ORIGINAL ARTICLE



# Synthesis and Optoelectronic Properties of Thiophene Donor and Thiazole Acceptor Based Blue Fluorescent Conjugated Oligomers

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Abstract We report on the synthesis and characterization of low band gap, blue light emitting and thermal stable conjugated oligomer by Wittig condensation. Thiophene and thiazole type of donor-acceptor based series of conjugated oligomers, Oligo-4,5-bis-[2-[5-[2-thiophene-2-yl-vinyl]thiophene-2-yl]vinyl]-thiazole (OBTV-TZ) and Oligo-2,4,5-Tris-[2-[5-[2thiophene-2-yl-vinyl]thiophene-2-yl]-vinyl]-thiazole (OTTV-TZ) were synthesized. These oligomers were confirmed by FT-IR and <sup>1</sup>H-NMR and LC/MS analysis. The effect of the number of thiophene rings on the optical, electrochemical, thermal and morphological properties of the oligomers were systematically investigated. Both oligomers were exhibited almost same absorption wavelength in methanol solution  $(\lambda_{\text{max}} = 365 \text{ nm and } 369 \text{ nm})$  which indicates both oligomers illustrate similar intra molecular charge transfer (ICT). In solid state, the oligomers were exhibited broadening peaks with higher onset absorptions ( $\lambda_{max} = 600$  nm and 580 nm). The photoluminescence absorption spectrum of the oligomers was observed at 433 nm and 434 nm respectively in methanol solution with blue emission. The electrochemical band gap  $(E_g^{ec})$  of the OBTV-TZ was 1.55 eV (low band gap) and OTTV-TZ was exhibited greater highest occupied molecular orbital (HOMO) value ( $E_{HOMO} = -6.6 \text{ eV}$ ). Moreover morphological parameters of both oligomer film of 2D and 3D diagrams were observed by using AFM studies.

Keywords Blue light emitting  $\cdot$  Conjugated oligomers  $\cdot$ Thiophene  $\cdot$  Thiazole  $\cdot$  Internal charge transfer  $\cdot$  Low band gap

#### Introduction

The design and synthesis of light emitting conjugated oligomers have been much focus of intense research over a last decade. Compared to oligomers, long chain polymers are having some complications such as polydispersity and purity. So it is mandatory to give more attention for smaller systems of oligomers which possess well-defined spectroscopic and chemical characteristics. The wide spread attention of the oligomers due to their optical, morphological, electrochemical and electrical properties [1]. These conjugated oligomeric materials may be applied in various optoelectronic devices such as organic photovoltaic devices (OPVs) [2] organic light emitting diodes (OLEDs) [3] organic thin film transistors (OTFTs) [4] and organic solar cells. These much electronic properties of oligomers are mostly regulated by delocalization of  $\pi$ -electrons in aromatic rings [1].

The large number of conjugated polymers and organic materials are displaying high fluorescent colours in the visible region such as green, orange and red. Mostly these three colours are well established in OLEDs. But even, they have few drawbacks such as high driven voltage, commercial value and less stability [5]. To achieve these problems and enhance properties of electroluminescence devices there is a demand for stable and strong blue-light emitting conjugated materials with great photoluminescence (PL). The current organic materials

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are combined with blue- light emitting efficiency includes polyphenylens [6], benzofurans [7], thiophenes [8], indoles [9], styryl arylenes [10], perylenes [11]. Among these, thiophenes are most widely studied classes of electron donors. Owing to the fact that of thiophene unit containing conjugated polymers are having excellent hole transporting ability, good photoconductivity, good light-harvesting properties, relatively strong inter chain interaction, excellent environmental and thermal stability [12].

Our main aim is lower band gap oligomers along with blue light emitting fluorescence. The low band gap (LBG) of the conjugated oligomers determined by interaction between the electron donor and electron acceptor units [13]. These type of lower band gap donoracceptor conjugated oligomers are capable of absorbing a broad range of solar photons, great photoluminescence and also having a good hole mobility. There is need of thiazole which is good electron acceptor to attach with thiophene (donor) unit to produce low band gap. Recently thiazole derivatives have been paid much attention as strong withdrawing moieties used for OLEDs, polymer solar cell, and light harvesting devices [14]. Thiazole derivatives has high electron transporting ability because of good electron delocalization with dynamic  $\pi$ -stacking and also has fluorescent chromophore because it contains two electron withdrawing atoms of carbon (C) and nitrogen (N) in one functional imine (C = N) group [15]. This imine group influences the interaction of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) causes to reduce the band gap. These types of fluorescence materials are also useful to interact between small probe molecules with nucleotide analogues [16] and human serum proteins [17–20].

In this research we have synthesized and designed two new low band gap blue emitting conjugated oligomers namely OBTV-TZ and OTTV-TZ which consisted repeating units of thiophene and thiazole linked directly with ethylene linkage. These ethylene linkages change the energy levels, increases the solubility, flexibility, planarity of the  $\pi$ -conjugated system and also tuning optoelectronic properties [21]. Actually these types of conjugated molecules were synthesized based on Pdcatalysed C-C coupling reactions with much cost such as heck reaction and Suzuki reaction [22]. In this paper, oligomers were synthesized without using metal catalyst with low cost of Wittig condensation route. Moreover, we investigated the surface morphology studies, optical, electrochemical and thermal properties of these oligomers.

# **Experimental Section**

# **Reagents and Solvents**

Thiophene 2-carbaldehyde, Zn powder, POCl<sub>3</sub>, TiCl<sub>4</sub>, 2,4,5tri methyl thiazole, 4,5-di methyl thiazole, Nbromosuccinimide, benzoylperoxide, sodium hydride, triphenylphosphine, were purchased from Sigma Aldrich, Bangalore, India. Solvents such as DCM, Ethyl acetate, THF, DMF, CCl<sub>4</sub>, and Acetonitrile respectively were purchased from Sd-fine chemicals, India. All solvents were dried and distilled before the synthesis as per standard procedures.

# **Characterization Methods**

FT-IR analysis was studied through Thermo Nicolet 330 FT-IR spectrometer with KBr pellets with midrange of (500-4000 cm<sup>-1</sup>). The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were analysed by using a Bruker Advanced III 400 MHz spectrometer. The UV-Visible absorption spectra were analyzed on Hitachi U2910 spectra photometer. The PL emissions were performed with Perkin elmer LS45 fluorescence spectrometer. The morphological (AFM) images were obtained using nanosurf easy scan II instrument. 0.10 mg/ml of oligomer sample was dissolved in methanol and spin coated onto clean glass substrate using apex spin NXG-P1 instrument. Thermal stability was performed on SDT Q600 V20.9 Build 20 instrument under nitrogen flow rate 100 ml/min. The molecular weight of the intermediate compounds were measured from Perkin Elmer Calarus 680 GC-MS spectrometer and the oligomers were observed from Shimadzu LC-MS-TOF-2010 mass spectrometry.

# **Synthetic Procedure**

#### Synthesis of Donor Molecule

**Preparation of (E)-1,2-Bis(2-Thienyl)Ethylene (2)** Zinc powder (5.53 g, 84.70 mmol) was dissolved in freshly distilled anhydrous THF (150 ml). To this stirred suspension TiCl<sub>4</sub> (8.45 g, 44.58 mmol) was dropped under nitrogen atmosphere at -10 °C. The resulting reaction mixture was refluxed under nitrogen atmosphere for 60 min. Then, 2-formyl thiophene (5 g, 44.58 mmol) was added drop wise. The resulting reaction mixture was refluxed for 2 h. After cooling, reaction mixture was diluted with water (300 ml) and extracted with diethyl ether (60 ml × 3). Finally organic layer was washed with brine solution and dried over Na<sub>2</sub>SO<sub>4</sub>. Resulting yellow colour crude product was purified by column chromatography through 60–120 mesh silica gel using hexane: ethyl acetate as an eluent and obtained colourless crystalline compound.

Yield: 65.2 %, mp. 133 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, <sup> $\delta$ </sup>ppm): 7.21 (d, 2 H, thiophene H), 7.06 (dd, 2 H, thiophene H), 7.05 (d, 2 H, thiophene H), 7.00 (s, 2 H, vinylene H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, <sup> $\delta$ </sup>ppm): 126.1, 121.45, 124.32, 142.41 (thiophene C), 127.62 (-CH = CH-). GC-MS calculated for C<sub>10</sub>H<sub>8</sub>S<sub>2</sub> (m/z) = 192.01, found, 192.30.

Preparation of (E)-1,2bis (5-Formyl-2-Thienyl)Ethylene (M<sub>1</sub>) 8.3 ml (73.3 mmol) of DMF was slowly added to a stirred solution of compound 1 (2.5 g, 13 mmol) in dichloroethane (DCE) and cooled at 0 °C. Then, POCl<sub>3</sub> (5.46 ml, 58.5 mmol) was dropped under protection of nitrogen and it was refluxed for 15 h. Resulting suspension was cooled to room temp, diluted with ice cold water and neutralised to P<sup>H</sup> 6-7 using saturated NaHCO<sub>3</sub> solution. Then product was extracted with dichloromethane (DCM), after evaporation of solvent crude product was washed with petroleum ether. Resulting brown colour powder was obtained. Yield: 56.25 %, mp: 196–198 °C. FT-IR: (KBr,  $\nu/cm^{-1}$ ): 1647.25 (-C = O), 1454.4 (C-C stretch in aromatic), 958.65 (transvinylene). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, <sup>8</sup>ppm): 7.20 (d, 2 H, thiophene H), 7.62 (d, 2 H, thiophene H), 7.16 (s, 2 H, vinylene H), 9.80 (s, 2 H, -CHO). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz, <sup>δ</sup>ppm): 182.62 (-CHO), 150.26, 137.0, 128.28, 142.80 (thiophene C), 124.01 (-CH = CH-). GC-MS calculated for  $C_{12}H_8O_2S_2$  (m/z) = 248, found, 248.80.

## Synthesis of Acceptor Molecule

**Preparation of 4,5-Bis-Bromo Methyl Thiazole (4)** 4,5dimethylthiazole (2 g, 17.67 mmol), N-bromosuccinimide (NBS) (6.2 g, 35.34 mmol) and benzoyl peroxide (BPO) (20 mg) were dissolved in 100 ml of CCl<sub>4</sub>. The reaction mixture was stirred at 70 °C for five hours. Formed succinimide salt was removed by water washing, product was extracted by DCM. Then solvent was removed under room temperature at atmospheric pressure. The resulting crude product was not stable at room temperature for long time and it was stable at below 15 °C in DCM. So the crude product was used for next synthesis without further purification.

**Preparation of 2,4,5-Tris Bromo Methyl Thiazole (6)** 2,4,5tris methyl thiazole (2.5 g, 19.65 mmol), N-bromosuccinimide (10.49 g, 58.96 mmol) and benzoyl peroxide (30 mg) were dissolved in 150 ml of CCl<sub>4</sub>. Resulting mixture was stirred at 70 °C for 5 h. After cooling, succinimide salt was removed by water washing and product was extracted by DCM (50 ml  $\times$  2). To this organic layer washed with brine solution and dried over Na<sub>2</sub>SO<sub>4</sub>. This product was also not stable at room temperature for long time and it was stable only at below 15  $^{\circ}$ C in DCM solvent. This crude product was also used for further synthesis without purification.

**Preparation of 4,5-(Tri Phenyl Phosphonium Di Bromo Methyl) Thiazole (M<sub>2</sub>)** In 100 ml round bottom flask, 4,5bis bromo methyl thiazole (4) (15 ml in DCM) and tri phenyl phosphine (1 g) were dissolved in 30 ml of acetonitrile. Then resulting suspension was stirred at room temperature. After 6 h white precipitation was formed, then filtered and washed with diethylether. White colour solid was obtained. FT-IR (KBr,  $\nu/cm^{-1}$ ): 3435.2 (aromatic C-H stretch), 1737.8 (C = C bending), 1587.4 (-C = N- stretch), 1435.04 (aromatic C-C stretch), 746.4 (C-P), 688.5 (C-Br), 553.5 (P-Br). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, <sup> $\delta$ </sup>ppm): 7.97–7.68 (m, all phenyl H), 5.44 (s, 2 H, -CH<sub>2</sub>-), 5.41 (s, 2 H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 400 MHz, <sup> $\delta$ </sup>ppm): 154.2, 154.1, 153.9, 153.8, 135.4, 135.3, 133.9, 133.8, 130.3, 130.2, 117.6, 116.7, 116.5, 116.4, 21.0, 14.1.

**Preparation of 2,4,5-(Tri Phenyl Phosphonium Tri Bromo Methyl) Thiazole (M<sub>3</sub>)** 2,4,5-Tris bromo methyl thiazole (6) (20 ml in DCM) and tri phenyl phosphine (1.5 g) were dissolved in 40 ml of acetonitrile. Then resulting suspension was stirred at room temperature for 6 h. White precipitation was formed, filtered and washed with diethylether. FT-IR (KBr,  $\nu/cm^{-1}$ ): 3051.2 (aromatic C-H stretch), 1716.6 (C = C bending), 1580.6 (-C = N- stretch), 1430.0 (aromatic C-C stretch), 749.5 (C-P), 689.7 (C-Br), 550.1 (P-Br). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, <sup>δ</sup>ppm): 7.99–7.69 (m, all phenyl H), 5.44 (s, 2 H, -CH<sub>2</sub>-), 5.38 (s, 2 H, -CH<sub>2</sub>-), 5.35 (s, 2 H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (DMSO-d6, 400 MHz, <sup>δ</sup>ppm): 165.64, 165.61, 152.3, 152.2, 135.39, 135.36, 133.9, 133.8, 130.3, 130.2, 117.7, 116.8, 115.5, 115.4, 21.71, 18.56, 13.95.

**Preparation of Oligomer OBTV-TZ** Monomer 2 ( $M_2$ ) (0.5 g, 0.57 mmol) was dissolved in 50 ml of THF. To this 60 % NaH (0.13 g, 5.72 mmol) was added pinch wise at -10 °C. Then monomer 1 ( $M_1$ ) (0.28 g, 1.14 mmol) was added and the reaction mixture was stirred at 70 °C for 24 h. After the reaction period, ethyl acetate was added slowly to get precipitate and filtered. Yellow coloured solid was obtained. FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3384 (aromatic C-H stretch), 3171 (=C-H stretch), 1637.9 (-C = N stretch), 1550.2 (C-C stretch in aromatic ring), 1338.6 (aromatic C = C), 1018.3 (=C-H bend), 925.9 (transvinylene). <sup>1</sup>H NMR (CH<sub>3</sub>OH-d<sub>4</sub>, 400 MHz, <sup>8</sup>ppm): 8.44 (s, thiazole H), 7.57–7.44 (m, all thiophene H nearer to N), 7.33–7.19 (m, all thiophene H nearer to S), 7.03–6.87 (m, all vinylene H). Anal. Calcd for C<sub>68</sub>H<sub>46</sub>N<sub>4</sub>S<sub>12</sub>: C 62.8; H 3.67; N 4.25; S 29.28 %. Found; C 62.25; H 4.62; N 4.52; S 28.61 %.

Preparation of Oligomer OTTV-TZ Monomer 3 (M<sub>3</sub>) (0.5 g, 0.43 mmol) was dissolved in 50 ml of THF. To this 60 % NaH (0.15 g, 6.52 mmol) followed by Monomer 1 (M<sub>1</sub>) (0.32 g, 1.30 mmol) was added. The reaction mixture was stirred at 70 °C for 24 h. Precipitation was formed while slow addition of ethyl acetate and then filtered to get a pale yellow coloured solid. FT-IR (KBr,  $\nu/cm^{-1}$ ): 3301 (aromatic C-H stretch), 3188.8 (=C-H stretch), 1641 (-C = N stretch), 1556.8 (C-C stretch in aromatic ring), 1330.3 (aromatic C = C), 1016 (=C-H bend), 933.9 (trans-vinylene). <sup>1</sup>H NMR (CH<sub>3</sub>OH-d<sub>4</sub>, 400 MHz,  $^{\delta}$ ppm): 7.86–7.79 (m, all thiophene H between of thiazole S and N), 7.57-7.41 (m, all thiophene H nearer to N), 7.33-7.18 (m, all thiophene H nearer to S), 7.05-6.89 (m, all vinylene H). Anal. Calcd for C<sub>73</sub>H<sub>51</sub>N<sub>5</sub>S<sub>13</sub>: C 61.96; H 3.63; N 4.95; S 29.46 %. Found: C 60.45; H 4.71; N 4.48, S 30.36 %.

#### **Results and Discussion**

# Synthesis and Characterization of Monomers and Oligomers

The general synthetic scheme for monomers and two oligomers are illustrated in scheme. 1. The structures of the monomers and target oligomers were confirmed by FT-IR. <sup>1</sup>H NMR spectroscopic techniques. Firstly, the donor type of intermediate (2) was synthesized from 2-formyl thiophene (1) using Zn powder, TiCl<sub>4</sub> via mcmurry coupling. Formed vinyl linkage was confirmed from <sup>1</sup>H NMR spectroscopy. Signal was appeared at 7.0 ppm (J=14) which indicates the intermediate (2) was in E- configuration and also appeared six thiophene proton signals at around 7.05–7.21 ppm. The monomer 1  $(M_{11})$ was synthesized from (E)-1,2-bis(2-thienyl)ethylene (2) in presence of DMF and POCl<sub>3</sub> by well-known Vilsmeier-Haack reacton. The aldehyde protons were observed at 1647.2 cm<sup>-1</sup> in FT-IR, 9.8 and 182 ppm was appeared in <sup>1</sup>H and C<sup>13</sup> NMR spectrum which confirms the newly formed formyl thiophene group. From the part of acceptor moiety, bromo methyl thiazole was firstly synthesized and then converted to monomers (M<sub>2</sub> & M<sub>3</sub>) using triphenylphosphine. The structure of M<sub>2</sub> & M<sub>3</sub> was confirmed by appearing the sharp absorption bands at 746.4, 749.5 (C-P band), 688.5, 689.7 (C-Br stretching) in FT-IR and 7.99-7.69 ppm (phenyl hydrogens of phosphonium salt) in <sup>1</sup>H NMR spectra. The molecular weights of the intermediate and monomers were well established using mass spectral analysis. The theoretical values was well agreement with the experimental value which confirms the structure of monomers  $(M_1, M_2)$  $M_2$  and  $M_3$ ).







Fig. 1  $\,$  FT-IR spectra of the oligomers OBTV-TZ and OTTV-TZ





8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 ppm Fig. 3 <sup>1</sup>H NMR spectra of OTTV-TZ

#### **Characterization of Oligomers**

The synthetic procedures of the both oligomers (OBTV-TZ, OTTV-TZ) were sketched in Scheme 1. The present oligomers were prepared from the thiophene dicarbaldehyde monomer ( $M_1$ ) and thiazole phosphonium salt monomers ( $M_2$  &  $M_3$ ) in dry THF solvent using well-known Wittig condensation route. Sodium hydride was selected as a base for deprotonation of phosphonium salt to prepare oligomer.

The oligomers were well soluble with water and methanol without introducing any solubilizing group in thiophene and thiazole moiety [23]. The structures of both oligomers were verified by FT-IR and NMR. The FT-IR spectra demonstrated (Fig. 1) that both oligomers (OBTV-TZ & OTTV-TZ) showed characteristic absorption bands formed at 3384, 3301 cm<sup>-1</sup> which indicates heterocyclic aromatic C-H stretching, 3171, 3188 indicates =C-H- stretching and 1637, 1641 cm<sup>-1</sup>



Fig. 4 Absorption spectra of the both oligomers in methanol solution and solid state

represents -C = N stretching. The sharp absorption peaks at around 925.9 and 933.9 cm<sup>-1</sup> which represents trans-vinylene was predominant among the newly developed vinylene double bonds. These IR values indicated for the successful reaction of monomers. The <sup>1</sup>H NMR spectrums of both oligomers are shown in Figs. 2 and 3. The oligomer OBTV-TZ exhibited down field peak at 8.44 ppm which indicates thiazole protons. All thiophene protons of both oligomers show multiple signals in between of 7.57–7.19 ppm. The signal formed at 7.03–6.76 due to trans-vinylene protons. The low molecular weight of the OBTV-TZ and OTTV-TZ was measured from mass spectrometry which was found to be 1330 m/z and 1398 m/z. The reason behind that wittig formed product usually oligomers were having low molecular weight [24].

#### **Optical Characterization**

#### Absorption Studies

The optical and photo physical properties of both oligomers were investigated by UV-visible spectroscopy and their optical absorption spectra were measured in methanol solution (5 mg mL<sup>-1</sup>) and thin films, which are shown in Fig. 4. Both oligomers displayed identical absorption peaks. This is the recognisable feature in donor-acceptor oligomers. Both oligomers were exhibited two types of absorption peaks, The first one is higher energy absorption peak (weak band) which was appeared at lower wavelength side. In absorption spectra it was observed at 244 to 297 nm, which is due to  $\pi$ - $\pi^*$ electronic transition of the conjugation. Second one is lower energy absorption peak (strong band) appeared at higher wavelength side. In absorption spectra it was observed at 300 to 420 nm which is responsible for the strong internal charge transfer (ICT) between donor (thiophene) and acceptor



Fig. 5 Fluorescence spectra of the both oligomers in methanol solution. Colour of the OBTV-TZ and OTTV-TZ solutions under **a** visible light **b** under UV-Lamp ( $\lambda_{max} = 365 \text{ nm}$ )





(thiazole) when compared with literature based benzo thiadiazole based co-oligomer [5].

The thin film absorption spectra of both oligomers were bathochromic shifted when compared with their solution absorption spectra. This demonstrate that the thin film states was shown strong intra or inter chain molecular interactions. Both oligomers were depicted a single absorption broadening peaks. In solid state  $\pi$ - $\pi^*$  transition peak was absent due to carbon-carbon bonds rotation was restricted leads to form aggregation or  $\pi$ - $\pi$  stacking.

The optical band gap values of both oligomers were calculated from the absorption onset of the thin film according to the equation  $E_g^{opt} = 1240/\text{absorption onset}$  [25]. The optical band gap values was observed as 2.0 and 2.13 eV which was calculated from their absorption onset values 600 and 580 nm respectively. These broadened peaks absorption onset values are greater than our previously reported carbazole and quinoline based donor-acceptor conjugated polymer ( $\lambda_{\text{onset}} = 460$  nm) [26].

#### **Photoluminescence Studies**

The fluorescence spectra for both oligomers in methanol are shown in Fig. 5. OBTV-TZ and OTTV-TZ oligomers exhibited blue light emission (Fig. 5b) with wavelength maxima at 433 nm and 434 nm respectively. It is highly expected that blue fluorescence is due to defined conjugation and fast intramolecular charge transfer among thiophene (donor) and thiazole (acceptor) moieties after photo excitation. Both oligomers showing pure fluorescence emission spectra without any shoulder peaks because of one kind of chromophore. Both oligomers exhibit almost similar emission values which indicate same conjugation length between thiophene and thiazole segments. These two oligomers were showed bathochromic shift when compared with thiophene based 2,5-di sustituted 1,3,4-oxazoles [27]. Moreover we investigated the three-dimensional fluorescence spectroscopy of both oligomers which is depicted in Fig. 6. The fluorescence parameters including peak intensity, peak locations, and fluorescence intensities were identified from 3D fluorescence spectra, which could be useful for quantitative analysis [28].

The oligomers OBTV-TZ and OTTV-TZ were not exhibited their emission in film and solid state. The reason may be due to the physical constraint in the solid state restricts their intermolecular rotations. This was blocked the nonradioactive channels and populating the radioactive decay thus making the oligomer and polymer non-emissive [29]. The photo luminescence of both oligomers could be favourable under solution state than film state.

Stokes shift is the difference between positions of the absorption and emission spectroscopy. Both absorption and emission energies were depend on the unique characteristics of particular oligomeric material structure. If the stokes shift is







#### номо

Fig. 8 Schematic diagram of HOMO/LUMO energy levels of OBTV-TZ, OTTV-TZ and comparison with  $PC_{61}BM$ 

very small, the overlapping of emission and absorption spectra will be more. Then luminescent efficiency will decrease in device because the emitting light will be self-absorbed by the material and the luminescent efficiency will be decreased [30]. In this study, stokes shift of OBTV-TZ and OTTV-TZ were found to have 85.4 and 82 nm. The longer stokes shift was observed in OBTV-TZ (85.4 nm) illustrate that the more structural adjustment among the ground state and excited state. So it was advised as best oligomeric material for organic light emitting diodes.

#### **Electrochemical Properties**

The electro chemical studies of both oligomers were investigated by the cyclic voltammetry (CV). The HOMO and LUMO energy values of the conjugated oligomers were calculated from oxidation and reduction potential values. The cyclic voltammograms of both oligomers and schematic diagram of HOMO/LUMO energy levels are depicted in Figs. 7 and 8. The CV is performed in 0.1 mol/L of tetra butyl ammonium hexa fluoro phosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile solution at scan rate 50 mV/S using platinum wire as a counter electrode and Ag/AgCl as reference electrode. The potentials were internally calculated using the Fc/Fc<sup>+</sup> redox couple. According to that, the electrochemical band gaps  $(E_g^{ec})$  of the both oligomers were calculated through following empirical equation [31].

$$E_{\text{HOMO}} = -(E_{\text{ox}} + 4.4)$$
$$E_{\text{LUMO}} = -(E_{\text{red}} + 4.4)$$
$$E_{\text{g}} = E_{\text{HOMO}} - E_{\text{LUMO}}$$

The electrochemical potential and energy levels of OBTV-TZ and OTTV-TZ are shown in Table. 1. The onset oxidation  $(E_{\text{ox}})$  and reduction  $(E_{\text{red}})$  potentials of OBTV-TZ are 1.05 V and -0.5 V respectively. The HOMO and LUMO energy levels of OBTV-TZ are calculated as 5.45 and -3.9 eV respectively and electrochemical energy band gap is 1.55 eV. This was lower compared to optical band gap which was measured from UV solid absorption spectra (2.00 eV). The difference between the optical band gap and electrochemical band gap is 0.45 eV. This may be accredited to the creation of free ions in cyclic voltammetry in electrochemical experiments which differentiate with solid UV absorption maxima. OBTV-TZ was also observed low band gap ( $E_g^{ec} = 1.55 \text{ eV}$ ) oligomer when compared with dithiazole and benzo di thiophene based conjugated polymer ( $E_g^{ec} = 2.86 \text{ eV}$ ) [14] and thieno pyrazine-based copolymers ( $E_g^{ec} = 1.84 \text{ eV}$ ,  $E_g^{ec} = 2.24 \text{ eV}$ ) [32]. These types of low band gap oligomers will be worked as good efficiency in the area of photovoltaic application.

The onset oxidation ( $E_{ox}$ ) potential of OTTV-TZ is 2.2 V. The HOMO value of OTTV-TZ is estimated to be -6.6 eV. This HOMO value is higher than thieno [3–4-b] pyrazine based polymer [33]. The LUMO level was calculated to be -4.5 eV according to the equation  $E_{LUMO} = E_{HOMO} + E_g^{opt}$  [34]. The higher HOMO level (-6.6 V) of OTTV-TZ is due to higher number of electron donating moieties (p-doped) respect to thiazole acceptor (n-doped). These types of highest HOMO value oligomers are acceptable for oxidative stable devices.

#### Surface Morphology Analysis

The morphology of both oligomers was investigated by AFM. This technique is important and useful for characterization of high resolution images of the surface of organic thin films. The thin films of both oligomers were coated on glass

Table 1 Electrochemical   property of both oligomers	Oligomers	$E_{\text{onset}}^{ox}$ (V)	$E_{\text{onset}}^{red}$ (V)	HOMO (eV)	LUMO (eV)	$E_g^{Ec}$ (eV)	$E_g^{Opt}$ (eV)
	OBTV-TZ OTTV-TZ	1.05 2.2	$-0.5$ 0.1(cal from $E_g^{Opt}$ )	-5.45 -6.6	-3.9 -4.5	1.55 2.13	2.0 2.1

Fig. 9 AFM images of oligomers OBTV-TZ and OTTV-TZ



substrate using spin coating technique. After evaporation of solvent it shows mainly three interactions those are molecule-solvent, molecule-surface and moleculemolecule interactions.

The surface morphology has been measured for two oligomers which are depicted in Fig. 9. The oligomer OBTV-TZ displayed rod shaped particle with size of width and length was measured as  $1.36 \ \mu m$  and  $6.36 \ \mu m$ . OTTV-TZ displayed micrometers sized long strip like structure that width was  $2.5 \ \mu m$  and length was  $8.5 \ \mu m$ .

AFM topography was also used to calculate the surface roughness (Sq), root mean square (RMS), average surface roughness (Sa), maximum peak height (Sp), peak-peak height (Sy), and maximum peak valley depth. These all surface measurements of both oligomers were depicted in Table. 2. The RMS surface roughness of OBTV-TZ and OTTV-TZ were noticed to be 13.6 nm and 10.6 nm respectively. These values were higher than thermally annealed and cast films of PPV with dithenyl(thienothiadiazole) copolymer [35]. Higher surface roughness of the oligomers leads to increase the photo current, internal light scattering light absorption and internal series resistance of the device [36, 37].

#### **Thermal Analysis**

The thermal properties of OBTV-TZ and OTTV-TZ oligomers were characterised by thermogravimetric analysis at a temperature ramp rate of 20 °C min<sup>-1</sup> under nitrogen atmosphere (Fig. 10). Both oligomers showed different curve shapes and thermal behaviour. OTTV-TZ has shown good thermal stability than OBTV-TZ. The degradation temperature ( $T_d$ ) with 13 % and 9 % weight loss at 350 °C was noticed for OBTV-TZ and OTTV-TZ. Obviously thermal stability of OTTV-TZ \ Both oligomers had higher thermal stability than dodecyl thieno[3,4-b]thiophene-2-carboxylate conjugated polymer ( $T_d = 350$  °C with 25 % weight loss) [38]. Final degradation temperatures of the oligomers were found to be 490 and

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Table 2
Surface morphology measurement of both oligomers
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Oligomers Average sur	face RMS roughness	s Peak-peak	m) Maximum pea	ak Maximum p	eak Maximum peak
roughness (S	Sa) (nm) (Sq) (nm)	height (Sy) (ni	m) height (Sp) (ni	m) valley depth	(Sv) (nm) valley (Sp-Sv) (nm)
OBTV-TZ 7.2 OTTV-TZ 4.5	13.6	211.3	183.4 238.6	-27.8	211.2



Fig. 10 TGA thermogram of both oligomers

500 °C with 40 % and 45 % weight loss for OTTV-TZ and OBTV-TZ oligomers. Both oligomers were shown good thermal stability compared to 2,5-bis(3-decylthiophen-2-y1) thiazole [5,4-d] thiazole and 2,6-(1,5didecyloxy)naphthalene containing conjugated polymer [39]. So, both oligomers are best material for making stable devices which is highly utilized material for OLED and photovoltaic application.

## Conclusions

We have successfully synthesized and characterized two thermally stable donor-acceptor conjugated oligomers OBTV-TZ and OTTV-TZ using Wittig condensation. We have achieved good solubility with methanol without introducing solubilizing groups. The optical band gaps of oligomers were 2.0 eV and 2.13 eV which was calculated from solid absorption onset. Both oligomers exhibited stronger blue light emission maxima with 433 and 434 nm wavelength. The optical and electrochemical characters of the both oligomers imply that the introduction of electron withdrawing thiazole and electron donating thiophene which both reduces the optical and electrochemical band gap of the oligomers (1.55 eV). Oligomer film displayed rod shaped particles and long strip like particles with lower surface roughness. Both oligomers were expressed good thermal stability with final decomposition temperature around 500 °C with 40-45 % weight loss. The result of both conjugated oligomers will be promised for future OLEDs and photovoltaic applications.

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