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Synthesis and characterization of thiophene and fluorene based donor–acceptor conjugated polymer containing 1,3,4-oxadiazole units for light-emitting diodes

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ABSTRACT

A new donor–acceptor (D–A) conjugated polymer (**PDTOF**) containing 3,4-didodecyloxythiophene, fluorene and 1,3,4-oxadiazole units is synthesized by using Wittig reaction methodology. The synthesized polymer is characterized by ^{1}H NMR, FTIR, GPC, and elemental analysis. The optical energy band gap of the polymer is found to be 2.42 eV as calculated from the onset absorption edge. The electrochemical studies of **PDTOF** reveal that, the HOMO and LUMO energy levels of the polymer are −5.45 eV and −3.58 eV, respectively. The polymer is thermally stable up to 320 °C. Polymer light-emitting diode devices are fabricated with a configuration of ITO/PEDOT: PSS/PDTOF/Al using **PDTOF** as the emissive layer. The electroluminescence (EL) spectrum of the device showed green emission with CIE coordinate values (0.34, 0.47). By current density–voltage characteristics, threshold voltage of the PLED device is found to be 6.5 V.

In the last two decades, the design and synthesis of electroluminescent conjugated polymers as the active materials in the field of polymer light-emitting diodes (PLEDs) have received much attention because these materials are potential candidates in flat panel display and lighting applications.[1,2] Extensive research has also been performed to develop highly efficient light-emitting polymers with tunable emission, long lifetimes, and color purity.[3] However the focus on the area of conjugated polymers has drawn great interest mainly because of easy processing, low operating voltages, faster response times, and facile color tuning over the full visible range, which makes them suitable for large-area flat panel displays.[4] Due to this reason, the design and synthesis of new conjugated polymers of varied optoelectronic properties play a vital role in the area of display technology.[5] In this regard, a wide range of conjugated polymers such as poly(*p*-phenylenevinylene) (PPV),[6] poly(thiophene) (PT),[7] poly(pyrrole),[8–10] poly(*p*-phenylene) (PPP),[11] poly(fluorene) (PF),[12] and their derivatives have been extensively investigated as emissive materials in LEDs. It is known that to obtain highly efficient light emitting devices, the balance in the injection and transportation of both holes and electrons into the polymer emissive layer is necessary. Several approaches have been used in order to achieve high electroluminescence efficiency in PLEDs.[13–15] Among them, donor–acceptor (DA) type polymers, introduced by Havinga et al.[16] in the macromolecular systems via alternating electron rich and electron deficient substituents along a polymer backbone are the well known approach to obtain efficient devices.[17] In this system, the electron or hole affinity can be enhanced simultaneously or controlled independently.[18,19] In the categories of conjugated polymers, polythiophene, and polyfluorene and their derivatives occupy a significant position. In particular, polythiophenes are more attractive candidates for PLEDs because of their good thermal stability both in the neutral and doped states and their wide electronic and optical tenability.[20–22] Also polyfluorene derivatives are attractive active materials for light-emitting diodes because of their thermal and chemical stability and their exceptionally high solution and solid-state fluorescence quantum yields.[12,23] Moreover, the facile substitution at the 9-position of the fluorene monomer allows the control of polymer properties such as solubility, processability, and morphology. Since 3,4-dialkoxythiophene and fluorene derivatives are both electron rich and hole transporting, it is necessary to introduce electron withdrawing units to the main chains or side chains to attain large electron affinities. The strong electron withdrawing 1,3,4-oxadiazole unit is the widely used electron injection and hole blocking material because of its high electron affinity, good thermal, and chemical stability.[24,25]

Herein we report the synthesis, characterization, and electroluminescent properties of a new donor–acceptor (D–A) type conjugated polymer **PDTOF**. The polymer structure consists of 3,4-didodecyloxythiophene and fluorene moieties as electron donor units and 1,3,4-oxadiazole moiety as the electron acceptor unit along with vinylene linkages. The thermal, optical, and electrochemical properties of the polymer are studied. Polymer light-emitting diodes are fabricated using **PDTOF** as emissive material

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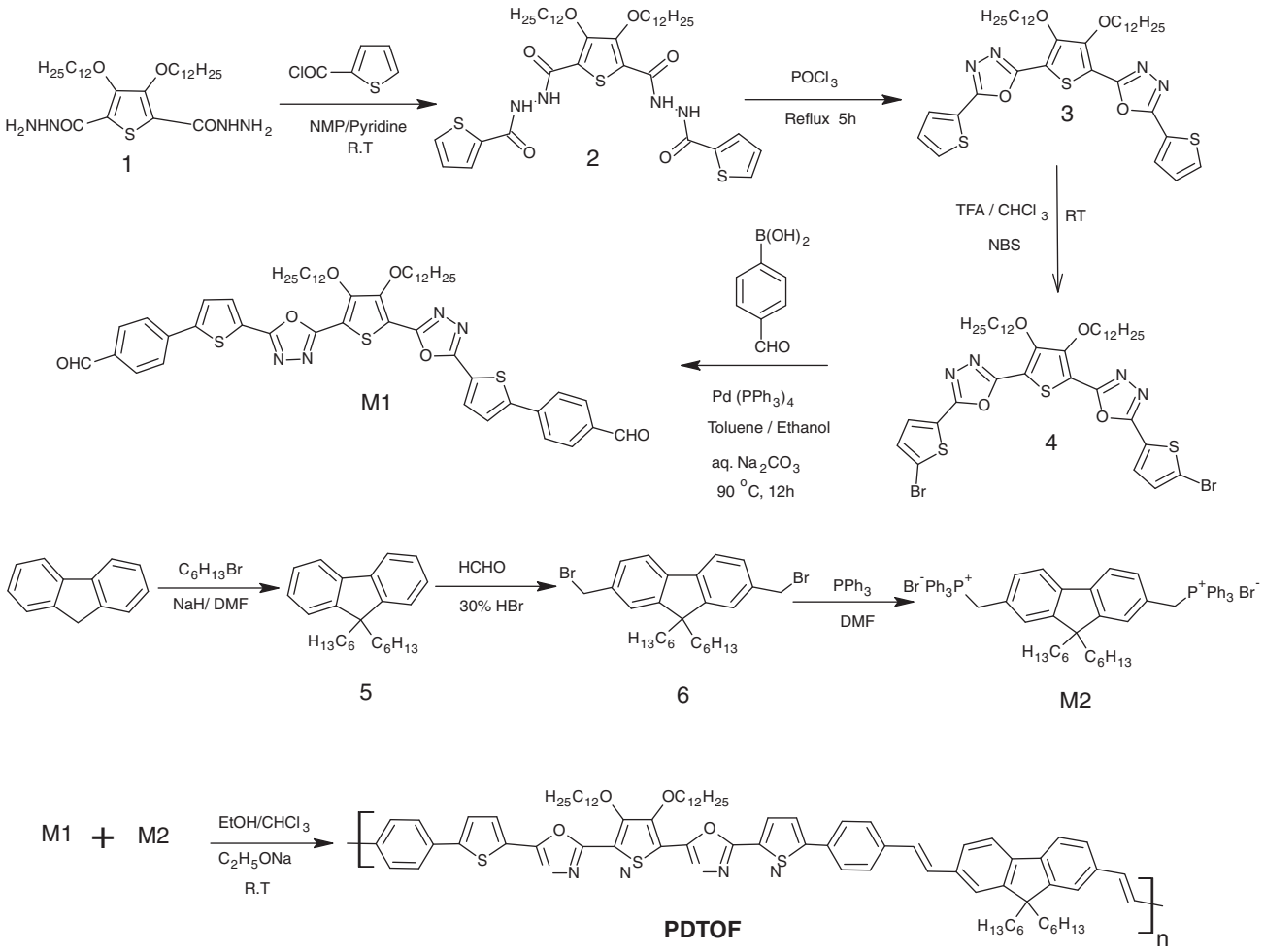
with a configuration of ITO/PEDOT: PSS/PDTOF/Al. The EL properties of **PDTOF** reveal that the polymer is a green light-emitting material for efficient light-emitting diodes.

The synthetic route for preparing the monomers and the polymer (**PDTOF**) are outlined in Scheme 1[26]. The detailed synthetic procedures of the intermediate compounds and their spectral data are given in the Supplementary data. The final conjugated polymer (**PDTOF**) containing 3,4-didodecyloxythiophene, fluorene, and 1,3,4-oxadiazole units is synthesized by using Wittig reaction method. The chemical structures of all the intermediates and the polymer were confirmed by NMR spectroscopy, FTIR spectroscopy, and elemental analysis. The compound 3,4-didodecyloxythiophene-2,5-carbonyldihydrazide (**1**) was prepared according to the previously reported method.[27] To prepare 3,4-bis(dodecyloxy)-*N*'2,*N*'5-di(thiophene-2-carbonyl)thiophene-2,5-dicarbohydrazide (**2**), the dihydrazide (**1**) was condensed with thiophene-2-carbonyl chloride in *N*-methylpyrrolidinone (NMP) in the presence of pyridine at room temperature. Conversion of dihydrazide to dicarbohydrazide was confirmed by ^{1}H NMR and FTIR studies. The ^{1}H NMR spectrum of **2** showed two >NH protons as singlet at δ 10 and 9.39. The three doublet peaks in the range of 7.69–7.68, 7.54–7.52, and 7.10–7.08 ppm are assigned to thiophene ring protons at positions 2, 4 and 3 respectively. The triplet peak at 4.29 ppm is due to the $-OCH_2-$ protons of the alkoxy chains of the thiophene ring and the multiple peaks in the range 1.96–0.87 ppm are due to the $-(CH_2)_{10}-CH_3$ protons of the alkoxy chains. The FTIR spectrum of **2** showed sharp peaks at 3380 and 1677 cm^{-1} due to >NH and >C=O groups, respectively. Cyclization of compound (**2**) to bisoxadiazole (**3**) was achieved by using $POCl_3$ and the completion of the reaction was confirmed by using ^{1}H NMR and FTIR spectral studies. In the ^{1}H NMR spectrum, the disappearance of two singlet peaks due to >NH protons confirms the cyclization. Further, the FTIR spectrum of (**3**) showed no absorption peaks corresponding to >NH and >C=O groups while a new peak appeared at 1568 cm^{-1} due to –C=N– stretching, indicating the formation of the oxadiazole ring. The synthesis of monomer **M1** from compound (**3**) requires two additional steps (Scheme 1). The first step consists of bromination of compound (**3**). The reaction of Br_2 in chloroform with (**3**) did not give the required brominated product (**4**). We have tried the method of *N*-bromosuccinimide (NBS) using different solvents like DMF, CCl_4, and benzene which were also unsuccessful. The failure of these methods could be due to the deactivation of thiophene rings in **3** toward bromination by the presence of electron deficient 1,3,4-oxadiazole units attached to the thiophene rings. However bromination reaction was successful when compound **3** is treated with NBS in trifluoroacetic acid/chloroform (3:1) solvent mixture, yielding the dibromo compound **4** in reasonable yield. The structure of compound **4** was confirmed by ^{1}H NMR spectrum, which showed the disappearance of double doublet peak of thiophene ring proton at position 2 and conversion of all double doublets into doublet peaks. The monomer **M1** was obtained by coupling between dibromo compound **4** and 4-formylphenylboronic acid through Suzuki coupling reaction. ^{1}H NMR spectrum of **M1** showed two (–CHO) protons as singlet at δ



Scheme 1. Synthetic route of monomers and the polymer.

10.05 ppm. The FTIR spectrum exhibited sharp peak at 1690 cm^{-1} due to >C=O groups. Alkylation of the fluorene was carried out with DMF, NaH, and *n*-hexyl bromide to afford compound **5**. The compound **6** and monomer **M2** were prepared according to the literature procedure.[28] Finally, the polymerization by Wittig reaction was confirmed by ^{1}H NMR, GPC, and elemental analysis. The ^{1}H NMR spectrum of the polymer displayed complex multiple peaks in the range δ 7.97–6.54 ppm corresponding to the aromatic and vinylic protons. A triplet peak at δ 4.32 ppm is due to $-OCH_2-$ protons of the alkoxy chains of the thiophene ring. The multiple peaks in the range 1.91–0.86 ppm are due to the protons of alkoxy and alkyl chains attached to thiophene and fluorene rings. The average molecular weight of the polymer was measured by gel permeation chromatography (GPC) with reference to polystyrene standards. The number averaged molecular weight (M_n) of the polymer is found to be 12200 with molecular weight distribution (PD) 7. The observed high polydispersity of the polymer may be due to the aggregation of polymer chains.[29] The overall yields for all the intermediates and polymer were between 55–90%. All the intermediate compounds and the polymer showed good solubility in common organic solvents, such as $CHCl_3$, THF, and chlorobenzene.

The optical properties of the polymer were studied by using UV–vis absorption and fluorescence emission spectroscopies. The UV–vis absorption spectra of monomer (M1) solution, **PDTOF** in chloroform solution (Ca. 10^{-4} g/l) and in thin film state are as shown in Figure 1. The monomer (M1) solution showed an absorption maximum at 390 nm. The absorption maximum of the polymer solution at 427 nm corresponds to the π–π^* transition in the polymer backbone. The polymer film displayed an absorption peak at 443 nm. Obviously, the red shift of about 16 nm in the film state is due to the π–π^* stacking effect. The optical band gap, defined by the onset absorption of the polymer in the film state is 2.42 eV. The polymer showed low band gap when compared to those of PFO, PFV, and some fluorene based conjugated polymers containing oxadiazole pendants.[30–32] This may be due to the strong interaction between electron donor segments (thiophene and fluorene) and strong electron acceptor segment (1,3,4-oxadiazole) in the polymer backbone. PDTOF emits green light under the irradiation of UV light. The polymer in solution showed emission maximum at 506 nm while in the film state a bathchromic shift of 7 nm is observed (Fig. 2). This can be attributed to the interchain or/ and intrachain mobility of the excitons and excimers generated in the polymer solid state.[33] The fluorescence quantum yields of the monomer (M1) and the polymer in chloroform solution are 23% and 40%, respectively, which were calculated by comparing with the standard of quinine sulfate (ca. 1×10^{-5} M solution in 0.1 M H_2SO_4 having a fluorescence quantum yield of 55%).[34] The optical properties of the polymer **PDTOF** is summarized in Table 1.

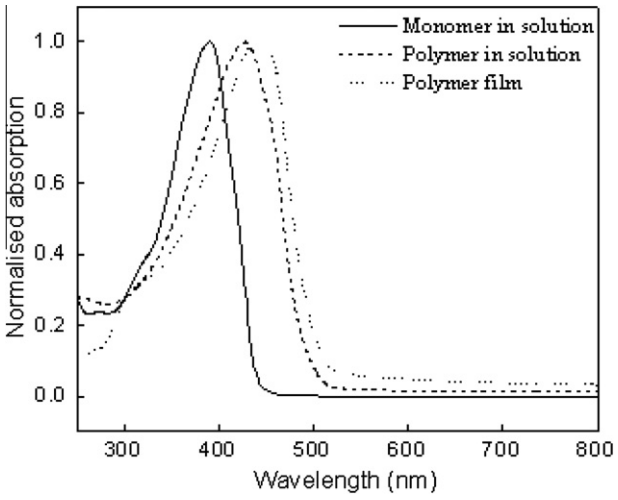


Figure 1. UV–vis absorption spectra of the monomer (**M1**) solution, polymer in chloroform solution and the polymer thin film.

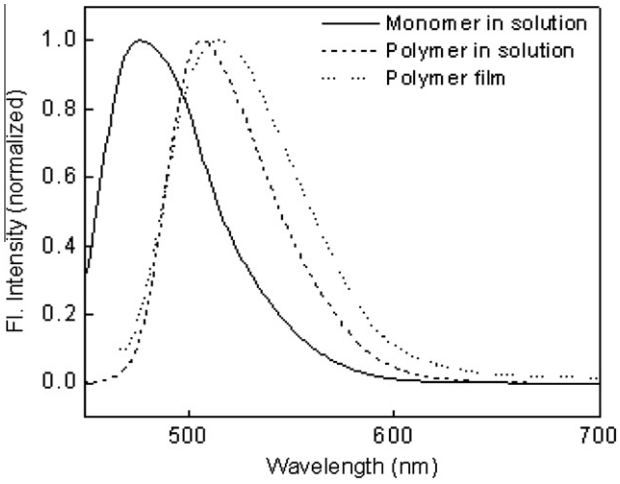


Figure 2. Fluorescence emission spectra of the monomer (**M1**) solution, polymer in chloroform solution and the polymer thin film.

Cyclic voltammetry (CV) was employed to investigate the redox behavior of conjugated polymers and to estimate their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, because the onset oxidation and reduction potentials obtained from the cyclic voltammograms correspond to the HOMO and LUMO energy levels, respectively.[35] Figure 3 shows the cyclic voltammogram of polymer (PDTOF) and monomer (M1) thin films coated on glassy carbon (GC) disk electrode with 0.1 M tetrabutylammoniumperchlorate (TBAPC)/CH_3CN as the electrolyte at a scan rate of 50 mV/s at room temperature. A platinum wire and Ag/AgCl were used as counter electrode and reference electrode, respectively. All measurements were calibrated with the ferrocene/ferrocenium (Fc/Fc^+) standard (E_{FOC} = 0.53 V vs Ag/AgCl).[36] As shown by the cyclic voltammogram, the monomer (M1) as well as the polymer showed both *n*-doping and *p*-doping processes. The monomer (M1) displayed an oxidation peak at 1.64 V and a small reduction peak at −1.44 V. These redox properties of the monomer (M1) could be attributed to the completely conjugated structure of the molecule and also to the presence of alternating donor and acceptor groups in the molecule. On sweeping the polymer cathodically, the onset of the n-doping process occurs at the potential of −0.69 V with a reduction peak at −1.00 V. In the anodic scan, the *p*-doping onset is observed at 1.18 V with an oxidation peak at 1.44 V. The onset potentials of *n*-doping and *p*-doping processes were used to estimate the HOMO and LUMO energy levels of the conjugated polymer according to the equations;[37]

$$E_{HOMO} = -[E^{ox}_{(onset)} + 4.8\ eV - E_{FOC}] \text{ and } E_{LUMO} = -[E^{red}_{(onset)} + 4.8\ eV - E_{FOC}], \text{respectively.}$$

Where $E^{ox}_{(onset)}$ and $E^{red}_{(onset)}$ are the onset potentials for the oxidation and reduction processes of the polymer, respectively. Accordingly, the HOMO and LUMO energy levels of the polymer are estimated to be −5.45 eV and −3.58 eV, respectively, and hence the electrochemical band gap is 1.87 eV. The difference between the electrochemical and optical band gaps can be attributed to the creation of free ions in the electrochemical experiment compared with the one measured through UV experiment, which refers to a neutral state.[38,39] The electron affinity of the polymer is lower than those of poly (fluorenevinylenes) (−2.6 eV), CN-PPV

Table 1
Optical and electrochemical properties of the polymer (PDTOF)

Absorption and fluorescence emission spectra							Cyclic voltammetry (vs Ag/Ag^+)				
λ_{max}[a] (nm)	λ_{max}[b] (nm)	λ_{em}[a] (nm)	λ_{em}[b] (nm)	E_g^{opt} (eV)	ϕ_{fl}[c] (%)	ϕ_{fl}[d] (%)	$E^{ox}_{(onset)}$ (V)	$E^{red}_{(onset)}$ (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{EC} (eV)
427	443	506	513	2.42	23	40	1.18	−0.69	−5.45	−3.58	1.87

E_g^{opt} optical band gap estimated from the onset wavelength of the optical absorption.
E_g^{Ec} Electrochemical band gap estimated from the difference between E_{HOMO} and E_{LUMO}.
[a] Measured in chloroform solution.
[b] Cast from chloroform solution.
[c] Fluorescence quantum yield of monomer (**M1**) in solution.
[d] Fluorescence quantum yield of the polymer (PDTOF) in solution.

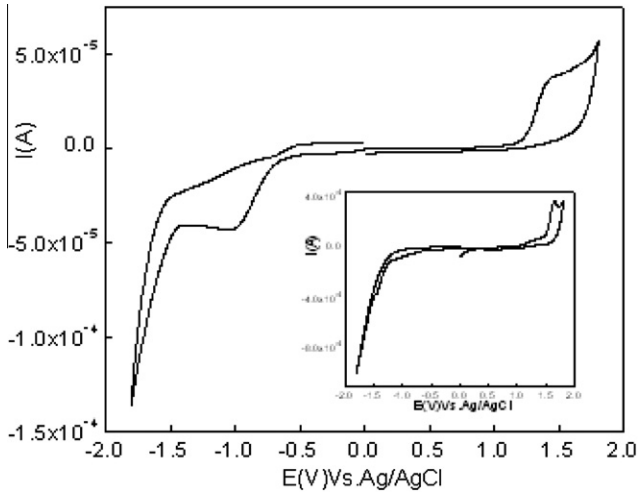


Figure 3. Cyclic voltammogram of the polymer film cast on glassy carbon disk in 0.1 M tetrabutylammoniumperchlorate (TBAPC)/CH_3CN solution at 50 mV/s. Inset shows the cyclic voltammogram of the monomer (**M1**).

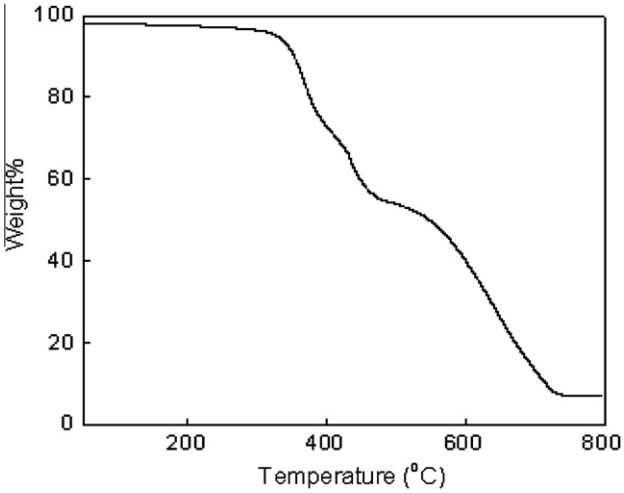


Figure 4. TGA plot of the polymer with a heating rate of 10 °C min^{-1}.

(−3.02 eV) and some poly (aromatic oxadiazole)s (−2.8 to −2.9 eV).[40,41] The lower LUMO level of the polymer indicates that the incorporation of electron withdrawing oxadiazole segment increases the electron affinity of the polymer and thus lowers the LUMO level of the polymer. From the high electron affinity value it can be expected that polymer may show an increased electron injection and transport properties. It should be noted that incorporation of the electron rich thiophene and fluorene segments in the polymer backbone raises the HOMO energy level, leading to a lower band gap polymer. The HOMO energy level of the polymer is almost similar to that of PPV (5.4 eV).[42] This means that the polymer has a good hole injection ability as PPV when it is used in the fabrication of PLEDs. The cyclic voltammetry data of PDTOF are summarized in Table 1.

Thermogravimetric analysis (TGA) was used to study the thermal property of the polymer **PDTOF** and was carried out under nitrogen atmosphere at a heating rate of 10 °C/min. The analysis reveals that, the polymer exhibits good thermal stability. The thermogram given in Figure 4 shows that there is no weight loss till 320 °C and there on the polymer starts decomposing.

To investigate the electroluminescent (EL) behavior of the polymer (**PDTOF**), PLED devices were fabricated with a configuration of ITO/PEDOT: PSS/PDTOF/Al where **PDTOF** was used as the emissive material. The detailed fabrication procedure is described in the Supplementary data. The typical EL spectrum of the polymer (**PDTOF**) at a driving voltage of 5 V is as shown in Figure 5 (inset). The EL maximum of polymer is centered at 524 nm. The PLEDs emitted green light with Commission Internationale De L'Eclairage (CIE) coordinates (0.34, 0.47) under a driving voltage of 5 V. The EL

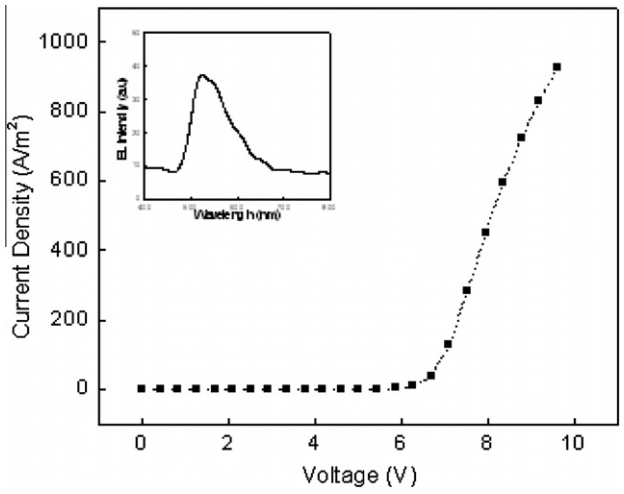


Figure 5. Current density–voltage characteristics and Electroluminescence (EL) spectrum (inset) of the ITO/PEDOT: PSS/ PDTOF/Al device.

spectra of the polymer were red shifted relative to the corresponding solid state PL spectra which probably result from the increased radiative decay from the longer conjugated segments during EL.[43] Moreover, the presence of longer alkoxy and alkyl chains attached to thiophene and fluorene rings improves the polymer solubility and film forming capability which leads to a change in the film morphology. The current density–voltage characteristics of the device are as shown in Figure 5 and shows that the current density of the polymer increases exponentially with the increasing forward

bias voltage, which is a typical diode characteristic. The polymer shows threshold voltage of 6.5 V. The lower threshold voltage can be attributed to the lower energy barrier for electron injection from the aluminum electrode.

In conclusion, we report the synthesis of a new donor–acceptor (D–A) type conjugated polymer (**PTDOF**) containing 3,4-didodecyloxythiophene, fluorene and 1,3,4-oxadiazole units via a Wittig method. The polymer was well characterized by ^{1}H NMR, FTIR, TGA, UV–vis absorption, fluorescence emission, and cyclic voltammetry techniques. The polymer (**PDTOF**) showed good solubility in the common organic solvents such as chloroform, tetrahydrofuran, and chlorobenzene with good film forming properties. The electrochemical properties revealed that the polymer possesses high lying HOMO energy levels of −5.45 eV and low-lying LUMO energy levels of −3.58 eV. The thermogravimetric studies indicated that the polymer is thermally stable upto ~320 °C. The optical band gap of the polymer is found to be 2.42 eV, which could be attributed to the D–A structure of the polymer backbone. The polymer light-emitting diode devices were fabricated with a configuration of ITO/PEDOT: PSS/PDTOF/Al using the polymer **PDTOF** as the emitting layer. The emission maximum of the EL spectra originated at 524 nm. The EL spectrum of the polymer was red shifted relative to its PL spectra. The PLEDs using **PDTOF** as the emissive layer emitted green light with a CIE coordinate of (0.34, 0.47) under a driving voltage of 5 V. These preliminary studies of EL properties of the PLED device show that the polymer **PDTOF** will be a good candidate as active material in the field of organic light-emitting diodes.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.10.157.

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26. The monomer **M1** was synthesized by Suzuki biaryl coupling reaction method. Under argon atmosphere, to a mixture of dibromo compound **4** (0.5 g, 0.548 mmol) and 4-formylphenylboronic acid (0.172 g, 1.2 mmol) in toluene and ethanol 10 ml (1:1 volume ratio), 2 M Na_2CO_3 (aq) was added. After 30 min of degassing with argon, 3 mol% (0.119 g, 0.164 mmol) of Pd $(PPh_3)_4$ was added. The reaction mixture was stirred at 80 °C for 12 h under argon. After completion of reaction (progress of the reaction was monitored by TLC), it was poured into distilled water and extracted with chloroform. The organic layer was dried with $MgSO_4$ and concentrated. The crude product was purified by silica gel column using a mixture of hexane and ethyl acetate (10/2) as an eluent, giving a yellow fluorescent solid. Yield: 70%. mp: 207–208 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.05 (s, 2H), 7.97–7.52 (m, 12H), 4.33 (t, J = 6.8 Hz, 4H), 1.92–1.24 (m, 40H), 0.86 (t, J = 6.4 Hz, 6H). FTIR ν (cm^{-1}): 2917 and 2849 (–C–H), 1690 (–C=O), 1570(C=N), 1513, 1457, 1379,1288, 1210 1020. Element. Anal. Calcd for $C_{54}H_{64}N_4O_6S_3$: C, 67.47; H, 6.72; N, 5.83; S, 9.99. Found: C, 67.35; H, 6.64; N, 5.92; S, 10.10. *Synthesis of monomer* **M2**: A mixture of **6** (1 g, 2.02 mmol) and triphenylphosphine(1.32 g, 5.06 mmol) in DMF (10 ml) was heated for 12 h at 105–110 °C under nitrogen. The reaction mixture was cooled to room temperature and added was slowly into 100 ml of diethyl ether while stirring. The white solid was filtered, washed with ether, and dried in a vacuum oven at 40 °C. Yield: 90%. mp:>200 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.02–7.82 (m, 30H), 7.58–7.17 (m, 6H), 5.6–5.56 (d, 4H), 1.54–1.50 (m, 4H), 1.16–0.78 (m, 16H), 0.2 (br, 6H). FTIR ν (cm^{-1}): 3407, 3340, 2921, 2852, 1434, 1109, 744. Element. Anal. Calcd for $C_{63}H_{66}Br_2P_2$: C 72.40, H 6.37. Found: C 72.32, H 6.42. *Synthesis of polymer* **PDTOF**: A solution of sodium(20 mg, 0.936 mmol) in 2 ml of anhydrous ethanol was added drop wise at ambient temperature under argon to a mixture of dialdehyde **M1** (0.3 g, 0.312 mmol) and phosphonium salt **M2** (0.35 g, 0.312 mmol) in 6 ml of dry chloroform. The mixture was stirred at room temperature for 12 h. The reaction mixture was slowly poured into 100 ml of methanol. The precipitated polymer was filtered off. The crude polymer was redissolved in chloroform and precipitated in methanol several times. The product was filtered vacuum dried to obtain the yellow powder. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.97–6.54 (m, 22H), 4.32 (t, 4H), 1.91–0.86 (m, 66H), 0.76 (t, 6H). FTIR ν (cm^{-1}): 2917 and 2848 (–C–H), 1573, 1482, 1452, 1368, 1027, 802. Element. Anal. Calcd for $C_{81}H_{98}N_4O_4S_3$: C, 75.54; H, 7.68; N, 4.35; S, 7.45. Found: C, 75.32; H, 7.54; N, 4.22; S, 7.52.
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