Substituent Effect on the Optoelectronic Properties of Poly(*p*-phenylenevinylene) Based Conjugated-Nonconjugated Copolymers

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ABSTRACT: Two classes of light emitting Poly(*p*-phenylenevinylene) (PPV) based conjugated-nonconjugated copolymers (CNCPs) have been synthesized. The conjugated chromophores containing 2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene (MEHPV) and 2,5-dimethyl-1,4-phenylenevinylene (DMPV) moieties are rigid segments and nonconjugated portion containing hexyl units are flexible in nature. All copolymers were synthesized by well-known Wittig reaction between the appropriate bisphosphonium salts and the dialdehyde monomers. The resulting polymers were found to be readily soluble in common organic solvents like chloroform, THF and chlorobenzene. The effect of chromophore substituents on the optical and redox properties of the copolymers has been investigated. Color tuning was carried out by varying the molar percentage of the comonomers. The UV-Vis absorption and PL emission of the copolymers were in the range 314–395 nm and 494–536 nm respectively. All the polymers show good thermal stability. Polymer light-emitting diodes (PLEDs) were fabricated in ITO/PEDOT:PSS/emitting polymer/cathode configurations of selected polymers using double-layer, LiF/Al cathode structure. The emission maxima of the polymers were around 499–536 nm, which is a blue-green part of the color spectrum. The threshold voltages of the EL polymers were in the range of 5.4–6.2 V. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2988–2998, 2009

Key words: poly(*p*-Phenylenevinylene) (PPV); conjugated-nonconjugated copolymers (CNCPs); color tuning; photoluminescence (PL); quantum yield

INTRODUCTION

Among organic conjugated polymers studied to date, poly(*p*-phenylenevinylene) (PPV) and its derivatives are the most promising candidates for efficient light emitting diodes (LEDs), due to high luminance and color tuning by easy modification of the chemical structure.[1–7] These materials have been easily tailored to show desired properties such as spectral line shape, high luminosity and quantum efficiency, relative indifference to impurities, processability and long-term stability. However, due to their extended conjugation, the emission of most polymeric materials is restricted to the green-red part of the spectrum while blue to green part of the visible spectrum is usually limited to shorter oligomers with shorter conjugation length. On the other hand, shorter oligomers usually exhibit poor processability and long term resistance towards crystallization, phase separation and other morphological degradations.

Color tuning of the EL emission combined with improved solubility from polymer based LEDs has been achieved mainly by "geometrical" control of conjugation length via several different routes. These include, among others, substitution of side groups, which enhances the steric hindrance and leads also to the decrease of the planarity.[8–12] A different approach is the development of polymers composed of short conjugated fluorescent segments interconnected via nonconjugated linkers.[13–19] Such polymers are expected to retain the electronic properties of the conjugated oligomer chain and possess the desired processibility and long-term morphological stability of higher molecular weight polymers. For example, incorporation of flexible nonconjugated segments into rigid conjugated polymer reduces the stiffness of the backbone and therefore affects the molecular order of the polymer. As many electronic properties of conjugated polymer depend on the degree of order,[20,21] this concept can be an important tool to tailor their optical properties. The electronic structure of the copolymers dominates the emission features and phenomena such as the formation of excimers,[22] energy transfer, and exciton migration[23] are of great interest. Hence, the study of these materials allows the investigation of various structural parameters on the electronic and physical properties of the polymers.

Though conjugated-nonconjugated copolymer (CNCP) systems are widely reported, 2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene (MEHPV) based conjugated blocks have not been explored to a great extent. Zyung et al. reported a CNCP system with MEHPV conjugated blocks and propyl nonconjugated blocks.[18] In a view to improve on the threshold voltage of EL device, we report the synthesis and properties of two classes of rigid-flexible PPV based CNCPs. The rigid segments are conjugated chromophores comprising of 2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene (MEHPV) and 2,5-dimethyl-1,4-phenylenevinylene (DMPV) moieties and flexible portion containing aliphatic nonconjugated hexyl units. The effect of substituents in the chromophore unit on optical and redox properties has been investigated. Color tuning has been achieved by varying comonomer feed ratio. PL quantum yield of the selected polymers has also been measured. The electroluminescent diodes were fabricated utilizing selected polymers. The EL properties and the characteristics of the devices have been measured and their results are discussed.

EXPERIMENTAL

Reagents

All the solvents were purified according to reported procedure.[24] All other chemicals were of analytical-reagent grade and used without further purification. The reactions were performed under a dry nitrogen atmosphere and the synthesized products were stored under nitrogen before use.

Characterization techniques

Thin-layer chromatography was performed with Merck silica gel 60 F254 aluminum sheets. Melting points were recorded on an S. D. Fines melting point apparatus and reported uncorrected. Elemental analysis was carried out using PerkinElmer CHNS analyzer. Fourier transform infrared (FTIR) spectra were obtained from a PerkinElmer 1600 series FTIR spectrophotometer with KBr pellets, where the percentage of transmittance versus wave number (cm^{-1}) was plotted. ^{1}H-NMR spectra were obtained using a Brucker 500 MHz FT-NMR spectrophotometer with chloroform-d and dimethylsulfoxide-d_6 (DMSO-d_6) as solvent. Chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. Gel permeation chromatography (GPC) was used to determine molecular weights of polymers with tetrahydrofuran (THF) as solvent and polystyrene as standard on a Waters GPC system. UV-Visible spectrum was taken on a Carry 500 Scan ultraviolet-Visible/near-infrared Spectrophotometer. PL spectra were obtained on a Flurolog Jobin spectrophotometer (Yvon-Horiba, model-3-11). Photoluminescence quantum yields of the polymer film coated on quartz plate were determined using an integrated sphere meant for quantum yield study. Thermo gravimetric analysis (TGA; Hi Res TGA 2950, TA Instruments) of the samples were carried out at a heating rate of 20°C/min in N_2 atmosphere. Cyclic voltammetry (CV) measurement was performed using an AUTOLAB potentiostat under argon atmosphere. Platinum plate coated with polymer film was used as working electrode. Platinum mesh electrode was used as counter electrode and Ag/AgCl electrode was used as reference. The films on the working electrode were prepared by dipping the platinum plate into a concentrated polymer solution in chloroform and drying in vacuum for several hours. CV measurements were performed in an electrolyte solution of 0.1 M tetraethylammonium tetrafluroborate (Et_4NBF_4) in acetonitrile.

EL device fabrication

The device was fabricated on the ITO substrate by a vacuum deposition method. The indium tin oxide (ITO) coated glass substrate was patterned by photolithographic technique and was cleaned following a chemical cleaning process with soap solution, followed by boiling in trichloroethylene and isopropyl alcohol and finally dried under vacuum. The cleaned and dried ITO substrate was Plasma treated for enhancing the work function of ITO electrode before PEDOT: PSS treatment. The double-layer LED with a configuration of ITO/PEDOT: PSS/emitting polymer/LiF/Al was fabricated by spin-coating the filtered polymer solution in chlorobenzene with a concentration of 8 mg/mL on the PEDOT: PSS pretreated ITO substrate. Then a thin buffer layer of LiF covered with a layer of aluminum was deposited as a cathode by thermal evaporation at a pressure below 10^{-6} Torr. The active area of the device was 4 mm^2. All fabrications were carried out inside glove box. The electrical measurement was done in the ambient atmosphere. The EL was recorded by using HR 2000 Ocean Optics Spectrometer, having a CCD array and fiber optic probe. The current-voltage characteristics were studied using a Keithley 617 electrometer interfaced with a PC. Voltage-luminescence characteristic of a representative polymer (CNCP10) was investigated using luminescence meter (LMT L1009).

Monomer synthesis

[(2,5-Bis(methyl)-1,4-xylene]bis(triphenylphosphonium chloride) (B1)

This compound was synthesized according to literature procedure.[25] All physical and spectral properties were in accordance with published values.

[(2-Ethylhexyloxy)-5-methoxy-1,4-xylene]bis (triphenylphosphonium bromide) (B2)

A solution of 4.3 g (10 mmol) of 2-ethylhexyloxy-5-methoxy-1,4-bis (bromomethyl)benzene and 7.8 g (30 mmol) of triphenylphosphine in 50 mL of toluene was stirred and heated to reflux for 24 h. The precipitate formed was collected by filtration and washed several times with diethyl ether. Finally after vacuum drying, the B2 was obtained as white powder. *Yield.* 65%. M.P: 213°C. ^{1}H-NMR (DMSO-d_6, ppm, δ): 7.91-7.51 (m, 30H, Ar-H), 6.72 (s, 1H, Ar-H), 6.50 (s, 1H, Ar-H), 5.06 (d, 2H, —CH$_2$P—), 4.95 (d, 2H, —CH$_2$P—), 2.90 (s, 2H, —OCH$_2$—), 2.79 (s, 3H, —OCH$_3$), 1.30-0.95 (m, 9H, —CH$_2$—, —CH), 0.82 (t, 3H, —CH$_3$), 0.69 (t, 3H, —CH$_3$). Elem. Anal. Calcd. for: C, 67.08%; H, 6.12%. Found: C, 66.32%; H, 5.91%.

(1,6-Bis(4-formylphenoxy)hexane) (D1)

6.1 g (25 mmol) of 1,6-dibromohexane was added dropwise to a solution of 6.1 g (50 mmol) of 4-hydroxybenzaldehyde and 10.5 g (75 mmol) of anhydrous potassium carbonate in 100 mL dry DMF with stirring and then heated to reflux under nitrogen for 24 h. The reaction mixture was cooled to room temperature and then poured in to ice water. The product precipitated was filtered and recrystallized twice from 100 mL of ethanol: chloroform (9 : 1 v/v) mixture to obtained pure white crystals. *Yield.* 87%. M.P: 110°C-120°C. ^{1}H-NMR (DMSO-d_6, ppm, δ): 9.85 (s, 2H, —CHO), 7.85 (d, 4H, Ar-H), 7.11 (d, 4H, Ar-H), 3.35 (s, Solvent), 2.5 (t, 4H, —OCH$_2$), 1.76 (q, 4H, —CH$_2$—), 1.44 (m, 4H, —CH$_2$—). Elem. Anal. Calcd. For: C, 73.59%; H, 6.79%. Found: C, 73.68%; H, 6.69%.

(1,6-Bis(4-formyl-2-methoxyphenoxy)hexane) (D2)

6.1 g (25 mmol) of 1,6-dibromohexane was added dropwise to a solution of 7.61 g (50 mmol) of 4-hydroxy-3-methoxybenzaldehyde and 10.5 g (75 mmol) of anhydrous potassium carbonate in 100 mL dry DMF with stirring and then heated to reflux under nitrogen for 24 h. The reaction mixture was cooled to room temperature and then poured in to ice water. The precipitate formed was filtered and recrystallized twice from 100 mL of ethanol: chloroform (9 : 1/v:v) mixture to obtained pure compound. *Yield.* 90%. M.P: 150°C-160°C. ^{1}H-NMR (CDCl$_3$, ppm, δ): 9.87 (s, 2H, —CHO), 7.45 (m, 4H, Ar-H), 7.00 (d, 2H, Ar-H), 4.15 (t, 4H, —OCH$_2$—), 3.95 (s, 6H, —OCH$_3$), 1.96 (q, 4H, —CH$_2$—), 1.60 (m, 4H, —CH$_2$—). Elem. Anal. Calcd. For: C, 68.37%; H, 6.78%. Found: C, 67.94%; H, 6.59%.

General procedure for polymerization

A solution of *t*-BuOK in anhydrous ethanol (3 *M* excess) was added dropwise to an equimolar mixture of dialdehyde and bisphosphonium salt in 40 mL anhydrous ethanol and chloroform (3/1) (v/v) at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 24 h. The reaction was quenched with 2% aq. HCl and stirred for 30 min. The organic layer was washed with 40 mL ethanol/water (3/1) (v/v) to remove the triphenylphosphine oxide and sodium salt. Solvent was removed under reduced pressure. The polymer was then dissolved in dry toluene containing a catalytic amount (5 mg per mol equiv of polymer) of iodine and the mixture was refluxed overnight. The solution was cooled, the solvent was evaporated and the residue was dissolved in chloroform. The polymer solution was concentrated and was added dropwise to a rapidly stirring methanol to precipitate. The resulting polymer was purified by Soxhlet extraction with methanol to remove byproduct and small molecules. The polymer was dissolved in chloroform, reprecipitated in methanol, and the process was repeated for three times. Finally the polymer was dried under vacuum at 40°C to obtain a yellow fibrous polymer. Polymer yields typically ranged from 40 to 60%. The feed compositions of CNCPs are summarized in Table I.

Polymer 1 (CNCP1)

^{1}H-NMR (CDCl$_3$, ppm, δ): 7.86-6.77 (m, 14H, Ar H, —CH=CH—), 4.09-4.01 (t, 4H, —OCH$_2$—), 2.47-1.55 (m, 14H, Ar-CH$_3$, —CH$_2$—). FTIR (KBr pellets): 964 cm^{-1} (*trans*-HC=CH—).

Polymer 2 (CNCP2)

^{1}H-NMR (CDCl$_3$, ppm, δ): 7.85-6.62 (m, 14H, Ar-H, —CH=CH—), 4.10-3.89 (m, 5H, —OCH$_2$—, —OCH$_3$), 2.45-1.08 (m, 15.8H, Ar-CH$_3$, —CH—, —CH$_2$—, —CH$_3$). FTIR (KBr pellets): 961 cm^{-1} (*trans*-HC=CH—).

Polymer 3 (CNCP3)

^{1}H-NMR (CDCl$_3$, ppm, δ): 7.86-6.72 (m, 14H, Ar-H, —CH=CH—), 4.10-3.91 (m, 6.5H, —OCH$_2$—, —OCH$_3$), 2.40-1.00 (m, 18.5H, Ar-CH$_3$, —CH—, —CH$_2$—, —CH$_3$). FTIR (KBr pellets): 964 cm^{-1} (*trans*-HC=CH—).

Polymer 4 (CNCP4)

^{1}H-NMR (CDCl$_3$, ppm, δ): 7.86-6.71 (m, 14H, Ar-H, —CH=CH—), 4.10-3.94 (m, 8H, —OCH$_2$—, —OCH$_3$),

TABLE I
Feed Composition of the Comonomers[a]

Polymers	Comonomer (D1) gram/(molar %)	Comonomer (B1) gram/(molar %)	Comonomer (B2) gram/(molar %)	Yield (%)
CNCP1	0.49 g (100)	1.1 g (100)	0.0 g	40
CNCP2	0.49 g (100)	0.87 g (80)	0.28 g (20)	44
CNCP3	0.49 g (100)	0.55 g (50)	0.71 g (50)	48
CNCP4	0.49 g (100)	0.22 g (20)	1.14 g (80)	52
CNCP5	0.49 g (100)	0.0 g	1.42 g (100)	55
Polymers	Comonomer (D2) gram/(molar %)	Comonomer (B1) gram/(molar %)	Comonomer (B2) gram/(molar %)	Yield (%)
CNCP6	0.58 g (100)	1.1 g (100)	0.0 g	42
CNCP7	0.58 g (100)	0.87 g (80)	0.28 g (20)	45
CNCP8	0.58 g (100)	0.55 g (50)	0.71 g (50)	52
CNCP9	0.58 g (100)	0.22 g (20)	1.14 g (80)	55
CNCP10	0.58 g (100)	0.0 g	1.42 g (100)	60

[a] In terms of the weight and mole % (given in parenthesis) and yield % of the polymers.

2.45-0.90 (m, 21.2H, Ar-CH$_3$, —CH—, —CH$_2$—, —CH$_3$). FTIR (KBr pellets): 963 cm^{-1} (*trans*-HC=CH—).

Polymer 5 (CNCP5)

^{1}H-NMR (CDCl$_3$, ppm, δ): 7.68-6.77 (m, 14H, Ar H, —CH=CH—), 4.02-3.50 (m, 9H, —OCH$_2$—, —OCH$_3$), 2.27-2.22 (m, 1H, —CH—), 1.83-1.29 (m, 16H, —CH$_2$—), 1.03-0.82 (t, 6H, —CH$_3$). FTIR (KBr pellets): 966cm^{-1} (*trans*-HC=CH—).

Polymer 6 (CNCP6)

^{1}H-NMR (CDCl$_3$, ppm, δ): 7.73-6.89 (m, 12H, Ar-H, —CH=CH—), 4.07-3.56 (m, 10H, —OCH$_2$—, —OCH$_3$), 2.45 (s, 6H, Ar-CH$_3$), 1.97-1.27 (m, 8H, —CH$_2$—). FTIR (KBr pellets): 967 cm^{-1} (*trans*-HC=CH—).

Polymer 7 (CNCP7)

^{1}H-NMR (CDCl$_3$, ppm, δ): 7.45-6.72 (m, 12H, Ar-H, —CH=CH—), 4.14-3.51 (m, 11H, —OCH$_2$—, —OCH$_3$), 2.45-0.89 (m, 15.8H, Ar-CH$_3$, —CH—, —CH$_2$—, —CH$_3$). FTIR (KBr pellets):964 cm^{-1} (*trans*-HC=CH—).

Polymer 8 (CNCP8)

^{1}H-NMR (CDCl$_3$, ppm, δ): 7.45-6.72 (m, 12H, Ar-H, —CH=CH—), 4.14-3.51 (m, 12.5H, —OCH$_2$—, —OCH$_3$), 2.45-0.89 (m, 18.5H, Ar-CH$_3$, —CH—, —CH$_2$—, —CH$_3$). FTIR (KBr pellets): 962 cm^{-1} (*trans*-HC=CH—).

Polymer 9 (CNCP9)

^{1}H-NMR (CDCl$_3$, ppm, δ): 7.46-6.75 (m, 12H, Ar-H, —CH=CH—), 4.15-3.51 (m, 14H, —OCH$_2$—, —OCH$_3$),

2.45-0.83 (m, 21.2H, Ar-CH$_3$, —CH—, —CH$_2$—, —CH$_3$). FTIR (KBr pellets): 966 cm^{-1} (*trans*-HC=CH—).

Polymer 10 (CNCP10)

^{1}H-NMR (CDCl$_3$, ppm, δ): 7.68-6.77 (m, 14H, Ar-H, —CH=CH—), 4.02-3.50 (m, 15H, —OCH$_2$—, —OCH$_3$), 2.25-2.22 (m, 1H, —CH—), 1.83-1.29 (m, 16H, —CH$_2$—), 1.03-0.80 (t, 6H, —CH$_3$). FTIR (KBr pellets): 965 cm^{-1} (*trans*-HC=CH—).

RESULTS AND DISCUSSION

Equimolar ratio of bisphosphonium salt and dialdehyde monomer synthesized as depicted in Scheme 1, has been used for synthesis of CNCP1-CNCP10 by adopting Wittig condensation method (Scheme 2). The composition of the copolymers was varied by changing the molar ratio of the bisphosphonium salts (Table I). The initial polymer, which contains a mixture of *cis*- and *trans*-olefin isomers, was then isomerized to the *trans* configuration by refluxing in toluene in the presence of catalytic amount of iodine.
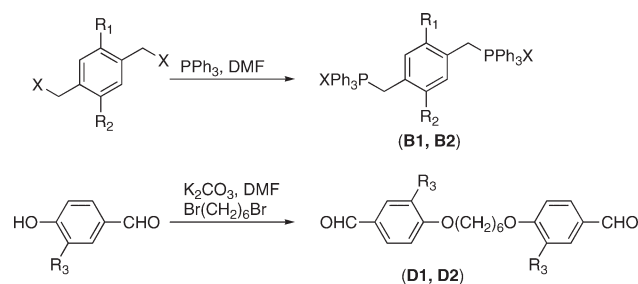
Where:
B1. R$_1$=R$_2$=Me, X=Cl, B2. R$_1$=OMe, R$_2$=OC$_8$H$_{17}$, X=Br and D1. R$_3$=H D2. R$_3$=OMe

Scheme 1 Synthetic route for monomers.
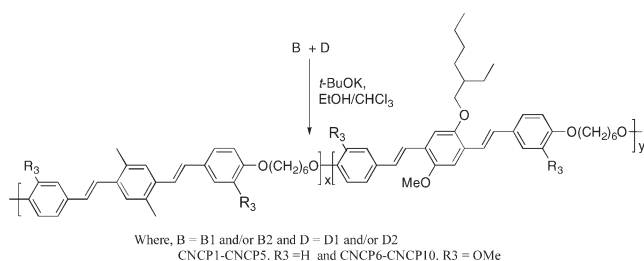
Scheme 2 Synthetic route for polymers (a) CNCP1-CNCP5 and (b) CNCP1-CNCP10.

The isomerized polymers were purified by multiple precipitations into methanol. The polymers synthesized were soluble in common organic solvents such as chloroform, tetrahydrofuran and chlorobenzene. The use of phenylenevinylene derivatives with asymmetric and branched substituents, 2-ethylhexyloxy, facilitates easy solubility. Good-quality polymer thin films could be obtained by spin coating the filtered polymer solution without any further thermal processes.

Characterization

The chemical structure of resulting copolymers was identified by FTIR and ^{1}H-NMR spectroscopy and the results were introduced in experimental section. The polymers showed peaks between 961 and 967 cm^{-1}, which corresponds to the out-of-plane bending mode of the *trans*-vinylene group. From the ^{1}H-NMR results it is observed that the vinylic and aromatic protons showed peaks between 6.62 and 7.86 ppm. This indicates that the newly formed vinylene bonds are mainly of *trans* configuration. FTIR and ^{1}H-NMR spectra revealed trace of carbonyl functionalities in these polymers, presumably due to the aldehyde end groups.

The weight average molecular weight (M_w) and polydispersity of the polymers obtained from GPC measurement are shown in Table II. From the results it is seen that the series of polymers (CNCP1-CNCP5) obtained by varying the DMPV and MEHPV fraction with respect to the dialdehyde D1 have M_w in the range of 5000-46,000. With increase in MEHPV content the M_w seems to increase monotonously. However, no particular trend in the molecular weight distribution, as reflected in the polydispersity values was observed. Similar trend of increasing M_w with increase in MEHPV fraction was observed in the second series of polymers CNCP6-CNCP10, obtained by varying the DMPV and MEHPV fraction with respect to dialdehyde D2. Molecular weight distributions are rather broad because of the limitation of the Wittig condensation.[26] It has also seen that DMPV rich polymers are basically oligomers. The relative lower molecular weight of DMPV rich polymers compared to MEHPV rich

polymers could be due to early precipitation in the polymerization solvents. Normally, when the polymer is not soluble in the medium, Wittig polycondensation yields polymer with lower molecular weights.[27] Formation of oligomers by Wittig polycondensation was also reported by Jung et al.[28] Higher molecular weight in case of polymers containing higher fraction of MEHPV moiety is accounted for by the presence of asymmetric and branched substituent, 2-ethylhexyloxy, which facilitates easy solubility in the polymerization solvents.

Thermal properties

TGA thermograms of the two series of polymers are presented in Figure 1. From the thermograms it is seen that CNCP4, CNCP5, CNCP9, and CNCP10 have distinctly higher thermal stability compared to the rest of the polymers. CNCP4 and CNCP5 correspond to the polymer having 80 and 100% MEHPV fraction with respect to dialdehyde D1. CNCP9 and CNCP10 correspond to polymers having MEHPV fraction 80 and 100% with respect to dialdehyde D2. This implies that higher MEHPV content imparts greater thermal stability to the polymers compared to DMPV fractions. As of the effect of dialdehyde type on thermal stability we observe that the decomposition temperature at 5% weight loss for CNCP5 is 331°C and that for CNCP10 is 390°C (Table II). It implies that methoxy-substituted dialdehyde (D2) imparts more thermal stability compared to D1.

Optical properties

Solution optical properties

The UV-Vis absorption spectra of the two series of polymers are represented in Figure 2. The relevant maxima are listed in Table III. Both the series of

TABLE II
Molecular Weight, Polydispersity Index (P_d), and Decomposition Temperature of Copolymers

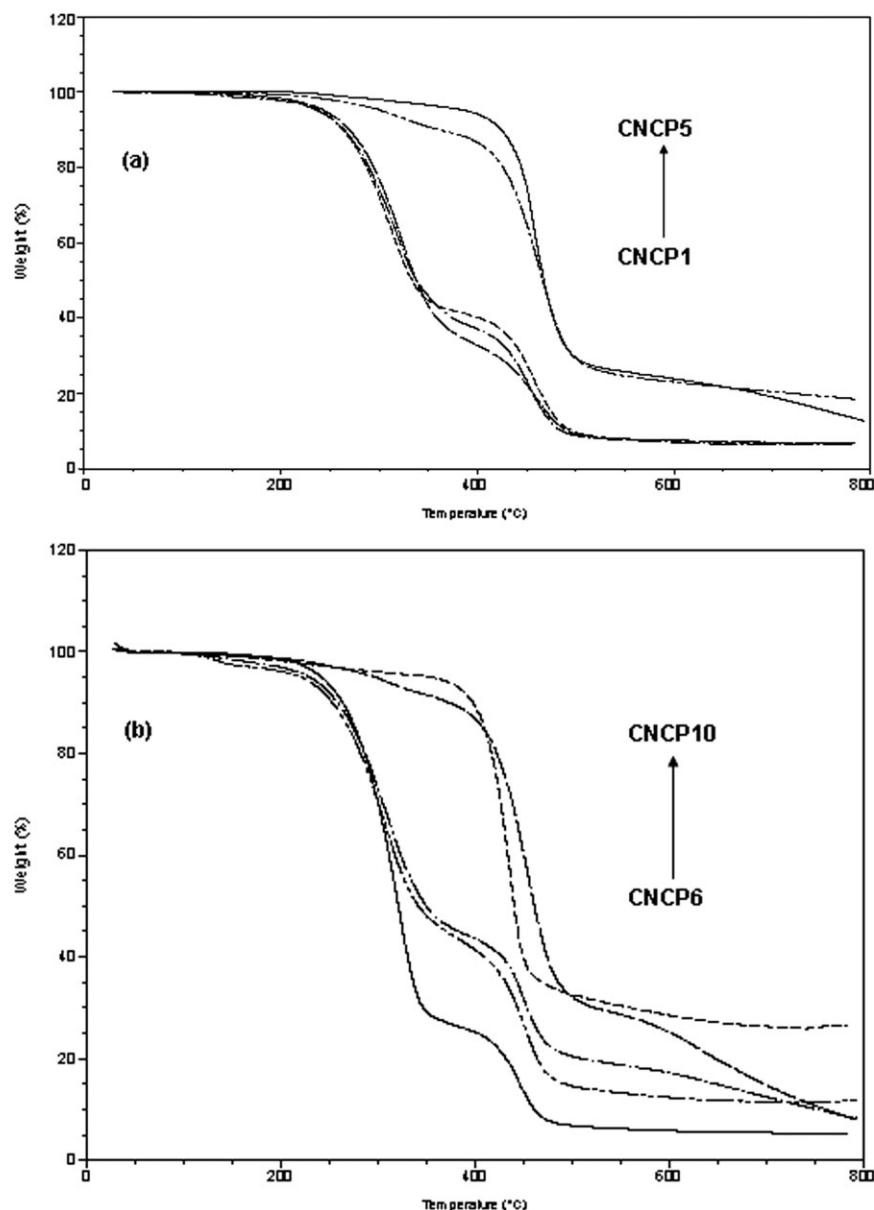| Polymers	M_w	P_d	Decomposition temperature (°C)	
			5 % weight loss	10 % weight loss
CNCP1	5050	2.1	220	253
CNCP2	5300	3.5	230	259
CNCP3	5700	2.4	243	268
CNCP4	12,800	3.3	280	348
CNCP5	46,200	2.6	331	396
CNCP6	5900	2.6	238	263
CNCP7	6250	3.4	240	265
CNCP8	6500	3.2	272	336
CNCP9	15,700	2.7	305	362
CNCP10	48,400	2.4	390	425

Figure 1 TGA trace of (a) CNCP1-CNCP5 and (b) CNCP6-CNCP10.

copolymers (CNCP1-CNCP5 and CNCP6-CNCP10) show monotonic red shift with increase in MEHPV content. For CNCP1-CNCP5, absorption maxima are in the range of 315–385 nm whereas for CNCP6-CNCP10, the absorption maxima are in the range of 320–395 nm. Comparison of the two series shows that methoxy substituted systems show a higher red shift. This shift in absorption maxima is due to comparatively higher electron donating effect of alkoxy groups.

The PL spectra of the copolymers were recorded for the polymers with an excitation wavelength corresponding to the absorption maxima. The emission spectrum follows the similar trend as the absorption spectrum in dilute solutions. The emission spectra of a few representative copolymers in chloroform are shown Figure 3(a). From the results it is seen that CNCP1 (D1 + B1) shows an emission maxima at 423 nm. A red shift is observed for CNCP6 (D2 + B1) system at an emission maximum of 458 nm. This could be attributed to the higher electron donating effect of the methoxy substituent in D2. CNCP5 (D1 + B2) and CNCP10 (D2 + B2) show emission maxima at 448 and 483 nm respectively. Thus a pronounced red shift of 25 nm is observed for this pair of polymers compared to CNCP1 and CNCP6. It could be because of the higher concentration of more electron donating methoxy group, leading to a higher increase in the HOMO level and consequently a red shift in emission. The emission maxima for the polymers CNCP1-CNCP10 in chloroform are summarized in Table III.
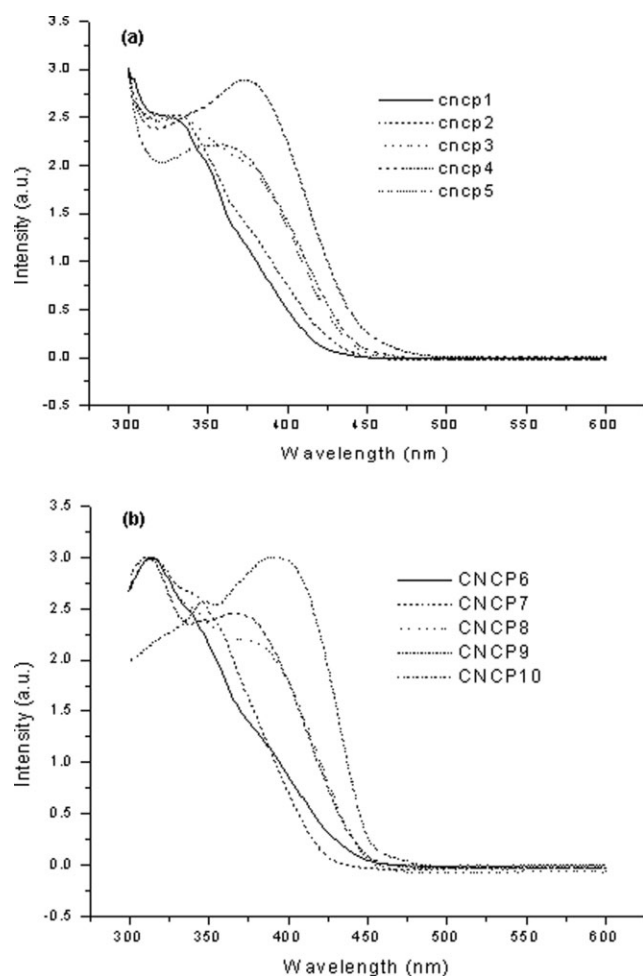
Figure 2 Absorption spectra of (a) CNCP1-CNCP5 and (b) CNCP6-CNCP10 in dilute chloroform solution (normalized).

Solid film optical properties

The absorption spectra of few representative copolymers CNCP1, CNCP5, CNCP6, and CNCP10 in solid films are shown in Figure 3(b). From the figure it was seen that absorption peak for solid films is characteristically broader compared to solution spectra.

The absorption peak of CNCP1 and CNCP5 in solid films are at 312 and 385 nm respectively. Whereas for CNCP6 and CNCP10, the absorption peaks are at 318 and 392 nm respectively. This hypsochromic shift in absorption spectra of solid films compared to solution absorption spectra could be due to the existence of solid-state aggregation.[29] The summary of absorption peak of polymer films is listed in Table III.

Figure 4 depicts the PL spectra of polymers CNCP1-CNCP5 and CNCP6-CNCP10 in solid films respectively. The corresponding emission maxima are listed in Table III. The emissions in the solid state are red-shifted relative to those of solution state. These shifts are due to intermolecular π-π interaction of the chromophores.[30] For CNCP1-CNCP5, emission maxima are in the range of 494–508 nm whereas for CNCP6-CNCP10, the emission maxima are in the range of 499–536 nm. The emission spectra of 100% MEHPV containing polymers (CNCP5 and CNCP10) exhibits emission peak at 508 and 536 nm respectively. Whereas the emission peak for 100% DMPV containing polymers (CNCP1 and CNCP6) is at 494 and 499 nm respectively. This bathochromic shift of 100% MEHPV containing polymers compared to 100% DMPV-containing polymers is due to the more electron-donating effect of alkoxy groups (methoxy and 2-ethylhexyloxy) present in MEHPV moiety than less electron-donating effect of methyl groups present in DMPV moiety. All the polymers show their emission in blue or blue-green region, but the changes of the emission maxima of the polymers are not so large as the absorption maxima in the absorption spectra. Red shifts of the emission maxima from the absorption maxima for all polymers mean the optical transitions between the subbands inside the π-π* optical gap.

The polymers, named CNCP1, CNCP5, CNCP6, and CNCP10 were taken for their quantum efficiency study. Using an integrated sphere meant for fluorescent quantum efficiency study, their quantum

TABLE III
Optical Properties of Copolymers

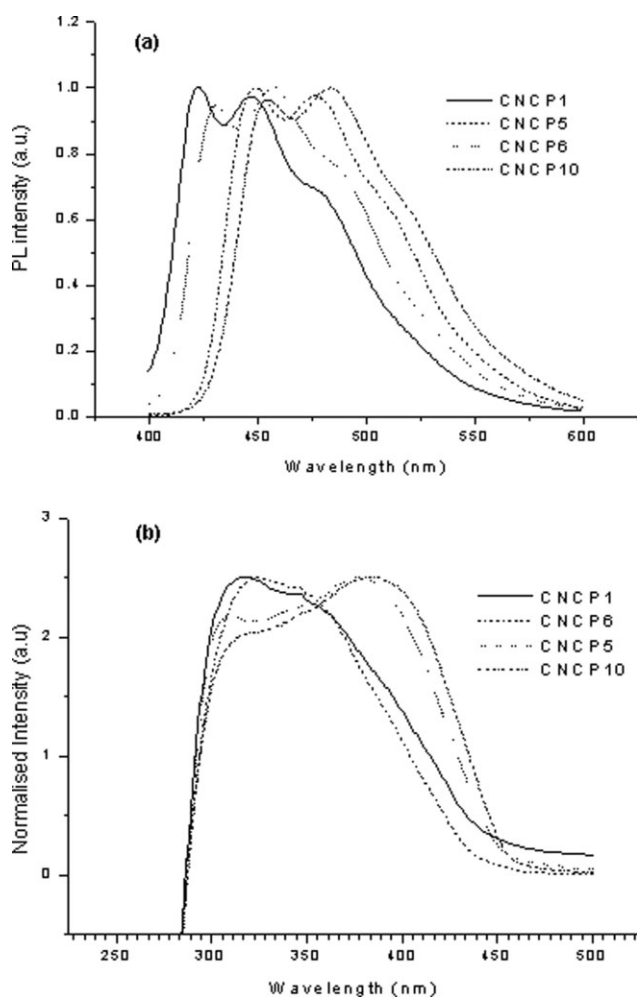| Polymer	λ_{max} (nm) absorption (solution)	λ_{max} (nm) absorption (film)	λ_{max} (nm) emission (solution)	λ_{max} (nm) emission (film)	Absorption edge (nm)	PL quantum yield (%)
CNCP1	314	312	423	494	428	42
CNCP2	331	330	430	496	432	–
CNCP3	333	333	432	499	439	–
CNCP4	355	350	445	502	446	–
CNCP5	385	385	449	508	456	50
CNCP6	321	318	458	499	431	45
CNCP7	325	325	460	500	428	–
CNCP8	351	350	464	502	435	–
CNCP9	365	370	472	506	442	–
CNCP10	395	392	483	536	460	53

Figure 3 PL spectra for (a) CNCP1, CNCP5, CNCP6, and CNCP10 in chloroform (normalized) and absorption spectra for (b) CNCP1, CNCP5, CNCP6, and CNCP10 films coated on quartz plate (normalized).

yield in solid state was carried out using the formula mentioned below.

The quantum yield,

$$\phi = \frac{E_i(\lambda) - (1 - A)\, E_0(\lambda)}{L_e(\lambda)\, A}$$

where $E_i(\lambda) = $ the integrated luminescence of the film caused by direct excitation.

$E_0(\lambda) = $ the integrated luminescence of the film caused by indirect illumination from the sphere.

$L_e(\lambda) = $ The integrated excitation profile from an empty integrated sphere (without the sample).

$\lambda = $ Wavelength.

Absorbance,

$$A = \frac{L_0(\lambda) - L_i(\lambda)}{L_0(\lambda)}$$

where $L_0(\lambda) = $ The integrated excitation profile when the sample is diffusely illuminated by the integrated sphere's surface.

$L_i(\lambda) = $ The integrated excitation profile when the sample is directly excited by the incident beam.

The photoluminescence quantum yields were obtained from three independent experiments and the average of the results are listed in Table III. The results are found to be in the same range as for other reported PPV based CNCPs.[31] The PL quantum yields of CNCP1 and CNCP6 are lower than that of CNCP5 and CNCP10. This could be attributed to the torsional twist in the chain by the methyl group, resulting in reduced planarity and less π-delocalization of the conjugated system.[32]

Electrochemical properties

The cyclic voltammetry (CV) measurement was carried out to employ the electrochemical properties of the polymers. The oxidation process corresponds to the removal of electrons from the highest occupied molecular orbital (HOMO), where as the reduction cycle corresponds to the filling by electrons of the lowest unoccupied molecular orbital (LUMO).
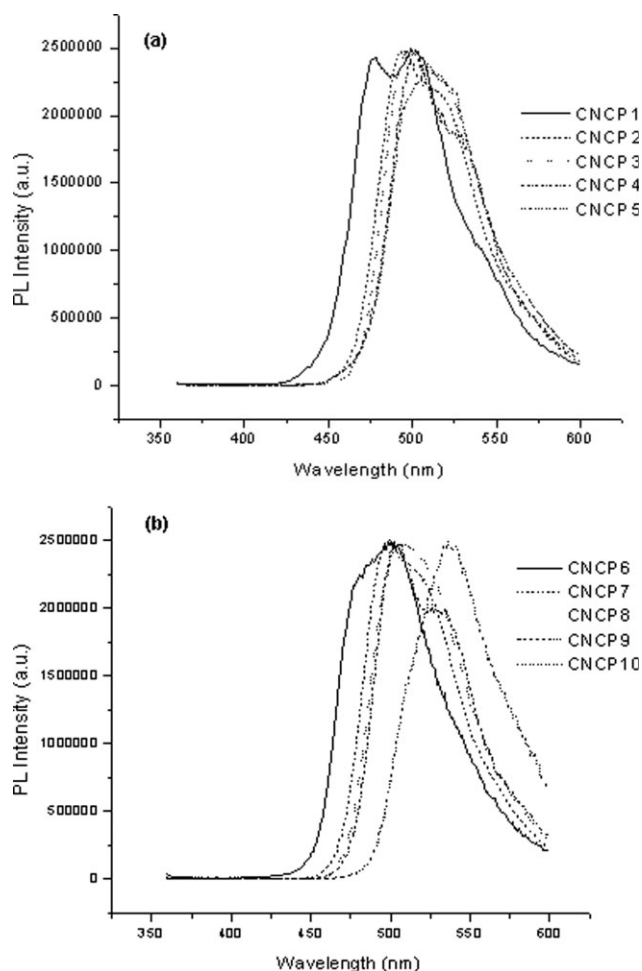

Figure 4 PL spectra of (a) polymers CNCP1-CNCP5 and (b) polymers CNCP6-CNCP10 in solid films (normalized).
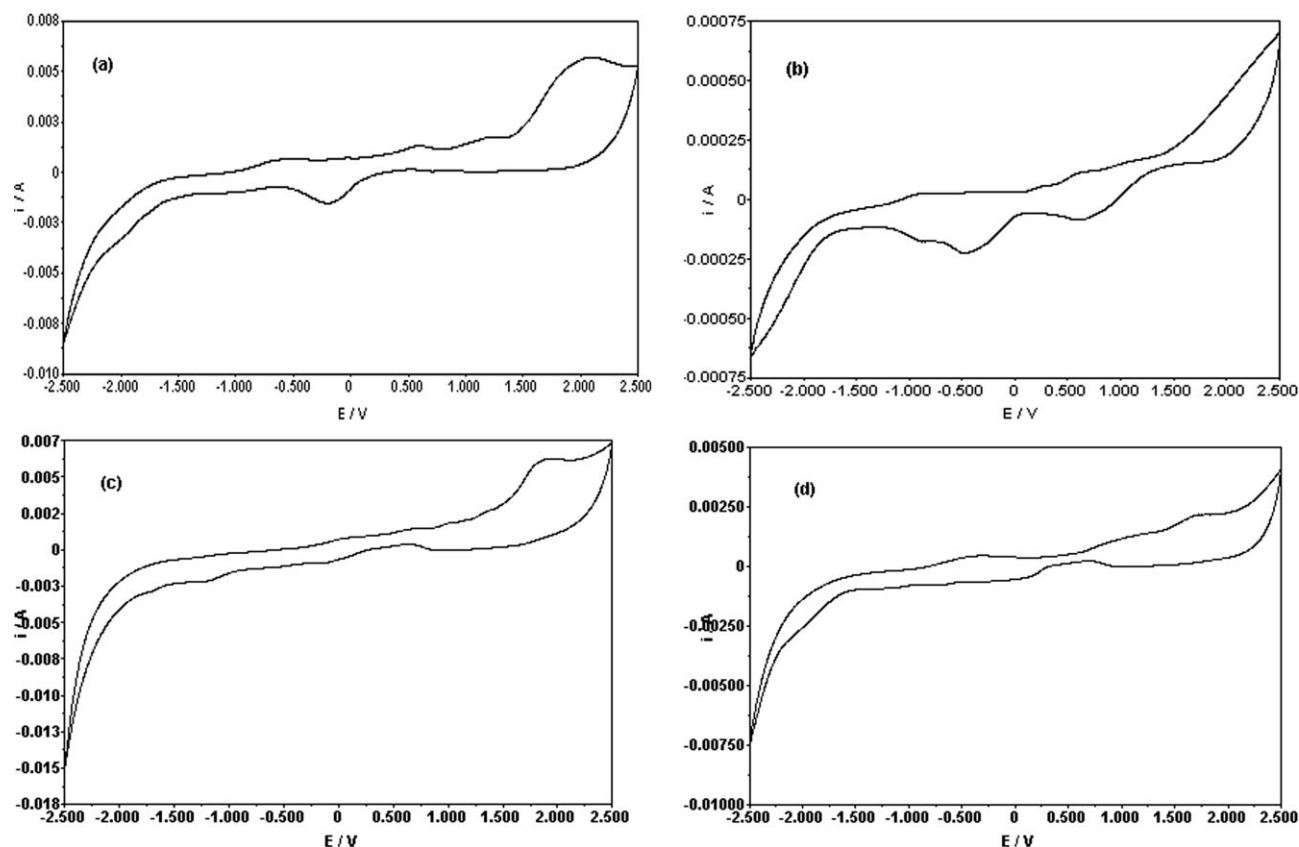
Figure 5 Cyclic voltammograms of CNCP1 (a), CNCP5 (b), CNCP6 (c), and CNCP10 (d).

Therefore, the onset oxidation and reduction potentials are closely related to the energies of the HOMO and LUMO levels of an organic molecule and thus can provide important information regarding the magnitude of the energy gap.

For comparison, the CV measurements of CNCP1, CNCP5, CNCP6, and CNCP10 were carried out at the same experimental conditions (scan rate, 50 mVs^{-1}) and their cyclic voltammograms are shown in Figure 5. The electrochemical band gaps ($E_{g(el)}$) obtained from the HOMO-LUMO energies are closer to those optical band gaps ($E_{g(op)}$) determined from the absorption edge of the solid state spectra.

HOMO and LUMO levels were derived from the onset oxidation potential and reduction potential respectively. They were measured by using an expical formula.[33]: HOMO = Ionization Potential (IP)(ev) = $E_{on(ox)}$ + 4.4 and LUMO = Electron Affinity (EA)(ev) = $E_{on(red)}$ + 4.4. The electrochemical prop-

erties are shown in Table IV. The onset oxidation potential of CNCP1 (D1 + B1) occurs at 1.40 V. However, the oxidation potentials for alkoxy substituted CNCP5 and CNCP10 are 1.09V, 1.06V, respectively, lower than that of CNCP1. This shows that alkoxy substituted polymers CNCP5 and CNCP10 have a ready hole injection ability than CNCP1, since the oxidation process is correlated with the removal of electrons (or hole injection) from the polymer at HOMO levels. The CV results indicate that the presence of more electron-donating alkoxy group compared to less electron-donating methyl group in polymers plays a dominating role in increasing its oxidation potential.

Electroluminescent properties

Polymer light emitting diode (PLED) with a configuration of ITO/PEDOT: PSS/emitting polymer/LiF/

TABLE IV
Electrochemical Properties of the Polymers

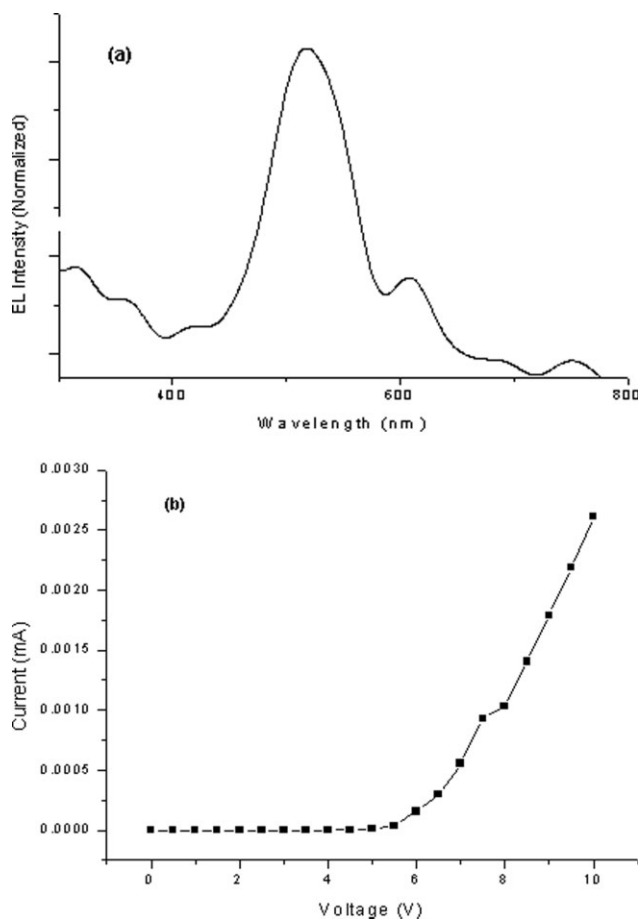| Polymer	$E_{on(red)}$ (V)	$E_{on(ox)}$ (V)	$E_{g(el)}$ (eV)	$E_{g(op)}$ (eV)	HOMO = IP (eV)	LUMO = EA (eV)
CNCP1	−1.62	1.40	3.02	2.90	5.8	2.78
CNCP5	−1.78	1.09	2.87	2.72	5.49	2.62
CNCP6	−1.72	1.21	2.93	2.88	5.61	2.68
CNCP10	−1.79	1.06	2.85	2.70	5.46	2.61

Figure 6 EL spectra of the ITO/PEDOT:PSS/CNCP5/LiF/Al device (a) and current-voltage characteristic of the ITO/PEDOT:PSS/CNCP5/LiF/Al (b).

Al was fabricated to investigate its electroluminescent characteristics. The concentration of the polymers in chlorobenzene solution was 8 mg/mL for all devices. A typical EL spectrum of CNCP5 is shown in Figure 6(a). The EL maxima are given in Table V. The polymers exhibit EL spectra similar to their PL counterpart, indicating that the same excited species (singlet excitons) are responsible for both processes. In the case of photoluminescence, the photoexcitation of the electron from HOMO to LUMO is known to generate a singlet exciton, which in turn decays radiatively with emission of light. The same species are formed in the case of EL, that is, the singlet excitons are formed in the polymer film by recombining the positive and negative polarons generated from the injected holes and electrons into the HOMO and the LUMO, respectively. The radiative decay from these singlet excitons is responsible for the EL.[34]

The forward bias current was obtained when the ITO is a positive electrode and the Al electrode is grounded. Figure 6(b) shows the current versus voltage characteristics of a typical CNCP (CNCP5). The forward current increases exponentially with the increasing forward bias voltage for all devices,

TABLE V
Characteristics of Devices Having Structure ITO/PEDOT: PSS/Polymer/LiF/Al

Polymer	Threshold voltage (V)	EL (nm)
CNCP1	6.2	499
CNCP5	5.8	508
CNCP6	6	503
CNCP10	5.4	536

which is a typical diode characteristic. The threshold voltages of the EL device from CNCP1, CNCP5, CNCP6, and CNCP10, were found to be 6.2, 5.8, 6, and 5.4 V respectively (Table V). These polymers show low threshold voltages in comparison with about 15–20 V of a dialkoxy-substituted PPV derivative (poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (PMEHPV) derivative.[18] The lower threshold voltage of the present systems is probably due to longer spacer length of the nonconjugated segment. The typical EL spectra and voltage-
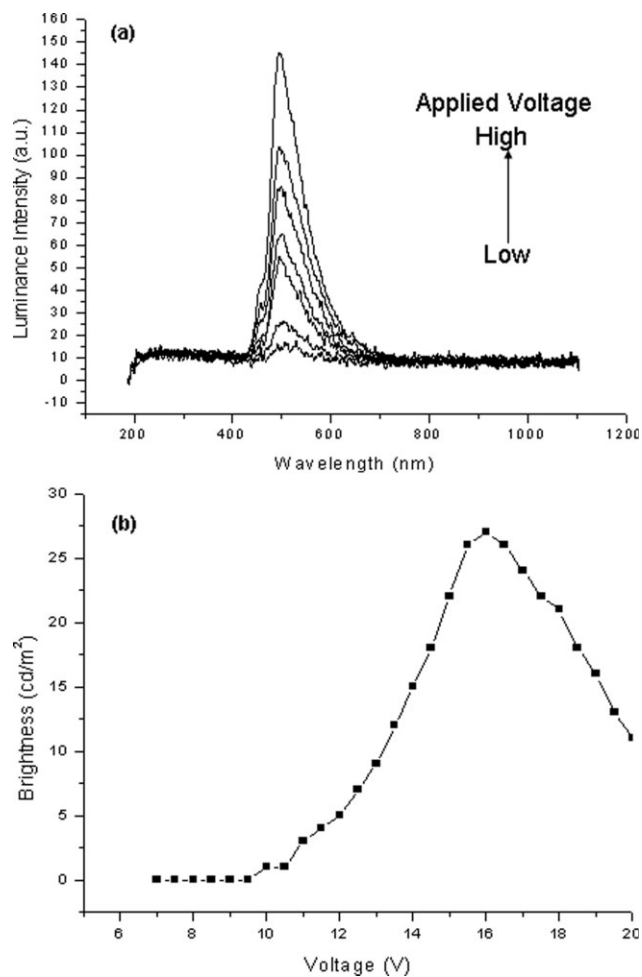

Figure 7 EL spectra of the ITO/PEDOT:PSS/CNCP10/LiF/Al device at varying forword applied bias voltage (a) and luminescence-voltage characteristic of the ITO/PEDOT:PSS/CNCP10/LiF/Al device (b).

luminescence curves for the ITO/PEDOT:PSS/ CNCP10/LiF/Al device is show in Figure 7. The device showed increase in brightness with increase in bias voltage. The characteristic shows highly nonlinear nature with ohmic conduction at low voltages and trap limited conduction at high voltages. The emission was uniform over the entire active area of the device pixel.

CONCLUSIONS

We have successfully synthesized and characterized two series of soluble PPV-based conjugated-nonconjugated copolymers (CNCPs) containing emitting MEHPV and 2,5-dimethyl-1,4-phenylenevinylene (DMPV) moieties in backbone through Wittig polymerization. They were designed by combining uniform conjugated units of specified length with intervening flexible-chain aliphatic oligomer segments. The present results confirm that it is possible to tune the color of the emission and improve physical properties by changing the substituents in the chromophore in an entirely systematic manner. We fabricated PLEDs in ITO/PEDOT:PSS/emitting polymer/cathode configuration with a bilayer LiF/Al, cathode structure. The threshold voltage is in the range of 5.4–6.2 V, which is considerably low compared with that of the PPV-based block copolymers. The introduction of the electron-donating alkyloxy substituents in the polymer backbone decreased the HOMO binding energy and thus decreased PLEDs threshold voltage.

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