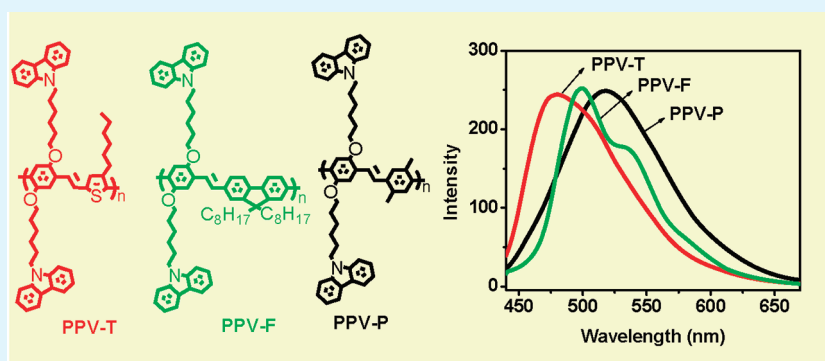


# Conjugated Polymer Network Films of Poly(*p*-phenylene vinylene) with Hole-Transporting Carbazole Pendants: Dual Photoluminescence and Electrochromic Behavior

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## Supporting Information



**ABSTRACT:** A series of poly(*p*-phenylene vinylene) (PPV) copolymers functionalized with hole-transport and electrochemically active carbazole units as pendant moieties is reported. These polymers exhibit photoluminescence properties by virtue of the PPV analogous backbone. They were also designed as precursor polymer bearing the electroactive carbazole group to form conjugated polymer network (CPN) films by electrodeposition. The electrochemical polymerization of the pendant units eventually lead to a dual property electro-optically active thin film — photoluminescence (PL) behavior that can be attenuated with CPN formation, and a reversible doping and dedoping processes at controlled potentials that lead to an electrochromic behavior. This reveals the ability to incorporate complementary optical and electro-optical properties within the same film using the CPN approach. It should be possible to design and synthesize other PPV  $\pi$ -conjugated polymers with efficient pendant hole-transport groups exhibiting tunable PL and electrochromism with cross-linking.

**KEYWORDS:** poly(*p*-phenylene vinylene), carbazole, electropolymerization, ITO, spectroelectrochemistry, fluorescence

## INTRODUCTION

Intrinsically conducting polymers (ICPs) or  $\pi$ -conjugated polymers have been utilized in light-emitting diodes, thin film transistors, chemical sensors, photonic, and photovoltaic devices.<sup>1</sup> For display devices, polymer light-emitting diodes (PLEDs) emitting light from blue to red with good external quantum efficiencies have been explored.<sup>2,3</sup> In principle, they are easier to fabricate as devices compared to small molecule organic materials because of their good thin film forming properties primarily by spin-coating or solution casting. Another solid-state device of importance is electrochromic display (ECD) devices. The significant amount of work on the electrochromic properties of conjugated polymers has led to the fine-tuning of several classes of polymers with a wide array of colors. A number of these polymers were obtained through electropolymerization or by chemical oxidation processes.<sup>4</sup> Although these techniques often are useful and easily

implemented, they possess several inherent drawbacks, such as nonuniform films and irregular linkages, that dramatically diminish the desired properties of the material such as color purity or switching rate.<sup>5</sup>

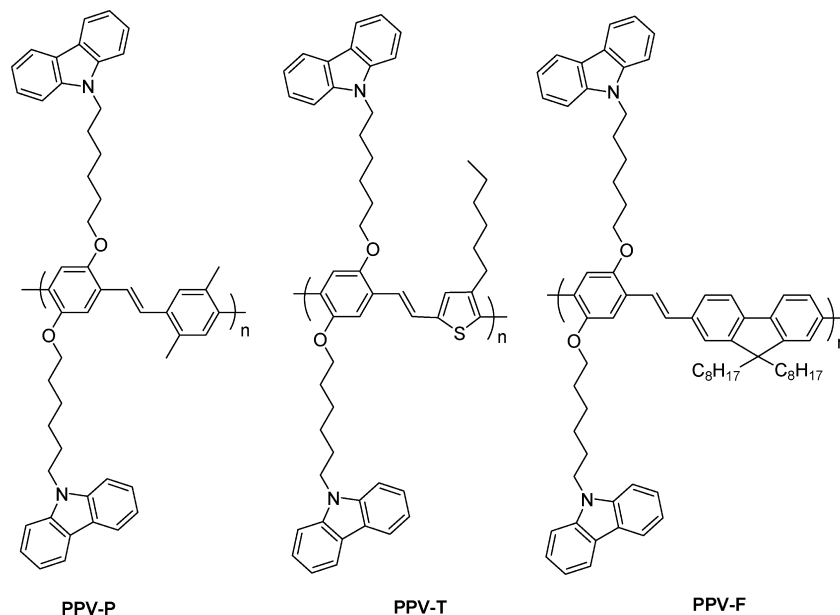
Among the conjugated polymers, poly(*p*-phenylene vinylenes) (PPVs) have been extensively studied because of their high stability, ease of synthesis, and strong electroluminescence properties.<sup>6</sup> Their emission properties are usually tailored by incorporation of aromatic moieties such as oxadiazole which is a known charge transport material. However, it is rare to see reports where the PPV itself or its copolymer intrinsically exhibits both electrochromic and PL properties unlike the polythiophenes.<sup>1e</sup> Previous reports involved the formation of

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Scheme 1. Structures of the PPV Copolymers with Pendant Carbazole Units



solid-state electrochromic devices based on blends of PPV and organic anions to achieve higher optical contrasts in electrochromic devices.<sup>7</sup> Other important classes of polymers that exhibit electrochromism include polycarbazoles, poly(3-alkyl thiophene)s, and the poly(2,2-dialkylpropylenedioxythiophene).<sup>1c</sup>

Herein, we have designed a series of PPV-based copolymers containing fluorene and thiophene units in the backbone and hole transporting carbazole units as the pendant groups in the same polymer (see Scheme 1). Intrinsically, the PPV copolymer exhibited PL properties in the emerald-green region (500–550 nm). In our design, we have a PPV backbone with built-in pendant carbazole units, and upon cross-linking the carbazole units form a robust and uniform electrodeposited film. By electrochemically cross-linking the carbazole units, interesting electrochromic properties were also observed.

## EXPERIMENTAL SECTION

**Materials.** All reagents were purchased from Aldrich, Fluka and/or Alfa Aesar and used without further purification. All reactions were carried out with freshly distilled anhydrous solvents under inert atmosphere. 1,4-Dimethyl-2,5-divinyl benzene<sup>8</sup> (4), 3-hexyl-2,5-divinyl thiophene<sup>9</sup> (5), and 9,9'-diethylhexyl-2,7-divinyl-9H-fluorene<sup>10</sup> (6) were synthesized by following literature procedures as enumerated below with their corresponding references.

**Characterization.** NMR spectra were recorded using a General Electric QE 300 spectrometer (<sup>1</sup>H 300 MHz). UV-vis spectra were recorded using an Agilent 8453 spectrometer. Fluorescence spectra were obtained on a Perkin-Elmer LS-45 luminescence spectrometer. Elemental analysis was done through Atlantic Microlabs. Cyclic voltammetry (CV) was performed on an Amel 2049 potentiostat and power lab/4SP system with a three-electrode cell. In all the measurements the counter electrode was platinum wire and indium tin oxide (ITO) or gold-coated glass as working electrode. The ITO was pretreated with the RCA recipe (H<sub>2</sub>O/H<sub>2</sub>O<sub>2</sub>/NH<sub>3</sub>: 15.1 g/26.6 g/8.57 g). The gold electrodes were cleaned with a plasma ion cleaner (Plasmod, March). Ag/AgCl was used as a reference electrode.

**Synthesis.** *Synthesis of 9-(6-Bromohexyl)-9H-carbazole (2).* The synthesis of 9-(6-bromohexyl)-9H-carbazole (Scheme 2) was accomplished by following a literature procedure.<sup>11</sup> A mixture of carbazole (10.32 g, 61.72 mmol) in toluene (100 mL) containing 1,6-dibromohexane (133.01 g, 547.4 mmol)

and TBAB (2 g), was stirred at 45 °C for 3 h and was left stirring at room temperature overnight. After the aqueous layer was removed and washed three times with water and brine, the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The organic solvent was evaporated and the unreacted 1,4-dibromobutane was removed by vacuum distillation. The residue was recrystallized from ethanol to give 17.31 g (85%) of the product. The characterization was found to be consistent with literature.

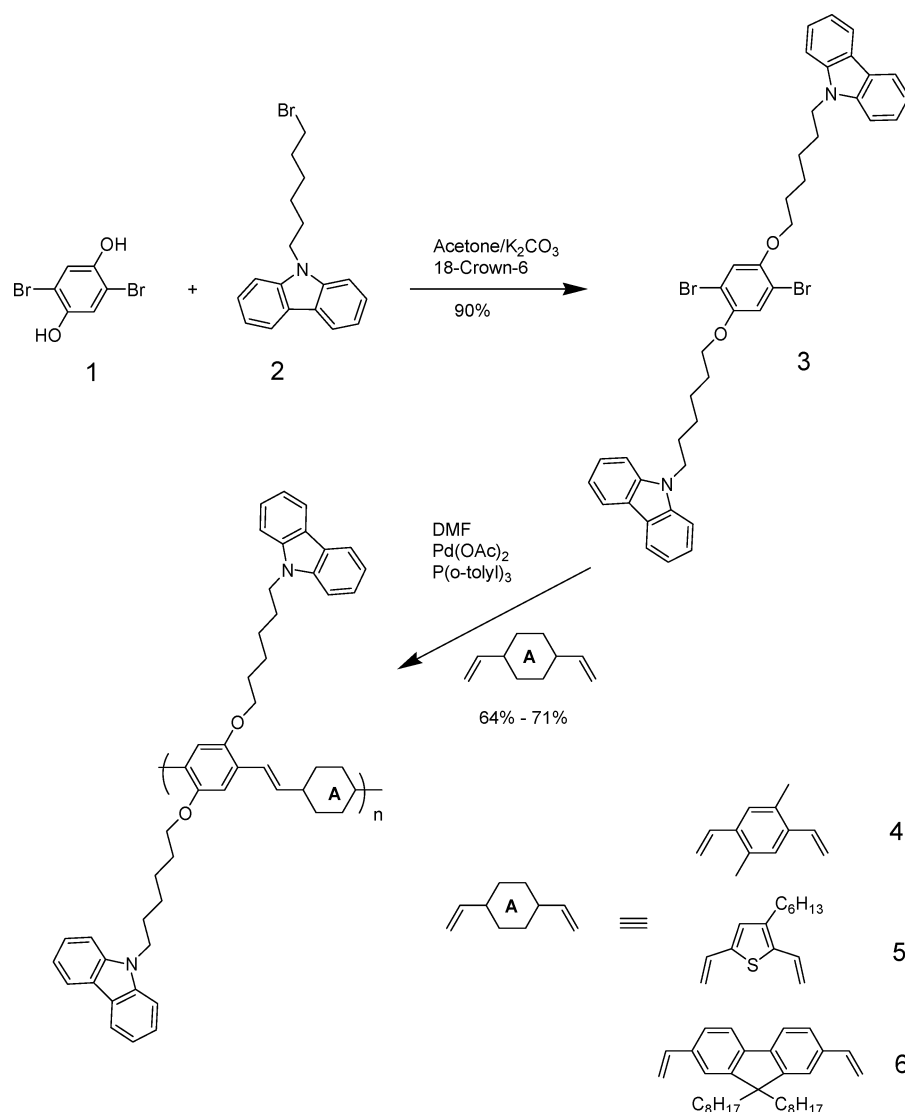
*Synthesis of 1,4-Dibromo-2,5-bis(9-(6-bromohexyl)-9H-carbazole) Benzene (3).* A mixture of dibromohydroquinone (1.0 g, 3.73 mmol), 9-(6-bromohexyl)-9H-carbazole (2.71 g, 8.21 mmol), potassium carbonate (1.55 g, 11.2 mmol), and a catalytic amount of 18-crown-6 in acetone was stirred at reflux for about 2 days. After the complete removal of the solvent, a large excess of water was added. The precipitate was filtered and recrystallized in methanol. The pale brown product was filtered. Yield: 2.60 g (90%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 8.11–8.09 (d, 4H, car-H), 7.45–7.43 (m, 8H, car-H), 7.26–7.24 (m, 4H, car-H), 7.04 (s, 2H, Ph), 4.35–4.30 (t, 4H, -NCH<sub>2</sub>), 3.91–3.87 (t, 4H, -OCH<sub>2</sub>), 1.93–1.91 (t, 4H, -CH<sub>2</sub>), 1.80–1.76 (t, 4H, -CH<sub>2</sub>).

*General Procedure for the Polymerization.*<sup>12</sup> The synthesis of PPV-P is given as a typical example for the preparation of polymers. A flask was charged with a mixture of 3 (1.0 g, 1.3 mmol), 4 (0.21 g, 1.3 mmol), Pd(OAc)<sub>2</sub> (0.02 g, 0.1 mmol), P(o-tolyl)<sub>3</sub> (0.15 g, 0.5 mmol), DMF (10 mL) and triethylamine (4 mL). The flask was degassed and purged with nitrogen and the mixture was heated at 90 °C under nitrogen. After 48 h, the solid was filtered, and the filtrate was poured into methanol. The resulting brownish precipitate was filtered and washed with methanol. The crude product was purified by dissolution in chloroform and precipitation in methanol (0.80 g, 68%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 8.22–8.16 (m, 4H, car-H), 7.45–7.33 (b, 18H, Car-H, Ph-H, vinyl), 4.40–4.30 (b, 4H, NCH<sub>2</sub>), 4.09–3.95 (b, 4H, -OCH<sub>2</sub>), 2.40–2.35 (b, 6H, -CH<sub>3</sub>), 2.00–1.39 (b, -CH<sub>2</sub>-). (See the Supporting Information.)

**PPV-T:** PPV-T was synthesized in a similar way by following the general procedure described above to give 64% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 8.18–8.17 (m, 4H, car-H), 7.54–7.24 (b, 17H, Car-H, Ph-H, Th-H, vinyl-H), 4.41–4.39 (b, 4H, -NCH<sub>2</sub>), 4.09–3.95 (b, 4H, -OCH<sub>2</sub>), 2.30–2.22 (b, 2H, Th-CH<sub>2</sub>), 1.70–1.33 (b, 8H, CH<sub>2</sub>), 0.94 (b, 3H, -CH<sub>3</sub>).

**PPV-F:** PPV-F was synthesized in a similar way by following the general procedure described above to give 71% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 8.32–8.30 (m, 6H, car-H, Flu-H), 7.69–7.41 (b, 20H, Car-H, Flu-H, Ph-H, vinyl-H), 4.56–4.53 (b, 4H, -NCH<sub>2</sub>),

Scheme 2. General Synthetic Scheme for the Polymers PPV-P, PPV-T, and PPV-F



4.20–4.15 (b, 4H,  $-OCH_2$ ), 2.14–2.13 (b, 8H, Flu- $CH_2$ , Car- $CH_2$ ), 1.70–1.33 (b, 24H,  $CH_2$ ), 0.94 (b, 6H,  $-CH_3$ ).

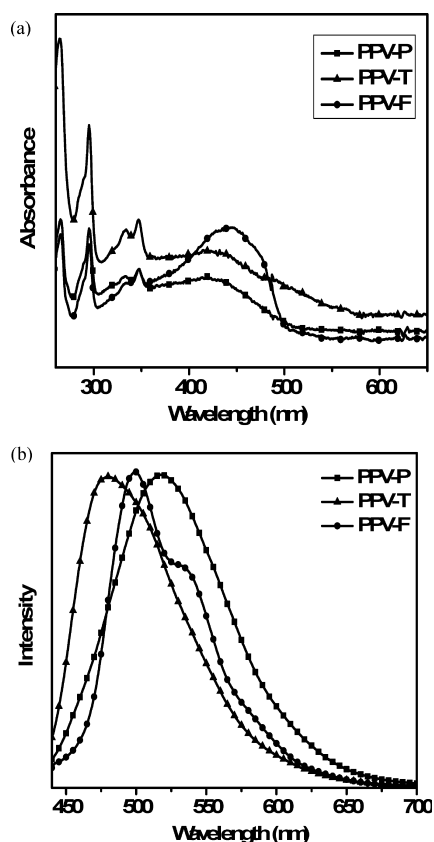
## RESULTS AND DISCUSSION

**Synthesis and Characterization.** The general synthetic route toward monomer and polymer synthesis is outlined in Scheme 2. Initially, 9-(6-bromohexyl)-9H-carbazole 2 was prepared following an established procedure. This was then reacted with each of the divinyl monomers 4, 5, and 6 synthesized via Stille coupling. Heck coupling was employed for all polymerization reactions. All polymers were characterized by NMR, GPC, TGA, UV–vis and fluorescence measurements. The number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) of the copolymers range from 9 to 12 kDa and 13 to 22 kDa, respectively, with polydispersity indices ranging from 1.2 to 1.9. These data are summarized in Table 1.  $^1H$  NMR confirmed the structures of the PPV-P polymers. The characteristic peaks at 8.22–8.16 ppm correspond to the protons on the carbazole units while peaks found at 7.44–7.33 ppm are assigned to the phenylene, remaining carbazole, and vinyl protons. Data for other polymers are also in good agreement with our proposed polymeric structures.

**Table 1. Properties of the Polymers, PPV-P, PPV-T, and PPV-F**

polymer	$\lambda_{abs}$ (nm)	$\lambda_{em}$ (nm)	onset temp. ( $^{\circ}C$ )	$M_n$ (kg/mol)	PDI
PPV-P	265, 296, 347, 425	516	375	9.1	1.4
PPV-T	265, 295, 347, 423	482	390	11.8	1.2
PPV-F	265, 296, 347, 445	498	385	11.4	1.9

**Absorption and Emission Properties.** The optical and spectroscopic properties of the synthesized polymers were investigated using UV–vis absorption and photoluminescence in dilute chloroform solution. Figure 1 shows the UV–vis absorbance and fluorescence spectra of the PPV polymers. All the copolymers showed peaks at 330 and 346 nm which are typically assigned to the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions of the carbazole species, whereas absorption peaks at 263 and 294 nm correspond to the benzenoid transitions at the backbone of the copolymers.<sup>13</sup> For the longer wavelength peaks, almost identical absorption spectra were observed for PPV-P and PPV-T, whereas a more red-shifted peak was observed for



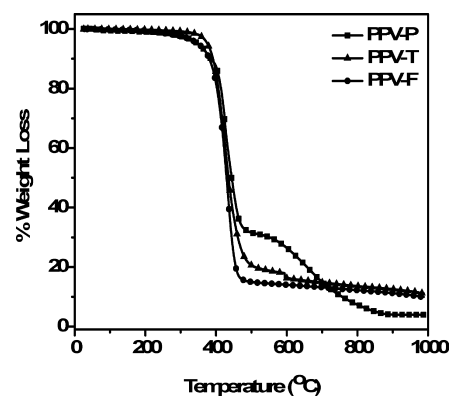
**Figure 1.** (a) UV-vis absorption and (b) emission spectra of the polymers in  $\text{CHCl}_3$  solution.

**PPV-F.** Structurally, the only difference among the copolymer species is the alternating unit - benzene in the case of **PPV-P**, thiophene in **PPV-T**, and fluorene in **PPV-F**. The longer wavelength  $\pi-\pi^*$  transition of the PPV backbone is indeed expected for **PPV-F** at 445 nm due to the comparatively longer conjugation segment of the fluorene backbone when compared to benzene and thiophene.

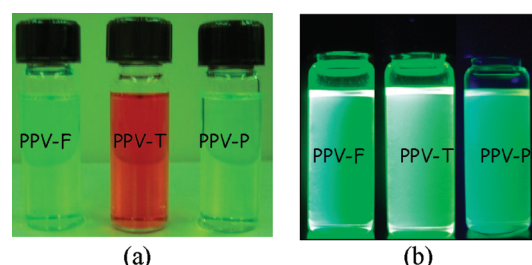
The fluorescence spectra recorded with the excitation wavelength corresponding to the maximum absorption wavelength of the polymers are shown in Figure 1b. For **PPV-P** and **PPV-T**, the emission peaks are observed at 516 and 482 nm, respectively. In the case of **PPV-F**, a shoulder peak around 534 nm was also detected in addition to the emission peak at 498 nm. The Stokes shifts observed for **PPV-P**, **PPV-T** and **PPV-F** are  $1.1 \times 10^5$ ,  $1.7 \times 10^5$  and  $1.9 \times 10^5 \text{ cm}^{-1}$ , respectively. The smallest Stokes shift exhibited by the **PPV-F** polymer may indicate a more favorable structure of the conjugated main chain leading to optimal ground-excited state energy transitions.<sup>14</sup>

**Thermal Properties.** The thermal stability of each polymer was further characterized by TGA. The polymer samples were heated up to 1000 °C at a heating rate of 10 °C under a dry nitrogen atmosphere. As illustrated by the TGA thermograms in Figure 2, the weight loss of the polymers was less than 10% upon heating to 400 °C, indicative of good thermal stability. The onset of thermal degradation temperatures are summarized in Table 1.

Figure 3a depicts a fluorescent solution of all copolymers when dissolved in chloroform. Remarkably, **PPV-T** showed a red colored solution instead of the usual green colored PPV polymers. The difference in color corroborates the data from



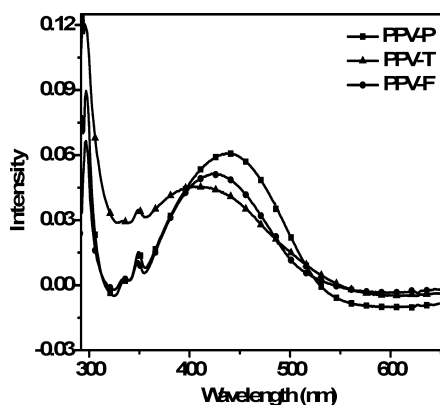
**Figure 2.** TGA traces for all three PPV polymers.



**Figure 3.** Digital photograph of PPV polymer solutions in chloroform (a) at room temperature and (b) fluorescence under long wavelengths (360 nm).

UV-vis spectra showing a strong blue shift (Figure 1a). Upon excitation under longer wavelength (360 nm), all polymers showed brighter fluorescence with different hues (Figure 3b). They typically show green fluorescence with variation in the intensities that may reflect in the device efficiency and true color. Interestingly, a transition from a red colored solution absorbance to a bright emitting green fluorescence is noticeable for **PPV-T** with a large Stokes Shift. The red color is a consequence of the contribution of the thiophene units. The fluorescence efficiency of the copolymers against 9,10-diphenylanthracene were determined to be 20.59, 16.32, and 32.42% for **PPV-P**, **PPV-T**, and **PPV-F**, respectively.

The advantage of the designed precursor polymer is the introduction of carbazole moieties that can be cross-linked electrochemically. The optical properties in solid state of these polymers were also investigated to determine the effect of cross-linking the carbazole pendant groups on the polymer chain. Chloroform solution of each of the polymers was used to spin-cast on an Indium Tin Oxide (ITO) substrate to obtain a thin film of 150–200 nm thickness. Figure 4 shows the absorbance spectra of the spin-coated polymer films. It can be clearly observed from these spectra that all polymers show similar absorbance behavior in both solution (Figure 1a) and solid state. The  $\pi-\pi^*$  transition of the PPV backbone for **PPV-F** and **PPV-T** are observed at 423 and 405 nm, with a hypsochromic shift of 22 and 18 nm, respectively. In the case of **PPV-P**, we have observed a bathochromic shift in the  $\pi-\pi^*$  transition peak by 15 nm. The observed shift in the  $\pi-\pi^*$  transition to a longer wavelength may indicate the presence of intermolecular interaction and/or increase in coplanarity of the polymer in the solid state.<sup>15</sup> Nevertheless, the differences in the absorbance behavior between solution and solid state is indicative of the conformational restriction and possible effect



**Figure 4.** UV-vis absorption of the spin-cast films of all three polymers on ITO substrate.

on increasing excitonic traps for the solid-state films due to aggregation.

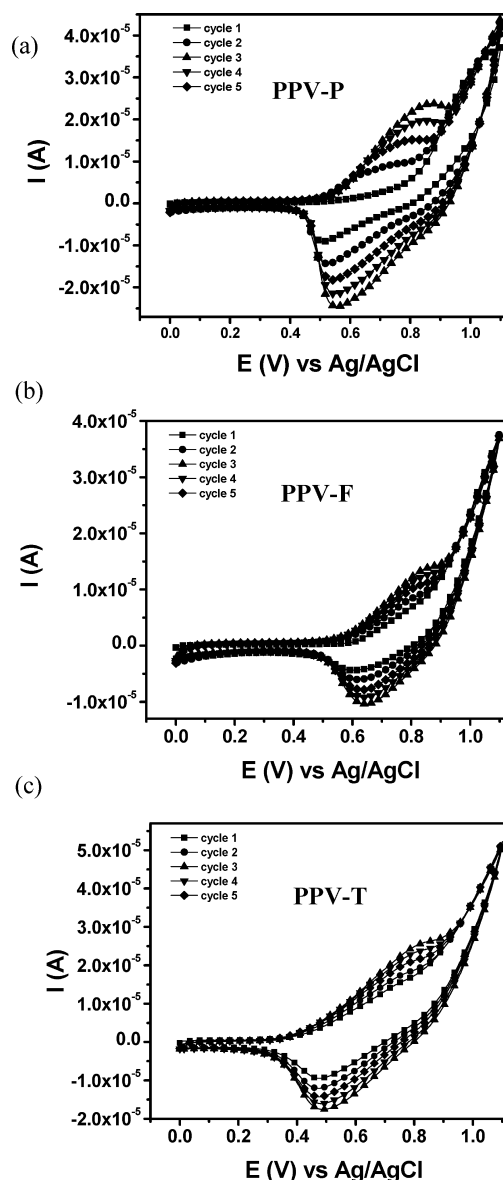
#### Electrochemical Polymerization of the Polymers.

Electrochemical polymerization is an important method in forming cross-linked films directly onto a conducting substrate. Typically, electrochemical polymerization entails oxidative coupling of monomers in a stepwise manner to produce insoluble oligomers that deposit on the working electrode surface. Our group has been investigating the precursor polymer approach to form conjugated polymer network (CPN) films through pendant electropolymerizable groups.<sup>13,16</sup>

The precursor approach is highly advantageous in terms of its versatility in utilizing the polymer backbone, which is useful in many ways such as imparting thermal stability/flexibility, adhesion, morphological modification, optical transparency and controlling ion permeability. This approach has recently been applied toward the electrochemical cross-linking and deposition of dendrimers.<sup>17</sup> The resulting cross-linked film is highly robust, mechanically stable, and insoluble in any organic solvents.

The electropolymerization (electrochemical cross-linking of the carbazole units) of all three polymers was performed in a three electrode cell, where the following electrodes were used: platinum as a counter electrode, Ag/AgCl as a reference electrode and ITO-coated glass substrate as anode. The electrochemical polymerization was performed using 0.5 mg/mL of each polymer in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. The scanning was performed at a scan rate of 50 mV/s from 0 to 1.1 V against a Ag/AgCl reference electrode.

Figure 5 shows the different CV traces for all three polymers and Table 2 summarizes the peak anodic and cathodic currents and potentials. All three precursor polymers show similar redox behavior. The CV traces show two oxidation peaks at 0.96 and 0.64 V vs Ag/AgCl. The two peaks are assigned to the electropolymerization of carbazole and p-doping of formed polycarbazole, respectively. Because it is known that carbazole can be electrochemically polymerized and the formed polycarbazole undergoes electrochemical oxidation at about 0.55 V vs Ag/AgCl, the growth of the peak at 0.64 V vs Ag/AgCl is attributed to p-doping of polymerized carbazole.<sup>18</sup> In the repeated scanning, the growth of the conducting polymer is reflected by gradually increasing currents corresponding to the peak at 0.64 V.<sup>19</sup> In addition, the slight increase in the peak separation potential reflected the increase in the polymer film



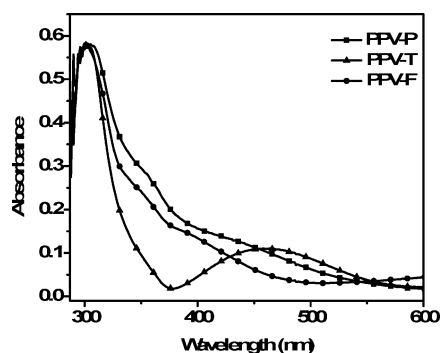
**Figure 5.** Cyclic voltammograms for: (a) PPV-P, (b) PPV-F, and (c) PPV-T in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAH as supporting electrolyte, Pt as counter electrode, Ag/AgCl as reference electrode, and ITO as working electrode.

**Table 2.** Cross-Linked Precursor Polymers Showing Peak Anodic and Cathodic Currents and Potentials

polymers	$E_{pa}$ (V)	$i_{pa}$ (mA)	$E_{pc}$ (V)	$i_{pc}$ (mA)	$\Delta E$ (V)
PPV-P	0.82	0.0025	0.51	-0.0025	0.31
PPV-T	0.83	0.0027	0.49	-0.0018	0.33
PPV-F	0.81	0.014	0.61	-0.0011	0.20

resistance as the thickness of the film increases with increasing number of cycles. These films showed good stability toward repeated redox cycling. A linear relationship between peak current and scan rate was observed for all these films suggesting that the redox-active polymer has been deposited to the electrode.

Figure 6 shows the UV-vis spectra of the cross-linked films of all three polymers. The extent of increasing  $\pi$  orbital overlap between neighboring repeat units on conjugated polymers can be directly assessed from their electronic spectra. The extent of

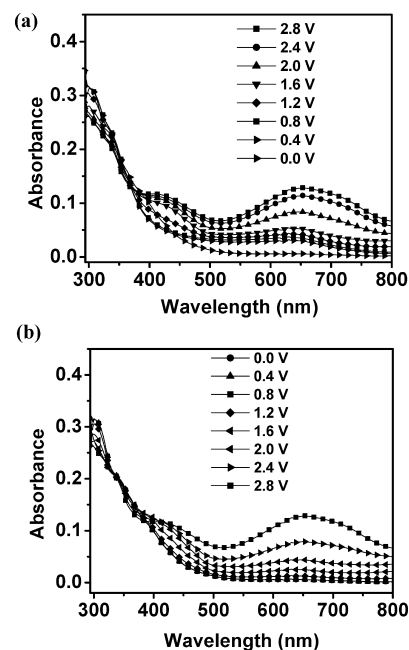


**Figure 6.** UV-vis absorption of the cross-linked films of all three polymers on ITO substrate.

electronic conjugation directly affects the observed energy of the  $\pi-\pi^*$  transition, which appears as the absorption maxima in these materials. The values of absorption maxima of the carbazole region indicate the degree of polymerization. After cross-linking, the  $\pi-\pi^*$  transition corresponding to carbazole is red-shifted and is observed as a broad shoulder. This indicated the formation of higher  $\pi$ -conjugated species.<sup>20</sup>

**Electrochromism.** Understanding the electrochromic property in both doped and undoped states of the copolymers was also done by passing current and monitoring the corresponding color change with UV-vis spectroscopy. The formation of radical cations during oxidation of the polymer essentially represents a trapped hole. The efficient migration of the hole along the polymer chain is an important criterion for charge transport in electronic devices. All three polymers were electrochemically deposited on an ITO-coated glass slide. At the same time, this enabled the formation of conjugated polycarbazole units which then facilitated the electrochromic behavior. The cross-linked films were analyzed under monomer-free conditions by applying a constant potential and the changes in the UV-vis absorption was monitored by in situ spectro-electrochemistry. The reversible changes in the absorption spectra induced by p-doping of PPV-P are presented in Figure 7 as a series of UV-vis absorbance spectra correlated to electrode potentials. In the neutral form at 0 V, the film exhibited strong absorption at a wavelength near 300 nm with a broad shoulder at 440 nm. Upon increasing the applied voltage from 0 to 1 V, no change was observed in the UV spectrum. The intensity of the spectrum starts to decrease at potentials around 1.2 V, where the polymer starts to be doped. As the intensity of the peak at 300 nm decreases, there is a simultaneous appearance of two new peaks at 420 and 680 nm, which increases with increase in the potential. The formation of new peaks was attributed to mono- and diradical cations.<sup>21</sup> The color changed simultaneously with the increase in the applied potential in a stepwise fashion, until it reached the instrument limit of 3 V. On reversing the potential to 0 V, the peak at 300 nm was fully recovered even after exposure to these high potentials. The ability of the polymer to undergo reversible oxidation shows its ability to promote hole transport without being attenuated by chemical oxidation conditions.<sup>22</sup> The electrochromic switching behavior appears to be of a highly reversible process similar to what has been observed with other electropolymerized polycarbazoles and CPN films previously reported.<sup>23</sup>

**Photoluminescence.** PL measurements on the films were made by comparing spin-cast films of the PPV materials with

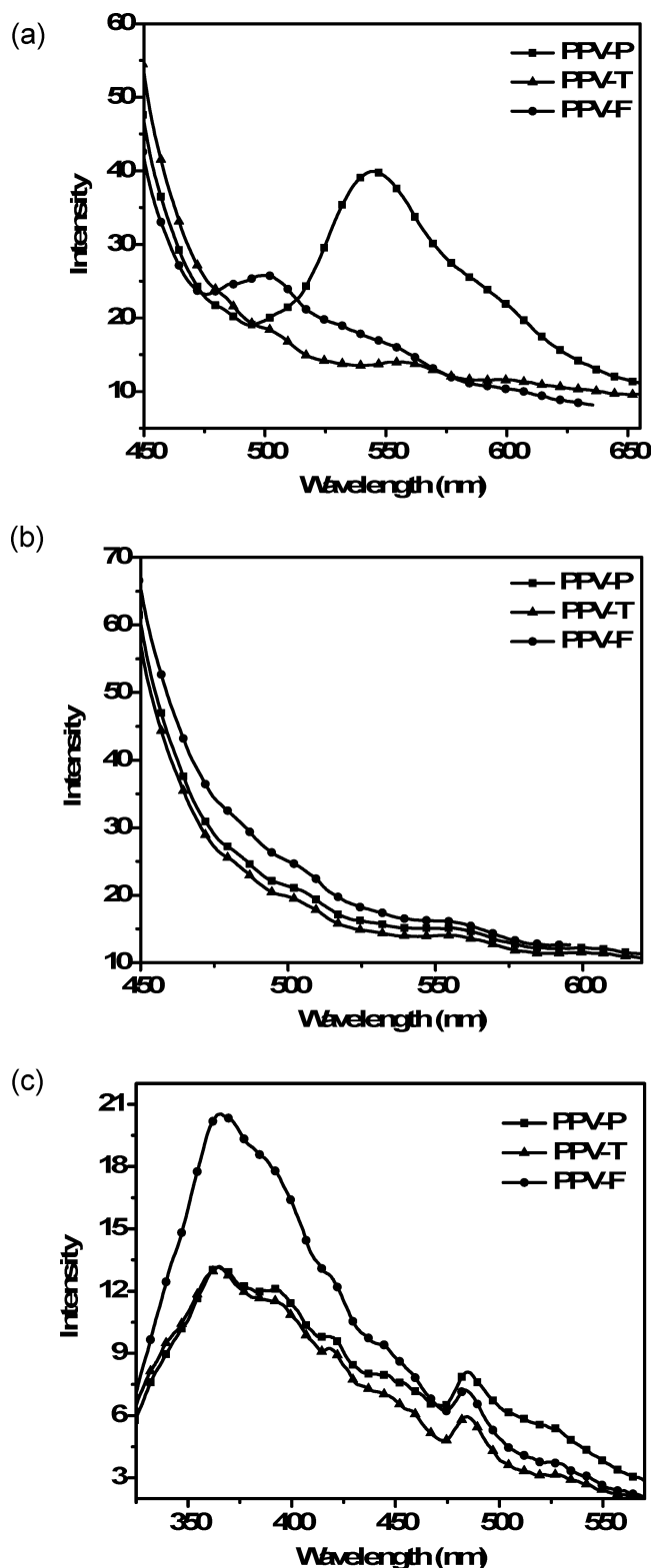


**Figure 7.** Spectro-electrochemical changes for the PPV-P at different constant voltages in (a) forward and (b) backward directions.

the electropolymerized films (Figure 8). The excitation was initially done at 420 nm, coincident with the absorbance observed for the PPV-F, PPV-P, and PPV-T spin-cast films as shown in Figure 4 (see the Supporting Information). Spin-cast films on ITO showed PL properties for PPV-P (550 nm) and PPV-F (500 nm) but have low intensity with PPV-T (500 and 550 nm). On the other hand, with the cross-linked films, the PL was generally quenched for all polymers with low peak intensities at 500 and 550 nm observed. However, excitation at 300 nm showed emission at 375 nm, which is characteristic of the phenylene species and the small peak at 475 nm, characteristic of the phenylenevinylene species that is still present for the three polymers but with attenuated intensity. In this case, the PL intensity is very much affected by the extent of cross-linking and solid state properties of a film which can be attributed to the following: (1) quenching observed because of field-induced dissociation of excitons as a result of the doped state of the film,<sup>6</sup> (2) increased aggregation state of the PPV polymers, which form excimer states that significantly reduce the photoluminescence efficiency from these materials,<sup>16</sup> and (3) influence of the ITO substrate used for the fabrication of the thin film and the effect of doping.<sup>27</sup> The results could indicate possible selective electric field or electropolymerization induced quenching of the PL.<sup>24–26</sup> This can be useful for patterning application of these films as well as different induced mechanisms for exciton trapping based on electrochemical cross-linking and redox reversibility. Recently, the electrochemical, electrochromic, and electrogravimetric responses of spin-cast MEH-PPV films (reddish brown color) have been reported, enabling stability suitable for light-emitting electrochemical (LEC) device applications.<sup>27</sup> The results reported here should complement a full color LEC application for these class of polymers.

## CONCLUSION

A new series of poly(*p*-phenylene vinylene) copolymers functionalized with the hole transport and electroactive



**Figure 8.** PL measurements for the PPV-P polymers as (a) spin-cast films at 420 nm and after electropolymerization and CPN film formation (b) at 420 nm and at (c) 300 nm.

carbazole units as pendant chains have been synthesized, characterized and electrochemically cross-linked. All copolymers differed with the alternating substituents in terms of absorption and fluorescence behavior where the highest Stokes shift was observed with the thiophene copolymer PPV-T. The

electrochemical polymerization of the pendant units has led to the formation of reversibly stable electrochromic thin films, i.e., the doping and dedoping processes in these materials are highly reversible. In this case, the formation of a radical cation during oxidation of the polymer essentially represents a trapped hole. However, cross-linking attenuated the PL behavior through a variety of possible mechanisms including excitonic traps that can lead to nonradiative pathways. Although the efficient migration of the hole along the polymer chain is an important criterion for charge transport in PLEDs, other applications including LEC devices can make use of the variable and reversible electron transport response. The synthesis of various  $\pi$ -conjugated polymers with efficient hole transport groups using this design parameters should be possible.

## ■ ASSOCIATED CONTENT

### Supporting Information

NMR data for the polymers and Fluorescence data on other excitation wavelengths. This material is available free of charge via the Internet <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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