.4 eV, based on the IP value of 5.1 eV and E_g^{opt} of 2.76 eV) as revealed by the previously discussed electrochemistry. These results also suggest that both PHPT and PPTF are promising as hole transport materials for LEDs and can be used effectively in multilayer devices[3g,h] or as blends[18] with electron transport materials.

Conclusions

New phenothiazine-containing conjugated polymers, poly(10-hexylphenothiazine-3,7-diyl) (PHPT) and poly(10-hexylphenothiazine-3,7-diyl-*alt*-9,9-dihexyl-2,7-fluorene) (PPTF), were synthesized by Ni(0)-catalyzed and Suzuki coupling polymerizations, respectively. The moderately high molecular weight polymers are amorphous with a glass transition temperature of 166 °C. Both polymers have identical solution and solid-state absorption and PL emission spectra, from which intermolecular aggregates and excimers can be excluded from their photophysics. This result is a consequence of the highly nonplanar geometry of the phenothiazine ring. The two polymers have low ionization potentials at 5.0−5.1 eV, suggesting good potential as p-type (hole transport) semiconductors in organic devices. Spectroelectrochemistry of PHPT showed that this polymer undergoes electrooxidation to radical cations at low potential (0.66 V vs SCE) and dications at much higher potentials (>0.83 V). Initial light-emitting diodes fabricated from PPTF showed blue-green electroluminescence that can be significantly enhanced to 320 cd/m^2 by using an electron transport polyquinoline to improve electron injection into the polymer.

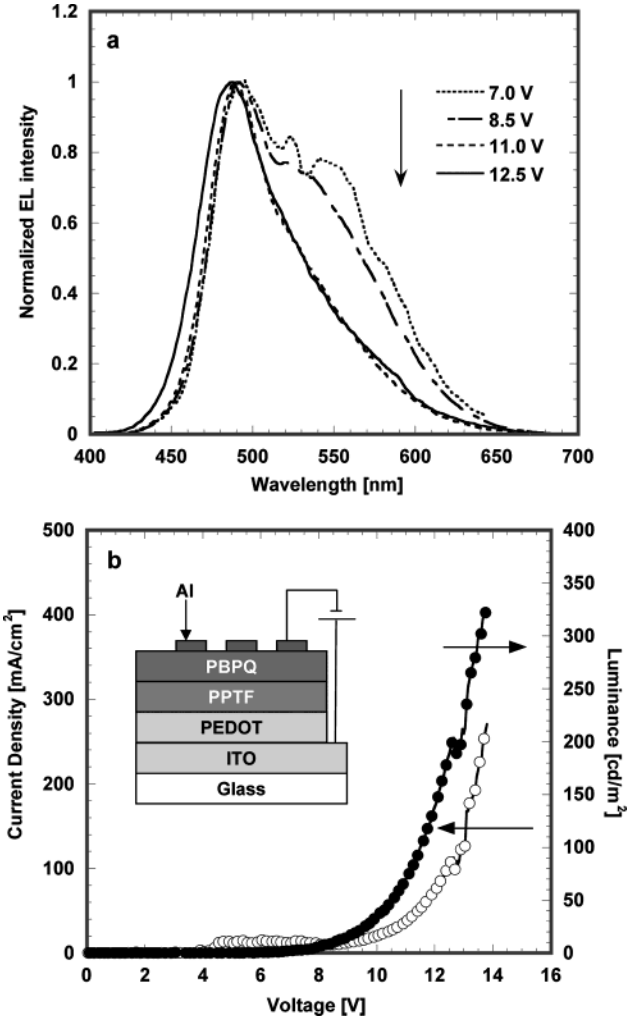


Figure 9. (a) EL spectra of bilayer LED from PPTF. (b) Current density−voltage−luminance characteristics of corresponding diode. The inset shows the device schematic.

Experimental Section

Chemicals. Phenothiazine, 10-methylphenothiazine, 1-bromohexane, Aliquat 336, Ni(COD)$_2$, 1,5-cyclooctadiene, tetrakis(triphenyl)phosphine palladium, and 2,2′-bipyridine were purchased from Aldrich. Tetrahydrofuran (THF) (99.8%, anhydrous) and *N*,*N*-dimethylformamide (DMF) (99.8%, anhydrous) were obtained from Aldrich and used as received. 9,9-Dihexylfluorene-2,7-bis(trimethylene boronate) was synthesized from 9,9-dihexylfluorene-2,7-diborionic acid by the method in the literature.[19] Methylene chloride and methanol (HPLC grade) were obtained from Fisher Chemicals.

Characterization. UV−vis absorption spectra were obtained on a Perkin-Elmer Lamda 900 spectrophotometer. Steady-state photoluminescence (PL) studies were done by using a PTI QM-2001-4 spectrofluorimeter (Photon Technology

International (PTI) Inc.). The PL quantum yields of the polymers were measured using 10^{-6} M solutions of the sample in THF and determined relative to 9,10-diphenylanthracene (DPA) as a standard ($\lambda_{ex} = 380$ nm; $\Phi_{dpa} = 0.91$ in benzene).[20]

Cyclic voltammetry (CV) was done on an EG&G Princeton Applied Research potentiostat/galvanostat model 273A. The redox properties of the polymer films were investigated by doing CV in acetonitrile solution with 0.1 M Bu_4NPF_6 at room temperature under nitrogen. A platinum wire electrode coated with a polymer thin film was used as the working electrode. Another platinum wire electrode was used as the counter electrode, and a Ag/Ag$^+$ (0.1 M $AgNO_3$ in acetonitrile) electrode was used as the reference electrode. The Ag/Ag$^+$ ($AgNO_3$) reference electrode was calibrated at the beginning of the experiments by running the CV of ferrocene as the internal standard in an identical cell without any polymer on the working electrode. The potential values obtained in reference to Ag/Ag$^+$ electrode were converted in reference to internal standard of ferrocene/ferrocenium ($E^{\circ\prime} = 0.424$ V vs NHE).[12a] GPC analysis of both polymers was done on a Waters GPC with Shodex gel columns and Waters 150 °C refractive index detectors at 30 °C with a THF flow rate of 1.0 mL/min. The molecular weight was calibrated by polystyrene standards.

Thermal analysis was carried out on TA Instruments model Q50 TGA and Q100 DSC. The TGA and DSC thermograms were obtained in nitrogen at a heating rate of 10 °C/min. Both ^{1}H NMR and ^{13}C NMR spectra were taken at 500 MHz on a Bruker WM500 spectrometer.

The light-emitting diodes were fabricated by sequential spin-casting of the polymer layers onto a cleaned ITO-coated glass substrate (Delta Technologies Ltd., Stillwater, MN), and an Al electrode was thermally evaporated through a shadow mask onto the polymer films by using an AUTO 306 vacuum coater (BOC Edwards, Wilmington, MA) at base pressures lower than 2×10^{-6} Torr. A 50 nm thick hole injection layer, poly(ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT) was spin-coated on top of ITO from a 1.3 wt % dispersion in water and dried at 200 °C for 1.5 h under vacuum. Electroluminescence (EL) spectra were obtained using a PTI QM-2001-4 spectrofluorimeter. Current−voltage characteristics and luminance of the LEDs were simultaneously measured using a HP4155A semiconductor parameter analyzer (Yokogawa Hewlett-Packard, Tokyo) and a model 370 optometer (UDT instruments, Baltimore, MD) equipped with a calibrated luminance sensor head (model 211), respectively. Further details of our polymer LED fabrication and characterization can be found in previous reports.[3f−h,13]

10-Hexylphenothiazine. In a flame-dried flask attached with a reflux condenser, 10 g (50 mmol) of phenothiazine was dissolved in 200 mL of anhydrous THF under argon. 2.2 g of sodium hydride (60% in mineral oil, 55 mmol) was added into the clear solution. After stirring for 1 h, 10.52 mL of 1-bromohexane (75 mmol) was added. The mixture was refluxed for 24 h and then poured into 200 mL of water. The product was extracted with methylene chloride (100 mL × 2), and the organic layer was dried over anhydrous sodium sulfate. After purification by silica gel column chromatography with hexane as eluent, 11.96 g of colorless oil was obtained with 84.5% yield. ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 7.14 (m, 4H, Ar−H), 6.89, (m, 2H, Ar−H), 6.85 (d, 2H, Ar−H), 3.82 (t, 2H, CH_2N), 1.79, (m, 2H, CH_2), 1.42 (m, 2H, CH_2), 1.30 (m, 2H, $2 \times CH_2$), 0.87 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS), δ (ppm): 145.31, 127.38, 127.12, 124.86, 111.25, 115.32 (Ar−C), 47.39 (CH_2N), 31.44, 26.87, 26.65, 22.57, 13.96 (CH_3).

3,7-Dibromo-10-hexylphenothiazine. 16 g of NaOH (0.4 mmol) was dissolved in 350 mL of acetic acid under argon and cooled to 5−10 °C with ice−water bath. 14.17 g (50 mmol) of 10-hexylphenothiazine was added, followed with 50 mL of chloroform under argon. After cooled back to 5−10 °C, 5.14 mL of bromine (100 mmol) in 50 mL of chloroform was added dropwise. The mixture was stirred for 2 h at room temperature. All of the solvent was removed by rotary evaporator, and then the residue solid was dissolved in 200 mL of chloroform and washed with 5% sodium carbonate solution (200 mL) and water (200 mL). The purple organic solution was dried over anhydrous sodium sulfate and purified by silica gel column flash chromatography with chloroform as eluent. The purple solution was concentrated and distilled out by Kugel Rohr distillation under vacuum. The pale yellow liquid was recrystallized in ethanol. 13.2 g of colorless crystal was obtained; yield 59.8%. ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 7.30 (m, 4H, Ar−H), 6.73 (d, $J = 8.65$, 2H, Ar−H), 3.78 (t, $J = 7.2$, 2H, CH_2N), 1.78 (m, 2H, CH_2CH_2N), 1.57 (m, 2H, CH_2), 1.32 (m, 4H, CH_2), 0.91 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$), δ (ppm): 143.83, 129.83, 129.47, 126.24, 116.44, 114.57 (aromatic C), 47.78 (CH_2N), 31.57, 26.89, 26.74, 22.81, 14.24 (CH_3). ESI-MS (M + 1): 439, 440, 441, 442; calcd M + 1: 439, 440, 441, 442.

Poly(10-hexylphenothiazine-3,7-diyl) (PHPT). In a dry flask, 515 mg of 2,2-bipyridine (3.3 mmol) and 825 mg of $Ni(COD)_2$ (3.0 mmol) were added in the glovebox. After taking out the flask from the glovebox, 357 mg of 1,5-cyclooctadene and 50 mL of anhydrous DMF were injected under argon. The mixture was stirred at 60 °C for half an hour to obtain a dark blue catalyst solution. In another dry flask, 1.103 g of 3,7-dibromo-10-hexylphenothiazine (2.5 mmol) was dissolved in a mixture of toluene (50 mL) and dry DMF (20 mL) under argon. The catalyst solution was slowly transferred into the monomer solution. After stirring for 24 h, the mixture was poured into 200 mL of methanol. The polymer was purified by precipitation from THF solution into methanol. After filtration and drying in a vacuum, 0.540 g of yellow powder was obtained; yield 77%. ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 7.30 (b, 4H, Ar−H), 6.86 (b, 2H, Ar−H ortho to MeN), 3.85 (b, 2H, CH_2N), 1.83 (b, 2H, CH_2CH_2N), 1.45 (b, 2H, CH_2), 1.32 (b, 2H, CH_2), 0.88 (b, 3H, CH_3). ^{13}C NMR ($CDCl_3$), δ (ppm): 143.96, 134.26, 125.21, 125.15, 124.72, 115.40, 47.59 (CH_2N), 31.49, 26.88, 26.70, 22.62, 14.02 (CH_3). GPC (THF, PSt standard) results: $M_w = 1.53 \times 10^4$, $M_w/M_n = 3.00$.

Poly(10-hexylphenothiazine-3,7-diyl-*alt*-9,9-dihexyl-2,7-fluorene) (PPTF). In a flask, 3,7-dibromo-10-hexylphenothiazine (1.103 g, 2.5 mmol), 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) (1.2558 g, 2.5 mmol), sodium carbonate (20 mmol, 2.12 g), and 0.15 g of Aliquat 336 were added under argon. 15 mL of degassed toluene and 10 mL of water were added in. The mixture was stirred until a solution was obtained, and then tetrakis(triphenyl)phosphine palladium [$Pd(PPh_3)_4$] was added. After the mixture was stirred at 100 °C for 6 h, another 30 mL of toluene was added. The mixture was stirred for another 66 h and was cooled to room temperature. It was poured into 200 mL of methanol and deionized water (10:1 v/v). A fibrous solid was obtained by filtration. The solid was washed with methanol, water, and then methanol. 1.32 g of polymer was obtained as a yellow fibrous solid; yield 86%. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.75 (m, 2H), 7.55 (m, 8H), 6.99 (d, 2H), 3.94 (s, 2H), 2.02 (b, 4H, CH_2CCH_2), 1.95 (b, 2H, CH_2CH_2N), 1.54 (b, 2H), 1.37 (b, 4H), 1.077 (b, 12H), 0.92 (b, 4H), 0.78 (b, 9H, $3 \times CH_3$). ^{13}C NMR ($CDCl_3$), δ (ppm): 151.69, 144.19, 139.82, 138.78, 136.04, 126.02, 125.85, 125.34, 124.73, 120.82, 119.93, 115.46, 55.26, 47.66, 40.50, 31.53, 31.48, 29.73, 26.92, 26.75, 23.81, 22.65, 22.60, 14.01. GPC (THF, PSt standard) results: $M_w = 1.83 \times 10^5$, $M_w/M_n = 6.45$.

Acknowledgment. This research was supported by a U.S. Army Research Office DURINT Program (DAAD19-01-1-0499) and in part by the U.S. Army Research Office TOPS MURI (DAAD19-01-1-0676).

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MA035087Y