

Synthesis and characterization of fluorescent poly(oxadiazole)s containing 3,4-dialkoxythiophenes

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Abstract

We report the synthesis, optical and electrochemical details, and properties of three conjugated copolymers (P1–P3) consisting of alternate hole-transporting thiophene derivative and electron-transporting 1,3,4-oxadiazole units. The polymers are prepared using the precursor polyhydrazide route. The polymers have well defined structure and exhibit good thermal stability with the onset decomposition temperature in nitrogen at around 300 °C. All the polymers are soluble in organic solvents such as DMF, DMSO, NMP and in strong organic acids like trifluoroacetic acid. The optical and charge-transporting properties of the polymers are investigated by UV–visible spectroscopy, fluorescence emission spectroscopy and cyclic voltammetry. The UV–visible absorption spectra of polymers in solution showed a maximum at around 400 nm. The polymers depicted green fluorescence both in solution and as thin films. Cyclic voltammetry studies reveal that these copolymers have low-lying LUMO energy levels ranging from –3.28 to –3.36 eV and high-lying HOMO energy levels ranging from –5.5 to –5.56 eV, which indicated that they may be promising candidates for electron-transporting or hole-blocking materials in light-emitting diodes.

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1. Introduction

Conducting polymers have received considerable attention in the past two decades due to their potential applications in light emitting diodes (LEDs), electrochromic devices, solar cells, electrochemical supercapacitors and field effect transistors [1–8]. Since the initial report of polymer light emitting diodes by the Cambridge group in 1990 [9], enormous efforts have been devoted to the synthesis of light emitting polymers. Polyparaphenylenevinylene (PPV) [10,11], polyparaphenylene (PPP) [12,13], polythiophene (PT) [14,15], polyfluorene (PF) [16] 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 [17]. In order to achieve high electroluminescent efficiency, it is necessary to balance the injection of electrons and holes at the opposite contacts in PLED devices. 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. To overcome this problem several approaches have been developed. One is to use metals with low work function such as calcium as cathode [18,19]. The major problem

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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 [20]. However the most promising approach of adjusting the HOMO and LUMO levels of the conjugated polymers involves the incorporation of both n- and p-dopable segments in to the polymer backbone. In this direction Yu et al. [21,22] and Huang et al. [23] have synthesized polymers containing oligothiophenes as electron rich p-dopable blocks and bis(1,3,4-oxadiazolyl)benzene as electron deficient n-dopable block. Reynolds et al. [24] have used 3,4-ethylenedioxythiophene as an electron rich block and pyridine as an electron poor block. Recently, Kumar and co-workers [25] have synthesized polymers having 3,4-alkylenedioxythiophene and 1,3,4-oxadiazole moieties. Ng et al. [26] have synthesized polymers comprising alternating electron donating thiophene and electron withdrawing oxadiazole units. Poly(3,4-ethylenedioxythiophene) (PEDOT), is thermally stable with low band gap and can be easily p-doped. Similarly 3,4-dialkoxy substituted polythiophenes show facile dopability and lower bandgap ascribe to the electron donating nature of the alkoxy moiety. In addition, introduction of long alkoxy pendants at the 3- and 4-positions of the thiophene ring improves the solvent processability of the corresponding polymer. In this report, we describe the synthesis and characterization of p- and n-dopable polymers where EDOT and 3,4-dialkoxythiophenes have been used as electron rich p-dope type segments and 1,3,4-oxadiazole as electron deficient n-type segment.

2. Experimental

Diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (1) was synthesized according to the literature procedure [27]. Dimethylformamide (DMF) and acetonitrile (ACN) were dried by distillation over CaH₂. 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. Diethyl 3,4-dialkoxythiophene-2,5-dicarboxylates (2a-c) were synthesized starting from compound 1 according to the reported procedure [28,29]. Infrared spectra of all intermediate compounds and polymers were recorded on a Nicolet Avatar 330 FT-IR (Thermo Electron Corporation). The UV-visible spectra of the polymers were measured using Varian CARY 500 spectrophotometer. Thermogravimetric analysis (TGA) was carried out with thermal analysis 2950 thermogravimetric analyzer (TA instruments). ¹H and ¹³C NMR spectra were obtained with AMX 400 MHz FT-NMR spectrometer using TMS/solvent signal as internal reference. Molecular weights of the polymers were determined by Shimadzu gel permeation chromatograph using polystyrene standards. Fluorescence

spectra of the polymers were recorded using 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 polymers were carried out using 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. General procedure for the synthesis of 3,4-dialkoxythiophene-2,5-carbonyldihydrazide, (3a-c)

Diethyl 3,4-dialkoxythiophene-2,5-dicarboxylate (0.5 g) was added into a solution of 10 ml of hydrazine hydrate in 40 ml of methanol. The reaction mixture was refluxed for 2 h. Upon cooling the solution to room temperature a white precipitate was obtained. The precipitate was filtered, washed with petroleum ether and dried under vacuum to get the product as white solid.

3,4-dihexyloxythiophene-2,5-carbonyldihydrazide (3a): yield: 90%, ¹H NMR (DMSO-*d*⁶) δ (ppm): 8.82 (s, 2H), 4.58 (s, 4H), 4.13 (t, 4H), 1.2–1.8 (m, 16H), 0.88 (t, 6H), ¹³C NMR (DMSO-*d*⁶) δ (ppm): 160.12, 147.03, 124.25, 73.46, 32.54, 31.05, 28.32, 22.21, 13.54. IR: 3408, 3328, 3293, 3197, 2931, 2862, 1652, 1507, 1369, 1307, 1057, 950, 631 cm⁻¹. Elemental (C₁₈H₃₂N₄O₄S). Calc: C, 54.0; H, 8.0; N, 14.0; S, 8.0. Found: C, 54.02; H, 7.73; N, 14.04; S, 7.99.

3,4-dioctyloxythiophene-2,5-carbonyldihydrazide (3b): yield: 85%, ¹H NMR (DMSO-*d*⁶) δ (ppm): 8.84 (s, 2H), 4.58 (s, 4H), 4.13 (t, 4H), 1.2–1.8 (m, 24H), 0.89 (t, 6H), ¹³C NMR (DMSO-*d*⁶) δ (ppm): 160.03, 147.03, 121.33, 73.72, 31.2, 29.28, 28.64, 25.63, 25.27, 22.06, 13.89. IR: 3407, 3331, 3289, 3194, 2920, 2858, 1653, 1508, 1369, 1304, 1055, 948, 629 cm⁻¹. Elemental (C₂₂H₄₀N₄O₄S). Calc: C, 57.9; H, 8.78; N, 12.28; S, 7.01. Found: C, 57.67; H, 8.77; N, 12.31; S, 6.64.

3,4-didecyloxythiophene-2,5-carbonyldihydrazide (3c): yield: 95%, ¹H NMR (DMSO-*d*⁶) δ (ppm): 8.9 (s, 2H), 4.6 (s, 4H), 4.12 (t, 4H), 1.3–1.8 (m, 32H), 0.93 (t, 6H), ¹³C NMR (DMSO-*d*⁶) δ (ppm): 160.01, 147.11, 126.42, 73.82, 32.65, 31.21, 30.59, 29.42, 28.86, 28.62, 25.2, 22.01, 13.84. IR: 3410, 3331, 3292, 3194, 2919, 2853, 1655, 1507, 1370, 1303, 1056, 953, 625 cm⁻¹. Elemental (C₂₆H₄₈N₄O₄S). Calc: C, 60.94; H, 9.44; N, 10.94; S, 5.64. Found: C, 60.87; H, 9.24; N, 10.75; S, 5.94.

2.2. Synthesis of 3,4-ethylenedioxythiophene-2,5-dicarboxylic acid (5)

Diethyl 3,4-ethylenedioxythiophene-2,5-dicarboxylate, 4, (0.5 g, 1.75 mmol) was refluxed with 20 ml of 10% sodium hydroxide solution for 8 h. The solution was then cooled to room temperature and was acidified with concentrated hydrochloric acid to get white precipitate.

The precipitate was filtered, washed with water and dried to get the product with 65% yield. Mp: 223 (dec.), ^1H NMR (DMSO- d^6) δ (ppm): 4.2 (s, 4H), 13 (s, broad), ^{13}C NMR (DMSO- d^6) δ (ppm): 161.69, 144.74, 111.72, 64.28. IR: 3559, 2948, 1681, 1574, 1309, 1098, 857, 831, 767 cm^{-1} . Elemental ($\text{C}_8\text{H}_6\text{O}_6\text{S}$). Calc: C, 41.74; H, 2.61; S, 13.91. Found: C, 41.46; H, 2.56; S, 13.94.

2.3. Synthesis of 3,4-ethylenedioxythiophene-2,5-dicarboxylic acid chloride (6)

Thionyl chloride (15 ml) was added to 0.5 g of 3,4-ethylenedioxythiophene-2,5-dicarboxylic acid (5). The reaction mixture was refluxed for 9 h, and then excess thionyl chloride was removed under reduced pressure. The residual green solid was extracted with dichloromethane and dried over anhydrous sodium sulfate. The solvent was evaporated using rotary evaporator to get 0.47 g (yield 80%) of the product. ^1H NMR (DMSO- d^6) δ (ppm): 4.5 (s, 4H), ^{13}C NMR (DMSO- d^6) δ (ppm): 161.59, 144.8, 111.61, 64.26, IR: 2945, 1748, 1570, 1299, 1092, 844 cm^{-1} . Elemental ($\text{C}_8\text{H}_4\text{O}_4\text{SCl}_2$). Calc: C, 32.21; H, 1.34; S, 10.74. Found: C, 32.45; H, 1.51; S, 10.67.

2.4. General procedure for the synthesis of polyhydrazides, (7a-c)

To a mixture of 1 equivalent of appropriate dihydrazide, 2 equivalent of anhydrous aluminum chloride and 0.1 ml of pyridine, 1 equivalent 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 70–85% yield.

7a: Yield: 85%. IR: 3349, 2954, 2871, 1637, 1559, 1451, 1282, 1096 cm^{-1} . 7b: Yield: 80%. IR: 3350, 2928, 2856, 1638, 1439, 1282, 1094 cm^{-1} . 7c: Yield: 70%. IR: 3340, 2981, 2881, 1635, 1444, 1283, 1094 cm^{-1} .

2.5. General procedure for the synthesis of polyoxadiazoles, (P1–P3)

The mixture of polyhydrazide and 50 ml of polyphosphoric acid was heated at 100 °C for 4 h. The reaction mixture was then cooled to room temperature and poured in to excess of water. The resulting precipitate was collected by filtration and was washed with water followed by acetone and dried in oven to get the polymers in 70–80% yield.

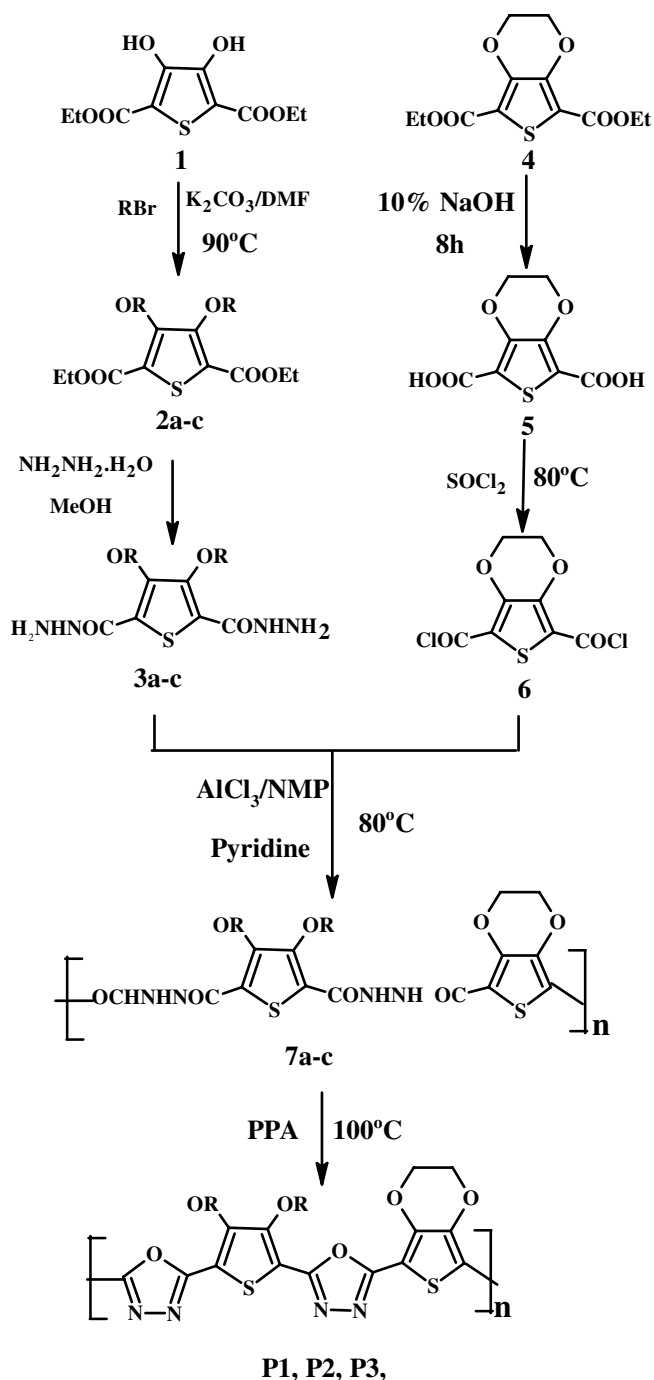
P1: ^1H NMR (DMSO- d^6) δ (ppm): 4.55 (s, 4H), 4.13 (t, 4H), 1.8–0.89 (m, 22H), ^{13}C NMR (DMSO- d^6) δ (ppm): 161.72, 160.05, 147.53, 144.52, 124.57, 112.1, 73.39, 63.52, 32.21, 30.96, 28.72, 22.59, 13.61, IR: 2952, 2873, 1538, 1440, 1363, 1161, 1077, 994 cm^{-1} . Elemental

($\text{C}_{26}\text{H}_{30}\text{N}_4\text{S}_2\text{O}_6$). Calc: C, 55.91; H, 5.38; N, 10.03; S, 11.47. Found: C, 55.65; H, 5.52; N, 10.65; S, 11.67. P2: ^1H NMR (DMSO- d^6) δ (ppm): 4.56 (s), 4.12 (t), 1.8–0.89 (m), ^{13}C NMR (DMSO- d^6) δ (ppm): 161.63, 160.23, 147.32, 144.85, 122.05, 112.23, 73.72, 64.58, 31.21, 29.24, 28.61, 25.67, 25.18, 22.03, 13.88. IR: 2951, 2867, 1538, 1440, 1363, 1159, 1075, 994 cm^{-1} . Elemental ($\text{C}_{30}\text{H}_{38}\text{N}_4\text{S}_2\text{O}_6$). Calc: C, 58.63; H, 6.19; N, 9.12; S, 10.42. Found: C, 57.92; H, 6.05; N, 9.45; S, 10.22. P3: ^1H NMR (DMSO- d^6) δ (ppm): 4.55 (s), 4.1 (t), 1.8–0.92 (m), ^{13}C NMR (DMSO- d^6) δ (ppm): 161.82, 160.21, 148.28, 144.92, 126.64, 112.34, 73.93, 65.18, 32.92, 31.31, 30.58, 29.56, 29.19, 28.89, 25.31, 22.08, 14.03. IR: 2886, 1534, 1442, 1361, 1164, 1081, 999 cm^{-1} . Elemental ($\text{C}_{34}\text{H}_{46}\text{N}_4\text{S}_2\text{O}_6$). Calc: C, 60.90; H, 6.87; N, 8.36; S, 9.55. Found: C, 60.23; H, 7.13; N, 8.54; S, 9.83.

3. Results and discussion

3.1. Synthesis and characterization of polymers

Synthetic routes of copolymers P1–P3 are shown in Scheme 1. Diethyl 3,4-dialkoxythiophene-2,5-dicarboxylates (2a-c) were prepared by treating the compound 1 with corresponding *n*-bromoalkane in presence of potassium carbonate and DMF. For the synthesis of 3,4-dialkoxythiophene-2,5-carbonyldihydrazides (3a-c), corresponding diethyl 3,4-dialkoxythiophene-2,5-dicarboxylates were treated with excess of hydrazine monohydrate in methanol. Hydrolysis reaction of diethyl 3,4-ethylenedioxythiophene-2,5-dicarboxylate using 10% sodium hydroxide solution yielded 3,4-ethylenedioxythiophene-2,5-dicarboxylic acid which was then treated with excess thionyl chloride to obtain 3,4-ethylenedioxythiophene-2,5-dicarboxylic acid chloride. Polyhydrazides (7a-c) were prepared by the polycondensation reaction of 3,4-ethylenedioxythiophene-2,5-dicarboxylic acid chloride with the corresponding 3,4-dialkoxythiophene-2,5-carbonyldihydrazide in *N*-methylpyrrolidone (NMP) in the presence of anhydrous aluminum chloride and pyridine. These polyhydrazides are insoluble in common organic solvents at ambient and at elevated temperatures, as observed for other polyhydrazides. The polyhydrazides were converted in to the corresponding poly (1,3,4-oxadiazole)s, (P1–P3), by cyclodehydration of the hydrazide group in to 1,3,4-oxadiazole ring, using polyphosphoric acid (PPA), which function both as solvent and dehydrating agent. The successful conversion of polyhydrazide in to polyoxadiazole was confirmed by FT-IR spectra. The stretching bands of C=O and N–H groups in polyhydrazides around 1637 and 3350 cm^{-1} , respectively, disappear in the IR spectra of corresponding polyhydrazides, where as the band corresponding to imine (C=N) in an oxadiazole ring around 1538 cm^{-1} , was newly generated. In addition, oxadiazole =C–O–C= stretching is observed around 1075 and 994 cm^{-1} for these polymers. The FT-IR spectrum of P2 is shown in Fig. 1. The polymers P1–P3 were obtained as black powders. All the poly-



2a, 3a, P1: R= -C₆H₁₃

2b, 3b, P2: R= -C₈H₁₇

2c, 3c, P3: R= -C₁₀H₂₁

Scheme 1. Synthesis of polymers.

mers 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. The chemical structures of the polymers were confirmed by ¹H and ¹³C NMR spectra. In the ¹H NMR spectra of the polymers P1–P3, a singlet peak was observed around δ

4.55 due to the –OCH₂– group on the EDOT ring. All the polymers showed a triplet peak around δ 4.1 due to the –OCH₂– protons of the alkoxy groups on the thiophene ring. In addition, multiple peaks were obtained in the range δ 1.8–0.9, due to –(CH₂)_n– protons of the alkoxy group. The ¹H NMR spectrum of P2 is shown in Fig. 2. The ¹³C NMR spectra of the polymers are consistent with their chemical structures. In particular, the ¹³C NMR spectrum of P2 (Fig. 3) showed characteristic peaks at δ 161.63, 160.23 (imine carbons, C=N, of 1,3,4-oxadiazole ring), 147.32 (C-3 and C-4 of 3,4-dioctyloxythiophene unit), 144.85 (C-3 and C-4 of EDOT ring), 122.05 (C-2 and C-5 of 3,4-dioctyloxythiophene unit), 112.23 (C-2 and C-5 of EDOT ring), 73.72 (–OCH₂– of octyloxy groups), 64.58 (ethylene carbons of EDOT ring), 31.21–14.03 (alkyl carbons, –(CH₂)₆CH₃, of octyloxy groups). The elemental analysis results for the polymers are in agreement with their expected empirical formula. Since the polymers are partially soluble in THF, only the molecular weights of the THF soluble parts were measured by means of gel permeation chromatography (GPC) using THF as eluant against polystyrene standards. The molecular weights of the THF soluble parts were measured as *M_n* = 3291 (PD = 1.34) for P1, 3465 (PD = 1.48) for P2 and 4149 (PD = 1.42) for P3. The actual molecular weights of the polymers should be higher than these measured values because of the insolubility of the parts with higher molecular weights. Although the results can not give accurate information on molecular weights of the polymers they convince us the polymeric structure of the obtained products. Thermogravimetric analysis (TGA) of all oxadiazole polymers was carried out under nitrogen atmosphere at a heating rate of 5 °C/min. All the polymers are found to be thermally stable up to ~300 °C. DSC studies were performed to observe glass transition temperature (*T_g*) of the polymers. 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 suggesting that the polymers are either having very high *T_g* or are highly crystalline in nature and decompose before melting.

3.2. Optical properties

3.2.1. Linear optical properties

The UV–visible absorption and fluorescence spectra of the polymers were recorded both in solution and in thin film, and the corresponding spectral data are summarized in Table 1. As shown in the Fig. 4, the absorption maxima of the polymers in dilute DMF solutions are 401 nm for P1, 408 nm for P2 and 415 nm for P3. These absorption maxima are comparable to those of some thiophene-1,3,4-oxadiazole copolymers [22,23]. The absorption spectra of the polymer thin films (Fig. 5) are similar to those in solutions, indicating that there is no much difference in the conformations of the polymer in the two states. Their optical energy band gaps (*E_g*) were calculated from the absorption edge in the thin films to be 2.23–2.28 eV (Table 1).

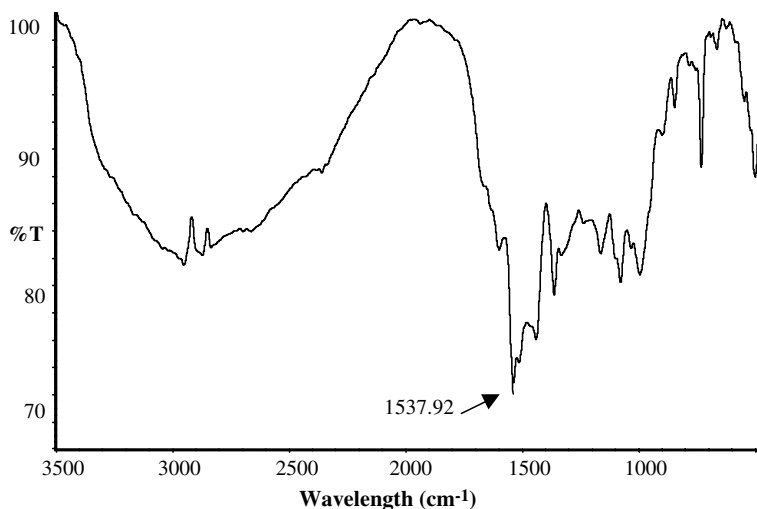
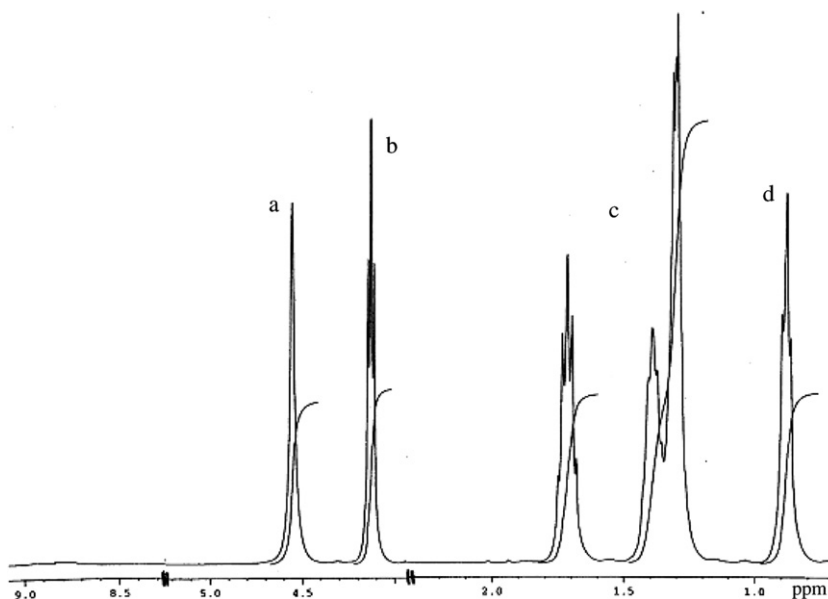


Fig. 1. FT-IR spectrum of P2.

Fig. 2. ^1H NMR spectrum of P2 ((a) OCH_2 of EDOT ring, (b) OCH_2 and (c) $-(\text{CH}_2)_6-$ of octyloxy groups, (d) $-\text{CH}_3$).

As shown in the Fig. 6, the emissive maxima (excitation wavelength 360 nm) of the polymers in dilute DMF solutions are 490 nm for P1, 492 nm for P2, and 495 nm for P3 with a shoulder at 446 nm for P3. The Stokes shift determined to be 89, 84 and 80 nm for P1, P2 and P3, respectively. The fluorescence emission spectra of these polymers in thin films are shown in Fig. 7. The polymers emit intense green light in solid state, with emission peaks at 516, 522 and 530 nm for P1, P2 and P3, respectively. 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, a sequential red shift in the λ_{max} was observed in both the UV–visible absorption spectra and fluorescence emission spectra of polymers P1–P3. The increase in the

length of the alkoxy side chains led to the red shift in the λ_{max} in UV–visible absorption and fluorescence emission spectra. This may be due to either an increase in the electron-donating property of the alkoxy group with increasing chain length or an expected better side chain interdigitation and interchain organization with increasing pendant chain length. The fluorescence quantum yields [30] of the polymers in solution were determined using quinine sulfate as a standard [31]. As shown in Table 1 the quantum yield of the polymers are in the range of 31–38%. These results indicate that the polymers can be used as light emitting materials in devices.

3.2.2. Non-linear optical properties

Conjugated polymers are a promising class of third-order non-linear optical (NLO) material because of their potentially large third-order susceptibilities associated with

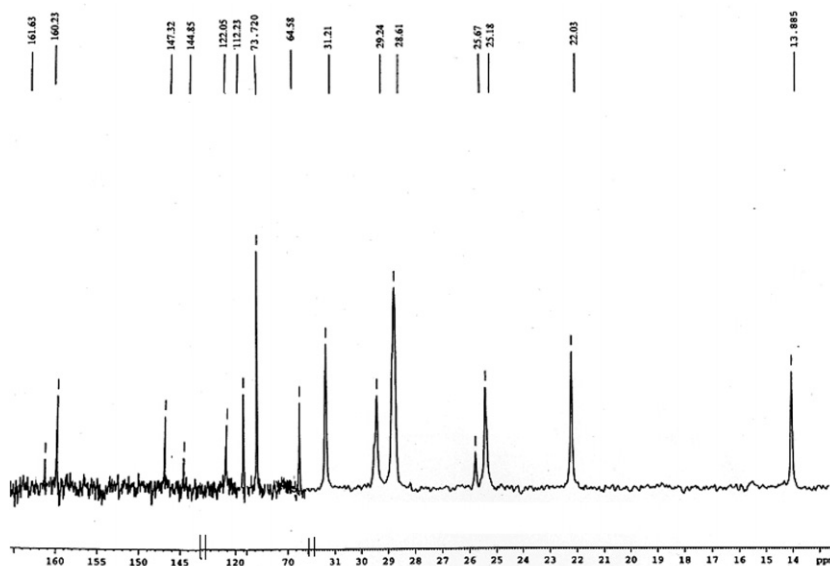
Fig. 3. ^{13}C NMR spectrum of P2.

Table 1
UV–visible absorption maxima, emission maxima and fluorescence quantum yields of the polymers

Polymer	UV–visible Spectroscopy		Fluorescence emission λ_{max}		Optical band gap E_g (eV)	Quantum yield ^a (%)
	λ_{max} (nm)		(nm)			
	Solution	Film	Solution	Film		
P1	401	401	490	516	2.28	38
P2	408	408	492	522	2.25	35
P3	415	415	495	530	2.23	31

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

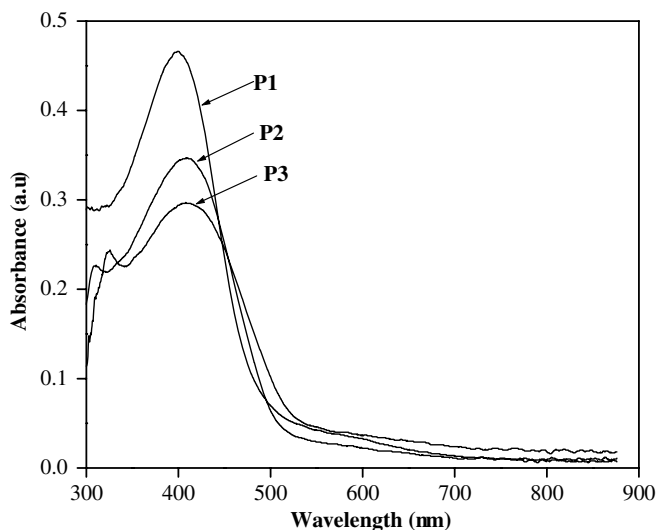


Fig. 4. UV–visible absorption spectra of P1–P3 in DMF solutions.

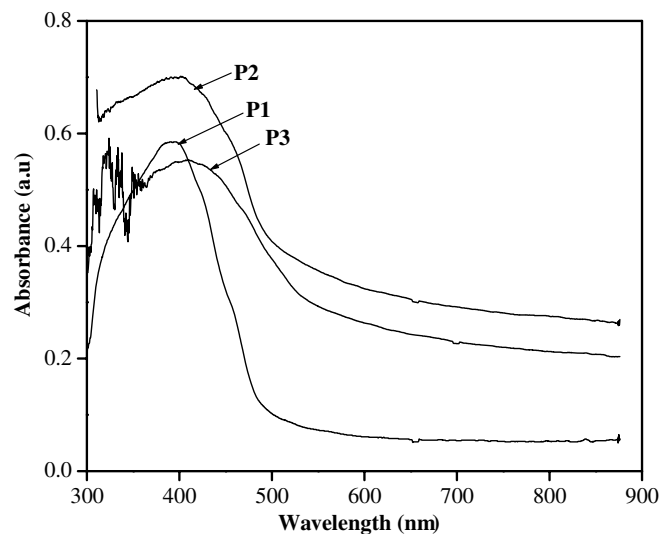


Fig. 5. UV–visible absorption spectra of the polymer thin films.

fast response time in addition to their variety, environmental stability and processability. Conjugated systems consisting of electron donor and electron acceptor units have showed enhanced third-order optical non-linearity [32]. Hence we expected that polymers P1–P3 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. Preliminary studies on these polymers using single beam Z-scan technique with Q-switched Nd:YAG nanosecond laser source yielded promising results. Further studies to determine third order optical susceptibility [$\chi^{(3)}$] and optical limiting behavior of the polymers are in progress.

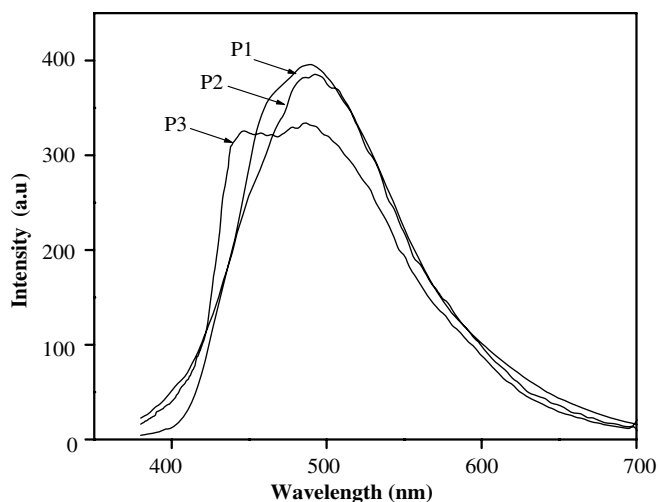


Fig. 6. Fluorescence emission spectra of P1–P3 in DMF solutions.

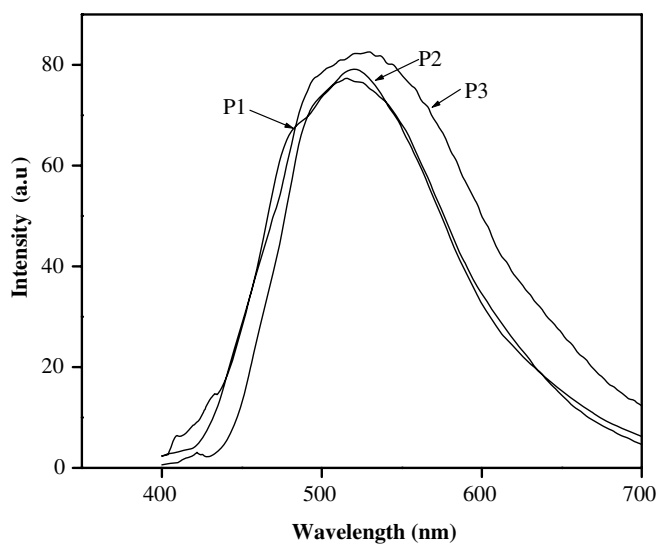


Fig. 7. Fluorescence emission spectra of the polymer thin films.

3.3. 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. While sweeping cathodically, the polymers showed reduction peak at around -1.3 V (Fig. 8). These reduction potentials are lower than those of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) [17,33], one of the most widely used electron transporting materials, and are comparable with those of some good electron transporting materials [17]. In the anodic sweep, polymers showed small oxidation peak at around $+1.26$ V (Fig. 9) comparable with those of

Table 2
Electrochemical potentials and energy levels of the polymers

Polymer	E (oxd)	E (red)	HOMO (eV)	LUMO (eV)	E_g (eV)
P1	1.26	-1.38	-5.50	-3.28	2.22
P2	1.27	-1.24	-5.55	-3.32	2.25
P3	1.24	-1.32	-5.56	-3.36	2.20

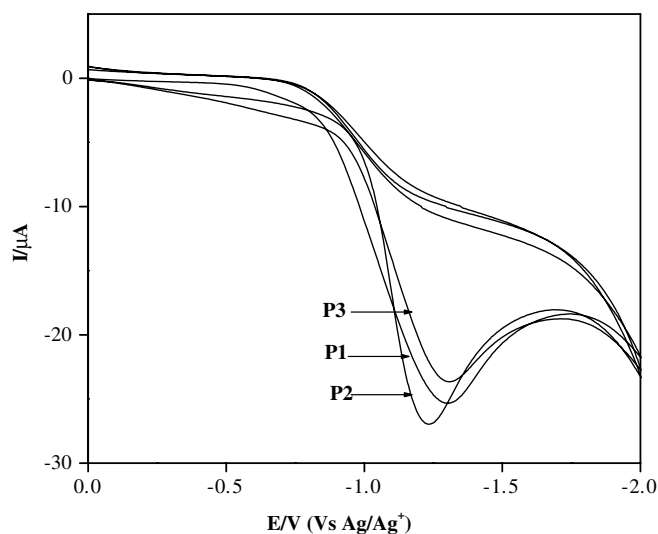


Fig. 8. Reduction cyclic voltammetry waves of the polymers at 25 mV/s scan rate in ACN/TBAPC (0.1 M) solution.

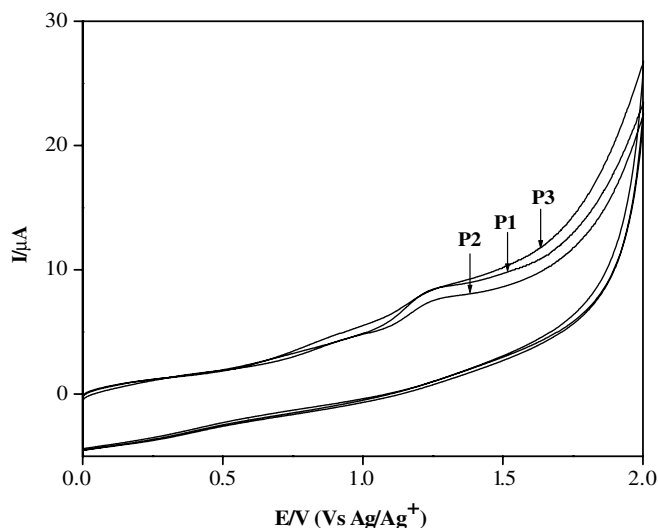


Fig. 9. Oxidation cyclic voltammetry waves of the polymers at 25 mV/s scan rate in ACN/TBAPC (0.1 M) solution.

some donor–accepter copolymers containing thiophene and oxadiazole units [22,23]. However, the redox behavior of these polymers is found to be independent of length of the alkoxy side chain on 3- and 4- positions of the thiophene ring. The onset potentials of n-doping and p-doping processes can be used to estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molec-

ular orbital (LUMO) energy levels of a conjugated polymer [34]. 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 versus SCE for the oxidation and reduction processes of a polymer respectively. The HOMO energy levels of polymers P1–P3 are estimated to be -5.5 , -5.55 and -5.56 eV respectively. These values 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 these values are higher than that of PPV [35]. 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 for some PPV-1,3,4-oxadiazole based copolymers. The LUMO energy levels of polymers P1–P3 are estimated to be -3.28 , -3.32 and -3.36 eV , respectively. These values are lower than those of PPV and other conjugated p-type polymers indicating that oxadiazole groups tend to decrease the barrier for electron injection and thus enhances the electron transporting properties of the corresponding polymers. 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) [36], indicating that these polymers have better electron-injection ability when they are used in PLEDs. A similar trend has been observed in some p–n diblock copolymers containing alternating electron donor and acceptor units [23]. Hence the high electron affinities of polymers P1–P3 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 polymers are comparable with those of some polyfluorene derivatives containing electron deficient 2-pyran-4-ylidene-malononitrile moiety [37]. From the onset potentials of oxidation and reduction processes, the band gaps of the polymers were estimated to be 2.22, 2.23 and 2.2 eV for polymer P1, P2 and P3 respectively. The values are quite close to those obtained by the optical method.

4. Conclusions

A new series of p- and n-dopable conjugated copolymers composed of 3,4-dialkoxythiophene, ethylenedioxythiophene (EDOT) and 1,3,4-oxadiazole units have been synthesized using precursor polyhydrazide route. The polymers have well defined structure and displayed good thermal stability. All the polymers showed a green fluorescence under the irradiation of UV light. The length of the electron-donating alkoxy chain at 3- and 4-positions of the thiophene ring influenced the optical properties of the polymers. Hence a sequential red shift was observed in the λ_{max} of the UV–visible absorption spectra and the fluorescence emission spectra of the polymers P1–P3. Electrochemical studies reveal that the polymers possess high-lying HOMO energy levels (from -5.5 to -5.56 eV) and

low-lying LUMO energy levels (from -3.28 to -3.36 eV) because of the alternate donor and acceptor conjugated units along the polymers' backbone, suggesting that the polymers are expected to provide enhanced charge transporting (electron transport/hole blocking) properties for the development of efficient LEDs.

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