

New blue light emitting cyanopyridine based conjugated polymers: From molecular engineering to PLED applications



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ABSTRACT

In this work, we report the design of three new cyanopyridine scaffold based polymers, viz. TP_y₁₋₃ as potential blue light emitters for PLED applications. The new polymer design comprise, a cyanopyridine core as an electron accepting entity, thiophene as an electron donating unit with different auxiliary donors, viz. phenylene (TP_y₁), biphenyl (TP_y₂), and fluorene (TP_y₃), and have been synthesized, following standard synthetic protocols including Suzuki-cross coupling polymerization reaction. Further, in order to assess all the prerequisites to act as an active emitter, the polymers TP_y₁₋₃, were subjected to structural, thermal, linear optical, electrochemical and computational studies. The results revealed that, all the polymers were thermally stable up to 300 °C and their estimated optical band-gaps were found to be 2.59–2.80 eV. Finally, new polymer light emitting diode (PLED) were fabricated by employing the polymers TP_y₁₋₃, as active emissive material with a configuration of ITO/PEDOT: PSS/Polymer/Al. Interestingly, all the fabricated devices, exhibited an intense blue electroluminescence at 12 V with low threshold voltages of 4.2–4.8 V, signifying an effective injection of electron in the device.

1. Introduction

Over the past few decades, PLEDs have gained substantial attention in the field of optoelectronics due to their cost-effective, light weight and ease of fabrication [1–4]. In PLED devices, photo functional conjugated polymers are considered to be prospective candidates as emitters due to their several advantages such as design versatility, tunable optical and electrochemical properties, good processability, low operating voltage and high flexibility, over the inorganic or organic small molecules [5,6]. Basically, such polymers comprise of a rigid backbone scaffold along with both electron rich donating and electron-deficient accepting moieties to facilitate optimum electron injection and transport, providing better charge carrier balance in the device [7,8]. Amongst them, the conjugated polymers carrying N-heterocyclic moieties have attracted significant interest as emitters in PLED devices, mainly due to their high electron-accepting abilities, good charge injection and excellent thermal as well as oxidation stability [9,10].

Recently, polymers centered on cyanopyridine core are being investigated widely for various optoelectronic applications owing to their high electron carrying ability as well as excellent fluorescence property [11]. Further, their photophysical behavior can be tuned easily by

incorporating various electron donor/ π -spacer functionalities in the polymer backbone [12]. Additionally, the inclusion of long chain alkoxy group to cyanopyridine scaffold would increase the polymer's solubility and film forming ability of polyme [13,14]. Also, it is well-documented that, the presence of highly stable thiophene ring in the conjugated polymer chain, leads to improvement in chemical stability and hole transporting ability of the polymers [15]. In fact, the high polarizability of sulphur (S) atom in thiophene stabilizes the macromolecule and improves charge transport behavior [16,17]. Moreover, in the literature, benzene and its derivatives have been effectively utilized as π conjugation linkers in conjugated polymers due to their electrochemical and thermal stability, tunable spectroscopic and electrochemical characteristics and good charge transporting ability [18]. Also, it is well-established that, fluorene and its derivatives are attractive materials mainly ascribed to their good stability (both thermal and chemical) and extremely high fluorescence quantum yields [19–22].

Against this background, in the present work, a new series of 2-hexadecoxylcyanopyridine based polymers, TP_y₁₋₃ carrying thiophene rings was designed. The new design includes phenylene (TP_y₁), biphenyl (TP_y₂) and fluorene (TP_y₃) moieties as π -conjugated auxiliary donors in the main chain primarily for enhancing the electrochemical

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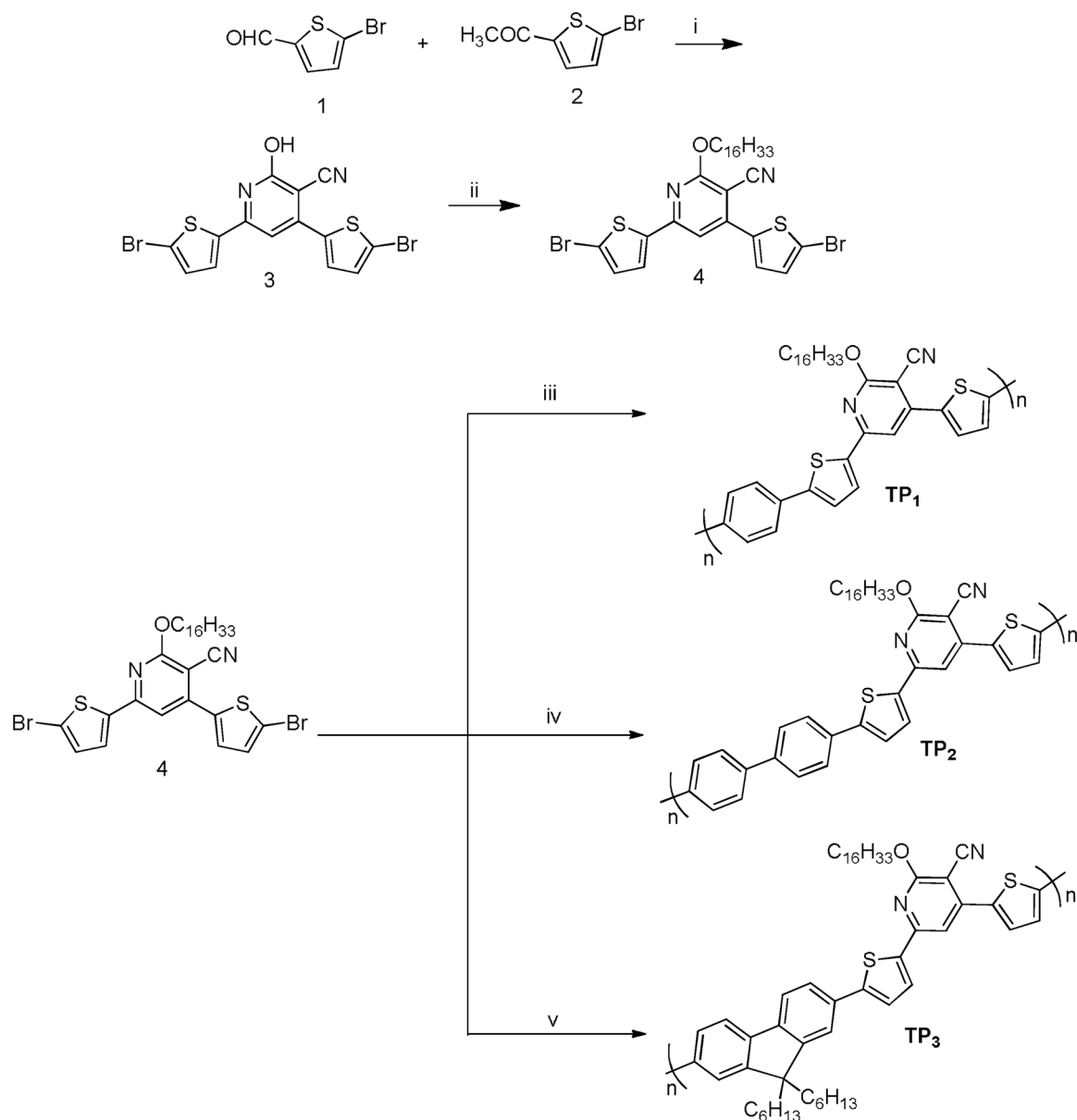
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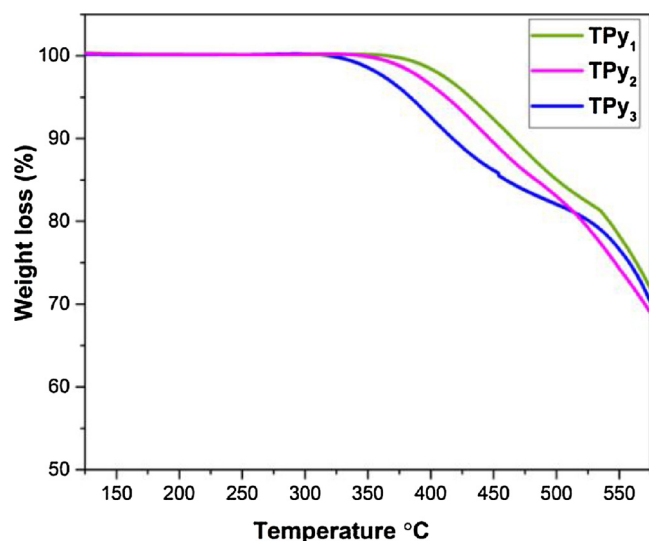
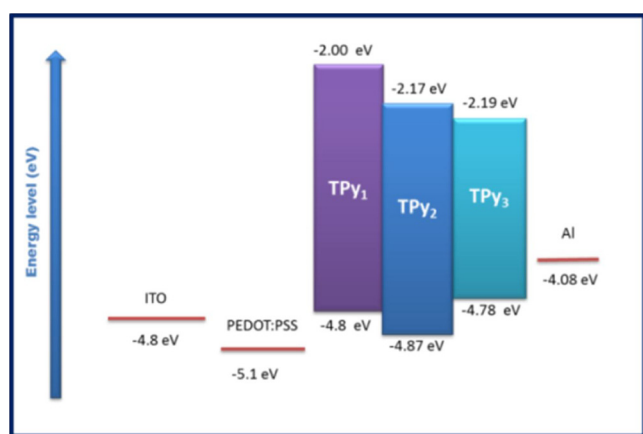


Scheme 1. Synthetic pathways of new polymers TP₁₋₃. Reaction conditions: (i) CNCH₂COOC₂H₅, CH₃COONH₄, 1,4-dioxane, 80 °C, 24 h; (ii) 1-bromohexadecane, K₂CO₃, DMF, 80 °C, 9 h; (iii) 1,4-phenylenebisboronic acid, Pd(PPh₃)₄, toluene-ethanol (1:1), Cs₂CO₃, 90 °C, 12 h; (iii) 4,4'-biphenyldiboronic acid, Pd(PPh₃)₄, toluene-ethanol (1:1), Cs₂CO₃, 90 °C, 12 h; (iii) 9,9-dihexylfluorene-2,7-diboronic acid, Pd(PPh₃)₄, toluene-ethanol (1:1), Cs₂CO₃, 90 °C, 15 h.

and optical properties as well as the overall stability and rigidity of resulting polymers. Here, cyanopyridine core being a strong electron acceptor, facilitates good charge transporting behavior, while thiophene rings on either side of cyanopyridine core act as strong electron donors. Further, presence of bulky alkoxy chain would bring good solubility as well as film forming nature of the polymers. The newly designed polymers were expected to own desired properties such as high molecular weight with great degree of solubility in common organic solvents, attractive charge carrying ability, good thermal stability, wide band gap, excellent quantum yield and blue fluorescence. The target polymers were synthesized from simple thiophene derivatives using standard synthetic protocols. We have employed the Suzuki cross-coupling method for the polycondensation of the cyanopyridines to achieve high molecular weight and low polydispersity index in the target polymers. However, there are no reports available in the literature on polymerization of cyanopyridine derivatives by Suzuki technique.

The new polymers and their intermediates were characterized using

NMR, FTIR spectral and elemental analysis. Their weight average molecular mass (M_w) along with polydispersity index (PDI) were determined from Gel permeation chromatography (GPC) technique. Their thermal stability with respect to temperature was investigated by the thermo gravimetric analysis (TGA). Further, their photophysical properties in both solution as well as solid film were studied by employing UV-vis. absorption as well PL emission spectroscopy. In addition, their HOMO-LUMO energy levels were determined using both spectral as well as cyclic voltammetric (CV) method. Further, DFT (density functional theory) studies were performed on the newly synthesized polymer, by considering the repeating units (monomers) at B3LYP/TZVP level using Tmolex. Finally, light emitting nature of newly synthesized polymers was determined by fabricating LED devices. The device was fabricated with the configuration, ITO/PEDOT: PSS/Polymer/Al, where the polymer functions as a light emissive layer in their respective device. In addition, the polymer structure and its effect on the various properties have been well explained.

Fig. 1. TGA traces of TPY₁₋₃.Fig. 2. Energy band diagram of TPY₁₋₃ based device.

2. Experimental

2.1. Materials and measurements

All the required chemicals are procured from companies such as Alfa Aesar, Sigma Aldrich, Spectrochem and TCI India. All the solvents used in the reaction were of synthetic grade and used without any further purification. The reaction progress was monitored by Thin Layer Chromatography (TLC) technique. The purification of monomer as well as its intermediate was done by column chromatography (100–200 mesh silica) and recrystallization techniques, respectively. The synthesized polymers TPY₁₋₃, were purified by Soxhlet extraction technique followed by re-precipitation method.

The FTIR (Bruker Alpha), ¹H NMR (Bruker Avance 300 MHz) and CHN analyzer (Thermo Fischer Flash EA1112) were used for the structural elucidation of new molecules. Further, Ultraviolet-Visible (UV–vis.) absorption and photoluminance (PL) emission spectra of the polymers TPY₁₋₃ using SPECORD S600 and Horiba Fluoromax-4 spectrophotometers respectively. Furthermore, the cyclic voltammetric (CV) measurements were carried out using Ivium Vertex electrochemical workstation. Moreover, the \bar{M}_w of polymers was determined against polystyrene standards with THF as an eluent using WATER's make GPC system. Finally, DFT calculations were executed for the repeating units of polymers TPY₁₋₃, by using Turbomole-7.2 V software.

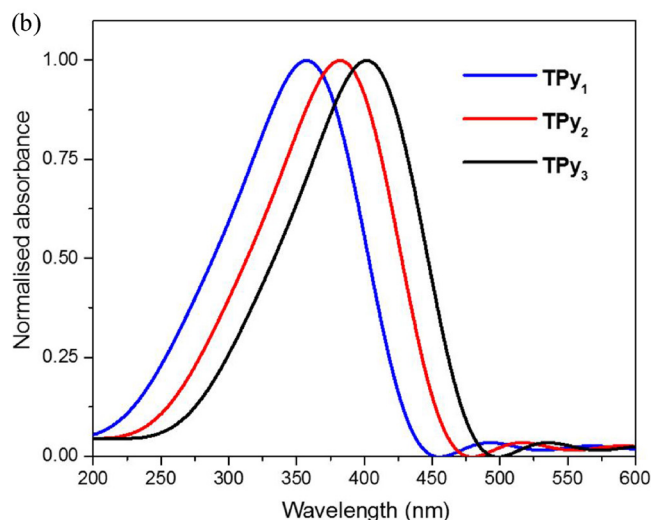
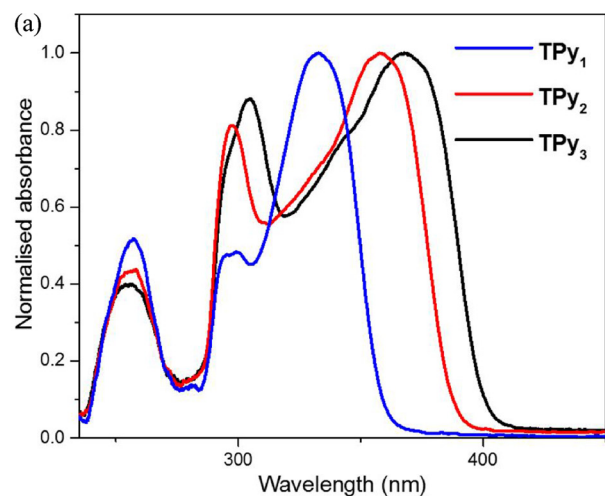
Fig. 3. (a) UV–vis spectra of polymers TPY₁₋₃ in THF (10^{-6} M conc.) solution. (b) UV–vis spectra of polymers TPY₁₋₃ in solid film state.

Table 1
Photophysical and electrochemical data of TPY₁₋₃.

Polymer		TPY ₁	TPY ₂	TPY ₃
UV -Visible	λ_{\max}^a nm	333	357	367
	λ_{\max}^b nm	356	382	402
	λ_{onset}^b nm	434	459	478
Fluorescence	λ_{em}^a nm	378	405	419
	λ_{em}^b nm	418	432	441
E_g^{opt} eV		2.80	2.70	2.59
E_g^{DFT} eV		3.30	3.14	3.31
LUMO (CV) eV		-2.00	-2.17	-2.19
LUMO (DFT) eV		-2.64	-2.42	-2.45
HOMO eV		-4.80	-4.87	-4.78
HOMO (DFT) eV		-5.94	-5.56	-5.76
Stoke Shift cm^{-1}		3575	3320	3380
Φ_f (%)		35.47	39.12	48.32
ϵ ($\text{M}^{-1} \text{cm}^{-1}$) at λ_{\max}^a		14,492 (360 nm)	15,258 (357 nm)	18,866 (367 nm)

a Polymer solution state.

b Polymer film state.

Φ_f : Fluorescence quantum yield.

ϵ : Molar absorption coefficient.

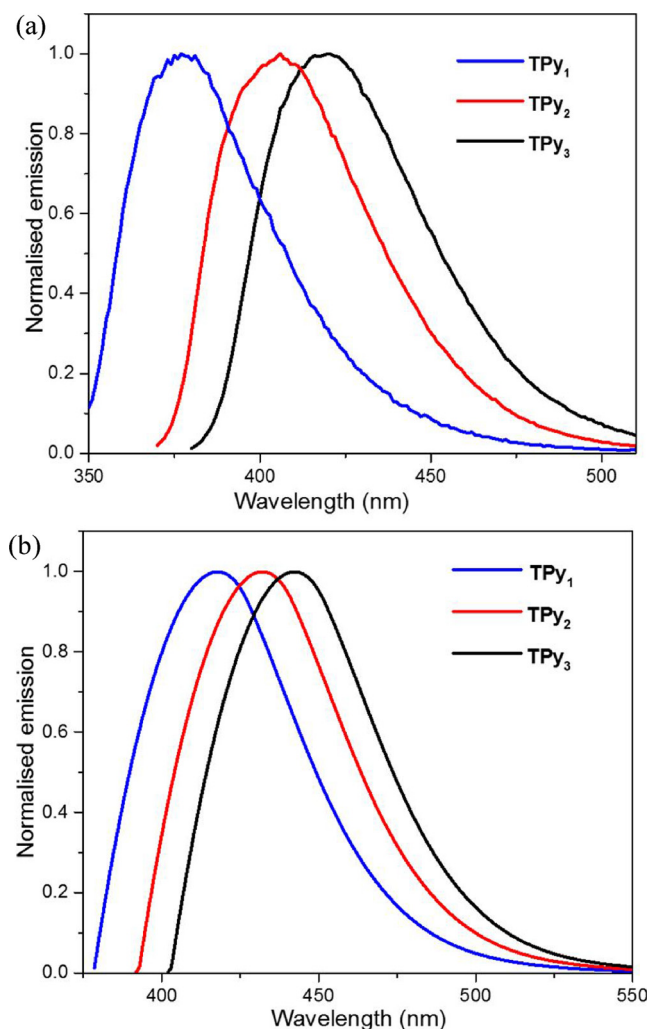


Fig. 4. (a) PL emission spectra of polymers **TPY**₁₋₃ in THF (10⁻⁶ M conc.) solution. (b) PL emission spectra of polymers **TPY**₁₋₃ in solid film state.

2.2. Synthesis

2.2.1. Synthesis of intermediate (3) and monomer (4)

The key intermediate **3** and cyanopyridine monomer **4** were synthesized as per reported procedure [23].

2.2.2. General synthesis of the polymer (TPY₁₋₃)

A mixture of cyanopyridine based monomer (**4**, 1 g, 1.5 mmol), Cs₂CO₃ (3.4 g, 10.5 mmol), and Pd(PPh₃)₄ (0.84 g, 0.75 mmol) in 20 mL of dried 1:1 mixture toluene and ethanol mixture was taken in 100 mL two neck round bottom flask. To above mixture, 1.5 mmol of respective boronic acid viz. 1,4-phenylenebisboronic acid (**TPY**₁), 4,4'-biphenyldiboronic acid (**TPY**₂) and 9,9-dihexylfluorene-2,7-diboronic acid (**TPY**₃) were added and refluxed under argon atmosphere. The reaction mixture was cooled down to room temperature, excess solvent was removed under reduced pressure. The obtained reaction mass was further dissolved in CH₂Cl₂ and filtered using the Celite bed to remove catalytic traces. The obtained filtrate was thoroughly washed with distilled water to remove traces of solvent and base. Then the solvent in the organic layer was removed under the vacuum. Further, to remove the lower weight oligomer fractions, the resultant crude product was subjected to Soxhlet extraction using solvents like methanol, acetone, and hexane. Finally, the crude product was dissolved in limited amount of chloroform, followed by re-precipitation using methanol to get the pure polymer.

TPY₁: Fluorescent yellowish color solid, Yield 65%. FTIR (cm⁻¹): 2221 (C≡N), 2918 (C-H). ¹H NMR (300 MHz, CDCl₃, δ ppm): 0.89–1.88 (m, 31 H), 4.55–4.61 (b, 2 H), 7.39–7.70 (m, 9 H). \bar{M}_w , 33,164 g/mol, PDI, 1.23. CHN, calculated: C, 74.46; H, 7.89; N, 4.57; found: C, 74.44; H, 7.88; N, 4.55.

TPY₂: Pale yellow color solid, Yield 68%. FTIR (cm⁻¹): 2218 (C≡N), 2918 (C-H). ¹H NMR (300 MHz, CDCl₃, δ ppm): 0.89–1.88 (m, 31 H), 4.56–4.61 (b, 2 H), 7.39–7.71 (m, 13 H). \bar{M}_w , 45,127 g/mol, PDI, 1.24. CHN, calculated: C, 76.70; H, 7.61; N, 4.07; found: C, 76.69; H, 7.60; N, 4.06.

TPY₃: whitish yellow powder, Yield 69%. FTIR (cm⁻¹): 2212 (C≡N), 2918 (C-H). ¹H NMR (300 MHz, CDCl₃, δ ppm): 0.89–1.95 (m, 43 H), 4.48–4.62 (b, 6 H), 7.52–8.05 (m, 11 H). \bar{M}_w , 52,763 g/mol, PDI, 1.21. CHN calculated for **TPY**₃: C, 78.75; H, 8.81; N, 3.22; found: C, 78.74; H, 8.80; N, 3.21.

3. Results and discussion

3.1. Synthesis of polymers TPY₁₋₃

The employed synthetic pathways for the preparation of the desired new intermediate/monomer as well as polymers are represented in Scheme 1. Initially, cyanopyridine intermediate (**3**) was synthesized from the 5-bromo-thiophene-2-carboxaldehyde (**1**) condensing with 2-acetyl-5-bromothiophene (**2**). Further, the intermediate **3** was O-alkylated using n-bromohexadecane to yield 2-hexadecylcyanopyridine (**4**). Furthermore, the targeted new polymers **TPY**₁₋₃ was obtained in good yield following renowned Suzuki coupling polymerization reaction, under anhydrous condition. Their chemical structures were well established using FTIR, ¹H NMR spectral and elemental analysis. Finally, all the polymers **TPY**₁₋₃ was subjected to GPC technique for determining \bar{M}_w and polydispersity of **TPY**₁₋₃. The GPC results revealed that, they have \bar{M}_w of 33,164, 45,127 and 52,763 g/mol, respectively and the polydispersity were in the order of 1.23, 1.24 and 1.21, respectively.

3.2. Solubility of polymers

The solubility of new polymers **TPY**₁₋₃ was tested in organic solvents viz. tetrahydrofuran (THF), dichloromethane (DCM), chloroform (CHCl₃), and dimethyl sulfoxide (DMSO). They displayed better solubility in aforementioned solvents, which can be ascribed to the bulkier hexadecoxyl alkyl chain present on cyanopyridine core. Hence all the synthesized polymers **TPY**₁₋₃, displayed good processability along with film forming nature. Amongst them, **TPY**₃ was found to show the highest solubility and good film forming ability due to presence of dihexyl fluorene units along with hexadecoxylcyanopyridine in polymer main chain.

3.3. Thermal analysis

In order to access the thermal stability of the synthesized polymers **TPY**₁₋₃, the TGA investigation were carried out in a nitrogen atmosphere by temperature ramp of 10 °C min⁻¹ ranging from 50 to 600 °C. Their thermograms are depicted in Fig. 1 and the thermal degradation temperatures of **TPY**₁, **TPY**₂ and **TPY**₃, were found to be 367, 351 and 318 °C, respectively. Interestingly, all the polymers **TPY**₁₋₃, demonstrated a high degree of thermal stability can be attributed to the presence of rigid aromatic heterocyclic ring systems in the polymer. Further, at 300 °C, about 20–25% of weight loss was observed mainly due to the degradation of the hexadecoxyl alkyl chain on the cyanopyridine scaffold. Finally, a gradual loss in weight was observed over 350 °C, which can be attributed to the further degradation of the macromolecular chain, which results in residue formation. Similar results were made for cyanopyridine based conjugated polymers reported earlier [23–25].

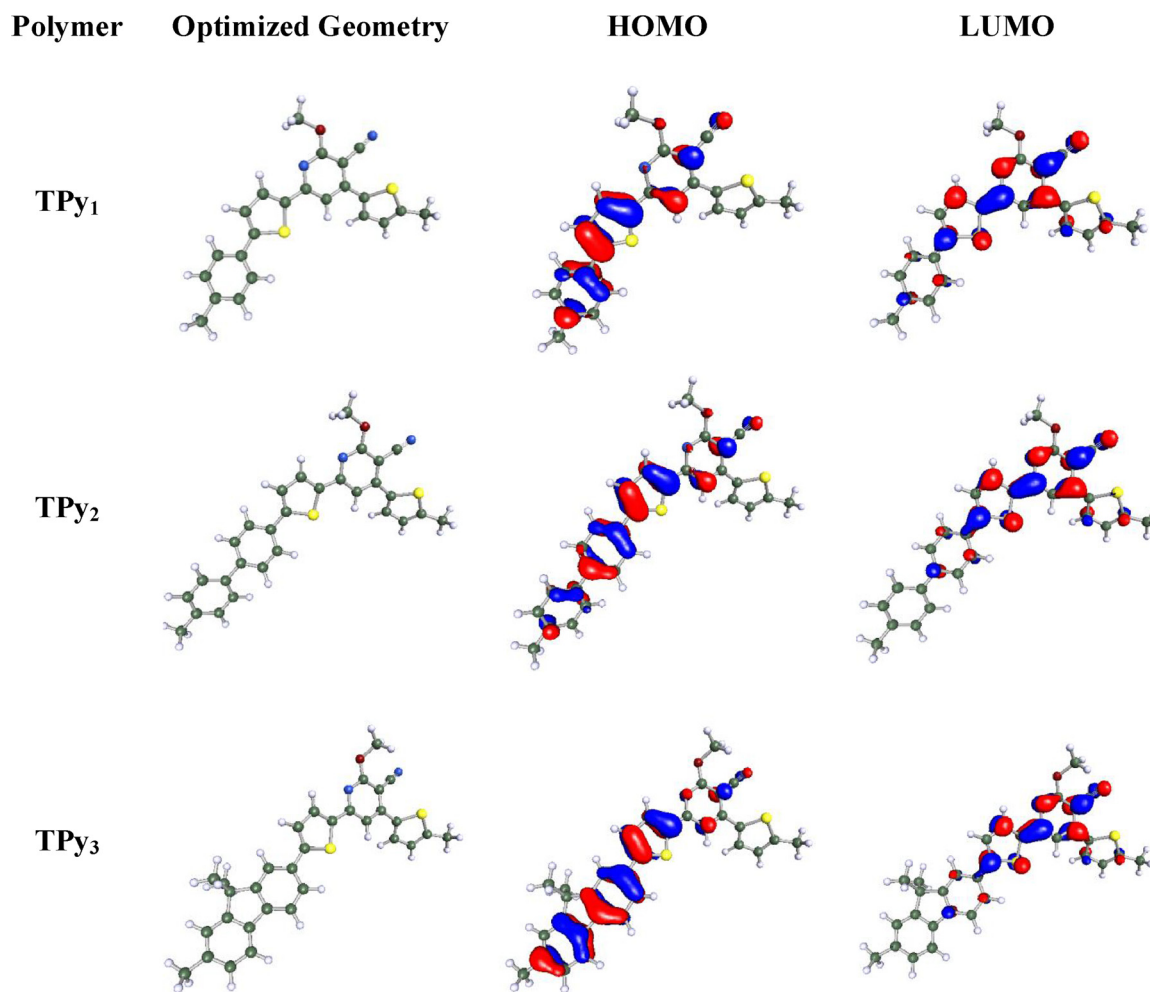


Fig. 5. Structurally optimized geometries along with simulated FMO levels of TPy₁₋₃.

3.4. Electrochemical studies

The electrochemical properties such as charge carrying and energy distributed in the FMO (Frontier molecular orbital) levels of polymers TPy₁₋₃, were investigated by CV measurements. In the current work, the cyclic voltammograms for polymer were recorded using standard three electrode system, consisting a working electrode (polymer coated on glassy carbon electrode), a reference electrode usually Ag/AgCl and a counter electrode (Pt electrode). These three electrodes were dipped in acetonitrile solution consisting of an electrolyte [0.1 M (n-Bu)₄N⁺PF₆⁻] and CV data were recorded at a scan rate of 100 mV/s. The resultant CV traces of TPy₁₋₃ were given in ESI (electronic supplementary information). From the results, it is quite evident that, the only reduction potential for TPy₁₋₃ were observed, which are in agreement with previously reported cyanopyridine based conjugated polymers [23].

The LUMO (Lowest unoccupied molecular orbital) energy levels of the TPy₁₋₃ were calculated by substituting the reduction potential value obtained from the CV traces into the equation: $E_{\text{LUMO}} = -e[E_{\text{red}} + 4.8 - E_{\text{FOC}}]$ [25]. Hence, the LUMO energy levels for TPy₁₋₃ and were estimated to be -2.00, -2.17 and -2.19 eV, respectively. Since CV traces of TPy₁₋₃ showed no oxidation potentials, the required HOMO (Highest occupied molecular orbital) levels were determined from their optical energy band gap. Thus, the HOMO energy levels for TPy₁₋₃ were found to be -4.8, -4.87 and -4.78 eV, respectively. Fig. 2 envisages energy level diagram of TPy₁₋₃, wherein FMO energy levels of polymers were compared with work functions of ITO and aluminum along with energy levels of hole injecting layer PEDOT:PSS of the PLED device.

3.5. Photophysical properties

The UV-vis, absorption spectra of polymers TPy₁₋₃, recorded in THF (10⁻⁶ M conc) solution and thin coated solid film, respectively were portrayed in the Fig. 3(a-b) and their pertaining spectral data were tabulated in Table 1. The absorption maxima λ_{max} obtained in solution state was found to be 333, 357 and 367 nm, where as a slightly red shifted absorption of 356, 382 and 402 nm were observed in thin film state, respectively. However, the observed red shift of about 23 nm (TPy₁), 25 nm (TPy₂) and 35 nm (TPy₃) in the absorption spectra confirms the effect of inter-chain interaction and inter-chain mobility of the excitons and excimers generated within the conjugated polymer in solid film state [23]. In addition, a small absorption maxima observed at lower energy level of film state can be attributed to the presence of trace of cyanopyridine monomer impurity trapped inside polymer chain. Moreover, the obtained results revealed that, the polymers TPy₁₋₃, displayed similar electronic behaviors both in solution as well in thin film states. Furthermore, their optical energy band gaps were calculated from the onset absorption edge $\lambda_{\text{onset}}^{\text{b}}$ of UV-vis. spectra obtained from thin film (Fig. 3b) [17]. Consequently, their optical energy band gap was found to be in the decreasing order of TPy₁ (2.80 eV) > TPy₂ (2.70 eV) > TPy₃ (2.59 eV). Typically, the polymers with wide energy band gap are highly preferred in blue light PLED applications. Finally, their molar extinction coefficients (ϵ) was determined by using Beer-Lambert law, and found to be 14,492 M⁻¹ cm⁻¹ (TPy₁), 15,258 M⁻¹ cm⁻¹ (TPy₂) and 18,866 M⁻¹ cm⁻¹ (TPy₃), respectively.

Fig. 4a and b, showcase the PL emission spectra of TPy₁₋₃ recorded at their respective excitation wavelengths in THF (10⁻⁶ M conc.)

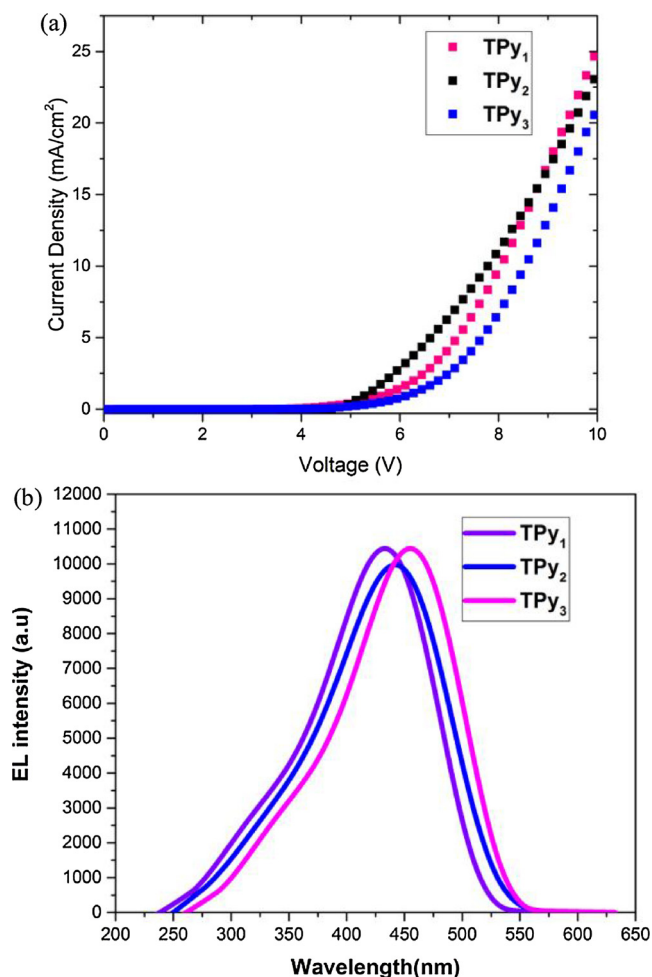


Fig. 6. (a) *J*-*V* curves of PLED device. (b) EL of TPY₁₋₃ at driving voltage of 12V.

solution and spin coated polymer film state, respectively, and their resultant spectral data are given in Table 1. From the Fig. 4a-b, it is clear that, the polymers displayed intense emission bands λ_{em} in THF solution at 378, 405, and 419 nm, while, in the thin film, λ_{em} was slightly red shifted to 418, 432 and 441 nm, respectively. This can be attributed to the π - π^* stacking of polymer chains in thin films. Further, the Stoke shifts of TPY₁₋₃ were calculated from the difference between the absorption maxima (λ_{max}) and emission maxima (λ_{em}) values obtained in solution state. The calculated Stoke shifts were found to be 3575, 3320 and 3380 cm^{-1} for TPY₁₋₃, respectively. Further, fluorescence quantum yield (Φ_f) determination for polymer solution was carried out using quinine sulphate as reference standard (degassed in 0.05 M sulfuric acid, with Φ_f of 52%). The Φ_f values for TPY₁₋₃, were found to be 35.47%, 39.12% and 48.32%, respectively. The obtained results were very much comparable to the previously reported conjugated polymers based on cyanopyridine scaffold [23]. Overall, these blue light emitting polymers, TPY₁₋₃, possess fairly good Φ_f values and therefore, they can be employed as potential emitter for PLED device applications.

3.6. Computational studies

The DFT simulations were performed with Turbomole V7.2 software package to get deeper insight into the electron density distributions in their FMO energy levels as well as optimized molecular geometry of the synthesized polymers TPY₁₋₃ [26,27]. In order to simplify the computational complexity, in the present work, only one repeating unit of the polymers TPY₁₋₃, were taken into the consideration and the long alkyl

chain present in the repeated units were subsequently replaced by methyl ($-\text{CH}_3$). To begin with, all the structures were first optimized in the gas phase with semi-empirical Austin Model 1 AM1/COSMO in 3D molecular builder of Tmole software at the B3LYP/TZVP level.

The Fig. 5 shows the optimized molecular geometries of the repeated units of the TPY₁₋₃, along with electronic distribution in their FMO energy levels. Their theoretically estimated FMO energy levels were tabulated in Table 1. The predicted FMO energy values of the TPY₁₋₃, moderately differs from experimental values, which may be ascribed to the fact that, while performing the simulations, the various realistic phenomenon such as effect of solvent, electrolyte and conformational order in bulk state were not taken into account [28–32]. From Fig. 5 it is quite evident that, in HOMO energy levels of TPY₁₋₃, the electron density is mainly concentrated on donor part. Whereas, in LUMO levels, the electron density is mostly localized on the electron deficient cyanopyridine scaffold.

3.7. I-V characteristics and electroluminescence studies

New ITO/PEDOT: PSS/Polymer/Al configured PLED devices were fabricated using TPY₁₋₃ as emissive material to study the electroluminescence (EL) characteristics. The devices fabrications was done following standard procedure and no protective encapsulation materials were used in this work [33–35]. The detailed procedure for device fabrication has been given in the ESI. Further, Figs. 6a and b, showcases the *J*-*V* (current-voltage) characteristic curves and EL emission spectra of the new PLED devices. Interestingly, Fig. 6a showed a steady rise in the current density with the increasing forward bias voltage indicating distinctive diode characteristic [36,37]. Further, the PLED devices showed low threshold voltage of 4.20, 4.55 and 4.80 eV for TPY₁, TPY₂ and TPY₃, respectively, which may be due to their low LUMO energy levels, which reduces the energy barrier of electron injection from the cathode [38–42]. The observed low threshold voltages are in very much comparable with previously reported PLED device [23]. Furthermore, their EL emission maxima were found to be 476 nm (TPY₁), 469 nm (TPY₂), and 471 nm (TPY₃) at driving voltage of 12 V. From Fig. 6b, it is quite evident that, the polymers TPY₁₋₃ displays a blue electroluminescence with a lower threshold voltage of 4.20–4.80 V when compare to similar reported polymers [25]. Conclusively, these cyanopyridine containing conjugated polymers as active emissive layers in the fabrication of new PLEDs has displayed better device performance when compared with that of previously reported similar type of polymers [25]. Consequently, these new polymers TPY₁₋₃ are considered to be promising emitters for the applications of PLED.

4. Conclusion

Conclusively, we have successfully designed, synthesized and characterized three new cyanopyridine based conjugated polymers, TPY₁₋₃ as blue light emitter. The polymers and their intermediate/monomers were synthesized by standard synthetic protocol including Suzuki cross coupling polycondensation technique. It is noteworthy that, the synthesis of TPY₁₋₃ proceeds in few steps with good yields and this polymerization methodology is different from the previous study [23]. Further, the TGA studies reveal that, the polymers are thermally stable up to 318–367 °C and the photophysical data indicate that, they exhibit a wide energy bandgap of 2.59–2.8 eV. Moreover, these polymers exhibited good light absorption and blue emission in the range of 356–402 nm and 418–441 nm, respectively. Furthermore, they displayed good fluorescence quantum yields of 35–48%. Finally, the PLED devices were fabricated using this polymer as a light emissive material and the device illustrated an enhanced performance at a threshold voltage of 4.20–4.80 V, demonstrating efficiently electron injection to the device. Conclusively, from the results, it is quite evident that, the polymers TPY₁₋₃, are promising candidates as emitters for electroluminescence device applications since they possess all the required

prerequisites.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jphotochem.2019.04.012>.

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