Design and synthesis of new donor–acceptor type conjugated copolymers derived from thiophenes

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ABSTRACT

A new series of donor-acceptor type poly(thiophene) derivatives (**P1–P3**) were synthesized starting from thiodiglycolic acid and diethyl oxalate through multistep reactions. In the final step, the polymerization was carried out using Wittig reaction. This is a good synthetic route for the preparation of any desired p- and n-type copolymers. The optical and potential charge-transporting properties of the copolymers were investigated by UV–vis, fluorescence emission spectroscopy and cyclic voltammetry. The copolymers exhibited bluish-green/green fluorescence in their thin film forms. Cyclic voltammetry experiments showed that these copolymers have low-lying LUMO energy levels ranging from −2.98 to −3.11 eV and high lying HOMO energy levels ranging from −5.45 to −5.65 eV. The optical and electrochemical studies reveal that new copolymers are new promising materials for the development of efficient polymer light emitting diodes.

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1. Introduction

Intense research activities have been carried out on conjugated polymers as promising materials for optoelectronic applications during the last decade. Amongst various newly developed polymers, poly(1,4-phenylenevinylene) (PPV) [1], poly(*p*-phenylene) (PPPs) [2], polyfluorenes (PFs) [3], and polythiophenes (PTs) [4] were in the focus of investigations. Currently, one of the main research objectives in this field is to develop light emitting polymers with both high thermal stability and emitting efficiency that are directly related to the performance and reliability of polymer light emitting devices (PLEDs) [5,6]. The development of more effective electron transporting polymers (n-type) which facilitate the use of air-stable cathodes such as aluminium is one of the challenges to develop efficient PLEDs [7]. Generally, in PLEDs, polymers such as polypyridines [8], polyquinoxalines [9], polyquinolines [10], polyoxadiazoles [11] containing elec-

tron-affinitive molecules have been widely used as electron transporting materials. An ideal electron transport polymer should permit efficient electron injection into it from an air-stable metallic electrode [12]. Also it must possess high mobility of electrons and effective transfer of electrons to the emissive polymer at the polymer/polymer interface.

In order to achieve high efficiency of PLED devices, it is necessary to balance the injection rate of electrons and holes. It has been reported that in most of the existing conjugated polymers the barrier between the Lowest Occupied Molecular Orbital (LUMO) of the polymers and the work function of the cathode is much larger than that between the Highest Occupied Molecular Orbital (HOMO) of the polymer and the work function of the anode. This causes an imbalance of the injection between electrons and holes, resulting in low efficiency of the PLED devices. Generally, there are two strategies to improve the efficiency of the PLEDs. The first approach is to utilization of the low work function metals like Ca, Li as cathode [13]. Insertion of an electron transporting/hole blocking layer between the emitter and cathode [14] is the second strategy. Main disadvantages of these two approaches are reduction in the

durability of devices due to reactive cathodes and difficulty involving in the fabrication of double layers PLEDs.

The latest approach involves the modification of chemical structure of emitting polymer molecules, i.e., design of new conjugated polymers with desired HOMO and LUMO levels. To achieve this, the polymer back-bone must involve both donor and acceptor segments. In this context, it is necessary to incorporate electron rich and electron deficient units in the polymer chain during the synthetic design. In the structural design, selection of p- and n-type segments plays an important role on their balanced charge transporting property. Based on this, synthesis of few conjugated donor–acceptor type copolymers containing π-excessive and π-deficient units have been reported and shown to possess unique electrochemical and optical properties [15–20]. Literature survey reveals that 3,4-dialkoxy substituted poly(thiophene)s show facile dopability and lower band gap ascribe to the electron donating nature of the alkoxy moiety. It has been also reported that introduction of long alkoxy pendants at 3- and 4-positions of the thiophene ring improves the solvent processability and hole carrying ability of the corresponding polymer [21,22]. Here, the insertion of oxadiazole ring in the polymer back-bone enhances the electron transporting property of the polymer, as oxadiazole ring possesses high electron affinity [21,22]. Further, incorporation of vinylene linkages facilitates to planarize the polymer back-bone by overcoming torsional interactions between rings that could help to alter the band gap [23].

Against this background, it has been thought of designing the synthesis of new PLED-oriented conjugated copolymers containing 3,4-dialkoxy thiophene ring, 1,3,4-oxadiazole moiety and vinylene linkage with both electron and hole transport architecture. It is hoped that the resulting polymers would show balanced charge carrying property and hence they would act as efficient light-emitting materials. In this communication, we hereby report the synthesis of new copolymers (**P1**–**P3**) carrying 2,2′-(3,4-dialkyloxythilene-2,5-diyl)bis[5-(2-thienyl)-1,3,4-oxadiazole units in their backbone structure and investigation of their optical (absorption as well as emission) and electrochemical (redox) properties. Here, the intermediate polymer precursor acts as a good starting material for the synthesis of desired copolymers containing n- and p-type segments. This is a convenient tool for the structural modification.

2. Experimental

2.1. Materials and instrumentation

Diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (**1**) was synthesized according to literature procedure [24] starting from thiodiglycolic acid and diethyl oxalate. Dimethylformamide (DMF) and acetonitrile were dried by distillation over CaH_2. TBAPC & *n*-bromo alkanes were purchased from Lancaster (UK) and were used as received. All other solvents and reagents are of analytical grade, were purchased commercially and used without further purification. Diethyl 3,4-dialkoxythiophene-2,5-dicarbox-

ylates (**2a**–**c**) were synthesized according to the reported procedures [25–27]. Infrared and NMR spectra were recorded on a NICOLET 5700 FTIR (Thermo Electron Corporation) and an AMX 400 MHz FT-NMR spectrophotometer, respectively. The Mass spectra were recorded on a Jeol SX-102 (FAB) Mass Spectrometer. The UV–vis and fluorescence emission spectra were measured using a GBC Cintra 101 spectrophotometer and a Perkin Elmer LS 55 Fluorescence spectrometer, respectively. Elemental analyses were performed on a Flash EA 1112 CHNS analyzer (Thermo Electron Corporation). The molecular weights of the copolymers were determined by Waters make GPC instrument using polystyrene as standards. The electrochemical studies were carried out using a AUTOLAB PGSTAT 30 electrochemical analyzer. Cyclic voltammograms were recorded using a three electrode cell system with a glassy carbon button working electrode, a Pt wire as counter electrode and an Ag/AgCl electrode as the reference electrode.

2.2. Synthesis of intermediates and monomers

2.2.1. General procedure for the synthesis of 3,4-dialkoxythiophene-2,5-carboxydihydrazides (**3a**–**c**)

Diethyl 3,4-dialkoxythiophene-2,5-dicarboxylate (**2a**–**c**) (0.5 g) was added into a solution of 10 mL hydrazine monohydrate 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, dried under vacuum and finally recrystallized from ethanol to get crystalline white solid. 3,4-Dipropyloxythiophene-2,5-carboxydihydrazide (**3a**): Yield: 90%, ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.34 (s, 2H, >NH), 4.98 (s, 4H, —NH_2), 4.11 (t, 4H, —OCH_2—, J = 6.8 Hz), 1.76–1.85 (m, 4H, >CH_2), 1.03 (t, 6H, —CH_3, J = 7.4 Hz). IR (KBr, cm^{-1}): 3338, 3290 (>N—H), 3195, 2966, 2931, 2875, 1656 (>C=O), 1503, 1375, 1306, 1062, 949, 637. Element. Anal. Calcd. For $C_{12}H_{20}N_4O_4S$: C, 45.56; H, 6.37; N, 7.71; S, 10.14. Found: C, 45.48; H, 6.46; N, 7.62; S, 10.02. 3,4-Dipentyloxythiophene-2,5-carboxydihydrazidde (**3b**): Yield: 90%, ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.33 (s, 2H, >NH), 4.09 (s, 4H, —NH_2), 4.14 (t, 4H, —OCH_2—, J = 6.8 Hz), 1.35–1.9 (m, 12H, —$(CH_2)_3$—), 0.94 (t, 6H, —CH_3, J = 7.0 Hz). IR (KBr, cm^{-1}): 3317, 3238 (>N—H), 2956, 2928, 2862, 1657 (>C=O), 1548, 1477, 1307, 1057, 962, 672. Element. Anal. Calcd. For $C_{16}H_{28}N_4O_4S$: C, 51.59; H, 7.58; N, 15.04; S, 8.61. Found: C, 51.42; H, 7.67; N, 14.97; S, 8.52. 3,4-Diheptyloxythiophene-2,5-carboxydihydrazide (**3c**): Yield: 88%, ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.32 (s, 2H, >NH), 4.05 (s, 4H, —NH_2), 4.14 (t, 4H, —OCH_2—, J = 6.9 Hz), 1.3–1.8 (m, —$(CH_2)_5$—, 20H), 0.90 (t, 6H, —CH_3, J = 7.1 Hz). IR (KBr, cm^{-1}): 3339, 3289 (>N—H), 3193, 2956, 2923, 2854, 1657 (>C=O), 1502, 1305, 1049, 956, 632. Element. Anal. Calcd. For $C_{20}H_{36}N_4O_4S$: C, 56.05; H, 8.47; N, 13.07; S, 7.48. Found C, 55.86; H, 8.56; N, 13.02; S, 7.40.

2.2.2. General procedure for the synthesis of N^2,N^5-di-(4-methylbenzoyl)-3,4-dialkoxythiophene-2,5-dicarbohydrazides (**4a**–**c**)

To a mixture of 1 equivalent of appropriate dihydrazide (**3a**–**c**), 0.1 mL of pyridine in 50 mL of NMP, 2 equivalents

of 4-methyl benzoyl chloride was added slowly at room temperature while stirring. The stirring was continued at room temperature for 1 h. The resulting solution was heated at 80 °C for 5 h. After cooling to room temperature, the reaction mixture was poured into excess of water to get a precipitate. The precipitate obtained was collected by filtration, washed with excess of water, dried in oven and recrystalized from ethanol/chloroform mixture. N^2,N^5-Di-(4-methylbenzoyl)-3,4-dipropyloxythiophene-2,5-dicarbohydrazide (**4a**): Yield: 82%, m.p.: 210–212 °C. FBHRMS: *m/z*, 553. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 10.23 (s, 2H, >NH), 9.70 (s, 2H, >NH), 7.76 (d, 4H, Ar, *J* = 8.2 Hz), 7.25 (d, 4H, Ar, *J* = 8.0 Hz), 4.28 (t, 4H, —OCH$_2$—, *J* = 7.0 Hz), 2.40 (s, 6H, Ar—CH$_3$), 2.0 (m, 4H, >CH$_2$), 1.09 (t, 6H, —CH3, *J* = 7.4 Hz). ^{13}C NMR (400 MHz, CDCl$_3$), δ (ppm) 10.2, 21.6, 23.2, 76.7, 123.5, 127.3, 128.3, 129.4, 143.0, 148.1, 157.1, 163.9. IR (KBr cm^{-1}): 3371, 3291 (>N—H), 2956, 2925, 2878, 1697 (>C=O), 1670 (>C=O), 1494, 1283, 1047, 969, 740 cm^{-1}. Element. Anal. Calcd. For C$_{28}$H$_{32}$N$_4$O$_6$S: C, 60.85; H, 5.84; N, 10.14; S, 5.80. Found: C, 60.81; H, 5.70; N, 10.07; S, 5.72. N^2,N^5-Di-(4-methylbenzoyl)-3,4-dipentyloxythiophene-2,5-dicarbohydrazide (**4b**): Yield: 85%, m.p.: 212–213 °C. FBHRMS: *m/z*, 609. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 10.25 (s, 2H, >NH), 9.42 (s, 2H, >NH), 7.76 (d, 4H, Ar, *J* = 8.1 Hz), 7.26 (d, 4H, Ar, *J* = 8.1 Hz) 4.32 (t, 4H, —OCH$_2$—, *J* = 7.0 Hz), 2.41 (s, 6H, Ar—CH$_3$), 1.45–2.0 (m, 12H, —(CH$_2$)$_3$—), 0.96 (t, 6H, —CH3, *J* = 7.1 Hz). IR (KBr, cm^{-1}): 3371, 3256 (>N—H), 2959, 2930, 2865, 1696 (>C=O), 1659 (>C=O), 1498, 1286, 1046, 923, 744, 623. Element. Anal. Calcd. For C$_{32}$H$_{40}$N$_4$O$_6$S: C, 63.14; H, 6.62; N, 9.20; S, 5.27. Found: C, 62.97; H, 6.70; N, 9.27; S, 5.34. N^2,N^5-Di-(4-methylbenzoyl)-3,4-diheptyloxythiophene-2,5-dicarbohydrazide (**4c**): Yield: 88%, m.p.: 163–165 °C. FABHRMS: *m/z*, 665. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 10.23 (s, 2H, >NH), 9.73 (s, 2H, >NH), 7.76 (d, 4H, Ar, *J* = 8.2 Hz), 7.22 (d, 4H, Ar, *J* = 8.0 Hz), 4.30 (t, 4H, —OCH$_2$—, *J* = 7.0 Hz), 2.39 (s, 6H, Ar—CH$_3$), 1.30–199 (m, —(CH$_2$)$_5$—, 20H), 0.95 (t, 6H, —CH3, *J* = 7.0 Hz). IR (KBr, cm^{-1}): 3310, 3209, 2952, 2924, 2858, 1685, 1646, 1464, 1283, 1047, 834, 740. Element. Anal. Calcd. For C$_{36}$H$_{48}$N$_4$O$_6$S: C, 65.03; H, 7.28; N, 8.43; S, 4.82. Found: C, 64.80; H, 7.17; N, 8.32; S, 4.96.

2.2.3. General procedure for the synthesis of 2,2′-(3,4-dialkoxythiophene-2,5-diyl)bis[5-(4-methylphenyl)-1,3,4-oxadiazole] (5a–c)

A mixture 10 mmol of compound **4a–c** and 50 mL of phosphorous oxychloride was heated at 80 °C for 6 h. The reaction mixture was then cooled to room temperature and poured into an excess of ice cold water. The resulting precipitate was collected by filtration, washed with water and dried in oven. Further purification was done by recrystalizing the obtained solid from ethanol/chloroform mixture. 2,2′-(3,4-Dipropyloxythiophene-2,5-diyl)bis[5-(4-methylphenyl)-1,3,4-oxadiazole] (**5a**): Yield: 90%, m.p.: 178–180 °C. FABHRMS: *m/z*, 517. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 8.01 (d, 4H, Ar, *J* = 8.0 Hz), 7.35 (d, 4H, Ar, *J* = 8.0 Hz), 4.30 (t, 4H, —OCH$_2$—, *J* = 6.8 Hz), 2.45 (s, 6H, Ar—CH$_3$), 1.92 (m, 4H, >CH$_2$), 1.10 (t, 6H, —CH$_3$, *J* = 7.3 Hz). ^{13}C NMR (400 MHz, CDCl$_3$), δ (ppm) 10.4, 21.7, 23.4, 76.4, 111.2, 120.7, 126.9, 129.9, 142.6, 150.9, 158.7,

164.4. IR (KBr, cm^{-1}): 2960, 2925, 2876, 1587 (C=N), 1495, 1460, 1278, 1035, 826, 733. Element. Anal. Cacld. For C$_{28}$H$_{28}$N$_4$O$_4$S: C, 65.10; H, 5.46; N, 10.85; S, 6.21. Found: C, 64.92; H, 5.40; N, 10.72; S, 6.14. 2,2′-(3,4-Dipentyloxythiophene-2,5-diyl)bis[5-(4-methylphenyl)-1,3,4-oxadiazole] (**5b**): Yield: 92%, m.p.: 126–128 °C. FABHRMS: *m/z*, 573. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 8.02 (d, 4H, Ar, *J* = 8.2 Hz), 7.34 (d, 4H, Ar, *J* = 8.0 Hz), 4.32 (t, 4H, —OCH$_2$—, *J* = 6.8 Hz), 2.46 (s, 6H, Ar—CH$_3$), 1.38–1.86 (m, 12H, —(CH$_2$)$_3$—), 0.96 (t, 6H, —CH$_3$, *J* = 7.0 Hz). IR (KBr, cm^{-1}): 2953, 2866, 1587 (C=N), 1495, 1464, 1279, 1054, 964, 822, 731. Element. Anal. Calcd. For C$_{32}$H$_{36}$N$_4$O$_4$S: C, 67.11; H, 6.34; N, 9.78; S, 5.60. Found: C, 67.00; H, 6.42; N, 9.62; S, 5.47. 2,2′-(3,4-Diheptyloxythiophene-2,5-diyl)-bis[5-(4-methylphenyl)-1,3,4-oxadiazole] (**5c**): Yield: 92%, m.p.: 87–89 °C. FABHRMS: *m/z*, 629. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.02 (d, 4H, Ar, *J* = 8.2 Hz), 7.35 (d, 4H, Ar, *J* = 8.0 Hz), 4.32 (t, 4H, —OCH$_2$—, *J* = 6.7 Hz), 2.46 (s, 6H, Ar—CH$_3$), 1.31–1.89 (m, 20H, —(CH$_2$)$_5$—), 0.95 (t, 6H, —CH$_3$, *J* = 7.0 Hz). IR (KBr, cm^{-1}): 2923, 2856, 1583 (C=N), 1521, 1494, 1469, 1280, 1049, 961, 825, 731. Element. Anal. Calcd. For C$_{36}$H$_{44}$N$_4$O$_4$S: C, 68.76; H, 7.05; N, 8.91; S, 5.10. Found: C, 68.62; H, 6.96; N, 8.99; S, 5.23.

2.2.4. General procedure for the synthesis of 2,2′-(3,4-dialkoxythiophene-2,5-diyl)bis[5-(4-bromomethylphenyl)-1,3,4-oxadiazole] (6a–c)

A mixture of 10 mmol of compound **5a–c**, 20 mmol of *N*-bromosuccinimide, 5 mg of benzoyl peroxide in 30 mL of benzene was refluxed for 5 h. After the solvent was removed, 20 mL of water was added with stirring for 1 h. The resulting crude product was recrystalized from methyl acetate/chloroform mixture. 2,2′-(3,4-Dipropyloxythiophene-2,5-diyl)bis[5-(4-bromomethylphenyl)-1,3,4-oxadiazole] (**6a**): Yield: 56%, m.p.: 199–202 °C. FABHRMS: *m/z*, 675. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.98 (d, 4H, Ar, *J* = 8.1 Hz), 7.32 (d, 4H, Ar, *J* = 8.0 Hz), 4.56 (s, 4H, Ar—CH$_2$Br), 4.33 (t, 4H, —OCH$_2$—, *J* = 6.8 Hz), 1.90 (m, 4H, >CH$_2$), 0.94 (t, 6H, —CH$_3$, *J* = 7.2 Hz). ^{13}C NMR (400 MHz, CDCl$_3$), δ (ppm): 10.7, 21.9, 24.2, 76.3, 110.9, 120.4, 126.5, 130.3, 142.9, 151.2, 158.6, 164.7. IR (KBr, cm^{-1}): 2966, 2878, 1589 (C=N), 1464, 1279, 1227, 1063, 961, 931, 849, 725, 603, 501. Element. Anal. Calcd. For C$_{28}$H$_{26}$Br$_2$N$_4$O$_4$S: C, 49.87; H, 3.89; N, 8.31; S, 4.75. Found: C, 49.70; H, 4.02; N, 8.39; S, 4.88. 2,2′-(3,4-Dipentyloxythiophene-2,5-diyl)bis[5-(4-bromomethylphenyl)-1,3,4-oxadiazole] (**6b**): Yield: 53%, m.p.: 165–167 °C. FABHRMS: *m/z*, 731. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 8.03 (d, 4H, Ar, *J* = 8.2 Hz), 7.32 (d, 4H, Ar, *J* = 8.1 Hz), 4.56 (s, 4H, Ar—CH$_2$Br), 4.31 (t, 4H, —OCH$_2$—, *J* = 6.9 Hz), 1.36–1.90 (m, 12H, —(CH$_2$)$_3$—), 0.95 (t, 6H, —CH$_3$, *J* = 7.1 Hz). IR (KBr, cm^{-1}): 2954, 2865, 1588 (C=N), 1463, 1278, 1227, 1053, 963, 851, 727, 603, 502. Element. Anal. Cacld. For C$_{32}$H$_{34}$Br$_2$N$_4$O$_4$S: C, 52.61; H, 4.69; N, 7.67; S, 4.39. Found: C, 52.37; H, 4.78; N, 7.72; S, 4.46. 2,2′-(3,4-Diheptyloxythiophene-2,5-diyl)bis[5-(4-bromomethylphenyl)-1,3,4-oxadiazole] (**6c**): Yield: 54%, m.p.: 148–150 °C. FABHRMS: *m/z*, 787. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 8.04 (d, 4H, Ar, *J* = 8.1 Hz), 7.30 (d, 4H, Ar, *J* = 8.1 Hz), 4.53 (s, 4H, Ar—CH$_2$Br), 4.32 (t, 4H, —OCH$_2$—, *J* = 7.0 Hz), 1.32–1.92 (m, 20H, —(CH$_2$)$_5$—), 0.92 (t, 6H, —CH$_3$, *J* = 7.3 Hz). IR

(KBr, cm^{-1}): 2925, 2856, 1587 (C=N), 1463, 1279, 1226, 1048, 961, 850, 726, 603, 502. Element. Anal. Calcd. For C$_{36}$H$_{42}$Br$_2$N$_4$O$_4$S: C, 54.97; H, 5.38; N, 7.12; S, 4.08. Found: C, 54.78; H, 5.48; N, 7.24; S, 3.97.

2.2.5. General procedure for the synthesis of 2,2′-(3,4-dialkoxythiophene-2,5-diyl)bis[5-((4-triphenylphosphonionmethyl)phenyl)-1,3,4-oxadiazole]dibromide (7a–c)

A solution of 10 mmol of dibromide compound **6a–c** and 20 mmol of triphenylphosphine in 20 mL of DMF was refluxed with stirring for 10 h. The reaction mixture was cooled to room temperature and poured in to 50 mL of ethyl acetate. The resulting precipitate was filtered off, washed with excess of ethyl acetate and dried at 40 °C for 10 h. 2,2′-(3,4-Dipropyloxythiophene-2,5-diyl)bis[5-((4-triphenylphosphonionmethyl)phenyl-1,3,4-oxadiazole] dibromide (**7a**): Yield: 72%, m.p.: 222–224 °C. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.20–7.92 (m, 38H, Ar), 6.10 (s, 4H, Ar—CH$_2$—), 4.26 (t, 4H, —OCH$_2$—, J = 6.9 Hz), 1.89 (m, 4H, >CH$_2$), 1.06 (t, 6H, —CH$_3$, J = 7.1 Hz). IR (KBr, cm^{-1}): 2965, 2876, 2776, 1588 (C=N), 1493, 1438, 1110, 1061, 854, 750, 721, 692, 509. Element. Anal. Calcd. For C$_{64}$H$_{56}$Br$_2$N$_4$O$_4$P$_2$S: C, 64.11; H, 4.71; N, 4.67; S, 2.67. Found: C, 63.96; H, 4.60; N, 4.62; S, 2.61. 2,2′-(3,4-Dipentyloxythiophene-2,5-diyl)bis[5-((4-triphenylphosphonionmethyl)phenyl-1,3,4-oxadiazole]dibromide (**7b**): Yield: 75%, m.p.: 188–190 °C. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.18–7.95 (m, 38H, Ar), 6.08 (s, 4H, Ar—CH$_2$—), 4.30 (t, 4H, —OCH$_2$—, J = 6.7 Hz), 1.29–1.92 (m, 12H, —(CH$_2$)$_3$—), 0.98 (t, 6H, —CH$_3$, J = 7.2 Hz). IR (KBr, cm^{-1}): 2962, 2865, 2773, 1587 (C=N), 1492, 1438, 1112, 1051, 963, 855, 750, 721, 692, 508. Element. Anal. Cacld. For C$_{68}$H$_{64}$Br$_2$N$_4$O$_4$P$_2$S: C, 65.07; H, 5.14; N, 4.46; S, 2.55. Found: C, 64.92; H, 5.20; N, 4.49; S, 2.65. 2,2′-(3,4-Diheptyloxythiophene-2,5-diyl)bis[5-((4-triphenylphosphonionmethyl)phenyl-1,3,4-oxadiazole]dibromide (**7c**): Yield: 76%, m.p.: 175–177 °C. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.24–7.90 (m, 38H, Ar), 6.10 (s, 4H, Ar—CH$_2$—), 4.29 (t, 4H, —OCH$_2$—, J = 6.9 Hz), 1.28–1.86 (m, 20H, —(CH$_2$)$_5$—), 0.88 (t, 6H, —CH$_3$, J = 7.1 Hz). IR (KBr, cm^{-1}): 2925, 2859, 2775, 1588 (C=N), 1493, 1437, 1278, 1111, 1050, 962, 853, 750, 722, 692, 509. Element. Anal. Cacld. For C$_{72}$H$_{72}$Br$_2$N$_4$O$_4$P$_2$S: C, 65.95; H, 5.53; N, 4.27; S, 2.45. Found: C, 65.70; H, 5.02; N, 4.37; S, 2.52.

2.3. Synthesis of copolymers (P1–P3)

General procedure: To a clear solution of 1 mmol of compound **7a–c** and 1 mmol of terephthlaldehyde in a mixture of 15 mL of ethanol and 5 mL of chloroform was added 10 mmol of sodium ethoxide solution, in 10 mL of ethanol at room temperature under nitrogen atmosphere. The mixture was stirred for 12 h. The solvent was removed and 10 mL of water was added and stirred for 1 h. The obtained polymer was redissolved in chloroform and poured into 50 mL of methanol. The precipitate was filtered off and dried at 40 °C under vacuum for 24 h to give fluorescent yellow to reddish yellow powders. **P1**: Yield: 52%, ^{1}H NMR (400 MHz, CDCl$_3$), δ 6.65–8.10 (m, 16H, Ar and —CH$_2$=CH$_2$—), 4.3 (t, 4H, —OCH$_2$—, J = 6.7 Hz), 1.90 (m, 4H, >CH$_2$), 0.89 (t, 6H, —CH$_3$— J = 7.2 Hz). IR (KBr, cm^{-1}): 2965, 2860, 2878, 2744, 1603 (C=N), 1492, 1211, 1060, 962, 841, 726. Element. Anal. Calcd. For C$_{36}$H$_{30}$N$_4$O$_4$S: C, 70.34; H, 4.92; N, 9.11; S, 5.22. Found: C, 69.72; H, 4.70; N, 9.37; S, 5.08. **P2**: Yield: 56%, ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 6.82–8.06 (m, 16H, Ar and —CH$_2$=CH$_2$—), 4.28 (t, 4H, —OCH$_2$—, J = 6.9 Hz), 1.28–1.90 (m, 16H, —(CH$_2$)$_3$—), 0.96 (t, 6H, —CH$_3$, J = 7.0 Hz). IR (KBr, cm^{-1}): 2954, 2865, 2756, 1605 (C=N), 1491, 1210, 1051, 964, 885, 842, 730. Element. Anal. Cacld. For C$_{40}$H$_{38}$N$_4$O$_4$S: C, 71.62; H, 5.71; N, 8.35; S, 4.78. Found: C, 71.36; H, 5.60; N, 8.21; S, 4.92. **P3**: Yield: 55%, ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm) 6.64–8.13 (m, 16H, Ar and —CH$_2$=CH$_2$—), 4.30 (t, 4H, —OCH$_2$—, J = 6.8 Hz), 1.28—1.89 (m, 20H, —(CH$_2$)$_5$—), 0.88 (t, 6H, —CH$_3$, J = 7.2 Hz). IR (KBr, cm^{-1}): 2857, 2752, 1604 (C=N), 1492, 1211, 1045, 962, 886, 843, 727. Element. Anal. Calcd. For C$_{44}$H$_{46}$N$_4$O$_4$S: C, 72.70; H, 6.38; N, 7.71; S, 4.41. Found: C, 72.32; H, 6.28; N, 7.56; S, 4.22.

3. Results and discussion

3.1. Synthetic plan

Scheme 1 shows the novel synthetic route for the preparation of monomers and copolymers. Diethyl 3,4-dialkoxythiophene-2,5-dicarboxylates (**2a–c**) were prepared by treating diethyl 3,4-dihydroxy thiophene-2,5-dicarboxylate (**1**) with corresponding *n*-bromoalkanes in presence of potassium carbonate and DMF. These diesters were readily converted to 3,4-dialkoxythiophene-2,5-carboxydihydrazides (**3a–c**), by the action of hydrazine hydrate in alcoholic medium. Then, compounds **3a–c** were benzoylated to yield N^2,N^5-di-(4-methylbenzoyl)-3,4-dialkoxythiophene-2,5-dicarbohydrazides (**4a–c**), which on treatment with phosphorus oxychloride afforded 2,2′-(3,4-dialkoxythiophene-2,5-diyl)bis[5-(4-methylphenyl)-1,3,4-oxadiazole] (**5a–c**) in good yield [28]. These bisoxadiazoles were Wohl–Ziegler brominated using *N*-bromo succinimide (NBS) in benzene and the resulting 2,2′-(3,4-dialkoxythiophene-2,5-diyl)bis[5-(4-bromomethylphenyl)-1,3,4-oxadiazole] (**6a–c**) were further transformed to the required precursors, 2,2′-(3,4-dialkoxythiophene-2,5-diyl)bis[5-((4-triphenylphosphonionmethyl) phenyl)-1,3,4oxadiazole] dibromides (**7a–c**) by treating them with triphenylphosphine in presence of DMF. The target copolymers **P1–P3** were obtained by Wittig reactions of the monomers **7a–c** with terphthalaldehyde (**8**) in presence of chloroform–ethanol under nitrogen atmosphere. The intermediates **7a–c** can readily react with substituted aldehydes and hence synthesis of any desired copolymer can be achieved. This is an excellent synthetic protocol for new copolymers.

3.2. Characterization

The structures of newly synthesized compounds were confirmed by their spectral and elemental analyses. Formation of 3,4-dipropyloxythiophene-2,5-carboxydihydrazide (**3a**) from diester (**2a**) was evidenced by its IR and ^{1}H NMR spectral data. Its IR spectrum showed sharp peaks at 3338 and1656 cm^{-1} indicating the presence of —NH$_2$
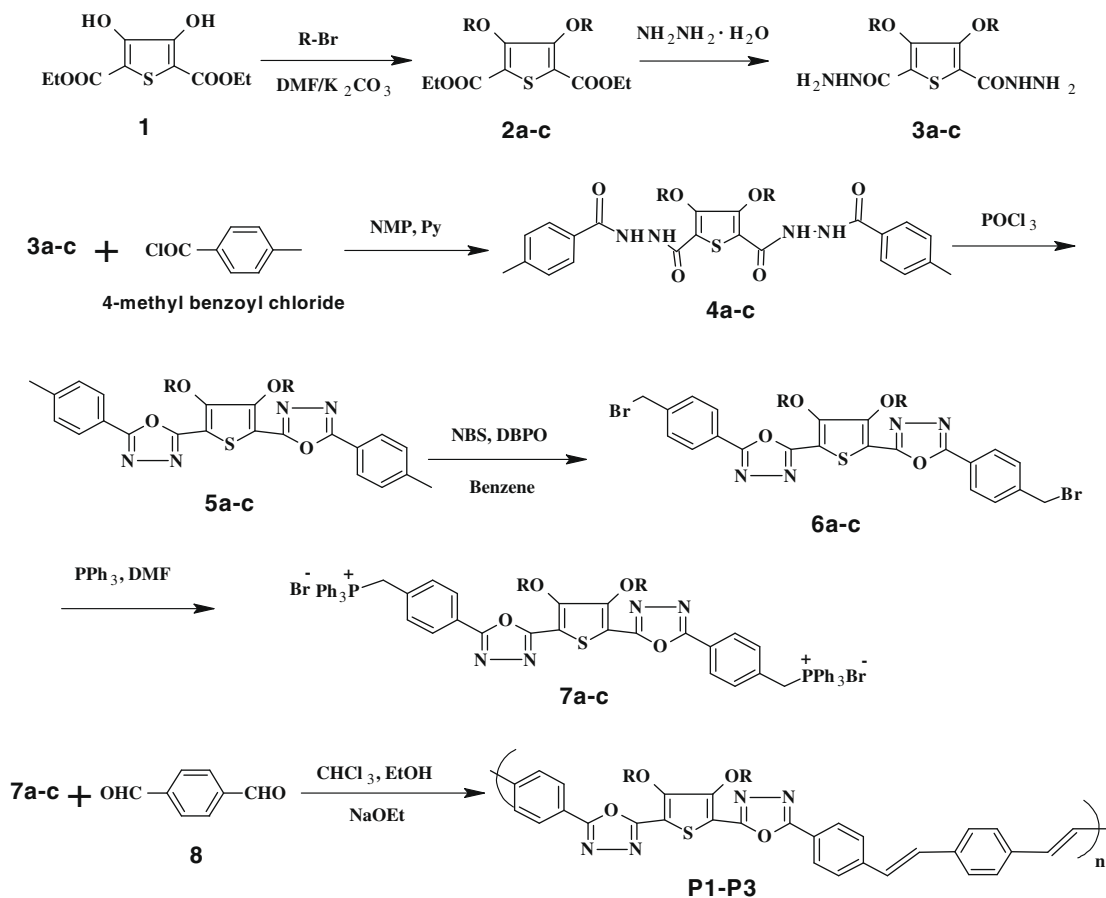
Scheme 1. Designed synthetic route for the preparation of copolymers.

and >C=O groups, respectively. ^{1}H NMR spectrum of it displayed peaks at δ 8.34 (s, 2H) and δ 4.98 (s, 4H) for >NH and —NH$_2$ protons respectively. Conversion of bishydrazide **3a** to biscarbohydrazide **4a** was confirmed by its IR, ^{1}H NMR and Mass spectral studies. Its IR spectrum exhibited sharp peaks at 3371 and 1697 cm^{-1} for >NH and >C=O groups respectively. ^{1}H NMR spectrum of it showed two >NH protons as singlet at δ values 10.23 and 9.70, aromatic protons as two doublets at δ 7.25 and 7.7 and tolual methyl protons at δ 2.40. Its mass spectrum showed the molecular ion peak at *m/z* 553.

Cyclization of biscarbohydrazide **4a** to form bisoxadiazole **5a** was established by its IR, ^{1}H NMR and Mass spectral data. Its IR spectrum showed no absorption peaks due to >NH and >C=O groups. The appearance of sharp peak at 1587 cm^{-1} indicated the formation of oxadiazole ring. Further, in its ^{1}H NMR spectrum two singlets corresponding to >NH protons disappeared confirming the cyclization. Mass spectrum of **5a** showed molecular ion peak at *m/z* 517

which corresponds to its molecular formula C$_{28}$H$_{28}$N$_4$O$_4$S. Bromination of bisoxadiazole **5a** to lead corresponding dibromide **6a** was confirmed by its ^{1}H NMR and Mass spectral data. It was observed that in its ^{1}H NMR spectrum the bromomethyl protons resonated at δ 4.56 and its molecular ion appeared at *m/z* 675 in its mass spectrum. The structure of the triphenyl phosphine salt **7a** was determined based on ^{1}H NMR spectral and elemental analyses. In its ^{1}H NMR spectrum, complex multiple peaks at δ 7.2–7.92 are due to the triphenyl phosphine and phenyl groups.

Finally, polymerization of **7a** to **P1** was confirmed by its IR, ^{1}H NMR, GPC and elemental analyses. IR spectrum of **P1** showed characteristic absorption peaks at 2965, 2860 cm^{-1} (C—H stretching aliphatic segments), 1603 cm^{-1} (1,3,4-oxadiazole), 1211 cm^{-1} (C—O—C stretching of ether bond), 1492, 962 cm^{-1} (aromatic and —CH=CH— trans). The ^{1}H NMR spectra of the copolymers in CDCl$_3$ displayed multiple peaks at δ 8.10–6.65, which

are due to aromatic and vinylic protons, a triplet at δ 4.3 which is due to —OCH$_2$— protons of alkoxy groups of thiophene ring. In addition multiplet peaks were observed in the range δ 1.9–0.89 due to —(CH$_2$)$_n$— protons of alkoxy group. The number and weight average molecular weights of the **P1** were found to be 2515 and 3420 respectively. Its polydispersity is 1.42. The molecular weights of the copolymers were found to be low. This is mainly attributed to the mild conditions and solvent systems used in the polymerization reaction. The molecular weight and polydispersity data of copolymers **P1**–**P3** are summarized in Table 1. Thermogravimetric analysis of all the copolymers was carried out under nitrogen atmosphere at a heating rate of 5 °C/min and they were found to be thermally stable up to $\sim$320 °C. The copolymers are readily soluble in conventional solvents such as CHCl$_3$ and THF.

3.3. Optical properties

The UV–vis absorption spectra of the copolymers were recorded both in solution and in thin films and the corresponding spectral data are summarized in Table 1. As shown in Fig. 1, the absorption maxima of the copolymers in dilute CHCl$_3$ solution are 380, 381, 381 nm for **P1**, **P2** and **P3** respectively. The absorption spectra of these polymers in thin film (Fig. 2) shows $\sim$20 nm bathochromic shift, indicating the presence of inter-chain interactions in the solid state. No red shift is observed on increasing the chain length of the alkyl group in position 3 and 4 of the thiophene ring. Their optical band gaps (E_g) were calculated from the absorption edge of the spectrum and found to be 2.53, 2.47 and 2.55 eV (Table 1) for **P1**, **P2** and **P3** respectively.

As shown in Fig. 3, the emissive maxima (excitation wavelength 360 nm) of the copolymers in dilute CHCl$_3$ solution are 480, 482 and 483 nm for **P1**, **P2** and **P3** respectively. The fluorescence emission spectra of these copolymers in thin film (Fig. 4) shows red shift ($\sim$15 nm) with respect to those obtained from their solutions. The copolymers emit intense bluish green–green fluorescence in solid state with emission peaks 495, 497 and 500 nm for **P1**, **P2** and **P3**, respectively. The Stokes shifts are found to be 97, 99, and 100 nm for **P1**, **P2** and **P3** respectively. The spectral results revealed that alkoxy chain length in the thiophene ring does not influence considerably on emission maxima of the polymers. The fluorescence quantum yields of the copolymers in solution were determined using quinine sulfate as a standard. As shown in Table 1 the quantum yield
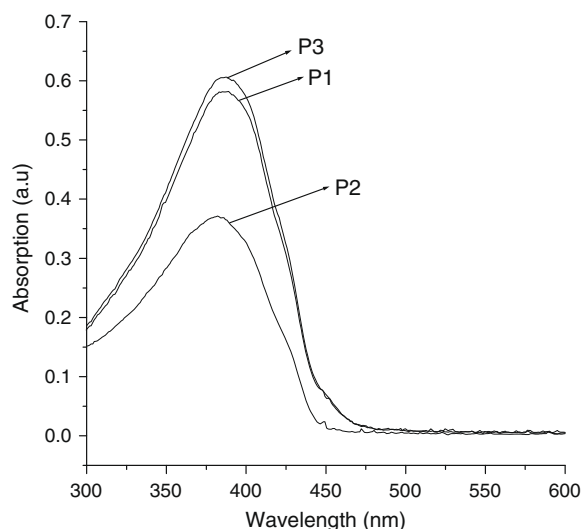

Fig. 1. UV–vis absorption spectra of the copolymers in CHCl$_3$ solution.
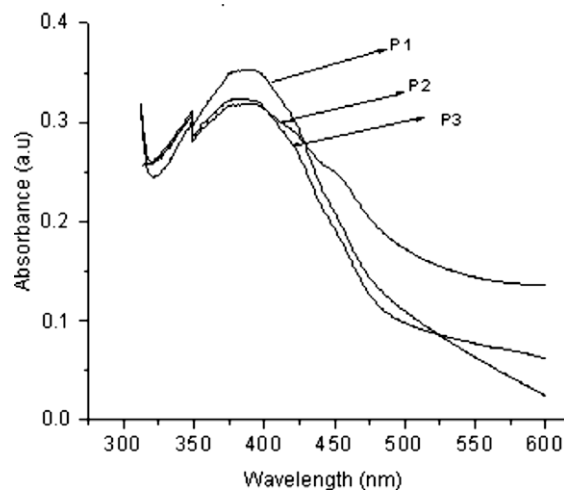

Fig. 2. UV–vis absorption spectra of the copolymer thin films.

of the polymers are in the range of 32–35%. These results clearly indicated that the newly synthesized copolymers are potential candidates for their applications in polymer LEDs.

Table 1
Molecular weight, UV–vis absorption maxima, emission maxima and fluorescence quantum yield of the copolymers.

Polymer	M_n[a]	M_w[b]	PD[c]	Absorption, λ_{max} (nm)		Emission, λ_{max} (nm)		Optical band gap, E_g (eV)	Quantum yield[d] (%)
				Solution	Film	Solution	Film		
P1	2415	3420	1.42	380	398	480	495	2.53	34
P2	2543	3572	1.40	381	398	482	497	2.47	32
P3	2516	3510	1.40	381	400	483	500	2.55	35

[a] Number average molecular weight.
[b] Weight average molecular weight.
[c] Polydispersity.
[d] Quantum yield relative to quinine sulfate (10^{-5} M quinine sulfate in 0.1 M H$_2$SO$_4$).
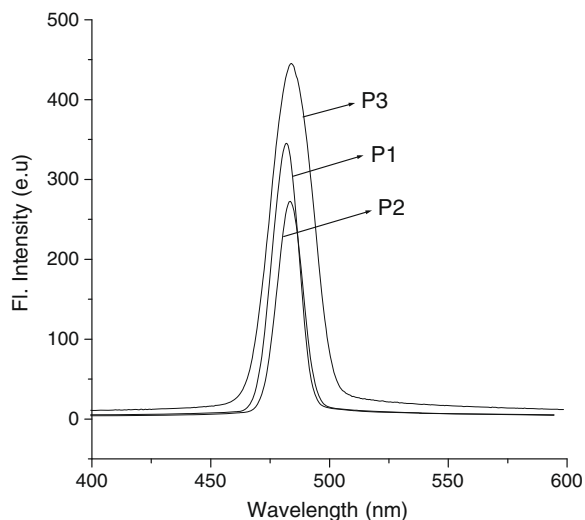
Fig. 3. Fluorescence emission spectra of **P1**–**P3** in CHCl$_3$ solution.
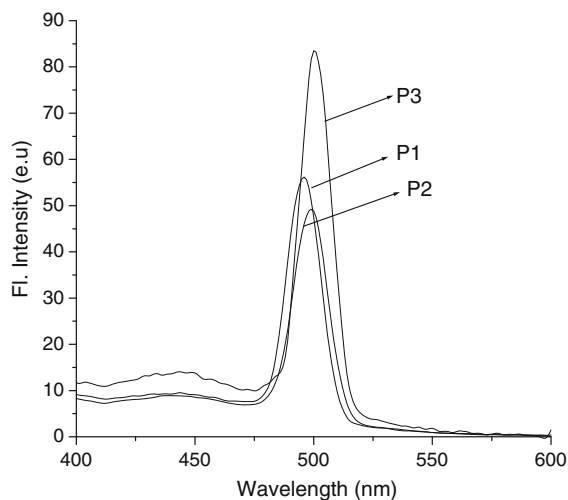

Fig. 4. Fluorescence emission spectra of the copolymer thin films.

Recently, it has been shown that conjugated polymers are promising class of third-order nonlinear optical (NLO) materials because of their potentially large third-order susceptibilities associated with fast response time. Further, their processability and thermal stability are added features for their selection. Conjugated systems consisting of electron donor and electron acceptor units were shown to possess enhanced third-order optical nonlinearity [29–33]. Hence we expect that copolymers **P1**–**P3** with conju-

gated donor–acceptor arrangement would show good third-order NLO properties. Preliminary studies on these polymers using Nd:YAG as laser source by *Z*-scan and degenerate four wave mixing (DFWM) techniques showed promising results. The detailed study of NLO properties of these copolymers will be discussed elsewhere.

3.4. Electrochemical properties

Cyclic voltametry (CV) was employed to determine redox potentials of new copolymers and then to estimate the HOMO and LUMO energy of the polymers, which are of crucial importance to the selection of cathode and anode materials for PLED devices. The cyclic voltammogram of the polymer coated on a glassy carbon electrode was measured on AUTOLAB PGSTAT 30 electrochemical analyzer, using a Pt counter electrode and a Ag/AgCl reference electrode, immersed in the electrolyte [0.1 M (*n*-Bu)$_4$NClO$_4$ in acetonitrile] at a scan rate of 25 mV/S. Electrochemical data of **P1**–**P3** are summarized in Table 2.

When the copolymers were swept cathodically, they showed reduction peaks at around −1.55 V (Fig. 5) with onset reduction potential at around −1.35 V. These reduction potentials are lower than those of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) [34,35], one of the most widely used electron transporting materials, and are comparable with those of some good electron transporting materials. While sweeping anodically, copolymers showed an oxidation peak at around 1.55 V with onset oxidation potential at around 1.2 V. These values are
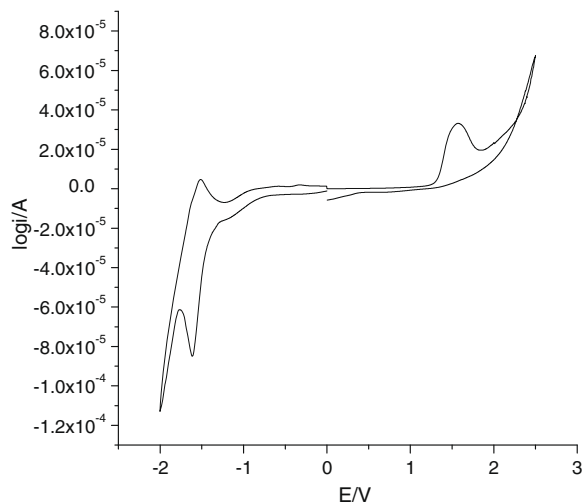

Fig. 5. Oxidation and reduction cyclic voltammetry waves of the copolymer **P2**.

Table 2
Electrochemical potentials and energy levels of the polymers.

Polymer	E_{oxd}^{onset}	E_{red}^{onset}	E_{oxd}	E_{red}	HOMO (eV)	LUMO (eV)	E_g (eV)	ΔE_h (eV)	ΔE_e (eV)	$\Delta E_e - \Delta E_h$ (eV)
P1	1.05	−1.42	1.48	−1.79	−5.45	−2.98	2.47	0.65	1.32	0.67
P2	1.25	−1.30	1.56	−1.61	−5.65	−3.10	2.55	0.85	1.2	0.35
P3	1.13	−1.29	1.62	−1.64	−5.53	−3.11	2.42	0.73	1.19	0.46

comparable with those of some reported donor acceptor polyoxadiazoles [21,22,36]. However length of the alkoxy side chain on 3- and 4-positions of the thiophene ring has not affected much on the oxidation–reduction potentials of the polymers. The onset potentials of oxidation and reduction processes are used to estimate the HOMO and LUMO energy levels of the copolymers.

According to the equations reported in the articles [37–39], i.e., $E_{HOMO} = -[E_{onset}^{oxd} + 4.4 \text{ eV}]$ and $E_{LUMO} = -[E_{onset}^{red} - 4.4 \text{ eV}]$, where E_{onset}^{oxd} and E_{oxd}^{red} are the onset potentials versus SCE for the oxidation and reduction processes of a polymer, respectively. The HOMO energy levels of the copolymers **P1**–**P3** were estimated to be −5.38, −5.58 and −5.46 eV respectively. The results indicate that the copolymers **P1**–**P3** possess almost same hole injection ability as that of CN–PPV and some reported polyoxadiazoles [21,22]. The LUMO energy levels of the copolymers **P1**–**P3** were estimated to be −2.91, −3.03 and −3.04 eV respectively. These values are very close to that of DIOX-A-PPV [6] indicating that new copolymers have similar electron transporting ability. Further, it has been noticed that values are lower than that of OXA-PPV (−2.58 eV) [40], showing that these polymers possess better electron-injection ability. Here, the high electron affinities of polymers **P1**–**P3** may be attributed to the incorporation of electron deficient oxadiazole moiety and also the alternating donor–acceptor arrangement along the polymers chains. The band gaps of the polymers were estimated to be 2.47, 2.55 and 2.42 eV for **P1**, **P2** and **P3** respectively. 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 LUMO energy levels of emitting polymers. Thus the hole-injection barrier is $\Delta E_h = E_{HOMO} - 4.8 \text{ eV}$, where 4.8 eV is the work function of the ITO anode and the electron-injection barrier is $\Delta E_e = 4.3 - E_{LUMO} \text{ eV}$, where 4.3 eV is the work function of aluminium 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. As shown in Table 2, the ΔE_e values of these copolymers are lower than PPV (1.8 eV) and some other p-type polymers indicating that the oxadiazole ring in the polymer backbone tend to decrease barrier for electron-injection and thus enhances the electron transporting properties of the corresponding polymer. The ΔE_h values of the copolymers are higher than PPV (0.3 eV) [41] due to the introduction of the oxadiazole rings along the polymer backbone. Further, these values are lower than those of PBD [42] and tris (8-hydroxyquinoline) aluminium (Alq₃) [43], which are widely used as electron transport hole blocking materials. The barrier energy difference $(\Delta E_e - \Delta E_h)$ is the lowest for **P2** among the copolymers. It is clear from these results that improved charge carrying property is expected for the new copolymers. The study reveals that donor–acceptor structure could be a promising molecular design for synthetically tuning HOMO and LUMO energy levels of conjugated polymers. In the present synthetic design, by taking different dialdehydes in the final step of polymerization it is possible to tune the HOMO and LUMO energy levels of the copolymers. Hence, this is a good synthetic route to obtain desired donor–acceptor type copolymers. Preliminary studies on light emitting device preparation and their characterization are on progress.

4. Conclusion

Three new conjugated copolymers (**P1**–**P3**) with donor (3,4-dialkoxy thiophene), acceptor (oxadiazole) with a divinylbenzene moiety architecture have been successfully synthesized through multistep reactions and newly synthesized compounds have been characterized. This is a good synthetic design to obtain desired donor–acceptor type copolymers. The optical properties revealed that all the copolymers emit bluish green–green fluorescence under the irradiation of light. The electrochemical properties showed that the copolymers **P1**–**P3** possess high-lying HOMO energy levels from −5.38 to −5.58 eV and low lying LUMO levels from −2.91 to −3.04 eV. This is attributed to the presence of alternate donor acceptor conjugated units along the polymer back-bone. From the results of electrochemical studies it can be concluded that the copolymers possess good charge carrying property. The light emitting and charge carrying properties revealed that the new copolymers are promising materials for the development of efficient PLEDS.

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