Chemical Science Review and Letters ISSN 2278-6783

Research Article

Hole Mobility Studies on Dehydrodivanillin based New Blue-green Emitting Poly(p-phenylenevinylenes)

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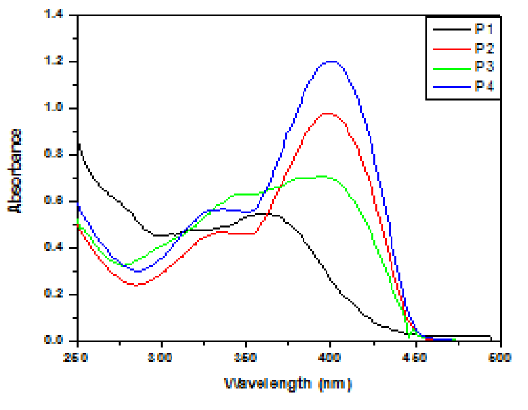
Abstract

New dehydrodivanillin based highly florescent blue-green emitting PPV oligomers have been synthesised and their hole mobilities were measured by fabricating the diode devices with structure Glass/ITO/oligomer/Al. These soluble materials have been fully characterized by UV, IR, thermal analysis, ^{1}H-NMR, ^{13}C-NMR and Raman spectroscopy. Their oligomeric characteristics have been assessed by MALDI-MS studies, while particle size measurements have been done using X-ray diffraction. The four oligomers are thermally stable and possess good film-forming properties. Their absorption spectra in the solution and thin film state show two strong absorptions at 200-240 and 400 nm while the emission spectra produced by excitation at 360 nm show λ_{max} at 450 nm and 500 nm, respectively. Diodes devices fabricated using these materials show low turn-on voltage (~1V) and hole mobility, assuming the hole current to be space-charge limited, in range of 10^{-3}-10^{-4} cm^{2}V^{-1}s^{-1}.



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Keywords: PPV oligomers, Hole Mobility, X-ray diffraction.

Introduction

In continuation of our work on use of natural products for electronic applications [1,2] we chose dehydrodivanillin (3, 3'-Diformyl- 6, 6'-dihydroxy-5, 5'-dimethoxybiphenyl), a commercially important molecule, as precursor to synthesise PPV oligomers. Conjugated organic materials have gained much importance over the years as semi-conducting materials due to their light weight, stability, ease of processing and color tunability through simple chemical modifications. They are used for photovoltaics, light-emitting devices (LEDs), as light-emitting electrochemical cells (LECs), field effect transistors (FETs), plastic lasers, batteries and sensors [3-8]. However, their limited self-luminescence restricts their use in large area display applications such as OLEDs. Poly(p-phenylenevinylene)s (PPVs) possessing good mechanical properties, high thermal stability in combination with good electrical conductivity have emerged as one of the most promising class of candidates for use as the active layer in devices [7,8]. Unsubstituted PPVs are commonly insoluble in nature which limits their use due to difficulties encountered in processability. To counter this problem introduction of alkyl side chain one of the method which is employed to improve their solubility as well as processability. Further, their elctronic structure and film morphology can be tuned by altering changes in their molecular structure, whereby not only the electroluminescent range but also the charge injection and transport properties of the active layer can be modified. For example, a biphenyl linkage introduced along the polymer backbone to enhance the exciton confinement also improves the morphology in the solid state by twisting the neighbouring chromophores onto different planes [9]. Such alterations for probing the structure-function properties can be accomplished using the ‘oligomer approach’ [10, 11]. Suitably functionalized oligomers, besides serving as model compounds, could also provide active new materials for various device applications. It has also been shown that low molecular weight PPVs show better structural order [12].

Recently, we have reported structural and electrical characterization of dehydrodivanillin, a natural product, which shows good hole mobility due to π-electron exchange between the two biphenyl rings [13]. In the present work, we report structural characterization, optical properties and hole mobility studies on four new PPV oligomers, synthesised using dehydrodivanillin, which emit in blue green region. To our knowledge, this is the first report describing the synthesis of conducting PPVs based on a natural product. The PPVs have been synthesised using Wittig-Horner procedure and hole mobility studies on thin films were carried out by fabricating Glass/ITO/PPV/Al devices. Also, hole mobility is another important criteria which determines the device performance [14]. The synthesis of PPV oligomers (P1-P4) using the new monomeric dialdehydes (1a-1d) is shown in **Figure 1**.

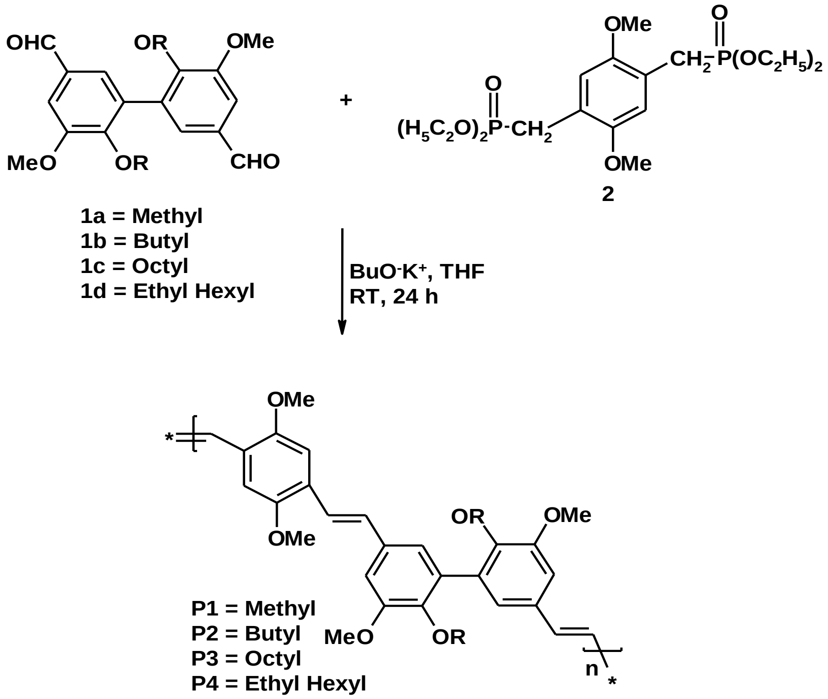


Figure 1 Synthesis of dehydrodivanillin based PPV’s

Experimental Section

The synthetic procedures described here were carried out in oven dried glassware. Chemicals and solvents, purchased from S.D. fine Chemicals, Sigma-Aldrich and Merck, were used without further purification. Optical measurements were made on a CARY-5E UV-Vis-NIR spectrophotometer in case the product being a film, and on a Hitachi AU-2700 spectrophotometer in the case of solution. IR spectra were recorded on Spectrum BX series spectrophotometer using KBr. NMR spectra were recorded on a Bruker 300 MHz instrument, using $CDCl_3$ as the solvent and TMS as the internal standard. TGA/DTA was done on a DTA-60 Shimadzu system at a heating rate of 20 ^{0}C min^{-1} in N_2 atmosphere. Differential scanning calorimetry (DSC) was performed under nitrogen atmosphere on Q200 instrument (TA waters Instrument, USA). X-Ray diffraction studies were performed on a Phillips X-ray diffractometer using $CuK_{\alpha 1}$ source, with typical scans in a 2d range of $\theta = 3^0–60^0$ with 0.05^0 increments. The wavelength of the incident beam is 1.5405 Å. For fluorescence measurements, a Biotek Synergy HP instrument was used, and photoluminescence (PL) experiments were performed on a Spex Flourlog F-112X instrument. Raman spectra were recorded on Renishaw FT-Raman instrument using the prepared materials in the form of compact disks. Mass spectra were recorded on Waters Microanalysis LCT Mass spectrometer (Model No. KC455) instrument and MALDI-MS was performed on a Shimadzu Biotech Axima-CFR Plus instrument using α-cyano-4-hydroxy cinnamic acid as matrix material.

General Procedure for Synthesis of oligomers (P1-P4):

A solution of dialdehyde (1a-d, 2 mmol) in anhydrous THF (5 mL) was added to a solution of the phosphonate derivative (2) (2 mmol) in THF (5 mL) under inert atmosphere. The solution was degassed at room temperature. To the stirred solution a degassed solution of *t*-BuO^-K^+ (6 mmol) in anhydrous THF (15mL) was added dropwise and the reddish reaction mixture stirred for 24 hr at room temperature. The reaction mixture was concentrated in vacuo and poured into methanol with stirring. The solid obtained was filtered, washed with water and methanol and dried under vacuum.

P1: yield 90.6 %; IR: 3424, 2937, 1687, 1583, 1498, 1463, 1413, 1266, 1141, 1046, 1003, 862, 818 cm^{-1}; ^{1}H-NMR: δ 3.6-3.9 (OCH_3), 5.1 (CH=CH), 6.9-7.6 (Ar-H), 9.9 (CHO); ^{13}C-NMR: 55.9, 60.5, 60.7, 84.19, 103.2, 111, 112.2, 112.6, 124.8, 130, 130.8, 131.9, 142.9, 147.5, 149.1, 152.1, 152.9 ppm
P2: yield 49.1%; IR: 3400, 3049, 2954, 2867, 1684, 1572, 1498, 1463, 1207, 1139, 1044, 961, 860 cm^{-1}; ^{1}H-NMR: δ 0.7-1.4 (alkyl chain), 3.8-4 (OCH_3), 4.6 (CH=CH), 6.8-7.7 (Ar-H); ^{13}C-NMR: 13.7, 18.8, 32.1, 56.0, 56.2, 68.7, 72, 109, 109.6, 112.9, 119.9, 122.2, 126.4, 128.8, 132.9, 146.1, 151.4, 153 ppm; DEPT-135: 13.7, 18.8 (down), 32.1 (down), 56 (up), 72 (down), 109.1, 109.6, 112.9, 120, 122.2, 128.5, 128.8 ppm
P3: yield 39 %; IR: 3435, 2926, 2852, 1685, 1574, 1500, 1464, 1408, 1252, 1143, 1046, 961, 865 cm^{-1}; ^{1}H-NMR: δ 0.82-1.85 (alkyl chain), 3.5-3.9 (OCH_3), 4.6 (CH=CH), 7.1-7.3 (Ar-H); ^{13}C-NMR: 14.2, 22.6, 25.8, 25.9, 29.3, 30.1, 31.8, 55.9, 73.3, 108.9, 109.3, 122.2, 126.4, 128.8, 132.9, 146, 151.4, 153 ppm; DEPT-135: 14.2, 22.6 (down), 25.8 (down), 25.9 (down), 29.3 (down), 30.1 (down), 31.8 (down), 55.9, 73.3, 108.9, 109.3, 122.2, 126.4, 128.8, 132.9, 146, 151.4, 153 ppm
P4: yield 37.1 %; IR: 3448, 2929, 1638, 1576, 1461, 1409, 1209, 1145, 1048, 962 cm^{-1}; ^{1}H-NMR: δ 0.7-1.37 (alkyl chain), 3.7-3.9 (OCH_3), 4.6 (CH=CH), 7-7.4 (Ar-H), 9.8 (CHO); ^{13}C-NMR: 10.7, 13.9, 22.7, 24.8, 28.7, 31.5, 39, 40, 55.7, 71.2, 114.6, 114.8, 115.4, 115.7, 116, 128.2, 149.6, 153.5 ppm DEPT-135: 10.8, 14, 22.8 (down), 25.1 (down), 28.8 (down), 31.6 (down), 39.1 (down), 41, 55.8, 71.3, 114.6, 114.8, 115.4, 115.7, 116, 128.2, 149.6, 153.5 ppm

Fabrication of devices

For device fabrication, indium tin oxide (ITO) coated glass substrates were thoroughly cleaned using the wet cleaning procedure. Thin films of the materials were prepared by spin-casting solutions containing 3 wt % of the oligomer in chlorobenzene on ITO coated glass. A typical film thickness was ~160 nm as determined by a Mickropack Nanocalc-2000 thin film reflectometer. Metallic electrode contacts were established by aluminum (~200 nm), which was formed by thermal evaporation of the metal in a vacuum coating unit, using a 2 x 10^{-6} mbar base pressure of the evaporation chamber and a deposition rate > 1 Å/s over the film through a shadow mask. The active area of the resulting devices was 0.04 cm^2. The samples, after deposition of the electrodes, were studied and kept under normal class 10000 clean room environmental conditions (temperature 25 ^{0}C and relative humidity ~ 45-50 %). Current-voltage (I-V) characteristics were recorded at ambient conditions using Keithley 2410 Sourcemeter.

Results and discussion

Synthesis and characterization of PPV

Dehydrodivanillin on alkylation yielded new alkoxy substituted derivatives, which were subjected to Wittig-Horner reaction with the diphosphonate derivative (monomer 2, Fig. 1), synthesised by bromomethylation of 1, 4-dimethoxybenzene followed by Arbuzov reaction [15]. Dehydrodivanillin, when used as dialdehyde, did not undergo any reaction as revealed by NMR spectroscopy. For emission in the blue region the most effective method is the shortening of conjugation length as it widens the band gap. The PPVs synthesised by us have short conjugation length and emit in the blue region of the visible spectrum, a property that is desirable especially for displays [16]. These materials are readily soluble in common organic solvents and their improved solubility is inferred due to the alkyl side chain (Table 1). Thermogravimetric analysis (TGA) shows that these materials possess good thermal stability and the weight loss is mainly due to loss of alkyl side chains corresponding to 65, 54 and 47% weight loss for P2, P3 and P4, respectively. The onset of decomposition temperatures indicates that the different side chains affect thermal stability to a considerable extent (Table 1). Even so, the thermal stability of these oligomers is enough for their use in electronic device applications. Melting temperatures (T_m) were determined by differential scanning calorimetry (Table 1, Fig. 2) and found to be in range of 57-113 ^{0}C. Molecular weights, as determined by MALDI-MS show values up to 10 kDa. The polydispersivities (PD) of these PPVs were found to be in the range 1.03-1.6 (Table 1). The low molecular weights are thought to be due to the steric hindrance in monomers. In spite of the low degree of polymerization, thin films were readily obtained from chloroform or chlorobenzene solutions.

Table 1 Solubility, thermal properties and molecular weight of the PPV oligomers

S.No.	Solubility^a	Thermal stability^b (^{0}C)	T_m^c (^{0}C)	P.D.^{d}
P1	partially soluble	--	88.2	1.04
P2	soluble	100	57.8	1.03
P3	soluble	260	65.6	1.04
P4	soluble	335	113.9	1.67

^{a}in chlorobenzene; ^{b}determined from TGA; ^{c}determined using DSC; ^{d}determined from MALDI-MS (M_w/M_n)

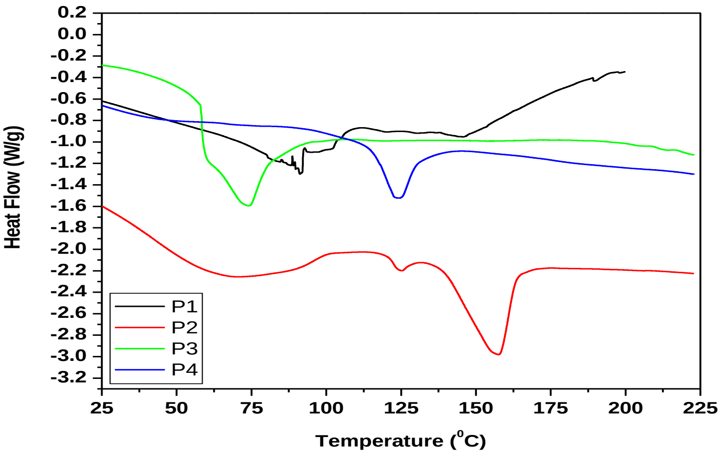
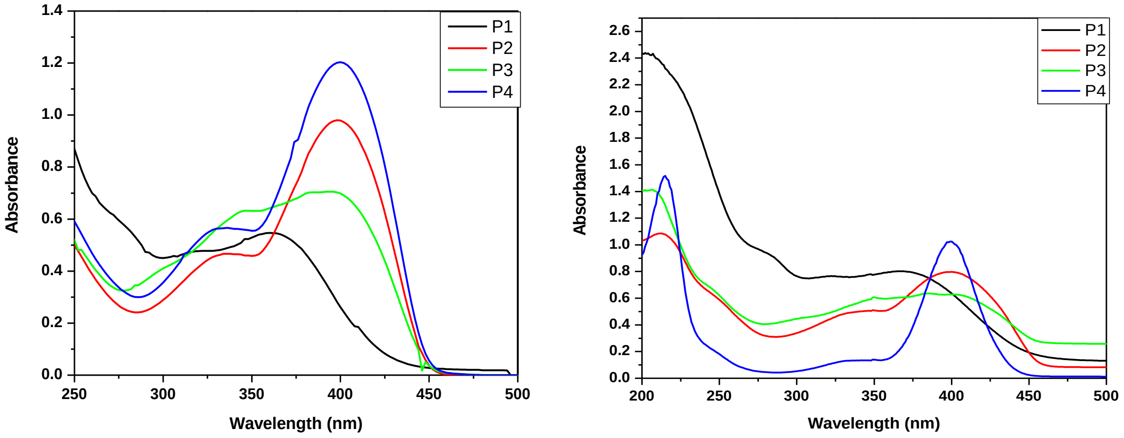


Figure 2 DSC curves of four oligomers (P1-P4).

The IR and NMR data of these four PPV oligomers are consistent with the proposed structures (Fig. 1). IR spectra of these materials showed three characteristics peaks at ~2931 cm^{-1} (C-H stretching of alkyl side chain), ~1203 cm^{-1} (C-O stretching) and ~962 cm^{-1} (C–H bending of trans vinylene) [17]. In the ^{1}H-NMR spectra, in addition to the expected aromatic (δ 6.8-7.6), methoxy (δ 3.5-4) and alkyl groups (δ 0.7-1.8), the vinyl protons appeared at δ 4.6 for P2-P4, while for P1 it appeared down field at δ 5.1. All the expected ^{13}C and CH_2 resonances were observed in the ^{13}C-NMR and DEPT-135 spectra, respectively. The ^{13}C-NMR spectra showed peaks for side chain in the region 10-40 ppm while peaks for alkoxy groups were observed in the region 55-60 ppm. Signals for aromatic moieties were observed in the region 100-155 ppm. Peaks for methylene carbons were observed pointing downwards, in the region 15-60 ppm, in DEPT-135 spectra. Raman spectra of the oligomers were recorded and the values obtained are in accordance with the reported values [17]. In addition to, three main bands at ~1629, ~1593 and 1306-1319 cm^{-1} (elongation of C=C trans vinyl bond), the spectra also show weak bands at ~1290 and 1120 cm^{-1} due to C-C stretching of the phenyl group (see supporting info). The absorption spectra of oligomers (Fig. 3), in thin film states, showed strong absorption peaks ~210, due to electronic transitions of aromatic units and 360-400 nm (π-π^* interactions) [18] along with a weak absorption at ~330 nm. The spectra in the region 300-450 nm exhibit similar features indicating that the conformation and intermolecular interactions are similar in both the states (Table 2) The long wavelength absorption edges of the spectra were used to determine band gaps (E_g), which are calculated to be in the range of 2.5-2.8 and 2.7-2.75 eV for solution and solid phase, respectively (Table 2). Absorption transition and the optical band gap together suggest that the oligomer backbone is coplanar with least disruption in conjugation in film state.



(a) (b)

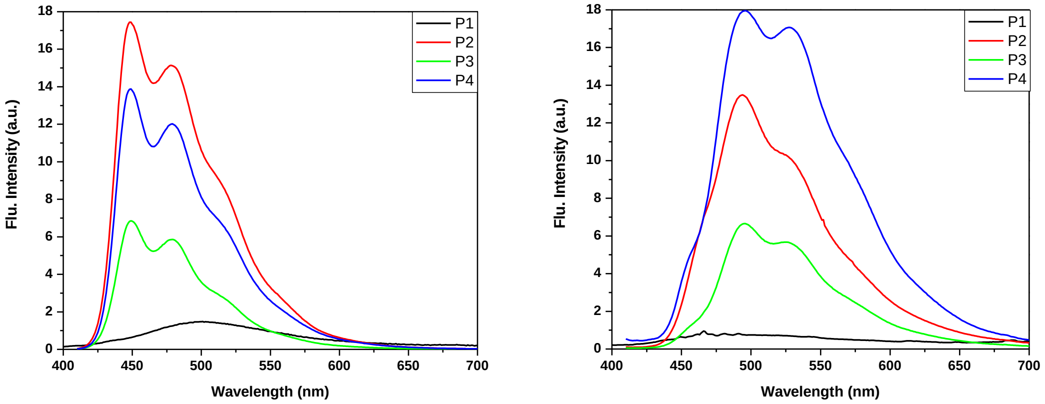
Figure 3 Absorption spectra of PPV oligomers (a) in $CHCl_3$ (b) spin coated thin film

Table 2 Absorption and emission properties of PPV oligomers

S. No.	UV-Vis (nm)		Band gap[c] (eV)		Emission (nm)	
	Solution[a]	Film[b]	Solution	Film	Solution[d]	Film
P1	363	204, 371	2.64	2.75	--	--
P2	398	213, 400	2.68	2.73	447, 478	492, 529
P3	398	207, 403	2.54	2.70	447, 478	495, 527
P4	401	214, 400	2.82	2.74	447, 479	495, 529

[a] in chloroform, [b] film cast from chloroform solution, [c] calculated from onset of absorption spectra, [d] in dichloromethane

The oligomers P2-P4 show strong blue green fluorescence in solution phase when excited at 366 nm, with P4 being the most fluorescent. Emission spectra (**Figure 4**), in solution state, show maxima at 495 and 527 nm when excited at 360 nm while in the solid state a bathochromic shift of ~50 nm was observed (Table 2). Oligomer P1 showed no emission while P2-P4 show very broad peaks, covering a large part of the visible spectrum form 450 nm to 650 nm.



(a) (b)

Figure 4 Emission spectra of PPV oligomers (a) in CH_2Cl_2 (b) spin coated thin film

To investigate the effect of structural modifications at the molecular level on structural disorder in the solid state, X-ray diffraction patterns have been recorded (**Figure 5**). In all cases, a broad peak centred at a 2θ value of 22-26^0 showed their amorphous character [19]. Elongation of side chain does not have any significant effect on molecular packing. The XRD crystallite size determined from Scherrer's formula found to be in range of 6.8-7.4 Å (**Table 3**).

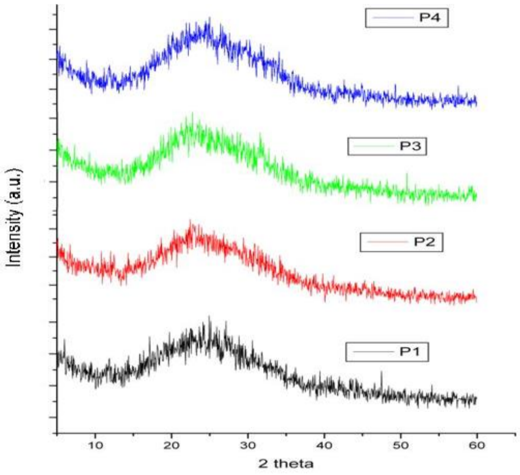


Figure 5 XRD patterns of thin films of oligomer over glass.

Table 3 XRD and hole mobility data of PPVs

	P1	P2	P3	P4
Dp^a (Å)	6.8	7.4	7.4	7.3
μ^b ($cm^2V^{-1}s^{-1}$)	8.5 x 10^{-10}	2.3 x 10^{-3}	9.3 x 10^{-4}	6.8 x 10^{-4}

^{a}calculated form XRD using Scherrer's formula, ^{b}calculated using Child's law

Studies on Glass/ITO/oligomer/Al

The devices studied consist of a single layer of π-conjugated material sandwiched between two electrodes. The organic material is spin coated over patterned ITO (acts as anode) on glass. Aluminum (as cathode material) was deposited over organic layer in high vacuum resulting in the device structure Glass/ITO/oligomer/Al (see supporting info). Current density-voltage (J-V) characteristics at room temperature are shown in fig. 6, where two separate voltage regions can be distinguished. The devices demonstrate nearly ohmic I-V dependence at voltage < 1 V while a distinct region with $I \propto V^2$ was observed at voltages > 1 V. Standard semiconductor theory predicts this type of I-V behavior in case of space charge limited current (SCLC) [20,21]. Considering the present SCLC as the trap-free limit, Child's Law is applied in its familiar form, which states that:

$$J = \frac{9}{8}\mu\varepsilon\varepsilon_0\frac{V^2}{d^3}$$

where, J is the current density, μ is the free carrier hole mobility, ε is the dielectric constant, ε_0 is the permittivity in a vacuum, V is the voltage applied across the electrodes and d is the film thickness, which acts as the drift space between the electrodes.

For electronic device applications, hole mobility is one of the important criteria which significantly affects performance of device [22]. Materials with good hole mobility are desirable so as to achieve better device performance. Using the above J-V relationship, hole mobility was calculated to be of the order of 10^{-3}-10^{-4} $cm^2V^{-1}s^{-1}$ for oligomers P2-P4 (**Table 3**), which can be due to their increased solubility and hence better film formation. For P1 the hole mobility was found to be low possibly due to decreased solubility and small crystallite size (Table 3), leading to poor intermolecular packing. The hole mobility values are found to be better than those reported for PPV and derivatives and are, in fact, comparable to values reported for conducting polymers [21-24]. No doping of materials was performed at any stage. One of key problems with majority of existing materials is that devices fabricated show large operating voltages. Devices fabricated by us using these materials show low turn-on voltage (~ 1 V), which is a distinct advantage for their use in low power electronic device applications. Further studies on their use for OLEDs and photovoltaic applications are currently in progress.

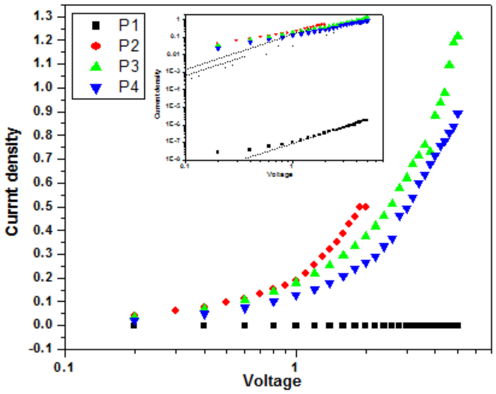


Figure 6 I-V characteristics of Glass/ITO/oligomer/Al diode devices (Inset shows the logrithmic plot).

Conclusions

New soluble PPV oligomers emitting in the blue-green region have been synthesised. The good hole mobility values at low turn-on voltages constitutes an encouraging result leading to the inference that these oligomers can serve as valuable compounds to be used as semiconducting materials for electronic device applications.

Acknowledgements

We thank the Principal, St. Stephen's College, Delhi and the Director, SSPL, Delhi for providing facilities. We thank DRDO and UGC for granting research funds. We are thankful to Dr. Suresh Das, NIIST, Trivandrum for help in Photoluminescene spectra and MALDI-MS results.

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Publication History

Received	01st July 2014
Revised	09th July 2014
Accepted	10th July 2014
Online	30th July 2014