

Synthesis and characterization of novel conjugated copolymers containing 3,4-dialkoxythiophene and 1,3,4-oxadiazole units

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Received 25 January 2007; received in revised form 28 March 2007; accepted 25 April 2007

Available online 3 May 2007

Abstract

In this report we describe the synthesis, optical and electrochemical properties of new conjugated copolymers (**P1–P4**) based on 3,4-dialkoxythiophene and 1,3,4-oxadiazole units. The copolymers are prepared using the precursor polyhydrazide route. The chemical structures of the copolymers are confirmed using FTIR, NMR spectroscopy and CHNS analysis. The polymers exhibit good thermal stability with the onset decomposition temperature in nitrogen at around 300 °C. The optical and charge-transporting properties of the copolymers are investigated by UV–visible absorption spectroscopy, fluorescence emission spectroscopy and cyclic voltammetry. The polymers depicted blue/green fluorescence under the irradiation of UV light. Cyclic voltammetry studies reveal that these copolymers have low-lying LUMO energy levels ranging from –3.28 to –3.32 eV and high-lying HOMO energy levels ranging from –5.26 to –5.62 eV, which indicated that they may be promising candidates for the fabrication of polymer light-emitting diodes. In addition, the copolymers showed good third-order non-linear optical properties.

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Keywords: Conjugated polymers; Polycondensation; Fluorescence; Cyclic voltammetry; Polythiophene; 1,3,4-Oxadiazole

1. Introduction

Since the initial report of conjugated polymer based light-emitting diodes (PLEDs) by the Cambridge group in 1990 [1], enormous efforts have been devoted to the synthesis of light-emitting polymers.

Polyparaphenylenevinylene (PPV) [2], polyparaphenylene (PPP) [3], polythiophene (PT) [4], polyfluorene (PF) [5] and their derivatives have been widely used as light-emitting materials in devices. However, all these polymers are π -excessive in nature and hence have greater tendency to transport holes than transporting electrons. Another series of polymers containing π -deficient heterocycles like pyridine, pyran, and oxadiazoles show greater tendency to transport electrons than holes [6]. In order to achieve high electroluminescent efficiency, it is

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necessary to balance the injection of electrons and holes at the opposite contacts in PLED devices. However, for most of the conjugated polymers, the barrier between the LUMO of the polymer and the work function of the cathode is much larger than that between the HOMO of the polymer and the work function of the anode that results in an imbalance of the injection between electrons and holes. Several approaches have been developed to overcome this problem. One is to use metals with low work function such as calcium as cathode [7]. The major problem with this method is that calcium is highly susceptible to atmospheric degradation resulting in much lowered device stability. Second approach is the design of multilayer devices, in which an additional electron-transporting layer is sandwiched between the emissive layer and cathode [8]. However the most promising approach to minimize the energy barriers between the fermi energy of the metallic electrodes and energy of the frontier levels of the polymer layer is to modulate the positions of the band edges of the polymer through proper derivatization of its conjugated backbone, for instance with π -electron donor and/or acceptor groups. In this direction few conjugated donor–acceptor copolymers constituted of π -excessive and π -deficient units were synthesized and showed unique electrochemical and optical properties [9–11]. Our interest is to synthesize copolymers containing 3,4-dialkoxythiophene as electron rich p-dope type segment and 1,3,4-oxadiazole as electron deficient n-type segment. 3,4-Dialkoxy substituted polythiophenes show facile dopability and lower bandgap ascribable to the electron donating nature of the alkoxy moiety. On the other hand, polyoxadiazoles, due to the high electron affinity of the oxadiazole moiety, are attractive candidates for n-type light-emitting and electron-transporting materials. However, in case of poly(3,4-dialkoxythiophene)s the steric interaction of alkoxy groups of adjacent thiophene rings reduces the coplanarity that decreases the effective conjugation length of the polymer. In order to minimize such steric interactions, we have introduced spacer units along the polymeric backbone so that the thiophene rings are well separated which thus minimizes the steric interactions of the alkoxy groups. In this report we describe the synthesis and characterization of four copolymers (**P1–P4**) based on 3,4-dialkoxythiophene and 1,3,4-oxadiazole units containing either 2,5-dialkoxybenzene or benzene moieties as spacer units.

2. Experimental part

Diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (**1**) was synthesized according to the literature procedure [12]. Dimethylformamide (DMF) and acetonitrile (ACN) were dried by distillation over CaH_2 . Diethyl 2,5-dihydroxyterephthalate was purchased from Aldrich. Tetrabutylammoniumperchlorate (TBAPC) and *n*-bromoalkanes were purchased from Lancaster (UK) and were used as received. All other solvents and reagents were of analytical grade, were purchased commercially and used without further purification. Infrared spectra of all intermediate compounds and polymers were recorded on a Nicolet Avatar 330 FTIR (Thermo Electron Corporation). The UV–visible absorption spectra of the copolymers were measured using a Varian CARY 500 spectrophotometer. Thermogravimetric analysis (TGA) was carried out with a thermal analysis 2950 thermogravimetric analyzer (TA instruments). ^1H NMR spectra were obtained with an AMX 400 MHz FT-NMR spectrometer using TMS/solvent signal as internal reference. Molecular weights of the copolymers were determined by a Shimadzu gel permeation chromatograph using polystyrene standards. Fluorescence emission spectra of the copolymers were recorded using a Perkin Elmer LS 50B luminescence spectrometer. Elemental analyses were performed on a Flash EA 1112 CHNS analyzer (Thermo Electron Corporation). The electrochemical studies of the copolymers were carried out using an AUTOLAB PGSTAT 30 electrochemical analyzer. Cyclic voltammograms were recorded using a three-electrode cell system, with a glass carbon button as working electrode, a Pt wire as counter electrode and an Ag/AgCl electrode as the reference electrode.

2.1. Synthesis of diethyl 2,5-dialkoxyterephthalates (**5a,b**)

2.1.1. Diethyl 2,5-dihexyloxyterephthalate (**5a**)

A mixture of diethyl 2,5-dihydroxy terephthalate (**4**) (1 g, 4 mmol), potassium carbonate (1.1 g, 8 mmol), potassium iodide (0.13 g, 0.8 mmol) and 20 ml of cyclohexanone was taken in a round bottom flask fitted with a condenser connected to a CaCl_2 guard. To this reaction mixture, 1-bromohexane (1.8 ml, 13.2 mmol) was added drop-wise with stirring and the mixture was refluxed for 20 h. The hot reaction mixture was filtered and washed with

cyclohexanone. The combined filtrate was vacuum distilled to remove the cyclohexanone and the excess 1-bromohexane. The pale yellow residue, which solidified on cooling, was then recrystallized from ethanol to get the pure compound **5a**.

^1H NMR (CDCl_3), δ (ppm): 7.28 (s, 2H), 4.2 (q, 4H), 3.95 (t, 4H), 1.71–1.26 (m, 22H), 0.87 (t, 6H). IR (KBr), ν (cm^{-1}): 2950, 2865, 1695, 1417, 1385, 1298, 1211, 1026, 951, 783, 735, 625, 556. Elem. Anal. Calcd for $\text{C}_{24}\text{H}_{38}\text{O}_6$: C 68.25; H 9.01. Found: C 68.45; H 8.92.

2.1.2. Diethyl 2,5-dioctyloxterephthalate (**5b**)

Compound **5b** was synthesized according to the procedure described for **5a** by reacting compound **4** (1 g, 4 mmol) with *n*-bromooctane (2.4 ml, 14 mmol).

^1H NMR (CDCl_3), δ (ppm): 7.34 (s, 2H), 4.26 (q, 4H), 3.97 (t, 4H), 1.82–1.31 (m, 30H), 0.89 (t, 6H). IR (KBr), ν (cm^{-1}): 2955, 2862, 1692, 1417, 1380, 1300, 1212, 1024, 948, 785, 730, 621, 552. Elem. Anal. Calcd for $\text{C}_{28}\text{H}_{46}\text{O}_6$: C 70.29; H 9.62. Found: C 70.38; H 9.79.

2.2. Synthesis of 2,5-dialkoxyterephthalic acids (**6a,b**)

Diethyl 2,5-dialkoxyterephthalate (0.5 g) was refluxed with 15 ml of 5% alcoholic potassium hydroxide solution for 4 h. The reaction mixture was cooled to room temperature and acidified with hydrochloric acid to give a white precipitate. The precipitates were collected by filtration, dried and recrystallized from ethanol to yield 2,5-dialkoxyterephthalic acids as white crystals.

2,5-Dihexyloxterephthalic acid (6a): ^1H NMR (CDCl_3), δ (ppm): 13 (s, 2H), 7.39 (s, 2H), 4.06 (t, 4H), 1.28–1.75 (m, 16H), 0.9 (t, 6H). IR (KBr), ν (cm^{-1}): 3375, 2950, 2868, 1685, 1508, 1472, 1418, 1390, 1295, 1232, 1134, 1074, 1020, 948, 782, 732, 620, 552. Elem. Anal. Calcd for ($\text{C}_{20}\text{H}_{30}\text{O}_6$): C 65.57; H 8.2. Found: C 64.72; H 8.19.

2,5-Dioctyloxterephthalic acid (6b): ^1H NMR (CDCl_3), δ (ppm): 13.1 (s, 2H), 7.38 (s, 2H), 4.03 (t, 4H), 1.26–1.72 (m, 22H), 0.91 (t, 6H). IR (KBr), ν (cm^{-1}): 3372, 2950, 2865, 1695, 1502, 1468, 1417, 1383, 1299, 1231, 1130, 1072, 1022, 946, 785, 736, 625, 554. Elem. Anal. Calcd for $\text{C}_{24}\text{H}_{38}\text{O}_6$: C 68.25; H 9.0. Found: C 68.42; H 8.79.

2.3. Synthesis of 2,5-dialkoxyterephthalic acid chlorides (**7a,b**)

A mixture of 2,5-dialkoxyterephthalic acid (0.5 g), 20 ml of thionyl chloride and three drops of DMF was refluxed for 5 h. The excess thionyl chloride was distilled off and the remaining solid residue was extracted with dichloromethane. The solvent was removed by rotary evaporation and the solid product obtained was recrystallized from hexane to yield diacid chlorides as yellow needles.

2,5-Dihexyloxterephthalic acid chloride (7a): ^1H NMR (CDCl_3), δ (ppm): 7.37 (s, 2H), 4.03 (t, 4H), 1.29–1.75 (m, 16H), 0.92 (t, 6H). IR (KBr), ν (cm^{-1}): 2953, 2872, 1705, 1678, 1514, 1442, 1316, 1248, 1224, 1150, 1050, 998, 945, 798, 762, 730. Elem. Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{O}_4\text{Cl}_2$: C 59.55; H 6.95. Found: C 59.38; H 7.08.

2,5-Dioctyloxterephthalic acid chloride (7b): ^1H NMR (CDCl_3), δ (ppm): 7.36 (s, 2H), 4.02 (t, 4H), 1.26–1.74 (m, 22H), 0.91 (t, 6H). IR (KBr), ν (cm^{-1}): 2945, 2875, 1708, 1680, 1507, 1443, 1310, 1246, 1223, 1152, 1048, 1000, 941, 792, 765, 735, 557. Elem. Anal. Calcd for $\text{C}_{24}\text{H}_{36}\text{O}_4\text{Cl}_2$: C 62.75; H 7.84. Found: C 62.84; H 7.68.

2.4. General procedure for the synthesis of polyhydrazides (**9a–d**)

To a mixture of 1 equiv of appropriate dihydrazide, 2 equiv of anhydrous aluminum chloride and 0.1 ml of pyridine, 1 equiv of the appropriate acid chloride was added slowly at room temperature. The reaction mixture was stirred at room temperature for 5 h. The resultant yellow solution was heated at 80 °C with stirring for 20 h. After cooling to room temperature the reaction mixture was poured into water to get a precipitate. The precipitate was collected by filtration and was washed with water followed by acetone and finally dried in vacuum to get the corresponding polyhydrazides in 75–85 % yield.

Compound 9a: Yield: 85%. IR (KBr), ν (cm^{-1}): 3366, 2930, 2803, 2715, 1627, 1507, 1462, 1359, 1206, 1056, 763, 496, 421. **Compound 9b**: Yield: 80%. IR (KBr), ν (cm^{-1}): 3362, 2934, 2814, 2718, 1628, 1509, 1458, 1357, 1210, 1058, 756, 492. **Compound 9c**: Yield: 75%. IR (KBr), ν (cm^{-1}): 3350, 2982, 2886, 1696, 1511, 1426, 1288, 1112, 937, 879, 782, 731 cm^{-1} . **Compound 9d**: Yield: 80%. IR: 3362, 2979, 2858, 1695, 1512, 1455, 1285, 1047, 1114, 930, 864, 720.

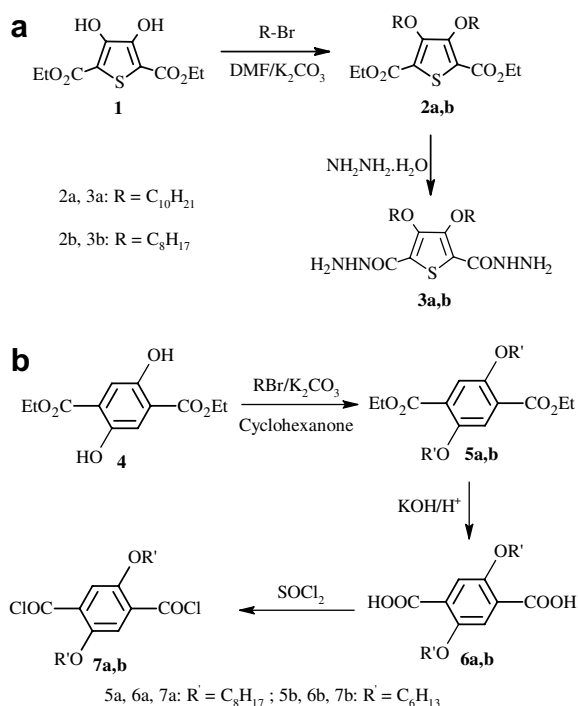
2.5. General procedure for the synthesis of polyoxadiazoles (**P1–P4**)

For the synthesis of polyoxadiazoles **P1** and **P2**, the appropriate polyhydrazide (0.5 g) was refluxed with phosphorous oxychloride (20 ml) for 20 h. The reaction mixture was then cooled to room temperature and poured in to excess of cold water. The resulting precipitate was collected by filtration and was washed with water and dried in oven to get the polymers in 70–80% yield. Polyoxadiazoles **P3** and **P4** were synthesized by heating the appropriate polyhydrazide with polyphosphoric acid (50 ml) at 100 °C for 4 h. The precipitate obtained by pouring the reaction mixture to excess of water was filtered, washed with excess water followed by acetone and dried at oven to get the copolymers in 80–90% yield.

Compound **P1**: ^1H NMR (DMSO- d_6), δ (ppm): 7.36 (s, 2H), 4.15 (t, 4H), 4.01 (t, 4H), 1.91–0.89 (m, 68H), IR (KBr), ν (cm^{-1}): 2925, 2854, 2786, 1744, 1541, 1484, 1354, 1098, 981, 767, 670. Elem. Anal. Calcd for $\text{C}_{50}\text{H}_{78}\text{N}_4\text{SO}_6$: C 69.61; H 9.05; N 6.5; S 3.71. Found: C 69.91; H 9.28; N 6.75; S 3.92. Compound **P2**: ^1H NMR (DMSO- d_6), δ (ppm): 7.34 (s, 2H), 4.16 (t, 4H), 4.02 (t, 4H), 1.9–0.91 (m, 60H). IR (KBr), ν (cm^{-1}): 2920, 2850, 2788, 1750, 1545, 1482, 1350, 1096, 978, 768, 670. Elem. Anal. Calcd for $\text{C}_{46}\text{H}_{70}\text{N}_4\text{SO}_6$: C 68.48; H 8.68; N 6.95; S 3.97. Found: C 68.72; H 9.04; N 6.83; S 4.18. Compound **P3**: ^1H NMR (DMSO- d_6), δ (ppm): 8.03 (s, 4H), 4.1 (t, 4H), 1.8–0.92 (m, 38H). IR (KBr), ν (cm^{-1}): 2928, 2856, 1697, 1535, 1488, 1428, 1373, 1278, 1174, 1052, 1012, 854, 728. Elem. Anal. Calcd for $\text{C}_{34}\text{H}_{36}\text{N}_4\text{SO}_4$: C 67.33; H 7.6; N 9.24; S 5.28. Found: C 67.54; H 7.45; N 9.36; S 5.42. Compound **P4**: ^1H NMR (DMSO- d_6), δ (ppm): 8.01 (s, 4H), 4.12 (t, 4H), 1.79–0.93 (m, 30H). IR (KBr), ν (cm^{-1}): 2989, 2883, 1696, 1544, 1510, 1426, 1289, 1112, 1007, 938, 880, 782, 731. Elem. Anal. Calcd for $\text{C}_{30}\text{H}_{38}\text{N}_4\text{SO}_4$: C 65.45; H 6.91; N 10.18; S 5.81. Found: C 64.87; H 7.31; N 10.36; S 5.46.

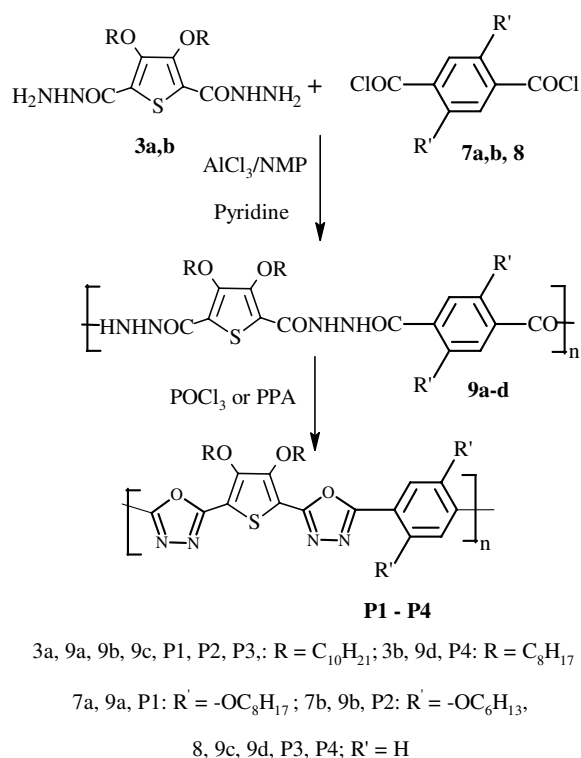
2.6. Synthesis and initial characterizations of copolymers

Synthetic routes for the synthesis of 3,4-dialkoxythiophene-2,5-carbonyldihydrazides (**3a,b**) are shown in Scheme 1a. Diethyl 3,4-dialkoxythiophene-2,5-dicarboxylates were prepared by treating diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (**1**) with the corresponding *n*-bromoalkanes in pres-



Scheme 1. (a) Synthesis of 3,4-dialkoxythiophene-2,5-carbonyldihydrazides (**3a,b**). (b) Synthesis of 2,5-dialkoxyterephthalic acid chlorides (**7a,b**).

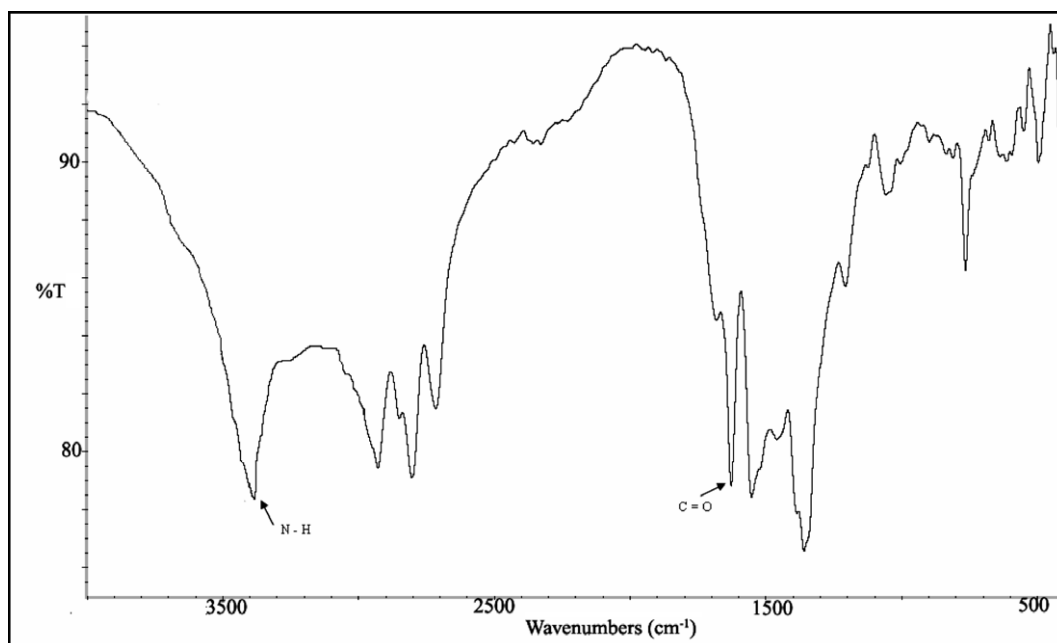
ence of potassium carbonate and DMF. For the synthesis of 3,4-dialkoxythiophene-2,5-carbonyldihydrazides, corresponding diethyl 3,4-dialkoxythiophene-2,5-dicarboxylates were treated with excess of hydrazine hydrate in methanol [11]. 2,5-Dialkoxyterephthaloyl chlorides (**7a,b**) were synthesized following the route depicted in Scheme 1b. Diethyl 2,5-dihydroxyterephthalate (**4**) was etherified with corresponding alkyl bromide in the presence of potassium carbonate to yield diethyl 2,5-dialkoxyterephthalates (**5a,b**). Saponification of **5a,b** with 10% aqueous potassium hydroxide yielded the 2,5-dialkoxyterephthalic acids (**6a,b**). The diacid chlorides (**7a,b**) were obtained by refluxing corresponding 2,5-dialkoxyterephthalic acids with excess of thionyl chloride. Synthetic routes of copolymers **P1–P4** are shown in Scheme 2. Precursor polyhydrazides (**9a–d**) were prepared by the polycondensation reaction of appropriate 3,4-dialkoxythiophene-2,5-carbonyldihydrazide with the corresponding diacyl chloride in *N*-methylpyrrolidone (NMP) in the presence of anhydrous aluminum chloride and pyridine. The polyhydrazides were converted in to the corresponding poly (1,3,4-oxadiazole)s, (**P1–P4**),

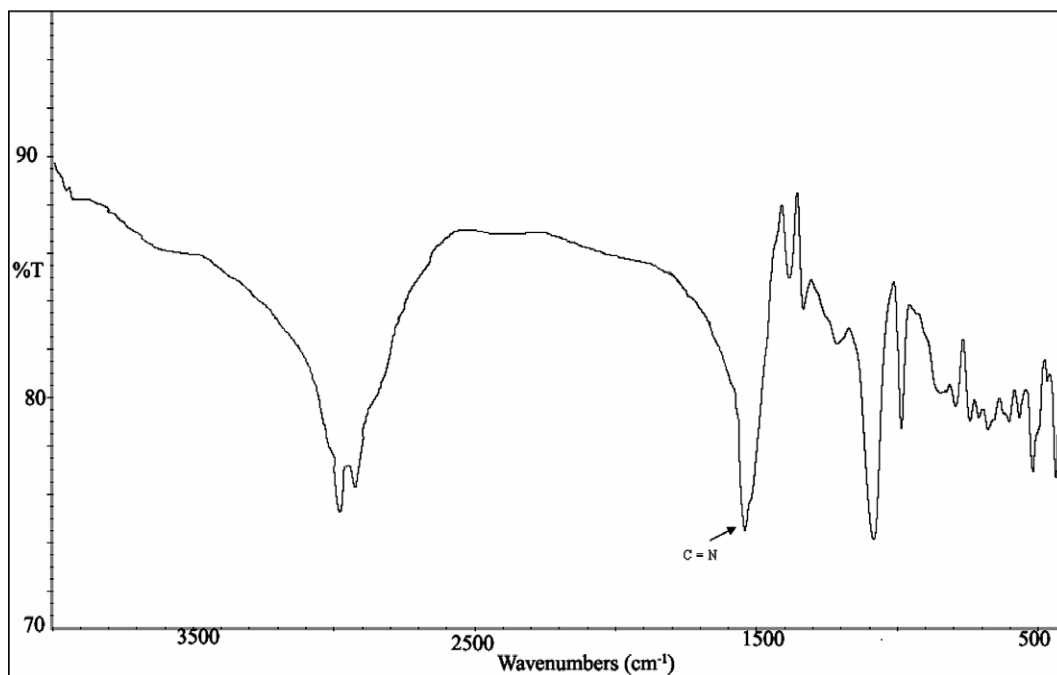


Scheme 2. Synthesis of polymers (P1–P4).

by cyclodehydration of the hydrazide group in to 1,3,4-oxadiazole ring, using a dehydrating agent.

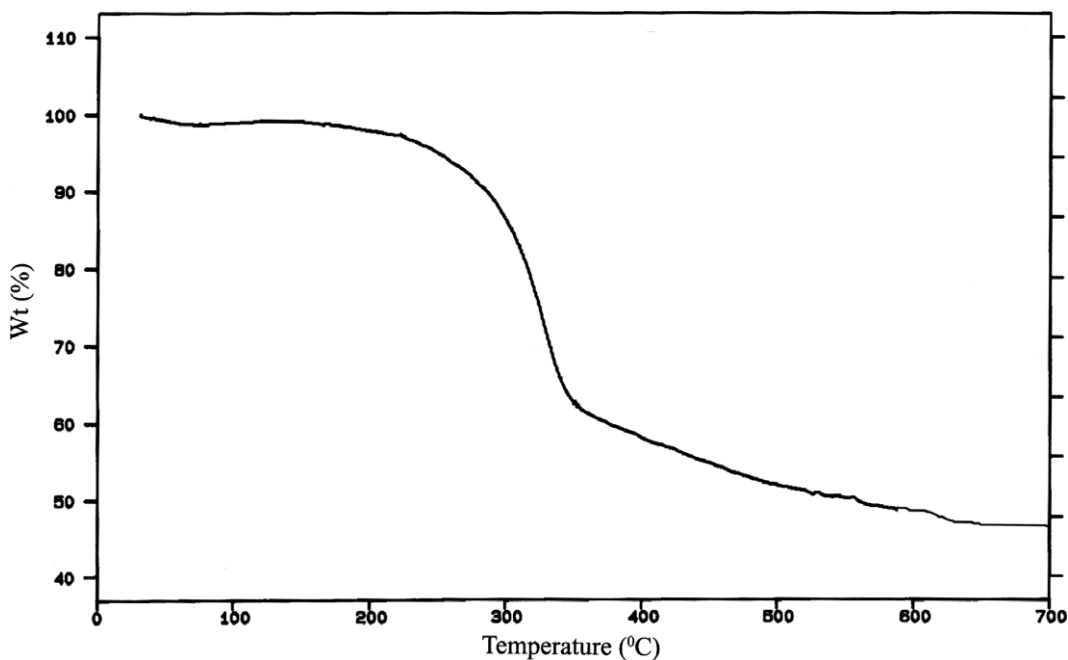
Polyphosphoric acid (PPA) was used for the cyclodehydration of polyhydrazides **9c,d**. As polyhydrazides **9a,b** were soluble, phosphorous oxychloride (POCl₃) was utilized for the cyclodehydration reaction. The successful conversion of polyhydrazides into polyoxadiazoles was confirmed by FTIR spectroscopy. The stretching bands of C=O and N–H groups in polyhydrazides disappeared in the FTIR spectrum of corresponding polyoxadiazoles, where as the band corresponding to imine (C=N) in an oxadiazole ring was newly generated. In addition, =C–O–C= stretching is also observed for these copolymers. Fig. 1 shows the FTIR spectrum of polyhydrazide **9a**. The FTIR spectrum of the corresponding polyoxadiazole (**P1**) is shown in Fig. 2. Copolymers **P1–P4** were obtained as brownish green powders. Copolymers **P3** and **P4** are partially soluble in conventional solvents such as CHCl₃ and THF, but readily soluble in DMF, DMSO, NMP, and in strong organic acids like trifluoroacetic acid. Whereas copolymers **P1** and **P2** are sparingly soluble in CHCl₃ and THF as expected from the solubilizing effect of alkoxy groups of 2,5-dialkoxybenzene units. The chemical structures of the copolymers were confirmed by ¹H NMR spectra. In ¹H NMR spectra of copolymers **P1** and **P2**, a singlet peak was observed at around δ 7.36 due to aromatic protons. The copolymers showed triplet

Fig. 1. FTIR spectrum of polyhydrazide **9a**.

Fig. 2. FTIR spectrum of polyoxadiazole **P1**.

peaks at around δ 4.15 and 4.01 due to the $-\text{OCH}_2-$ protons of the alkoxy groups on the thiophene and phenyl rings, respectively. In addition, multiple peaks were obtained in the range δ 1.91–0.89, due

to $-(\text{CH}_2)_n-$ protons of the alkoxy groups. The ^1H NMR spectra of polymers **P3** and **P4** showed characteristic peaks; a singlet at around δ 8.03 due to aromatic protons, a triplet at around δ 4.12 due to

Fig. 3. TGA curve of polyoxadiazole **P1**.

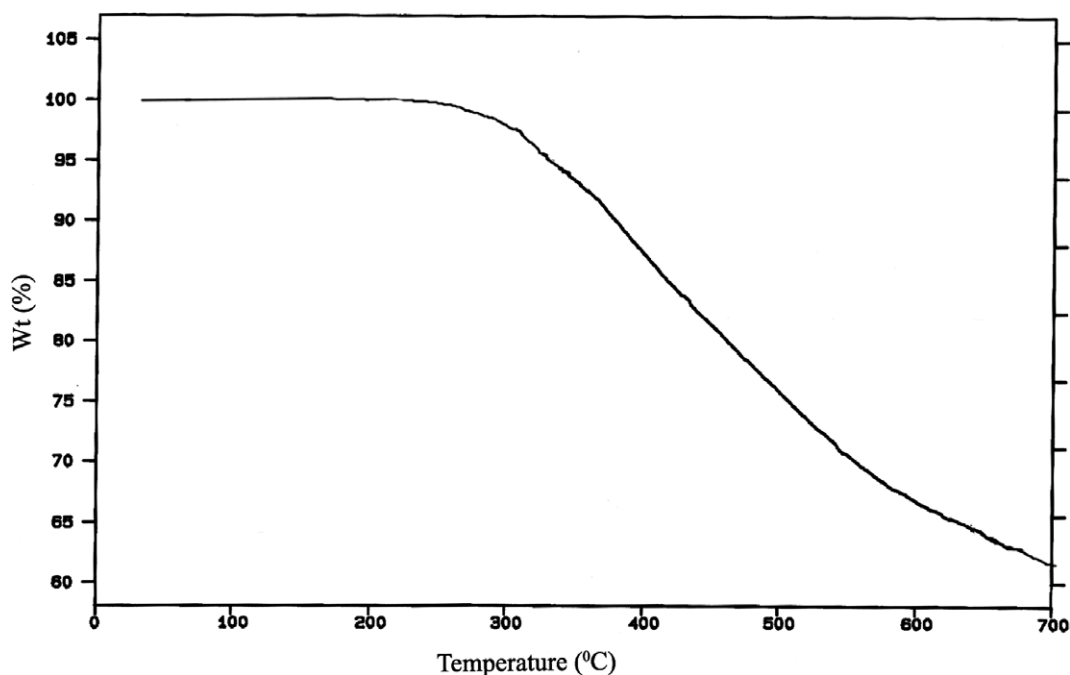


Fig. 4. TGA curve of polyoxadiazole **P3**.

–OCH₂– protons of the alkoxy group and multiple peaks in the range δ 1.8–0.92 due to –(CH₂)_n– protons of the alkoxy groups. The elemental analysis results for the copolymers are in agreement with their expected empirical formula. The molecular weights of the copolymers were determined by means of gel permeation chromatography (GPC) using THF as eluant against polystyrene standards. The molecular weights of **P1** and **P2** are found to be $M_n = 8840$ ($M_w/M_n = 1.41$) and $M_n = 9260$ ($M_w/M_n = 1.48$), respectively. Since copolymers **P3** and **P4** are partially soluble in THF, only the molecular weights of the THF soluble parts were measured and the corresponding molecular weights were measured as $M_n = 4260$ for **P3** ($M_w/M_n = 1.43$) and $M_n = 3980$ for **P4** ($M_w/M_n = 1.38$). The actual molecular weights of these copolymers should be higher than these measured values because of the insolubility of the parts with higher molecular weights. Although the results cannot give accurate information on molecular weights of the polymers they convince us the polymeric structure of the obtained products. Thermogravimetric analysis (TGA) of all the copolymers was carried out under nitrogen atmosphere at a heating rate of 5 °C/min. Copolymers **P1** and **P2** are found to be thermally stable up to ~270 °C whereas the thermal decompo-

sition starts above 300 °C for copolymers **P3** and **P4**. TGA curves of copolymers **P1** and **P3** are shown in Figs. 3 and 4, respectively. DSC studies were performed to observe glass transition temperature (T_g) of the copolymers. The samples were heated up to 300 °C under nitrogen atmosphere at a heating rate of 5 °C/min. No T_g or melting point was observed for these copolymers.

3. Results and discussion

3.1. Optical properties

3.1.1. Linear optical properties

The UV–visible absorption and fluorescence emission spectra of the copolymers were recorded both in solution and in thin film, and the corresponding spectral data are summarized in Table 1. The absorption spectra of the polymers in dilute DMF solution are shown in Fig. 5. The absorption maxima of copolymers **P1** and **P2** are 432 and 421 nm, respectively. These absorption maxima are red shifted compared with those of some thiophene-1,3,4-oxadiazole copolymers [13]. Copolymers **P3** and **P4** showed absorption maxima at 363 and 358 nm, respectively. The absorption spectra of the polymer thin films (Fig. 6) are similar

to those in solutions, indicating that there is no much difference in the conformations of the polymers in the two states. Their optical energy band gaps (E_g) were calculated from the absorption edge in the thin films to be 2.04–2.36 eV (Table 1). As shown in Fig. 7, the emissive maxima of the copolymers in dilute DMF solutions are 530 nm for **P1**, 521 nm for **P2**, 456 nm for **P3** and 452 nm for **P4**. The Stokes shift determined to be 98, 103, 93 and 94 nm for **P1**, **P2**, **P3** and **P4**, respectively. The fluorescence emission spectra of these copolymers in thin films are shown in Fig. 8. Copolymers **P1** and **P2** emit intense green light in the solid state, with emission peaks at 536 and 530 nm for **P1** and **P2**, respectively, whereas **P3** and **P4** show bluish fluorescence in the solid state. Consequently, the fluorescence spectra of the polymer thin films exhibit a red shift with respect to those obtained from their solutions. This can be attributed to the interchain or/and intrachain mobility of the excitons and excimers generated in the polymer in the solid stated phase. As depicted in Table 1, the UV–visible absorption and fluorescence emission spectra of copolymers **P1** and **P2** showed a red shift compared with those of **P3** and **P4**. The introduction of 2,5-dialkoxybenzene units in place of unsubstituted benzene moiety led to a red shift in the absorption as well as in the emission maxima, which can be attributed to the electron releasing effect of alkoxy groups of the 2,5-dialkoxybenzene units. The fluorescence quantum yields [14] of the copolymers in solution were determined using quinine sulfate as a standard [15]. As shown in Table 1 the quantum yield of the copolymers are in the range of 32–42%. These results indicate that the polymers can be used as light-emitting materials in devices.

3.1.2. Non-linear optical properties

Organic materials exhibiting strong non-linear optical (NLO) properties have attracted considerable interest in recent years because of their possible

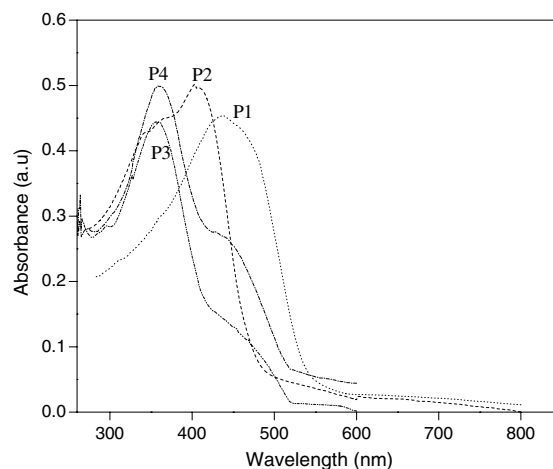


Fig. 5. UV–visible absorption spectra of **P1–P4** in DMF solutions.

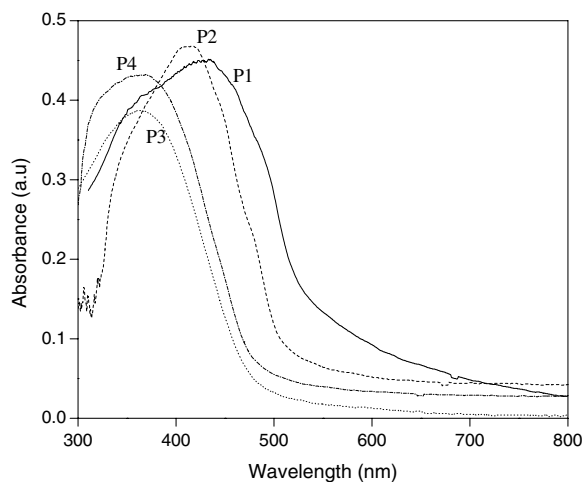


Fig. 6. UV–visible absorption spectra of the polymer thin films.

Table 1

UV–visible absorption maxima, emission maxima and fluorescence quantum yields of the copolymers

Polymer	UV–visible spectroscopy λ_{max} (nm)		Fluorescence emission λ_{max} (nm)		Optical band gap E_g (eV)	Quantum yield ^a (%)
	Solution	Film	Solution	Film		
P1	432	434	530	536	2.04	42
P2	421	424	524	530	2.05	38
P3	363	364	456	482	2.28	34
P4	358	358	452	478	2.36	32

^a Quantum yield relative to quinine sulfate. 10^{-5} M quinine sulfate in 0.1 M H_2SO_4 .

applications in opto-electronic and all-optical devices such as optical limiters, optical switches and optical modulators [16,17]. Conjugated polymers

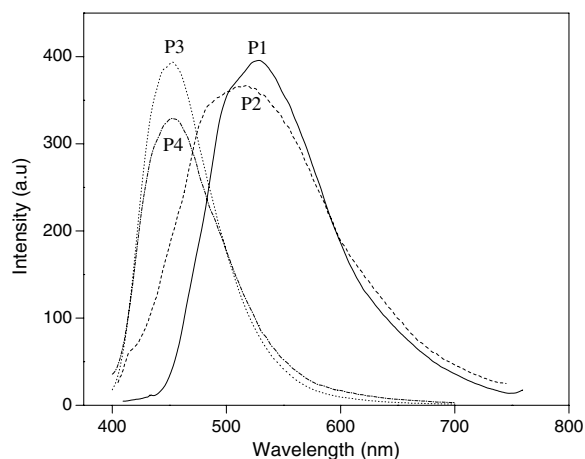


Fig. 7. Fluorescence emission spectra of **P1–P4** in DMF solutions.

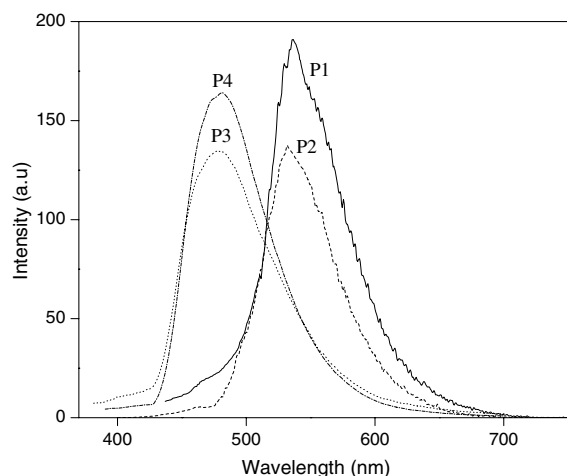


Fig. 8. Fluorescence emission spectra of the polymer thin films.

are a promising class of third-order non-linear optical (NLO) materials because of their potentially large third-order susceptibilities associated with fast response time in addition to their variety, environmental stability and processability [18,19]. Conjugated systems consisting of electron donor and electron acceptor units have showed enhanced third-order optical non-linearity [20,21]. Hence we expected that the newly synthesized polymers (**P1–P4**) with fully conjugated donor–acceptor arrangement might show good third-order non-linear optical properties due to increase in the π -electron delocalization along the polymer chain. We investigated third-order non-linear optical properties of the copolymers in DMF solution by using single

beam Z-scan technique with a Q-switched Nd:YAG nanosecond laser source at 532 nm. The Z-scan results with and without an aperture indicated that the copolymers exhibit both non-linear absorption and non-linear refractive behavior. The value of third-order non-linear susceptibility ($\chi^{(3)}$) is determined to be of the order of 10^{-12} esu for the copolymers. Non-linear refractive index, n_2 , of investigated copolymers is found to be negative and the magnitude is as high as 10^{-10} esu. The non-linear absorption is found to be originating from reverse saturable absorption. The copolymers exhibited good optical limiting properties at 532 nm. The experimental setup used for the measurements and the detailed study of third-order NLO properties of these copolymers will be discussed elsewhere.

3.2. Electrochemical properties

To study the electrochemical behavior, polymer thin films were coated on glassy carbon (GC) button electrode by evaporating the DMF solution of the polymers. The cyclic voltammetry (CV) was conducted in 0.1 M tetrabutylammoniumperchlorate (TBAPC) solution in acetonitrile at a scan rate of 25 mV/s and the corresponding electrochemical data is summarized in Table 2. The cyclic voltammogram of **P1** is shown in Fig. 9a. In positive bias, **P1** showed an oxidation peak at +1.71 V. This value is higher when compared with other conjugated polymers. The high oxidation potential implies that within a solid state device, the copolymer may possess good hole blocking properties. In negative bias, two distinct irreversible reduction peaks at –1.01 and –1.84 V are observed. The two-step reduction process can be assigned to the n-doping of two different heteroaromatic rings. This is in contrast to PPV and PT, where the two-step reduction process has rarely been observed [22]. However, in conjugated heteroaromatic alternating copolymers, such as poly(furanquinoxaline)s, and poly(phenylene-1,3,4-oxadiazole)s, a main peak with a shoulder in the cyclic voltammogram has been observed [23,24]. Copolymer **P2** exhibited similar redox behavior and the corresponding cyclic voltammogram is shown in Fig. 9b. In case of **P3** and **P4** a reduction peak was observed at around –1.6 V in the cathodic sweep. These reduction potentials are lower than those of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) [6,25], one of the most widely used electron-transporting materials, and are comparable with those of some good

Table 2
Electrochemical potentials and energy levels of the copolymers

Polymer	E_{oxd} (V)	E_{red} (V)	HOMO (eV)	LUMO (eV)	E_g (eV)	ΔE_h (eV)	ΔE_e (eV)	$\Delta E_e - \Delta E_h$ (eV)
P1	1.71	−1.84, −1.01	−5.26	−3.31	1.95	0.46	0.99	0.53
P2	1.73	−1.81, −1.01	−5.34	−3.32	2.02	0.54	0.98	0.44
P3	1.48	−1.61	−5.58	−3.31	2.27	0.78	0.99	0.21
P4	1.50	−1.58	−5.62	−3.28	2.34	0.82	1.02	0.2

electron-transporting materials [6]. In anodic sweep, the copolymers showed an oxidation peak at around +1.26 V, which are comparable with those of some donor–acceptor copolymers containing thiophene and oxadiazole units [13]. The cyclic voltammogram of **P3** is shown in Fig. 9c. The onset potentials of n-doping and p-doping processes can be used to estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of a conjugated polymer [26]. According to the equations reported by de Leeuw et al., $E_{\text{HOMO}} = -[E_{(\text{onset})}^{\text{ox}} + 4.4 \text{ eV}]$ and $E_{\text{LUMO}} = -[E_{(\text{onset})}^{\text{red}} + 4.4 \text{ eV}]$, where $E_{(\text{onset})}^{\text{ox}}$ and $E_{(\text{onset})}^{\text{red}}$ are the onset potentials vs. SCE for the oxidation and reduction processes of a polymer, respectively. The HOMO energy levels of copolymers **P1–P4** are estimated to be −5.26, −5.34, −5.58 and −5.62 eV, respectively. It can be seen that copolymers **P1** and **P2** possess higher-lying HOMO energy levels compared with those **P3** and **P4** probably due to the electron releasing effect of additional alkoxy groups of 2,5-dialkoxybenzene units. The HOMO energy levels of **P3** and **P4** are almost the same as that of poly(cyanoterphthalylidene) (CN-PPV), indicating that the polymers have similar hole-injection ability with CN-PPV when they are used in PLEDs. However all these values are higher than that of PPV [27] and other p-type conjugated polymers. This could be due to the introduction of 1,3,4-oxadiazole units along polymers' backbone, which unavoidably increases the energy barrier for hole-injection as observed in some PPV-1,3,4-oxadiazole based copolymers. The LUMO energy levels of polymers **P1–P4** are estimated to be −3.31, −3.32, −3.31 and −3.28 eV, respectively. These values are lower than those of PPV and other conjugated polythiophenes. Further, the values are lower than those of CN-PPV, (−3.02 eV) and some poly(aromatic oxadiazole)s (−2.8 to −2.9 eV) [28], indicating that these copolymers have better electron-injection ability when they are used in PLEDs. A similar trend has been observed in some p–n diblock copolymers contain-

ing alternating electron donor and acceptor units [29]. Hence the high electron affinities of polymers **P1–P4** may be attributed to the incorporation of electron deficient oxadiazole moiety and also the alternating p- and n-type arrangement along the polymers' backbone. However, the LUMO energies of these copolymers are comparable with those of some polyfluorene derivatives containing electron deficient 2-pyran-4-ylidene-malononitrile moiety [30]. The band gaps of the copolymers were estimated from the onset potentials of oxidation and reduction processes and the corresponding values are tabulated in Table 2. The values are quite close to those obtained by the optical method.

The energy barriers between the emitting polymers and electrodes can be estimated by comparing the work functions of the electrodes with the HOMO and the LUMO energy levels of emitting polymers. Thus, the hole-injection barrier is $\Delta E_h = E_{\text{HOMO}} - 4.8 \text{ eV}$, where 4.8 eV is the work function of the ITO anode and the electron-injection barrier is $\Delta E_e = 4.3 - E_{\text{LUMO}} \text{ eV}$, where 4.3 eV is the work function of aluminum cathode. The difference between the electron- and hole-injection barriers ($\Delta E_e - \Delta E_h$) is a useful parameter for evaluating the balance in electron and hole injection. Lower ($\Delta E_e - \Delta E_h$) values indicate improved injection balance of electrons and holes from the cathode and anode, respectively. The band structures of polymers **P1–P4** are depicted in Fig. 10 and the barrier energies are listed in Table 2. It is evident from Table 2 that there is no much difference in ΔE_e values among the copolymers. This is understood from the fact that all the copolymers contain 1,3,4-oxadiazole as the electron-transporting unit. Moreover, these values are lower than those of PPV and other conjugated p-type polymers indicating that the oxadiazole groups tend to decrease the barrier for electron-injection and thus enhances the electron transporting properties of the corresponding polymers. Copolymers **P1** and **P2** show lower ΔE_h values compared with those of **P3** and **P4**, due to electron releasing alkoxy groups

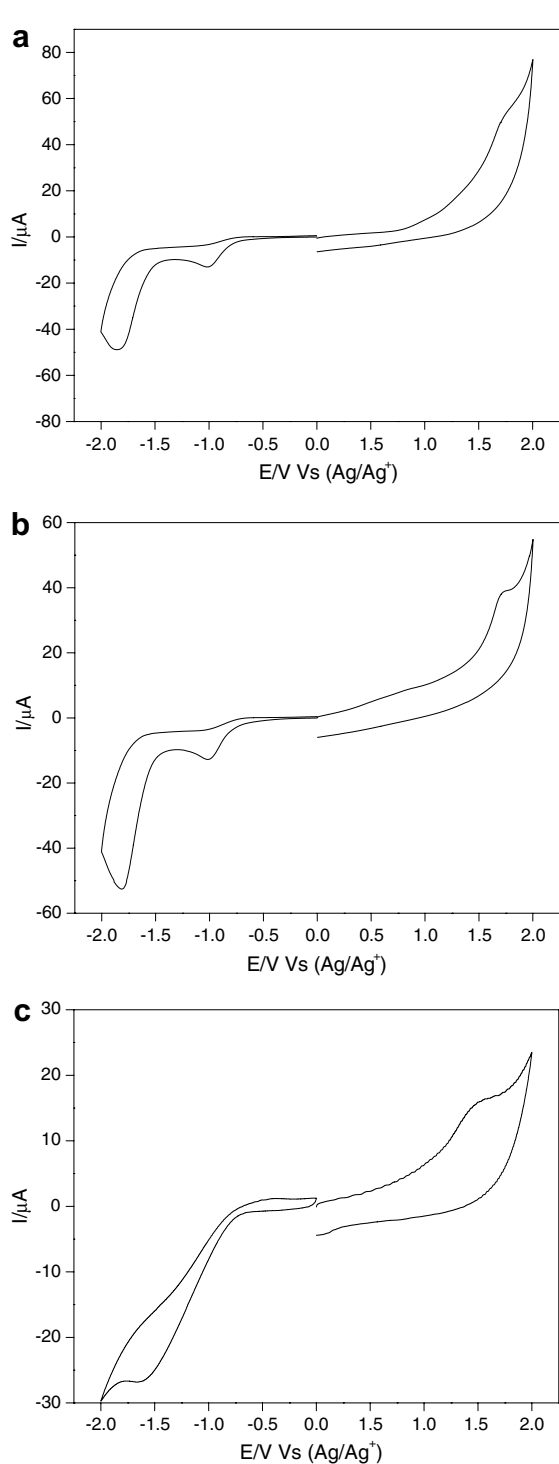


Fig. 9. Cyclic voltammograms of (a) **P1**, (b) **P2** and (c) **P3** in 0.1 M TBAPC in acetonitrile at a scan rate of 25 mV/s.

of 2,5-dialkoxybenzene units. The barrier is lowest for **P1** (0.46 eV) and highest for **P4** (0.82) among

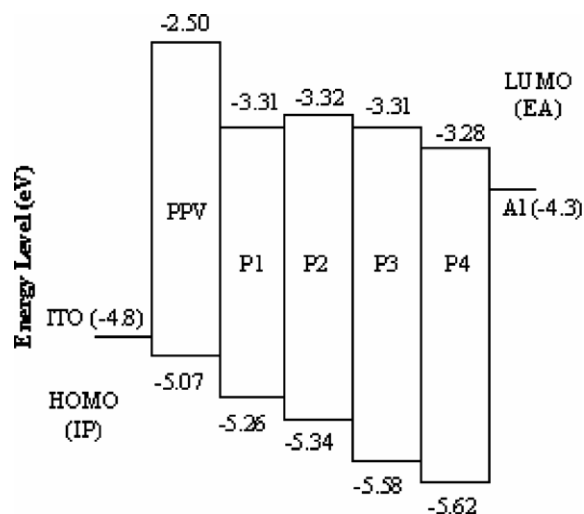


Fig. 10. Band diagrams of **P1–P4** as determined from the electrochemical data. The band structure of PPV is given for comparison.

the copolymers. All these values are higher than that of PPV (0.3 eV) [28] which could be due to the introduction of 1,3,4-oxadiazole units along polymers' backbone. However these values are lower than those of PBD [31], bathocuproine [32], and tris(8-hydroxyquinoline) aluminum (Alq_3) [33], which are widely used as electron transport hole blocking (ETHB) materials. The barrier energy difference ($\Delta E_e - \Delta E_h$) is the highest for **P1** and the lowest for **P4** among the copolymers. These results suggest that the copolymers are expected to provide enhanced charge-transporting properties for the development of efficient PLEDs. The study reveals that donor–acceptor structure could be a promising molecular design for synthetically tuning HOMO and LUMO energy levels of conjugated polymers.

4. Conclusions

Both p- and n-dopable conjugated copolymers based on 3,4-dialkoxythiophene and 1,3,4-oxadiazole units have been synthesized using precursor polyhydrazide route. The copolymers have well defined structure and displayed good thermal stability. Copolymers containing 2,5-dialkoxybenzene units (**P1**, **P2**) are sparingly soluble in common organic solvents like THF and CHCl_3 whereas copolymers **P3** and **P4** are partially soluble in these solvents. The copolymers showed blue/green fluorescence under the irradiation of UV light. Electrochemical studies reveal that the copolymers possess

high-lying HOMO energy levels (from -5.26 to -5.62 eV) and low-lying LUMO energy levels (-3.28 to -3.32 eV) because of the alternate donor and acceptor conjugated units along the polymers' backbone, suggesting that the copolymers are expected to provide enhanced charge-transporting properties for the development of efficient PLEDs. Further, the copolymers exhibited good third-order NLO properties.

Acknowledgements

We thank DRDO, India for the financial support. We are grateful to NMR research center and IPC Department of IISc Bangalore, CDRI Lucknow and CECRI Karaikudi for instrumental analyses.

References

- [1] Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, et al. *Nature* 1990;347:539.
- [2] Curtis MD. *Macromolecules* 2001;34:7905.
- [3] Benincori T, Consinni V, Gramatica P, Pilati T, Rizzo S, Sanniccolo F, et al. *Chem Mater* 2001;13:1665.
- [4] Berggren M, Inganäs O, Gustafsson G, Rasmussen J, Anderson MR, Hjertberg T, et al. *Nature* 1994;372:444.
- [5] Pei Q, Yang Y. *J Am Chem Soc* 1996;118:7416.
- [6] Strukelj M, Papadimitrakopoulos F, Miller TM, Rotheberg LJ. *Science* 1995;267:1969.
- [7] Braun AD, Heeger AJ. *Appl Phys Lett* 1991;58:1982.
- [8] Brown AD, Bradley DDC, Burroughes JH, Friend RH, Greenham NC, Burn PL, et al. *Appl Phys Lett* 1999;261:2793.
- [9] Yu WL, Meng H, Pei J, Huang W. *J Am Chem Soc* 1998;120:11808.
- [10] Ojha UP, Krishnamoorthy K, Kumar A. *Synth Met* 2003;132:279.
- [11] Udayakumar D, Adhikari AV. *Synth Met* 2006;156:1168.
- [12] Lima A, Schottland P, Sadki S, Chevrot C. *Synth Met* 1998;93:33.
- [13] Yu WL, Meng H, Pei J, Huang W, Li Y, Heeger AJ. *Macromolecules* 1998;31:4838.
- [14] Davey AP, Elliott S, O'Connor O, Blau WJ. *Chem Soc Chem Commun* 1995:1433.
- [15] Demas JN, Grosby GA. *J Phys Chem* 1971;75:991.
- [16] Munn RW, Ironside CN, editors. *Principles and applications of nonlinear optical materials*. Chapman and Hall: CRC Press; 1993.
- [17] Zyss J. *Molecular nonlinear optics materials, physics, and devices*. Academic Press; 1994.
- [18] Bredas JL, Chance RR, editors. *Conjugated polymeric materials: opportunities in electronics, optoelectronics, and molecular electronics*. USA: Kluwer Academic publishers; 1989.
- [19] Prasad PN, Williams DJ. *Introduction to nonlinear optical effects in molecules and polymers*. New York: John Wiley and Sons; 1992.
- [20] Chen Q, Sargent EH, Leclerc N, Attias A-J. *Appl Opt* 2003;42:7235.
- [21] Johnkiran A, Udayakumar D, Chandrasekharan K, Adhikari AV, Shashikala HD. *J Phys B At Mol Opt Phys* 2006;39:3747.
- [22] Moratti SC, Bradley DDC, Cervini R, Friend RH, Greenham NC, Holmes AB. *Advanced Materials for Information Technology*. In: Estemad S, editor. SPIE proceedings 1994; 2144: 108.
- [23] Janietz S, Schulz B, Torronen M, Sundholm G. *Eur Polym J* 1993;29:545.
- [24] Kanbara T, Miyazaki Y, Yamamoto T. *J Polym Sci Part A Polym Chem* 1995;33:999.
- [25] Janietz S, Wedel A. *Adv Mater* 1997;9:403.
- [26] De Leeuw DM, Simenon MMJ, Brown AB, Einerhand REF. *Synth Met* 1997;87:53.
- [27] Cervini R, Li X, Spencer GWC, Holmes AB, Moratti SC, Friend RH. *Synth Met* 1997;84:359.
- [28] Bradley DDC. *Synth Met* 1993;54:401.
- [29] Chen S-H, Chen Y. *Macromolecules* 2005;38:53.
- [30] Peng Q, Lu Z-Y, Huang Y, Xie M-G, Han SH, Peng J-B, et al. *Macromolecules* 2004;37:260.
- [31] Okumoto K, Shirota Y. *Appl Phys Lett* 2001;79:2131.
- [32] Wang Y, Herron N, Grushin VV, LeCloux D, Petrov D. *Appl Phys Lett* 2001;79:449.
- [33] Im W-B, Hwang H-K, Lee J-G, Han K, Kim Y. *Appl Phys Lett* 2001;79:1387.