# Accepted Manuscript

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\$1010-6030(18)30432-5
https://doi.org/10.1016/j.jphotochem.2018.05.037
JPC 11307
Journal of Photochemistry and Photobiology A: Chemistry
3-4-2018
3-5-2018
23-5-2018

Please cite this article as: Pilicode N, K M N, M N S, Adhikari AV, New cyanopyridine based conjugative polymers as blue emitters: Synthesis, photophysical, theoretical and electroluminescence studies, *Journal of Photochemistry and Photobiology, A: Chemistry* (2018), https://doi.org/10.1016/j.jphotochem.2018.05.037

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# New cyanopyridine based conjugative polymers as blue emitters: Synthesis, photophysical, theoretical and electroluminescence studies

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## **GRAPHICAL ABSTRACT:**

Three new conjugative polymers **Th-Py-1**, **Th-Py-2** and **Th-Py-3**, were designed, synthesized and characterized. Their thermal, photophysical, theoretical and electroluminescence studies were carried out.



### HIGHLIGHTS

- Designed and synthesized new 3 cyanopyridine based polymers for PLED applications
- Polymers display light absorption at 377-397 nm and emission at 432-482 nm
- They possess optical band gap of 2.55-2.64 eV with good thermal stability
- Their EL maxima range is 469-476 nm with blue emission in their PLED devices
- Their fluorescence quantum yield varies in the range of 21-45%

### **ABSTRACT**:

Herein, we report the design of three new blue light emitting conjugated polymers (Th-Py-1, Th-Py-2 and Th-Py-3), carrying cyanopyridine ring as a strong electron accepting unit and thiophene as well as phenylene vinylene scaffolds with different substituents, as electron donating moieties. The newly designed monomers/polymers were synthesized using well-known synthetic protocols such as cyclocondensation, Oalkylation, Suzuki cross coupling, Wittig and Knoevenagel reactions. They were well-characterized by spectral, thermal, photophysical, electrochemical and gel permeation chromatography (GPC) techniques. Further, they were subjected to theoretical studies using DFT simulations, performed at B3LYP/TZVP level using Turbomole 7.2V software package. The new polymers were tested in PLED devices (ITO/PEDOT: PSS/Polymer/Al) as emissive materials. Optical studies revealed that, all the polymers displayed light absorption in the range of 377-397 nm and blue light emission in the order of 432-482 nm, respectively. Further, their band-gaps were calculated to be in the order of 2.55-2.64 eV using both optical and electrochemical data. Furthermore, the TGA study indicated that, they possess good thermal stability with onset decomposition temperature, greater than 300 <sup>0</sup>C under nitrogen atmosphere. Interestingly, use of these polymers in new PLEDs as emissive layers, has shown improved performance when compared to previously reported polymers in similar type of devices. They show blue light emission with a low threshold voltage of 3.5-3.9 V, affirming an efficient electron injection in the diodes.

Keywords: Conjugative polymers, Blue light emitter, Cyanopyridine, DFT, PLED.

### 1. Introduction

Conjugated polymers based on heteroaromatics are of prime importance in the last few decades due to their remarkable optical and electrochemical properties. These polymers were shown to possess many optoelectronic applications, which include mainly electroluminescent devices [1-2], photovoltaic cells [3] and field effect transistors, sensors [4]. Such polymers are prospective candidates for optoelectronic devices because of their many obvious advantages such as mechanical flexibility, impact resistance, optical transparency, thermal as well as photochemical stability, film forming ability, ease of fabrication, ability to form radical cations and hence possession of high charge carrier mobility. In addition, their optical and electronic properties can be fine-tuned by functionalization of their backbone structures as well as by unique combination of the donor and acceptor units in their structural designs.

Pyridine has attracted much attention of many researchers for designing new conjugated polymers, as it is thermally stable *n*-type heterocyclic system. Due to its high electron deficient nature, pyridine acts as a very strong electron withdrawing moiety with good electron transporting property. It shows very good optical properties because of localization of lone pair of  $sp^2$  orbital electrons of the nitrogen atom [5-7]. Further,

presence of the electron withdrawing nitrile (CN) substituent on the pyridine ring enhances its electrontransporting nature [8]. Consequently, polymer with cyanopyridine in the main chain would increase its charge carrying property [9]. Also, as cyanopyridine itself exhibits very good fluorescence property, its presence in polymer chain would further enhance light emitting characteristics of the resulting conjugative macromolecules.

Among the  $\pi$ -conjugated systems, thiophene based polymers have gained intense interest among researchers all over the world and actually being advanced to be most frequently investigated structures [10-13]. Consequently, they are the most frequently used conjugative materials, particularly as an active component in organic electronic devices and molecular electronics. Indeed, they display the best combination of efficient electronic conjugation, chemical stability and incredible synthetic versatility, which allows their significant properties to be accessed through proper substitution. Thiophene chemistry is well-established and has been under development for a long time [14]. Highly stable thiophene ring acts as a powerful electron donor and also a good hole transporting system. Moreover, they are ideal building blocks in transition metal-catalyzed crosscoupling reactions which have been developed enormously in past two decades and nowadays, provides basis for synthesis of most of the polymers. Evidently, such polymers are normally stable both in conducting and in semiconducting states and can be readily characterized by many methods. Their unique optical, electronic, redox, charge carrying and self-assembling properties are quite interesting in addition to their exceptional arrangement and stacking behavior on solid surfaces as well as in the bulk. Further, the high polarizability of S atoms in thiophene ring leads to the stabilization of the conjugated chain and excellent charge transport properties, which are crucial assets for their optoelectronic applications. In addition, they possess enormous and attractive potential of structural variation leading to different architectures which allow tuning of electronic properties over a wide range and outstanding physical as well as chemical properties.

Conducting polymers derived from phenylene vinylene are attractive class of materials for their applications in the field of optoelectronics, mainly due to their efficient electroluminescent property. They are good conducting polymers of rigid-rod polymer family and their physical, as well as electronic properties can be altered by the inclusion of functional side groups. The repeating phenylene vinylene units act as strong electron donors and also, function as good hole transporting systems in the polymer backbone. Obviously, they possess highly ordered crystalline film-forming ability, improved mechanical properties and excellent luminescent behavior [15-16]. Further, presence of the vinylene linkage along with phenylene ring in the polymer main chain increases the planarity and hence conjugation length of the molecule, causing enhanced optoelectronic properties. Moreover, vinylene linkage functions as an excellent fluorophore *via* charge transfer, making the polymer highly luminescent.

Against this background, in quest of new efficient blue light emitters, it has been aimed at designing three new donor-acceptor type conjugated polymers, *viz.* **Th-Py-1**, **Th-Py-2** and **Th-Py-3** carrying cyanopyridine ring as a strong electron acceptor, thiophene and phenylenevinylene units as strong electron donors. In fact, such designs carrying cyanopyridine system with two thiophene rings on either sides, have not yet been reported in the literature, however copolymers containing thiophene, phenylenevinylene and cyanopyridine systems in sequence were well-known [17-20]. In the new design, presence of electron withdrawing nitrile group (-CN) on vinylene unit of **Th-Py-1**, as well as electron accepting bromo (-Br) functionality on phenyl ring of **Th-Py-3** is expected to improve charge carrying ability of polymer chains.

Further, hexadecyl side chain ( $-C_{16}H_{33}$ ) on cyanopyridine ring would bring about good solubility and film forming ability for the polymers. Thus, the resulting polymers have been predicted to possess promising structural requirements for exhibiting favorable optical properties with wide band gap and thermal stability, which arise from both the backbone and functional groups. As a result, we hoped these new polymers are potential candidates for application in PLEDs, as blue emissive materials.

In the present work, the required monomers as well as polymers, **Th-Py-1**, **Th-Py-2**, and **Th-Py-3** were designed and synthesized starting from simple derivatives of thiophene and xylene using routine synthetic protocols. Polymerization of monomers was achieved by Knoevenagel and Wittig methods. Newly synthesized monomers/polymers were well-characterized by FTIR, NMR spectral and elemental analysis techniques. Weight average molecular masses and polydispersity index (PDI) of polymers were determined using GPC method and their thermal stability was evaluated by thermo gravimetric analysis (TGA). Their photophysical properties were investigated using UV-Vis and fluorescence spectral studies. Their optical and electrochemical bad gaps along with HOMO-LUMO energy levels were obtained by spectral and cyclic voltammetric (CV) methods, respectively. Further, theoretical studies of these polymer structures were carried out using DFT simulations, performed at B3LYP/TZVP level using Turbomole 7.2V software. Finally, their electroluminescence behavior was explored by fabricating new PLED devices with configuration, ITO/PEDOT: PSS/Polymer/Al, where polymers **Th-Py-1**, **Th-Py-2** and **Th-Py-3** function as light emissive layers in respective diodes. Based on the experimental results, correlation between the polymer structures and various above mentioned properties was discussed in detail.

### 2. Experimental section

#### 2.1. Materials and methods

The starting materials 5-Bromo-2-thiophenecarboxaldehyde, 2-Acetyl-5-bromothiophene, 3bromobenzaldehyde, p-xylylene dibromide and 1,4-phenylenediacetonitrile ( $M_1$ ) were procured from Sigma Aldrich and was used without purifying further. All the solvents were dried prior to use. The reactions were performed under inert atmosphere and completion of reaction was confirmed by Thin Layer Chromatography (TLC) method. Compounds were purified using column chromatography and recrystallization techniques.

### 2.2. Instrumentation

The melting points of the final products were determined using SMP-10 melting point apparatus (Stuart Make) and were uncorrected. FTIR spectra were run using Bruker Alpha spectrophotometer. <sup>1</sup>H NMR spectra were recorded using Bruker Advance 300 MHz using deuterated chloroform (CDCl<sub>3</sub>) as solvent and TMS as an internal standard whereas the elemental analysis was carried out on Flash EA1112 CHNSO analyzer (Thermo Electron Corporation). UV-Vis and Fluorescence spectra were recorded in 10<sup>-5</sup> M THF solution/thin film using SPECORD S600 and Horiba Fluromax-4 spectrophotometers. CV measurements were performed on an IVIUM Vertex Electrochemical Workstation by using the three electrode system consisting of polymer film casted on glassy carbon electrode as a working electrode, Pt electrode as a counter electrode and Ag/AgCl as a reference electrode. All three electrodes are immersed in acetonitrile solution consisting of an electrolyte [0.1M (*n*-Bu)<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup>] and CV data were recorded at a scan rate of 100 mV/s. Molecular weights of polymers were

determined with WATER's make Gel Permeation Chromatograph (GPC) against polystyrene standards with THF as an eluent. Finally, DFT calculations were performed using Turbomole, 7.2V software package.

#### 2.3. Synthetic plan

### 2.3.1. Synthesis of intermediates, monomers and polymers.

All the required intermediates (3, 4, and 6), monomers ( $\mathbf{M}$ ,  $\mathbf{M}_2$  and  $\mathbf{M}_3$ ) and polymers (**Th-Py-1**, **Th-Py-2** and **Th-Py-3**) were synthesized through series of reactions as summarized in **Schemes 1** and **2**. Monomer  $\mathbf{M}_1$  was procured directly from the vender while  $\mathbf{M}_2$  and  $\mathbf{M}_3$  were prepared as per the reported procedures [21-22].

### 2.3.2. Synthesis of 2,5-bis(4-bromothiophene)-2-hydroxypyridine-3-carbonitrile (3)

A mixture of 5-Bromo-2-thiophenecarboxaldehyde (**1**, 1.86 g, 9.74 mmol) and 2-Acetyl-5-bromothiophene (**2**, 2 g, 9.75 mmol) was dissolved in 35 mL of 1,4-dioxane. To this ammonium acetate (6.77 g, 87.7 mmol) was added slowly with shaking followed by 1.25 mL of ethyl cyanoacetate (11.7 mmol) and the temperature was raised to 80 °C. The reaction mixture was kept at 80 °C under stirring for 24 h. Progress of the reaction was monitored using TLC. The content was then cooled and poured onto 100 mL of ice-cold water and stirred for about 10 min. The obtained precipitate was filtered, and thoroughly washed with 1,4-dioxane and finally dried to afford a white solid product **3**. Yield 36%; mp 310.7 °C; ATR-IR (cm<sup>-1</sup>):1635 (C=N), 2220 (C=N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 6.97 (s, 1H), 7.62-7.67 (d, 4H). Elemental Analysis calculated for C<sub>14</sub>H<sub>6</sub>Br<sub>2</sub>N<sub>2</sub>OS<sub>2</sub>: C, 38.03; H, 1.37; N, 6.34; S, 14.50; found: C, 38.01; H, 1.36; N, 6.33; S, 14.52.

### 2.3.3. Synthesis of 2, 5-bis (4-bromothiophene)-2-(hexadecoxyl)pyridine-3-carbonitrile (4)

2,5-*bis*(4-bromothiophene)-2-hydroxypyridine-3-carbonitrile (**3**, 0.5 g, 1.131 mmol) was dissolved in 8 mL of DMF. To this 1-bromohexadecane (0.35 mL, 1.146 mmol) was then added, followed by 148 mg of potassium carbonate (1.072 mmol) and the reaction mixture was stirred at 80 °C for overnight. Progress of the reaction was monitored using TLC. After cooling, it was then cooled and poured onto 150 mL of ice cold water with constant stirring. The obtained precipitate was filtered, washed with water and dried to obtain creamy yellow product. It was recrystallized using chloroform-methanol to give product **4.** Yield 75%; mp 71.1 °C; ATR-IR (cm<sup>-1</sup>): 2220 (C=N), 2919 (C-H). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 0.81-1.86 (m, 31H), 4.56-4.58 (t, 2H), 7.73-7.86 (m, 5H). Elemental Analysis calculated for C<sub>30</sub>H<sub>38</sub>Br<sub>2</sub>N<sub>2</sub>OS<sub>2</sub>: C, 54.06; H, 5.75; N, 4.20; S, 9.62; found: C, 54.05; H, 5.76; N, 4.21; S, 9.63.

#### 2.3.4. Synthesis of 3-(4,4,5,5-tetramethy-1,3,2-dioxaborolan-2-yl)-benzaldehyde (6)

A mixture of 3-bromo benzaldehyde (5, 1.68 g, 9.08 mmol), bis(pinacolato)diboron (3.4 g, 13.4 mmol), catalyst Pd(dppf)Cl<sub>2</sub> (199 mg, 0.27 mmol), and potassium acetate (2.67 g, 27.24 mmol) in degassed 1,4-dioxane (50 ml) was stirred at 80 °C for 6 h under N<sub>2</sub> atmosphere. Progress of the reaction was monitored using TLC. The reaction mixture was quenched by adding cold water to it and the separated the product was extracted by

dichloromethane (25 mL x 3). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified by silica gel (60-120 mesh) chromatography (petroleum ether, 60-80 °C/dichloromethane, 1:3) to give compound **6** (1.86 g, 88.9%) as pale white solid; mp 51 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 1.36 (s, 12H), 7.51-8.31 (m, 4H), 10.1 (s, 1H).

### 2.3.5. Synthesis of 1,4-bis-(2'-formyl-phenylene-thiophene-5-yl)-2-hexadecoxyl-nicotinonitrile (M)

A clear solution of cyanopyridine derivative (**4**, 1 g, 1.5 mmol), 3-formylphenylboronic ester (**6**, 0.77 g, 3.3 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.17 g, 0.15 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (3.4 g, 10.4 mmol) in 20 mL toluene was refluxed under argon atmosphere for 5 h. Progress of the reaction was monitored by TLC. After completion of the reaction, toluene was removed under reduced pressure to get the crude product. It was then dissolved in dichloromethane and passed through Celite bed to remove Pd traces. Obtained filtrate was washed with excess of distilled water to remove traces of base and toluene. The crude product was extracted using dichloromethane (25 mL x 3) and the combined organic layer was dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica (60-120 mesh) with hexane/ethyl acetate mixture (100:25). The product was obtained as off-white solid; Yield 59%; mp 79.2 °C; ATR-IR (cm<sup>-1</sup>): 1692 (C=O), 2213 (C=N). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 0.81-1.86 (m, 31H), 4.54-4.58 (t, 2H), 7.69-8.16 (m, 13H), 10.1(d, 2H). Elemental Analysis calculated for C<sub>44</sub>H<sub>48</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>: C, 73.71; H, 6.75; N, 3.91; O, 6.69; S, 8.94; found: C, 73.72; H, 6.74; N, 3.92; O, 6.68; S, 8.93.

### 2.3.6. Synthesis of polymer Th-Py-1

Cyanopyridine dialdehyde derivative (**M**, 0.5 g, 0.68 mmol) and phenylene diacetonitrile (**M**<sub>1</sub>, 0.13 g, 0.83 mmol) were dissolved in a mixture of 5 mL of chloroform and 15 mL of ethanol. Freshly prepared sodium ethoxide (0.06 g, 2.6 mmol in 10 mL of ethanol) was added to the reaction mixture at room temperature under nitrogen atmosphere. The content turned to yellow color and it was further stirred for 12 h at room temperature. Reaction was monitored by TLC. After completion of the reaction, solvent was removed under reduced pressure. The crude reaction mass was poured onto excess of methanol and stirred for 20 min. The obtained polymer **Th-Py-1** was filtered and washed thoroughly with acetone to remove traces of monomers. The crude precipitate was filtered off and dried at 40 °C under vacuum for 20 h to give fluorescent yellow color powder. Yield 65%. ATR-IR (cm<sup>-1</sup>): 2217 (C=N), 2917 (C-H). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 1.18-1.86 (m, 31H), 4.54-4.58 (b, 2H), 7.23-8.1 (m, 20H). Elemental Analysis calculated for **Th-Py-1**: C, 77.56; H, 6.74; N, 6.46; S, 7.39; found: C, 77.52; H, 6.72; N, 6.43; S, 7.37.  $\overline{M}_w$ , 18,932 g/mol, PDI, 1.62.

### 2.3.7. Synthesis of polymer Th-Py-2

А of cyanopyridine dialdehyde (**M**, 0.5 0.68 mmol) 1,4 mixture g, and bis{(bromotriphenylphosphoranyl)methyl}benzene (M2, 0.95 g, 1.05 mmol) was dissolved in a mixture of 5 mL of chloroform and 15 mL of ethanol. Freshly prepared sodium ethoxide (0.1 g, 4.3 mmol in 10 mL of ethanol) was added drop wise to the reaction mixture under nitrogen atmosphere. Reaction mixture turned to pale yellow color after 30 min rigorous stirring. It was further stirred for 9 h at room temperature to complete

polycondensation reaction. Then, solvent was removed under reduced pressure. The crude reaction mass was thoroughly washed with excess of methanol followed by acetone to remove traces of monomers. Crude product was purified by re-precipitation technique using chloroform and methanol solvent system. The obtained precipitate **Th-Py-2** was filtered off and dried at 40 °C under vacuum for 20 h to give pale yellow powder. Yield 59%. ATR-IR (cm<sup>-1</sup>): 2219 (C=N), 2919 (C-H). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 1.18-1.87 (m, 31H), 4.54-4.58 (b, 2H), 6.93-8.1 (m, 21H). Elemental Analysis calculated for **Th-Py-2**: C, 79.37; H, 7.40; N, 3.43; S, 7.85; found: C, 79.33; H, 7.39; N, 3.42; S, 7.84.  $\overline{M}_w$ , 15267 g/mol, PDI, 1.73.

### 2.3.8. Synthesis of polymer Th-Py-3

The monomers, *i.e.* cyanopyridine dialdhyde 0.5g, 0.68 mmol) 1,4 (**M**, and bis((bromotriphenylphosphoranyl)methyl)bromobenzene (M3, 0.91 g, 1.04 mmol) were dissolved in a mixture of 5 mL of chloroform and 15 mL of ethanol. Freshly prepared sodium ethoxide (0.1 g, 4.3 mmol in 10 mL of ethanol) was added drop wise to the reaction mixture at room temperature under nitrogen atmosphere. Reaction mixture turned to light pale yellow color after continuous stirring for 30 min. Further condensation reaction was continued for 12 h at room temperature. Progress of reaction was monitored by TLC. After completion of the reaction, solvent was removed and crude reaction mass was poured onto excess of methanol under stirring for 20 min. The obtained polymer Th-Py-3 was filtered and washed thoroughly with acetone to remove traces of monomers. Crude product was re-dissolved in chloroform and poured onto excess of methanol to precipitate the pure polymer. The precipitate was filtered off and dried at 40 °C under vacuum for 20 h to give whitish yellow coloured powder. Yield 55%. ATR-IR (cm<sup>-1</sup>): 2222 (C≡N), 2918 (C-H). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ ppm): 1.18-1.87 (m, 31H), 4.54-4.58 (b, 2H), 6.93-8.1 (m, 20H). Elemental Analysis calculated for Th-Py-3: C, 72.38; H, 6.64; N, 3.13; S, 7.16; found: C, 72.36; H, 6.62; N, 3.12; S, 7.15. M<sub>w</sub>, 15175 g/mol, PDI, 1.81.

### 3. Results and discussion

#### 3.1. Structural and thermal characterization

Schemes 1 and 2 depict the synthetic routes for the preparation of new monomers and polymers, respectively. As shown in Scheme 1, 5-bromo-thiophene-2-carboxaldehyde was condensed with 2-acetyl-5-bromothiophene in presence of ethyl cyanoacetate to form cyanopyridine derivative (3), which was further converted into alkylated cyanopyridine derivative (4) by O-alkylation, in good yield. Separately, boronic ester derivative (6) of 4-bromobenzaldehyde was prepared using Pd(dppf)Cl<sub>2</sub> as a catalyst. The monomer M was synthesized by coupling thiophene substituted cyanopyridine (4) with freshly prepared boronic ester (6) using Pd(PPh<sub>3</sub>)<sub>4</sub> as a catalyst, under anhydrous condition, in presence of cesium carbonate following renowned Suzuki method. Polycondensation of monomer M with 1,4-phenylenediacetonitrile (M<sub>1</sub>) to form Th-Py-1 was achieved by Knoevenagel condensation technique. Whereas copolymerization of monomer M with co-monomers M<sub>2</sub> and M<sub>3</sub> to yield Th-Py-2 and Th-Py-3, respectively was carried out by Witting method. The structures of the new intermediates and the target polymers were established by <sup>1</sup>H NMR, FTIR, elemental analysis and gel permeation chromatographic techniques. The weight-average molecular weights of the polymers Th-Py-1, Th-Py-2 and Th-Py-3 were found to be 18,932, 15,267 and 15,175, respectively. The polydispersity of these polymers were 1.62, 1.73 and 1.81, respectively.

The solubility of polymers in common organic solvents is one of the important desired parameters for their selection in device fabrication, particularly by drop casting technique. Interestingly, all the three polymers showed good solubility in organic solvents such as chloroform, dichloromethane, tetrahydrofuran, and dimethylsulfoxide and hence these polymers displayed good processability and film-forming ability. The observed solubility is attributed to the presence of bulky hexadecoxyl substituent on cyanopyridine ring of the polymer chain.

The thermal studies of the polymers were carried out by thermogravimetric analysis (TGA), using a 10 °C min<sup>-1</sup> temperature ramp starting from 50 to 550 °C in a nitrogen atmosphere. The thermograms (**Fig. 1**) indicate that all the polymers exhibit a high degree of thermal stability up to 300 °C mainly due to presence of rigid heterocyclic ring system in the main chain. Further, the observed 15-20% weight loss after 300 °C may be attributed to the degradation of the alkoxy side chains in the polymers. The gradual weight loss above 350 °C may be ascribed to the slow degradation of the main polymer chain, which led to the final residue. Similar observations have been reported for some of the cyanopyridine based polymers [21]. The degradation temperatures of polymers were found to be 325, 309 and 305 °C for polymers **Th-Py-1**, **Th-Py-2** and **Th-Py-3** respectively.

### 3.2. Electrochemical studies

The electrochemical properties of polymers were studied using cyclic voltammetry measurements in order to determine their HOMO and LUMO energy levels, which are very crucial to design the polymers for application in LEDs. In the present study, cyclic voltamograms were obtained for polymers coated on glassy carbon electrode from their chloroform solution (2 mg/mL) with Ag/AgCl as reference electrode [16-20] and calibrated against  $Fc/Fc^+$  redox couple, for which ionization energy is presumed to be 4.80 eV [23]. Fig. 2 depicts CV traces of Th-Py-1, Th-Py-2 and Th-Py-3. From the results, it is clear that only reduction potentials were observed for all the polymers but not oxidation potentials. Similar observations were reported for some of the cyanopyridine based polymers [21]. Using the reduction potential data, the required LUMO energy levels of the polymers were calculated following the equation:  $E_{LUMO} = -e[E_{red} + 4.33]$ . Here, measured ionization potential (E<sub>FOC</sub>) for Fc/Fc<sup>+</sup> was 0.47 V vs. Ag/AgCl electrode. Accordingly, the calculated LUMO energy levels for Th-Py-1, Th-Py-2 and Th-Py-3 were found to be -2.65, -2.25 and -2.49 eV, respectively. From the results it is evident that Th-Py-2 showed the highest energy level among the three polymers, which is attributed to presence of unsubstituted vinylene group in polymer chain, while other two structures possess electron withdrawing CN/Br group attached to vinylene group causing little higher levels. Further, since their CV traces show no oxidations potentials, required HOMO energy levels of polymers were calculated from their optical band gaps, obtained from UV-Vis absorption spectra of polymer films. Thus, the calculated values for Th-Py-1, Th-Py-2 and Th-Py-3 were found to be -4.70, -4.59 and -4.7 eV, respectively.

### 3.3. Linear optical properties

The photophysical properties of new polymers were evaluated using UV-Vis absorption and emission spectroscopy both in THF solution and thin film states, in order to assess their optical band gaps. **Figs 3** (**a**) and (**b**) display UV-Vis spectra of polymers recorded at room temperature, in  $10^{-6}$ M THF solution and thin film states, respectively. Their corresponding spectral data are summarized in **Table 1**. It is seen that the absorption

maxima obtained for solution of **Th-Py-1**, **Th-Py-2** and **Th-Py-3** at 360, 353 and 355 nm, have been red shifted to 397, 377 and 390 nm in their film state, respectively. Evidently, the red shift of about 37, 24 and 35 nm for the polymers confirms the presence of inter-chain interactions and inter chain mobility of the excitons and excimers generated within the polymer molecules in solid state [24-25]. Further, in case of **Th-Py-1** and **Th-Py-3**, the  $\lambda_{max}$  values are red-shifted due to presence of electron withdrawing cyano and bromo groups respectively, when compared to that of **Th-Py-1**. Similar trend has been observed for the  $\lambda_{max}$  obtained for the polymers measured in film state also. These results clearly indicate that all the polymers exhibit identical electronic properties both in solution and solid states. Furthermore, the optical band gaps of these polymers were calculated from the onset absorption maximum  $\lambda_{max}$  of the thin film using  $E_g^{opt}=1240/\lambda_{max}$  where  $\lambda_{max}$  being the absorption onset wavelength of the polymers are highly preferred in LED applications. The observed high values may be due to extended conjugation and structural combinations of different hole and electron transporting moieties in the polymer chain. Further, molar extinction coefficients of polymers were determined according to Lambert-Beer law. The molar extinction coefficients were found to be 12,232, 14,193 and 16,212 M<sup>-1</sup>cm<sup>-1</sup> for **Th-Py-1**, **Th-Py-2** and **Th-Py-3** respectively.

Fluorescence emission spectra of **Th-Py-1**, **Th-Py-2** and **Th-Py-3**, obtained by irradiative excitation at their respective wavelengths of the absorption maxima are given in **Fig. 4** (a) (at concentration of 10<sup>-6</sup>M in THF), and **Fig. 4** (b) (at film state) and their corresponding data are summarized in **Table 1**. As seen from the spectra, the polymers display characteristic intense emission bands  $\lambda_{em}$  at 465, 418, and 442 nm, in solution state and fluorescent bands at 482, 432 and 457 nm in film state, respectively. The observed bathochromic shift in emission maxima of film form is mainly attributed to  $\pi$ - $\pi$ \* stacking of polymer chains. Thus, the photophysical study clearly reveals that the new polymers are good blue light emitters both in solution and film states, when irradiated with UV light.

Further, Stoke shifts of **Th-Py-1**, **Th-Py-2** and **Th-Py-3** were calculated using their  $\lambda_{max}$  and  $\lambda_{em}$  values, measured in their dilute THF solutions at concentration 10<sup>-6</sup> M and their values are summarized in **Table 1**. The calculated values were found to be 6272, 4405 and 5545 cm<sup>-1</sup> for **Th-Py-1**, **Th-Py-2** and **Th-Py-3**, respectively. The observed highest value in case of **Th-Py-1** is ascribed to the presence of strong electron withdrawing cyanovinylene linkage in the polymer chain. Furthermore, the fluorescence quantum yield ( $\Phi_f$ ) of polymer solution was calculated by comparing with reference standard quinine sulphate (dissolved in 0.05 M sulfuric acid, having fluorescence quantum yield of 52%). The fluorescence quantum yields of **Th-Py-1**, **Th-Py-2** and **Th-Py-3** were found to be 21.38%, 36.07% and 44.65%, respectively. All the polymers exhibited good fluorescence quantum yield in the range of 21-45% compare to some of the previously reported cyanopyridine based conjugated polymers [22]. Conclusively, these blue light emitting polymers with good fluorescence quantum yield are potential candidates for PLED applications as emitters.

### 3.4. Computational studies

DFT calculations with hybrid functional are considered to be one of the reliable computational approaches and are generally used in the field of optoelectronics in order to gain deeper insight into the

molecular geometry and electron distribution in the polymer as well as its optical behavior in the excited state. To estimate the electron density distribution of the frontier orbitals of the polymer, DFT calculations were performed at the B3LYP/TZVP level using Turbomole 7.2V software [27-28]. Only one repeating unit of each polymer was subjected to the calculation, with alkyl chains replaced by CH<sub>3</sub> groups hypothetically in order to minimize the computational complexity without compromising the quantitative picture. The geometries were first optimized with semi empirical AM1/COSMO basis using MOPAC in Tmolex. The optimized geometries as well as electronic distribution in HOMO and LUMO levels of repeating unit of polymers are portrayed in Fig 5. The calculated HOMO levels of Th-Py-1, Th-Py-2 and Th-Py-3 were found to be -5.94, -5.56 and -5.76 eV, whereas their LUMO levels were obtained to be -2.64, -2.42 and -2.45 eV, respectively. Their band gaps were shown to be 3.29, 3.13 and 3.31 eV, respectively. All these data are summarized in Table 1. The present predicted HOMO/LUMO values of the polymer repeating unit moderately differ from their experimentally obtained values, which may be due to various effects such as conformational order in bulk state, effect of solvent and electrolyte that were not taken into account [29-30]. From the data, it is clear that the electron density in HOMO levels of Th-Py-2 and Th-Py-3, is found to be high on donor part indicating that the HOMO energy level is affected by both the electron donor units in the polymer chain. However, the electron density of their LUMO levels is almost localized on the electron withdrawing cyanopyridine unit. Interestingly, in case of Th-Py-1 electron density of HOMO is localized on cyanopyridine ring while that of LUMO is confined on cyanovinyelene linkage, indicating that electron withdrawing ability of cyanovinylene moiety dominates over that of cyanopyridine ring.

#### 3.5 Electroluminescence studies

PLED devices were fabricated with a configuration of ITO/PEDOT:PSS/Polymer/Al under ambient conditions to investigate the electroluminescent (EL) behavior of the emissive polymers Th-Py-1, Th-Py-2 and Th-Py-3. In the device, PEDOT:PSS works as a hole injecting layer, ITO acts as a transparent anode and aluminum functions as a cathode. Fabrication was done without using any protective encapsulation material. A detailed fabrication procedure has been described in the Supplementary information. The current density-voltage characteristics of the PLED device (Fig 6a and b) indicate that the current density of the polymer increases exponentially with the increasing forward bias voltage, which is a typical diode characteristic [31]. The polymer light emitting diode shows low threshold voltage of 3.5, 3.75 and 3.9 eV for Th-Py-1, Th-Py-2 and Th-Py-3, respectively, which can be attributed to the lower energy barrier for electron injection (due to low lying LUMO level of the polymer) from the aluminum electrode [32-38]. The obtained low threshold voltage values are comparable with some of the previously reported light-emitting polymers showing good EL performance. The EL emission maximum of polymers Th-Py-1, Th-Py-2 and Th-Py-3 were found to be 476, 469 and 471 nm, respectively at driving voltage of 5V. The EL spectra depict that, all the polymers display blue electroluminescence at low threshold voltage of 3.5-3.9 V. Conclusively, use of these cyanopyridine based polymers in new PLEDs as emissive layers has shown improved device performance when compared to previously reported polymers in similar type of device structure [23]. Consequently, these polymers are considered to be potential emissive materials for the efficient PLED devices.

### 4. Conclusion

We have successfully synthesized three new blue light emitting conjugated polymers, viz. **Th-Py-1**, **Th-Py-2** and **Th-Py-3**, carrying cyanopyridine ring as a strong electron accepting entity, thiophene and phenylenevinylene scaffolds with different substituents, as electron donating units, starting from simple organic molecules. Because of presence of long chain alkoxy group, they showed good solubility in the common organic solvents such as chloroform, tetrahydrofuran and chlorobenzene with good film forming property. Their thermal analysis indicated that, the polymers possess good thermal stability with degradation temperature ranging from 305 to 325° C due to structural rigidity and peculiarity of having strong electron withdrawing as well as powerful electron donating units in the backbone. The photophysical studies revealed that, polymers display light absorption in the range of 377-397 nm and blue light emission in the order of 432-482 nm, with a wide optical band gap of 2.55-2.64 eV; fluorescence quantum yield varies in the range of 21-45%. The PLED devices (ITO/PEDOT: PSS/Polymer/Al) fabricated using new polymers as an emissive layer displayed intense light emission with EL emission maximum ranging from 469-476 nm at driving voltage of 5V. The polymers display blue electroluminescence at low threshold voltage of 3.5-3.9 V, indicating an efficient electron injection in the diodes. Amongst the three polymers, **Th-Py-2** has emerged as the best blue emitter under the lowest driving voltage when used in PLEDs.

### Acknowledgement

The authors are highly grateful to the NITK, Surathkal, India, for providing necessary laboratory facility. NP is highly in debt to BASF India Ltd and BASF Innovation Campus (Centre), Mumbai for their moral, and technical support including essential instrumental analysis.

### References

- 1. E. Cells, Polymer Light-Emitting, Science. 269 (1995) 1086-1088.
- L.J. Rothberg, A.J. Lovinger, Status of and prospects for organic electroluminescence, J. Mater. Res. 11 (1996) 3174-3187. doi:10.1557/JMR.1996.0403.
- Z. Fang, A.A. Eshbaugh, K.S. Schanze, Low-bandgap donor-acceptor conjugated polymer sensitizers for dye-sensitized solar cells, J. Am. Chem. Soc. 133 (2011) 3063-3069. doi:10.1021/ja109926k.
- G. Liu, Q.D. Ling, E.T. Kang, K.G. Neoh, D.J. Liaw, F.C. Chang, C.X. Zhu, D.S.H. Chan, Bistable electrical switching and write-once read-many-times memory effect in a donor-acceptor containing polyfluorene derivative and its carbon nanotube composites, J. Appl. Phys. 102-112 (2007). doi:10.1063/1.2756386.
- X. Pan, S. Liu, H.S.O. Chan, S.C. Ng, Novel fluorescent carbazolyl-pyridinyl alternating copoloymers: Synthesis, characterization, and properties, Macromolecules. 38 (2005) 7629-7635. doi:10.1021/ma050425b.
- K.L. Wang, W.T. Liou, D.J. Liaw, W.T. Chen, A novel fluorescent poly(pyridine-imide) acid chemosensor, Dye. Pigment. 78 (2008) 93-100. doi:10.1016/j.dyepig.2007.10.015.
- K.L. Wang, W.T. Liou, D.J. Liaw, S.T. Huang, High glass transition and thermal stability of new pyridinecontaining polyimides: Effect of protonation on fluorescence, Polymer (Guildf). 49 (2008) 1538-1546.

doi:10.1016/j.polymer.2008.01.039.

- M.S. Liu, X. Jiang, S. Liu, P. Herguth, A.K.Y. Jen, Effect of cyano substituents on electron affinity and electron-transporting properties of conjugated polymers, Macromolecules. 35 (2002) 3532-3538. doi:10.1021/ma011790f.
- H. Wang, Z. Li, B. Huang, Z. Jiang, Y. Liang, H. Wang, J. Qin, G. Yu, Y. Liu, Y. Song, Synthesis, lightemitting and optical limiting properties of new donor-acceptor conjugated polymers derived from 3,5dicyano-2,4,6-tristyrylpyridine, React. Funct. Polym. 66 (2006) 993-1002. doi:10.1016/j.reactfunctpolym.2006.01.008.
- A. Ricci, M. Chiarini, C. Lo Sterzo, R. Pizzoferrato, S. Paoloni, Synthesis and photophysical properties of poly(arylene ethynylene) small-molecules and polymers derivatized with leucine substituents, J. Photochem. Photobiol. A Chem. 298 (2015) 1-8. doi:10.1016/j.jphotochem.2014.10.003.
- J.F. De Deus, G.C. Faria, R.M. Faria, E.T. Iamazaki, T.D.Z. Atvars, A. Cirpan, L. Akcelrud, White light emitting devices by doping polyfluorene with two red emitters, J. Photochem. Photobiol. A Chem. 253 (2013) 45-51. doi:10.1016/j.jphotochem.2012.12.018.
- Marrocchi, A. Spalletti, S. Ciorba, M. Seri, F. Elisei, A. Taticchi, Synthesis and photophysical properties of conjugated anthracene-based compounds, J. Photochem. Photobiol. A Chem. 211 (2010) 162-169. doi:10.1016/j.jphotochem.2010.03.002.
- M.R. Raj, S. Anandan, R.V. Solomon, P. Venuvanalingam, S.S.K. Iyer, M. Ashokkumar, Conjugated polymer based on oligobenzo[c]thiophene with low-lying HOMO energy level as potential donor for bulk heterojunction solar cells, J. Photochem. Photobiol. A Chem. 262 (2013) 34-44. doi:10.1016/j.jphotochem.2013.04.013.
- M. Melucci, P. Frère, M. Allain, E. Levillain, G. Barbarella, J. Roncali, Molecular engineering of hybrid πconjugated oligomers combining 3,4-ethylenedioxythiophene (EDOT) and thiophene-S,S-dioxide units, Tetrahedron. 63 (2007) 9774-9783. doi:10.1016/j.tet.2007.07.006.
- D. Braun, G. Gustafsson, D. McBranch, A.J. Heeger, Electroluminescence and electrical transport in poly(3-octylthiophene) diodes, J. Appl. Phys. 72 (1992) 564-568. doi:10.1063/1.351834.
- 16. J.H. Cook, J. Santos, H. Li, H. a. Al-Attar, M.R. Bryce, A.P. Monkman, Efficient deep blue fluorescent polymer light-emitting diodes (PLEDs), J. Mater. Chem. C. 2 (2014) 5587-5592. doi:10.1039/c4tc00896k.
- J.H. Cook, J. Santos, H.A. Al-Attar, M.R. Bryce, A.P. Monkman, High brightness deep blue/violet fluorescent polymer light-emitting diodes (PLEDs), J. Mater. Chem. C. 3 (2015) 9664-9669. doi:10.1039/C5TC02162F.
- 18. J. Roncali, Synthetic Principles for Bandgap Control in Linear  $\pi$ -Conjugated Systems, Chem. Rev. 97 (1997) 173-206. doi:10.1111/j.1754-4505.2009.00107.x.
- M.G. Murali, P. Naveen, D. Udayakumar, V. Yadav, R. Srivastava, Synthesis and characterization of thiophene and fluorene based donor-acceptor conjugated polymer containing 1,3,4-oxadiazole units for light-emitting diodes, Tetrahedron Lett. 53 (2012) 157-161. doi:10.1016/j.tetlet.2011.10.157.
- D. Bondarev, J. Zedník, Influence of covalent structure and molecular weight distribution on the optical properties of alternating copolymers and oligomers with 1,2,3-triazole and 1,3,4-oxadiazole side groups, Polym. (United Kingdom). 124 (2017) 107-116. doi:10.1016/j.polymer.2017.07.045.
- 21. B. Hemavathi, T.N. Ahipa, S. Pillai, R.K. Pai, Cyanopyridine based conjugated polymer-synthesis and

characterization, Polym. (United Kingdom). 78 (2015) 22-30. doi:10.1016/j.polymer.2015.09.053.

- K.A. Vishnumurthy, M.S. Sunitha, K. Safakath, R. Philip, A.V. Adhikari, Synthesis, electrochemical and optical studies of new cyanopyridine based conjugated polymers as potential fluorescent materials, Polymer 52 (2011) 4174-4183. doi:10.1016/j.polymer.2011.07.012.
- M.G. Murali, P. Naveen, D. Udayakumar, V. Yadav, R. Srivastava, Synthesis and characterization of thiophene and fluorene based donor-acceptor conjugated polymer containing 1,3,4-oxadiazole units for light-emitting diodes, Tetrahedron Lett. 53 (2012) 157–161. doi:10.1016/j.tetlet.2011.10.157.
- F. Chen, P.G. Mehta, L. Takiff, R.D. McCullough, Improved electroluminescence performance of poly (3alkylthiophenes) having a high head-to-tail (HT) ratio, J. Mater. Chem. 6 (1996) 1763-1766. doi:10.1039/jm9960601763.
- R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, M. Lo, W.R. Salaneck, D.A. Dos Santos, J.L. Bre, Electroluminescence in conjugated polymers, (1999) 121-128.
- G.A. Crosby, J.N. Demas, Measurement of photoluminescence quantum yields. Review, J. Phys. Chem. 75 (1971) 991–1024. doi:10.1021/j100678a001.
- 27. N. Martin, J.L. Segura, C. Seoane, E. Orti, P.M. Viruela, R. Viruela, A. Albert, F.H. Cano, J. VidalGancedo, C. Rovira, J. Veciana, Synthesis, characterization, and theoretical study of sulfur-containing donor-acceptor DCNQI derivatives with photoinduced intramolecular electron transfer, J. Org. Chem. 61 (1996) 3041-3054.
- A.D. Becke, A new mixing of Hartree-Fock and local density-functional theories, J. Chem. Phys. 98 (1993) 1372–1377. doi:10.1063/1.464304.
- 29. P. Naik, R. Su, M.R. Elmorsy, D.D. Babu, A. El-Shafei, A.V. Adhikari, Molecular design and theoretical investigation of new metal-free heteroaromatic dyes with D-π-A architecture as photosensitizers for DSSC application, J. Photochem. Photobiol. A Chem. 345 (2017) 63-73. doi:10.1016/j.jphotochem.2017.05.033.
- 30. M.G. Murali, A.D. Rao, P.C. Ramamurthy, New low band gap 2-(4-(trifluoromethyl)phenyl)-1Hbenzo[d]imidazole and benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole based conjugated polymers for organic photovoltaics, RSC Adv. 4 (2014) 44902-44910. doi:10.1039/C4RA08214A.
- J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, A.B. Holmes, Light-emitting diodes based on conjugated polymers, Nature. 347 (1990) 539-541. doi:10.1038/347539a0.
- 32. B.M.T. Bernius, M. Inbasekaran, J.O. Brien, W. Wu, Progress with Light-Emitting Polymers, (2000) 1737-1750.
- 33. L. Yang, Y. Liao, J.K. Feng, A.M. Ren, Theoretical studies of the modulation of polymer electronic and optical properties through the introduction of the electron-donating 3,4-ethylenedioxythiophene or electronaccepting pyridine and 1,3,4-oxadiazole moieties, J. Phys. Chem. A. 109 (2005) 7764-7774. doi:10.1021/jp0515277.
- H.J. Jiang, Z.Q. Gao, F. Liu, Q.D. Ling, W. Wei, W. Huang, Novel photoluminescent polymers containing fluorene and 2,4,6-triphenyl pyridine moieties: Effects of noncoplanar molecular architecture on the electrooptical properties of parent matrix, Polymer (Guildf). 49 (2008) 4369-4377. doi:10.1016/j.polymer.2008.07.023.
- 35. H.J. Jiang, J.L. Zhang, J. Sun, W. Huang, Novel amphipathic photoluminescent copolymers containing

fluorene, pyridine and thiophene moieties: Synthesis, characterization and self-assembly, Polym. (United Kingdom). 53 (2012) 5684-5690. doi:10.1016/j.polymer.2012.10.007.

- 36. J. He, L. Du, C. Wang, M. Jiang, L. Liu, Y. Mo, Z. Xie, B. Yang, Y. Ma, Conformation pre-organization in fluorene-based conjugated polymer for simultaneous enhancement of luminescence and charge mobility, Polym. Chem. 8 (2017) 1255-1262. doi:10.1039/c6py01995a.
- 37. X. Pan, S. Liu, H. Yan, Synthesis and properties of fluorenyl-pyridinyl alternatingcopolymers for lightemitting diodes, Polym. Int. 63 (2014) 1105–1111. doi:10.1002/pi.4621.
- B. Liu, S. Ye, Y. Zou, B. Peng, Y. He, K. Zhou, A dithienyl benzotriazole-based polyfluorene: Synthesis and applications in polymer solar cells and red light-emitting diodes, Macromol. Chem. Phys. 212 (2011) 1489-1496. doi:10.1002/macp.201100080.

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Fig 1 Thermogravimetric traces of polymers Th-Py-1, Th-Py-2 and Th-Py-3



Fig 2 Cyclic voltamograms of polymers Th-Py-1, Th-Py-2 and Th-Py-3



Fig 3 (a) UV-Vis spectra of polymers Th-Py-1, Th-Py-2 and Th-Py-3 in solution state; (b) UV-Vis spectra of polymers Th-Py-1, Th-Py-2 and Th-Py-3 in film state



Fig 4 (a) Fluorescence spectra of polymers Th-Py-1 (360 nm), Th-Py-2 (353 nm) and Th-Py-3 (355 nm) in solution (THF); (b) Fluorescence spectra of polymers Th-Py-1 (397 nm), Th-Py-2 (377 nm) and Th-Py-3 (390 nm) in film state



Fig 5 Optimized geometry and simulated FMO energy levels of one repeating unit of Th-Py-1, Th-Py-2 and Th-Py-3



Fig 6. (a) Electroluminescence spectra of Th-Py-1, Th-Py-2 and Th-Py-3 at driving voltage of 5 V; (b) Current density-voltage characteristics of ITO/PEDOT: PSS/Polymer/Al devices





Scheme 2 Synthetic routes of polymers Th-Py-1, Th-Py-2 and Th-Py-3

	UV -Visible			Fluorescence		opt		LUMO	LUMO			Stoke		ε( <b>M</b> <sup>-1</sup> cm <sup>-1</sup> )
Polymer	$\lambda^a_{max}$ nm	$\lambda_{max}^b$ nm	$\lambda^b_{onset}$ nm	$\lambda^a_{em}$ nm	$\lambda^b_{em}$ nm	eV	E <sup>DFT</sup> eV	(CV) eV	(DFT) eV	HOMO eV	HOMO (dft) eV	Shift cm <sup>-1</sup>	$\Phi_{\rm f}$ (%)	at $\lambda^a_{max}$
Th-Py-1	360	397	486	465	482	2.55	3.29	-2.65	-2.64	-4.70	-5.94	6272	21.38	12,232 (360 nm)
Th-Py-2	353	377	469	418	432	2.64	3.13	-2.25	-2.42	-4.59	-5.56	4405	36.07	14,193 (353 nm)
Th-Py-3	355	390	481	442	457	2.58	3.31	-2.49	-2.45	-4.71	-5.76	5545	44.65	16,214 (355 nm)

## Table 1 Optical, electrochemical and DFT data of Th-Py-1, Th-Py-2 and Th-Py-3

<sup>a</sup> Solution state

<sup>b</sup> Film state

 $\Phi_f$  Fluorescence quantum yield of polymer in solution.

 $\epsilon$  Molar absorption coefficient at respective absorption wavelength in solution.

DFT Density Functional Theory

CV Cyclic voltammetry