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Fluorene-based conjugated poly(arylene ethynylene)s containing heteroaromatic bicycles: preparation and electro-optical properties

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Abstract A series of high molecular weight fluorene-based soluble poly(arylene ethynylene)s (PAEs) have been prepared and characterized. The polymers consist of 2,5-bis(3-tetradecylthiophen-2-yl)-3a,6a-dihydrothieno[3,2-b] thiophene, 2,5-bis(3-tetradecylthiophen-2-yl)-3a,6a-dihydrothiazolo[5,4-d]thiazole, or 4,7-bis(3-tetradecylthiophen-2-yl)benzo[c] [1, 2, 5] thiadiazole unit with an electron donor 9,9-bis(2-ethylhexyl)-9H-fluorene unit connected via electron accepting ethynylene linkage. The molecular weights (M_w) of the polymers were found to be in the range of 103600–179000 g/mol with polydispersity index (PDI) of 3.9–5.0. Optical and redox properties have been investigated by UV–visible, fluorescence spectroscopy, and cyclic voltammetry (CV) measurements. Combination of experimental and density functional theory (DFT) calculations indicated that the benzothiadiazole unit incorporated polymer has lowest band gap with most stable lowest unoccupied molecular orbital (LUMO) energy level. Polymer light emitting diode properties have been investigated for the polymer having highest molecular weight with device configuration ITO/PEDOT:PSS/Polymer/LiF/Al. Well-behaved diode characteristics with EL maxima at 600 nm were observed.

Introduction

In recent times, π-conjugated materials have attracted tremendous scientific research interest due to their remarkable opto-electronic and electrochemical applications in organic field-effect transistors (OFETs) [1, 2], polymer light emitting diodes (PLEDs) [3, 4], solar cells [5, 6], molecular sensors [7, 8], electrochromic devices [9, 10], etc. Conjugated polymers (CPs) are very desirable for above said advanced devices in terms of their flexibility, large-area applicability, and easy solution processability [11, 12]. Among various CPs, poly(arylene ethynylene)s (PAEs) have become materials of choice for various opto-electronic device applications [13, 14]. Also, they have been commercialized in chemical and biological sensors [15, 16]. PAEs are known to show high solution state quantum yield than its poly(arylene vinylene) (PAV) counterpart [17]. It often adopts a planar structure that facilitates crystalline packing of the chain in the solid state [18]. Compared to PAVs, they exhibit enhanced electron affinity attributed to the electron accepting nature of triple bonds, makes them as potential candidates for low voltage operating opto-electronic devices [1, 19]. Guo et al. have reported tuning of optical energy gap via variation of donor co-monomers in a series of donor–acceptor PAEs [20]. Swager group has achieved efficient electroluminescence from a series of grafted PAEs [21].

Nowadays, fluorene-based CPs have commercialized as a very promising candidate for polymer-based opto-electronic devices due to their combined desirable properties, such as high fluorescence efficiency, electrochemical stability, good solubility in common organic solvents, excellent film forming, and charge mobility properties [22, 23]. Watters et al. have reported a fluorene-based copolymer with high hole mobility [24]. Cao group has reported all

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solution processed polymer light emitting diodes (PLEDs) using fluorene-based copolymers [25]. Osken et al. [26] have studied the fine-tuning properties of a series of fluorene-based copolymers. Recently, Reynolds group has also used fluorene containing polymers for solar energy harvesting [27]. Most of the fluorene-based copolymers reported in recent past is mainly synthesized either by Suzuki or Stille cross-coupling polycondensation reaction [28, 29]. However, incorporation of various heteroaromatic bicyclic units into fluorene-based PAEs and extensive study of their physico-chemical and electro-optical properties have not been fully explored [30].

Here we report the design and synthesis of a series of PAEs based on 9,9-bis(2-ethylhexyl)-9H-fluorene. PAEs were prepared by Sonogashira coupling reaction using chlorobenzene as a solvent. Molecular weights of these new PAEs were investigated by gel permeation chromatography (GPC) and are found to be high in nature. The high weight average molecular weight (M_W) facilitates in forming uniform thin films, which is vital for processing and application of polymer thin film technologies. Electrochemical and spectroscopic properties of synthesized copolymers were systematically evaluated and discussed in detail. DFT calculation analysis of the simplified model molecules was performed to understand the photophysical and electronic properties of these polymers. In addition, a bi-layered PLED was fabricated, and diode properties were analyzed.

Experimental

Materials

2,5-Bis(5-bromo-3-tetradecylthiophen-2-yl)-3a,6a-dihydrothieno[3,2-b]thiophene [31], 2,5-bis(5-bromo-3-tetradecylthiophen-2-yl)-3a,6a-dihydrothiazolo[5,4-d]thiazole [32], 4,7-bis(5-bromo-4-tetradecylthiophen-2-yl)benzo[c] [1, 2, 5] thiadiazole [33], and 9,9-bis(2-ethylhexyl)-2,7-diethynyl-9H-fluorene [34] were prepared according to the previous report. Anhydrous chlorobenzene, $(PPh_3)_2PdCl_2$ and CuI were purchased from Aldrich. Diisopropylamine was dried over sodium-benzophenone ketyl radical.

Characterization

Thin layer chromatography was performed with Merck silica gel 60 F254 aluminum sheet. Chromatographic separations were carried out using Merck silica gel 100–200 mesh. Fourier transform infrared (FTIR) spectra of polymer films were recorded on KBr pellet using a Nicolet 5700 FTIR spectrophotometer. ^{1}H NMR spectra were recorded using Brucker 500 and 300 MHz FT-NMR spectrometer with chloroform-*d* as solvent. Chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. Molecular weights of the polymers were determined by GPC on Waters 2690 separations module apparatus using Waters Styragel column and 2410 refractive index detector. All the measurements were carried out at 35 °C using THF as solvent and polystyrene as standard. UV–visible and PL spectra were recorded using Varian Carry 5000 scan and Spex Flurolog-3-11 spectrometers. Thermogravimetric analysis (TGA; Hi Res TGA 2950, TA Instruments) of the samples was carried out at a heating rate of 10 °C/min under nitrogen atmosphere. Cyclic voltammetry (CV) was performed on an AUTOLAB/PGSTAT30 potentiostat with a three-electrode cell in a solution of Et_4NBF_4 (0.10 M) in acetonitrile at a sweep rate of 50 mV/s. Platinum electrode coated with polymer film was used as working electrode. Platinum mesh electrode was used as counter electrode, and Ag/Ag$^+$ electrode was used as reference. The measurements were calibrated using ferrocene as standard.

Synthesis of **F3**

The compound **F2** (1.5 g, 2.7 mmol) was dissolved in a mixture of toluene and isopropyl alcohol (30 mL, 2:1). KOH (0.6 g, 10.83 mmol) was added to the mixture and refluxed for 2 h. The reaction mixture was cooled to room temperature and poured into water (100 mL). The compound was extracted with ethyl acetate, washed with water, dried over Na_2SO_4, and evaporated to obtain brown oil. The crude compound was then purified by column chromatography (silica gel), and a mixture of petroleum ether and ethyl acetate (98:2) as eluent to afford the compound **F3** as orange viscous oil. Yield: 81 %. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.47 (t, 6H), 0.88-0.63 (m, 22H), 1.26 (s, 2H), 1.96 (br, 4H), 3.10 (s, 2H), 7.23 (dd, 2H), 7.33 (d, 2H), 7.64 (d, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 10.23, 13.92, 22.63, 26.97, 27.98, 33.52, 34.62, 44.40, 54.87, 77.05, 84.42, 119.30, 120.42, 127.72, 131.08, 141.03, 150.83.

General method of polymerization for **PAE1-PAE3** and characterization

Under nitrogen atmosphere, anhydrous chlorobenzene (4 mL) and diisopropylamine (2 mL) were added by syringe into a thoroughly dried 25 mL Schlenk flask charged with 9,9-bis(2-ethylhexyl)-2,7-diethynyl-9H-fluorene (105.28 mg, 0.24 mmol), $(PPh_3)_2PdCl_2$ (2.24 mg, 0.0032 mmol), CuI (1.22 mg, 0.0064 mmol), and bisbrominated monomer 2,5-bis(5-bromo-3-tetradecylthiophen-2-yl)-3a,6a-dihydrothieno[3,2-b]thiophene, 2,5-bis(5-bromo-3-tetradecylthiophen-2-yl)-3a,6a-dihydrothiazolo[5,4-d]thiazole, or 4,7-bis(5-bromo-3-tetradecylthiophen-2-yl)benzo[c] [1, 2, 5] thiadiazole;

0.24 mmol. The mixture was stirred for 1 h at room temperature and then heated at 100 °C for 72 h. The reaction mixture was cooled to room temperature and poured into methanol (100 mL). The precipitate was filtered, and the residue was soxhlet extracted with methanol and hexane to remove inorganic impurities and oligomers. Finally, the pure dark polymer was collected from Soxhlet thimble and dried under vacuum for several hours till constant weight.

Synthesis of **PAE1**

2,5-bis(5-bromo-3-tetradecylthiophen-2-yl)-3a,6a-dihydrothieno[3,2-b]thiophene (205.20 mg, 0.24 mmol) was used. Yield: 78 %. FTIR (cm^{-1}, KBr): 2923, 2852, 2361, 2337, 1460, 1300, 1029, 819, 521. ^1H NMR ($CDCl_3$, 300 MHz), ppm: 7.76–7.61 (br, 6H), 7.53 (br, 2H), 7.27 (br, 2H), 2.86 (br, 4H), 2.65 (br, 4H), 2.00 (br, 4H), 1.25 (br, 54H), 0.87-0.55 (br, 26H). GPC: $M_w = 103{,}600$, $M_w/M_n = 3.9$ (polystyrene calibration). T_d (°C, 5 % weight loss): 364.

Synthesis of **PAE2**

2,5-bis(5-bromo-3-tetradecylthiophen-2-yl)-3a,6a-dihydrothiazolo[5,4-d]thiazole (205.68 mg, 0.24 mmol) was used. Yield: 82 %. FTIR (cm^{-1}, KBr): 2927, 2856, 2360, 2338, 1639, 1457, 1026. ^1H NMR ($CDCl_3$, 300 MHz), ppm: 7.69 (br, 2H), 7.55 (br, 2H), 7.26 (br, 2H), 7.18 (br, 2H), 2.96 (br, 4H,), 2.01 (br, 4H), 1.74 (br, 4H), 1.27 (br, 54H), 0.88–0.56 (br, 26H). GPC: $M_w = 179000$, $M_w/M_n = 5.6$ (polystyrene calibration). T_d (°C, 5 % weight loss): 362.

Synthesis of **PAE3**

4,7-bis(5-bromo-3-tetradecylthiophen-2-yl)benzo[c] [1, 2, 5] thiadiazole (204.24 mg, 0.24 mmol) was used. Yield: 73 %. FTIR (cm^{-1}, KBr): 2921, 2851, 2358, 2337, 1650, 1540, 1460, 1036, 832, 523. ^1H NMR ($CDCl_3$, 300 MHz), ppm: 7.96 (br, 2H), 7.81 (br, 2H), 7.66 (br, 2H), 7.56 (br, 2H), 7.26 (br, 2H), 2.86 (br, 4H), 2.65 (br, 4H), 2.00 (br, 4H), 1.25 (br, 54H), 0.87–0.55 (br, 26H). GPC: $M_w = 129600$, $M_w/M_n = 4.7$ (polystyrene calibration). T_d (°C, 5 % weight loss): 336.

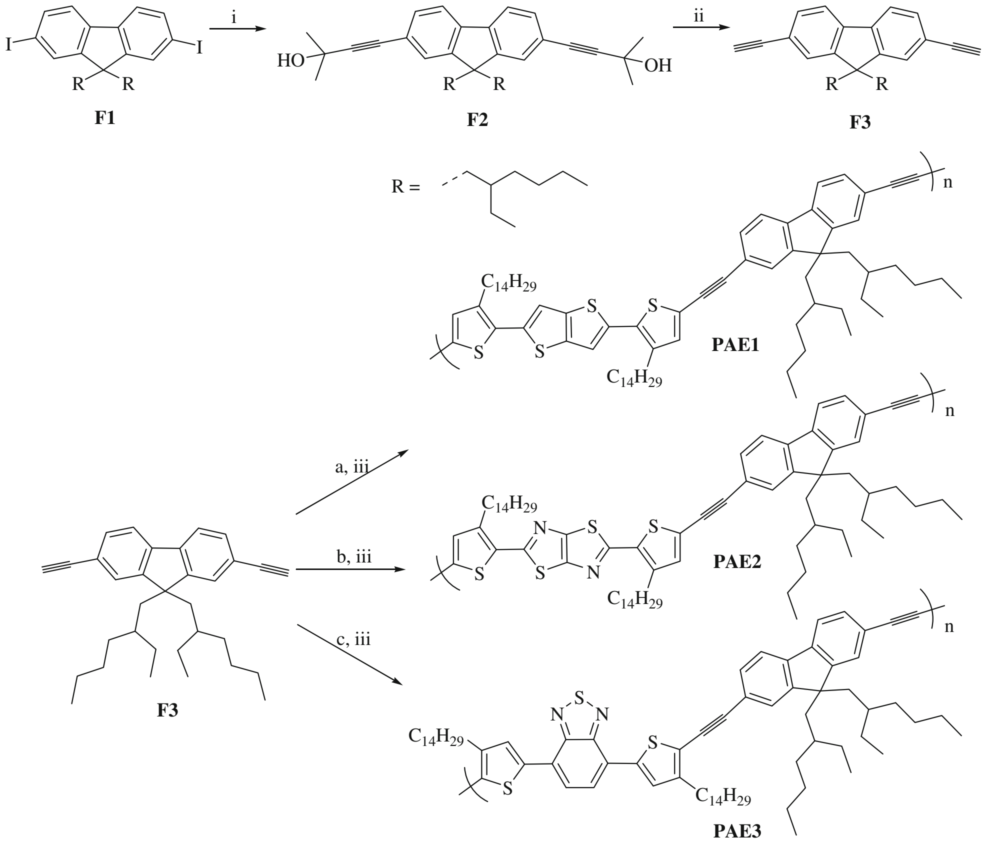
Device fabrication and measurements

The bi-layered PLED device having configuration ITO/PEDOT:PSS/PAE/LiF/Al was fabricated and characterized. The cleaned and patterned indium tin oxide (ITO) was used as anode and LiF/Al as cathode. The polymer films (65 nm) were deposited by spin coating and LiF/Al by thermal deposition. PEDOT:PSS acts as a hole transporting and synthesized polymer as emissive layer materials, respectively. The fabrication of the device followed our earlier reported procedure [35, 36]. Active area of all the fabricated devices was 4 × 4 mm^2 and all electrical measurements were performed under ambient condition without encapsulation. Electroluminescence (EL) spectra of the devices were obtained using HR 2000 Ocean Optics spectrometer, having a CCD array and fiber optic probe. The current–voltage characteristics were studied using Keithley 2400 programmable voltage-current digital source meter.

Results and discussion

Polymer synthesis, characterization, and thermal stability

The synthesis of **PAE1**, **PAE2**, and **PAE3** was started from compound 9,9-bis(2-ethylhexyl)-2,7-diethynyl-9H-fluorene (**F3**) as shown in Scheme 1. Fluorene derivative (**F3**) was synthesized from its parent diiodinated compound (**F1**) via (**F2**) following a reported procedure (see experimental part) with acceptable yield. Then, PAE polymers were synthesized by Sonagashira polycondensation reaction between **F3** and the respective bisbrominated reagent in good yield. In this method, equimolar ratio of bisbrominated reagent (0.24 mmol) and **F3** (0.24 mmol) was allowed to react in the presence of catalytic amount of $(PPh_3)_2PdCl_2$ and CuI in anhydrous chlorobenzene and diisopropylamine at 100 °C for 72 h. 2,5-Bis(5-bromo-3-tetradecylthiophen-2-yl)-3a,6a-dihydrothieno[3,2-b]thiophene (205.20 mg, 0.24 mmol), 2,5-bis(5-bromo-3-tetradecylthiophen-2-yl)-3a,6a-dihydrothiazolo[5,4-d]thiazole (205.68 mg, 0.24 mmol), and 4,7-bis(5-bromo-3-tetradecylthiophen-2-yl)benzo[c] [1, 2, 5] thiadiazole (204.24 mg, 0.24 mmol) were used as bisbrominated reagent led to **PAE1**, **PAE2**, and **PAE3** in 78, 82, and 73 % yields, respectively. These new polymers are found to be soluble in toluene, tetrahydrofuran (THF), and chlorinated organic solvents such as chlorobenze and chloroform. All the synthesized polymers were analyzed by FTIR and ^1H NMR spectroscopy. In IR spectra, the presence of two bands (due to Fermi resonance) around 2300 cm^{-1} assignable to disubstituted ethynylene moiety ($-C\equiv C-$) at the main chain and the absence of peaks attributed to monosubstituted ethynylenes ($\equiv C-H$ stretching vibration around 3300 cm^{-1} and $-C\equiv C$ stretching vibration around 2100 cm^{-1}) support the formation of polymers. A representative FTIR spectrum of the polymer **PAE1** is given in Fig. 1. The molecular structure of the polymers was also confirmed by ^1H NMR spectroscopy. From ^1H NMR spectra, the peaks show broader spectra due to polymeric character. A representative ^1H NMR spectrum of polymer **PAE2** is also shown in Fig. 2.



i) Di-isopropylamine, 2-methylbut-3-yn-2-ol, $(PPh_3)_2PdCl_2$, CuI, THF; ii) Isopropanol, KOH, Toluene, reflux;
iii) $(PPh_3)_2PdCl_2$, CuI, Diisopropylamine, Chlorobenzene, 100 °C,
a) 2,5-bis(5-bromo-3-tetradecylthiophen-2-yl)-3a,6a-dihydrothieno[3,2-b]thiophene,
b) 2,5-bis(5-bromo-3-tetradecylthiophen-2-yl)-3a,6a-dihydrothiazolo[5,4-d]thiazole,
c) 4,7-bis(5-bromo-4-tetradecylthiophen-2-yl)benzo[c][1,2,5]thiadiazole

Scheme 1 Synthesis of the fluorene-based poly(arylene ethynylene)s

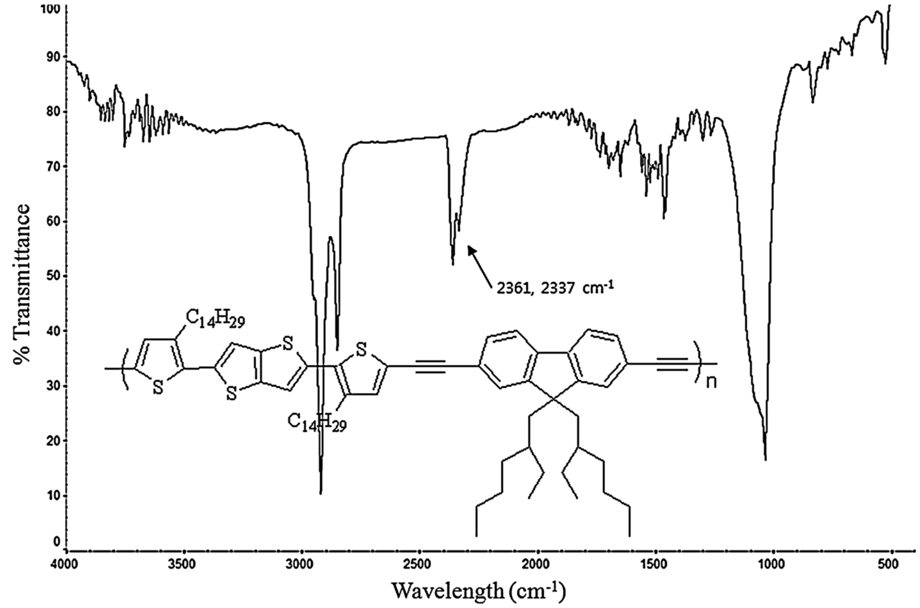


Fig. 1 IR spectrum of the polymer (**PAE1**)

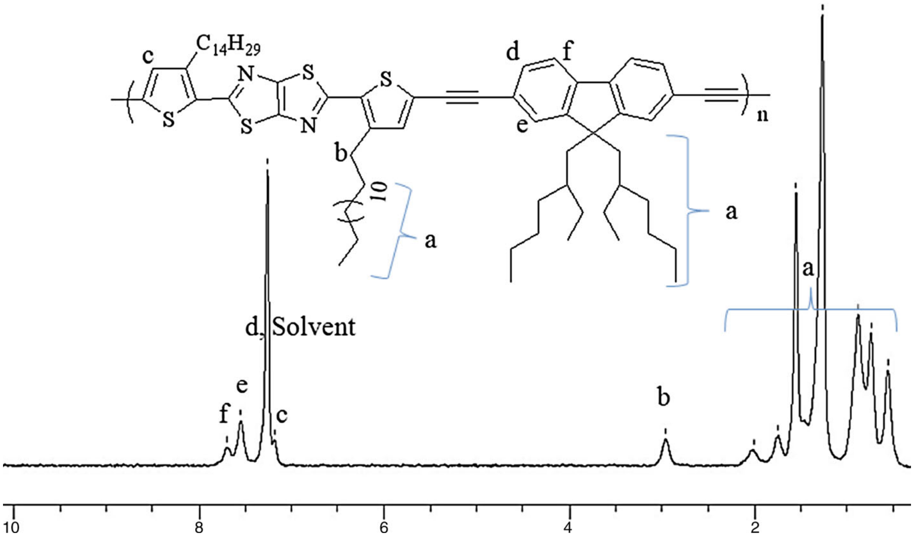


Fig. 2 ^{1}H NMR spectrum of the polymer (**PAE2**)

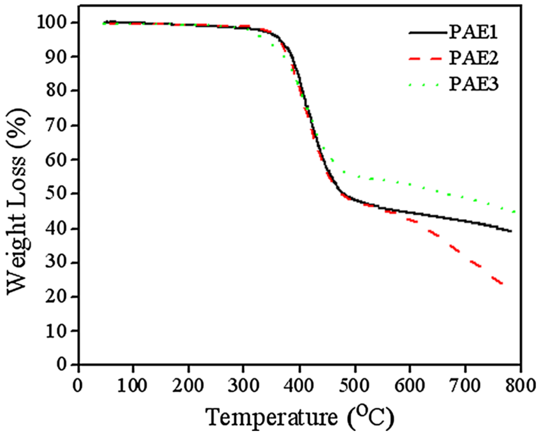


Fig. 3 TGA thermograms of the polymers (**PAE1-PAE3**)

The number-average molecular weights (M_n) and polydispersity index (PDI) of the polymers were estimated by GPC using a polystyrene standard in THF. The M_n was determined to be 26560 g/mol (PDI = 3.9) for **PAE1**, 35800 g/mol (PDI = 5.0) for **PAE2**, and 27570 (PDI = 4.7) for **PAE3**. These new synthesized polymers are found to be having high molecular weight than that of similar type of polymers reported in the literature [37]. The thermal properties of the targeted polymers (**PAE1-PAE3**) were determined by TGA under nitrogen atmosphere, as shown in Fig. 3. All these copolymers have good thermal stability with onset decomposition temperature (T_d) with 5 % weight loss at 364, 362, and 336 °C for **PAE1**, **PAE2**, and **PAE3**, respectively. When investigating the thermal behavior of the polymer using DSC, we observed no clear thermal transitions in the temperature range from room temperature to 300 °C. The resulting polymers can provide desirable thermal properties for opto-electronic device applications. The yield, molecular weight, and decomposition temperature of the polymers are summarized in Table 1.

Polymer optical properties

Figure 4a shows the UV–visible absorption spectra of the polymers in chloroform solution. In solution, the polymers exhibit absorption maxima ranging from 387 to 480 nm. Among the synthesized polymers, the benzothiadiazole containing polymer (**PAE3**) shows two absorption maxima in the range of 350–600 nm. It is also reported that benzothiadiazole containing copolymers show two maximum peaks in their absorption spectrum [38]. In solid film, the absorption maxima are red shifted from their solution counterpart and ranging from 391 to 500 nm (Fig. 4b). This red shift in absorption may be attributed to the traditional pi-conjugated polymers due to aggregation of the polymer main chain in the film form. All the absorption maxima values are summarized in Table 1. The optical band gaps ($E_{g,opt}$) determined from the onset of absorption of the polymers film are in the order **PAE3** (2.01 eV) < **PAE2** (2.23 eV) < **PAE1** (2.36 eV). Compared to reported PAEs [37] (with TPD, Cz, Th, Ph, and BN moiety), our PAEs having 2,5-bis(3-tetradecylthiophen-2-yl)-3a,6a-dihydrothieno[3,2-b]thiophene, 2,5-bis(3-tetradecylthiophen-2-yl)-3a,6a-dihydrothiazolo[5,4-d]thiazole, or 4,7-bis(3-tetradecylthiophen-2-yl)benzo[c] [1, 2, 5] thiadiazole unit show red shift in absorption maxima and low band gap (Table 1). Among the polymers, the benzothiadiazole containing polymer (**PAE3)** shows the narrowest band gap with broader absorption spectrum. These results also suggest that the optical properties could be tuned by varying the heteroaromatic segment in the copolymer system.

Photoluminescence (PL) properties of the polymers (**PAE1-PAE3**) were studied by fluorescence spectrometer.

Table 1 Physico-chemical and electro-optical properties of the polymers (**PAE1-PAE3**)

	Solution[a]		Film[b]				M_w[c]	M_n	$E_{g(opt)}$[d]	T_d[e]	E_{ox}[f]
	λ_{max}^{abs} (nm)	λ_{max}^{pl} (nm)	λ_{max}^{abs} (nm)	λ_{max}^{pl} (nm)	CIE_x	CIE_y	g/mol	g/mol	eV	°C	V
PAE1	412	541	417	542	0.29	0.47	103600	26560	2.36	364	1.45
PAE2	462	519, 555	480, 513 (s)	541 (s), 595	0.44	0.53	179000	35800	2.23	362	1.48
PAE3	387, 480	613, 652 (s)	391, 500	616, 654 (s)	0.51	0.47	129600	27570	2.01	336	1.49
[g]**PFE**	313	424	312	530	–	–	19200	–	2.76	381	0.72
[g]**TPD-PFE**	347	444	358	495	–	–	17600	–	2.90	388	0.42
[g]**Cz-PFE**	297	470	300	525	–	–	22500	–	2.67	371	0.62
[g]**Th-PFE**	312	447	311	519	–	–	19700	–	2.70	398	0.63
[g]**Ph-PFE**	312	444	312	524	–	–	23300	–	2.71	385	0.84
[g]**BN-PFE**	312	455	312	540	–	–	15800	–	2.68	398	0.66

[a] Measured in chloroform solution

[b] Cast from chloroform solution; s = Shoulder peak

[c] Optical band gap E_g (opt) estimated from the onset of electronic absorption of polymer film

[d] Determined by GPC relative to polystyrene standards

[e] Temperature at 5 % weight loss

[f] All potentials are reported versus Ag/Ag$^+$

[g] Values taken from reference no. 37

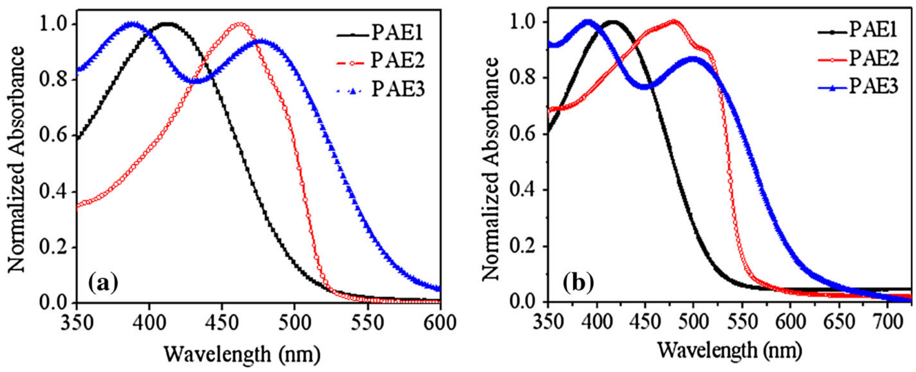


Fig. 4 UV-visible spectra of the polymers (**PAE1-PAE3**) in chloroform (**a**) and in solid film (**b**)

The PL spectra of the polymers were also recorded in solution as well as in film form and are reported in Fig. 5a and b. These polymers are fluorescent in nature and show PL maxima in the range of 519–613 nm in chloroform solution and 541–616 nm in solid film. Similar to the trend in absorption, emission maxima also show red shift in comparison to the reported PAEs (Table 1). The CIE color co-ordinates are also calculated for PL in film for the polymers and are represented in CIE color triangle (Fig. 5c). The calculated CIE colors co-ordinated are found to be $x = 0.29$, $y = 0.47$ for **PAE1**; $x = 0.44$, $y = 0.53$ for **PAE2**, and $x = 0.51$, $y = 0.47$ for **PAE3**. The color co-ordinates are also according to the optical band gap of the polymers. The detailed optical properties are summarized in Table 1.

Electrochemical properties of the polymers

From the onset oxidation potential in the cyclic voltammogram, energy level of the highest occupied molecular orbital (HOMO) can be readily estimated. A representative cyclic voltammogram of the **PAE3** film versus Ag/Ag$^+$ is shown in Fig. 6. The HOMOs energy levels calculated from onset oxidation potential (E_{ox}) according to the equation, HOMO $= -e(E_{ox} + 4.71)$ eV, are found to be 6.16, 6.19, and 6.20 eV for **PAE1**, **PAE2**, and **PAE3**, respectively. The low-lying HOMOs corresponding to higher oxidation onsets indicate a better environmental stability of these new polymers compared to earlier reported PAEs [37] and thus that devices based on these polymers would be stable under ambient conditions. The

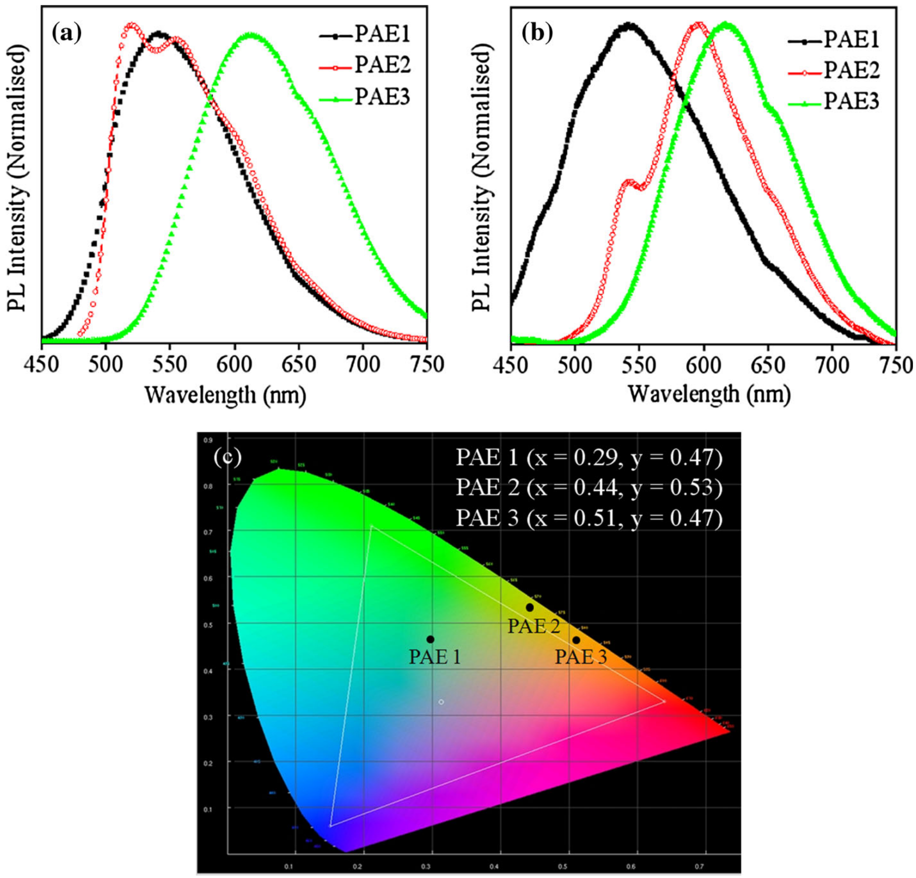


Fig. 5 PL spectra of the polymers (**PAE1-PAE3**) in chloroform (**a**) and in solid film (**b**)

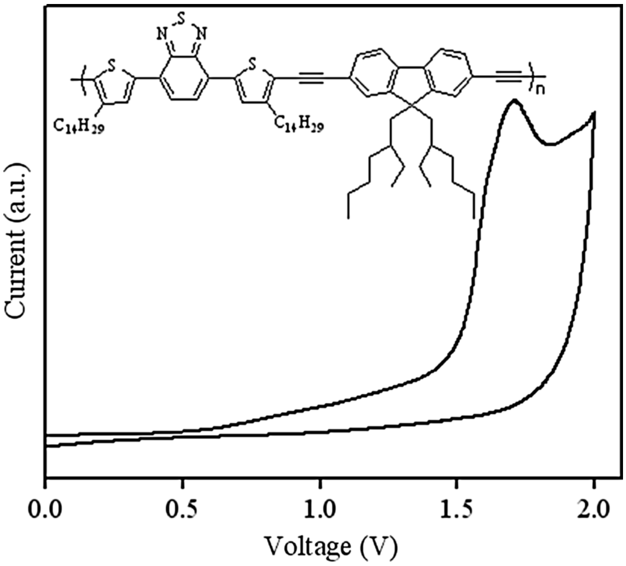


Fig. 6 Cyclic voltammogram of the polymer (**PAE3**)

Table 2 HOMO, LUMO energy values and corresponding band gaps of the polymers (**PAE1-PAE3**)

	From Experiments			From Calculation[d] (model)		
	HOMO[a]	LUMO[b]	$E^{c}_{g(opt)}$	HOMO	LUMO	E_g
PAE1	−6.16	−3.80	2.36	−4.8	−2.1	2.7
PAE2	−6.19	−3.96	2.23	−5.0	−2.4	2.6
PAE3	−6.20	−4.19	2.01	−4.89	−2.72	2.2

[a] HOMO = $-e(E_{ox} + 4.71)$ eV calculated from CV experiment

[b] LUMO energy levels were calculated from the HOMO values and optical band gap

[c] Optical band gap E_g (opt) estimated from the onset of electronic absorption of polymer film

[d] DFT quantum mechanical calculations (B3LYP/6-31G*)

lowest unoccupied molecular orbital (LUMO) energy level of the polymers is estimated from the HOMO energy level and optical band gap. The calculated LUMO energy levels of the polymers (**PAE1-PAE3**) are found to be in the range of 3.80–4.19 eV. The electrochemical data are summarized in Table 1 and 2. Among all, **PAE3** shows low-lying LUMO energy level possibly due to the presence of strong electron accepting benzothiadiazole moiety.

DFT analysis

A theoretical calculation analysis on the simplified model molecule model 1, model 2, and model 3 were performed in order to obtain a better understanding of the photo-physical and electronic properties of the synthesized polymers. All the straight and branched alkyl chains were

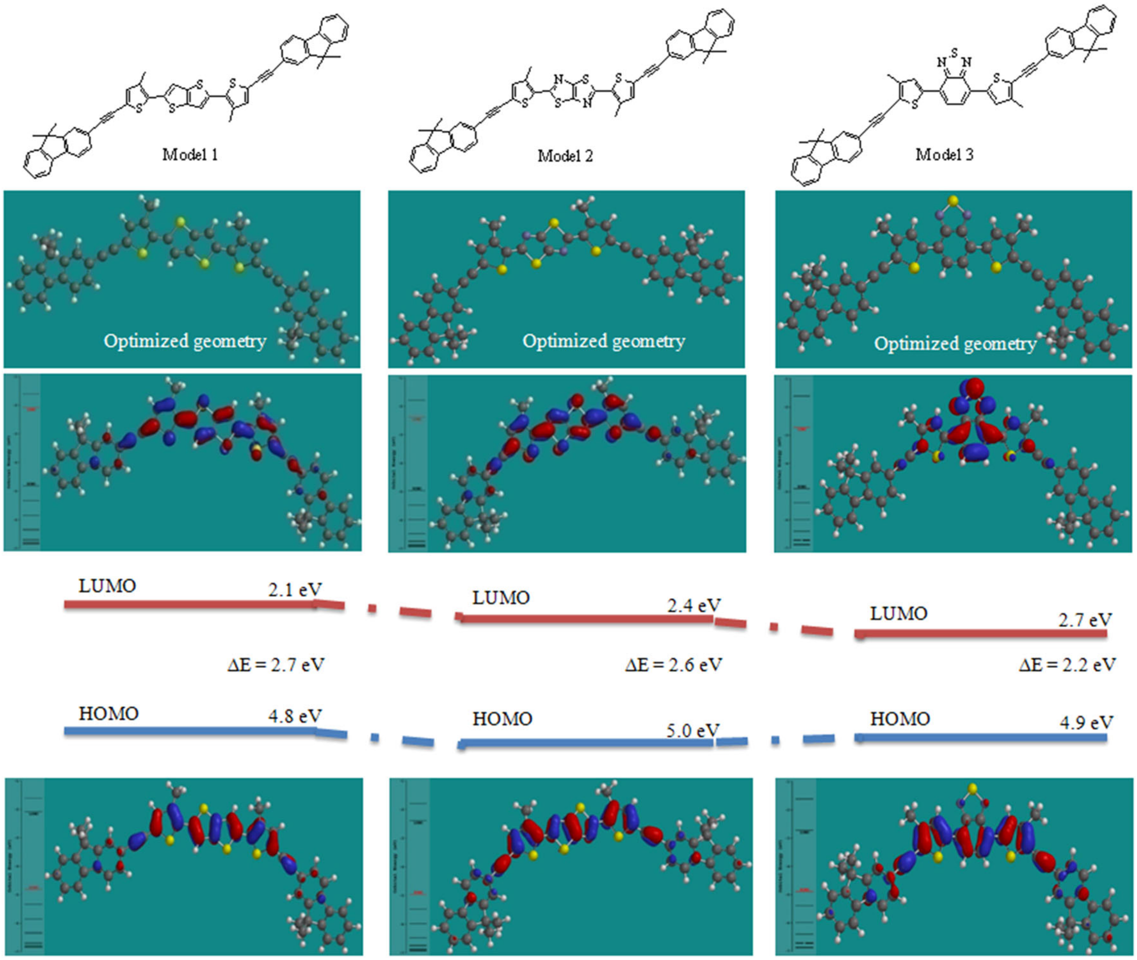


Fig. 7 Structures, optimized geometry and molecular orbital diagrams for the HOMO and LUMO of the designed model 1, 2 and 3 from density functional theory calculations

replaced with simplest methyl group to reduce the calculation time, and a B3LYP method was used with a 6-31G*(d,p) basic set. The molecular structures for model 1, model 2, and model 3 with optimized geometry along with calculated electron density distribution and the HOMO and LUMO energy levels are shown in Fig. 7 and respective values are summarized in Table 2. As depicted in Fig. 7, the LUMO of the model 3 compound is more strongly concentrated on the central benzothiadiazole core with a strong contribution on S and N atoms in comparison to other thienothiophene and thiozolothiazole based models. Although in model 1 and model 2 the LUMO is also centered on thienothiophene and thiozolothiazole moiety, in all the three models the HOMOs are broadly delocalized over the polymer backbone showing the consistency with HOMO–LUMO energy distribution in several other ethynylene-based polymers [39]. As shown in Fig. 7, the HOMO–LUMO energies are calculated for model 1, model 2, and model 3 are 4.8, 2.1 eV; 5.0, 2.4 eV; and 4.9, 2.7 eV, respectively. The synthesized polymers are of very high molecular weight, result higher calculated energy levels for model compounds in comparison to the energy levels calculated for polymers experimentally based on CV and UV–visible, but follow the same trend (i.e., LUMO = 3.80, 3.96 and 4.19 eV, respectively). Out of the three polymer models, the one having central benzothiadiazole core exhibits strong donor–acceptor interaction between the benzothiadiazole unit and fluorene unit, results in the smallest HOMO–LUMO band gap (2.2 eV) in comparison to model having thienothiophene (2.7 eV) and thiozolothiazole (2.6 eV) as central moiety. The band gap values for the synthesized polymers obtained experimentally are 2.36, 2.23, and 2.01 eV, respectively, and are in well agreement with the values calculated theoretically for models. From the optical properties of synthesized polymers, it is also seen that **PAE3** having smallest band gap value, because of the presence of strongest donor–acceptor pair among the polymers, which is well supported by theoretical calculations.

Electroluminescence properties of the polymers

The optical and electrochemical properties of our synthesized polymers suggest their possible use in opto-electronic

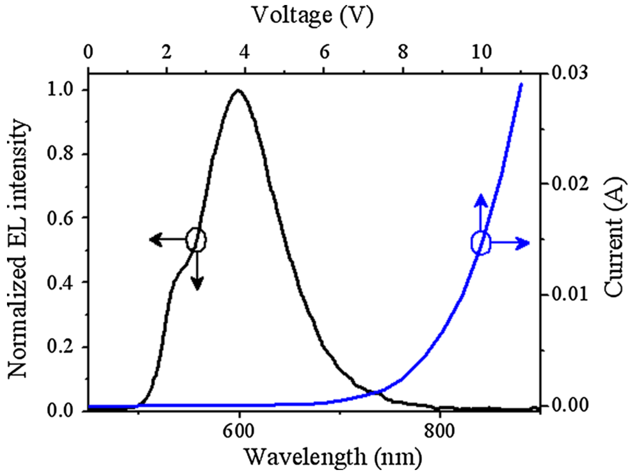


Fig. 8 EL spectrum and corresponding I–V curve of the polymer (**PAE2**) in device configuration ITO/PEDOT:PSS/**PAE2**/LiF/Al

device applications. The optical band gap of our synthesized polymers lies in between 2.0 and 2.5 eV, suggests that the polymers can show electroluminescence in visible region of electromagnetic spectrum. Hence, a bi-layer polymer light emitting diode (PLED) was fabricated to investigate the electroluminescence (EL) properties. The highest molecular weight polymer was chosen among all and applied as emissive layer material in PLED having device configuration ITO/PEDOT:PSS/**PAE2**/LiF/Al. ITO and Al were used as anode and cathode for hole and electron injection, respectively, during the device operation. PEDOT:PSS was used as hole transporting layer. Both the polymers (hole transporting and emissive material) were deposited on pre-cleaned patterned ITO electrode using spin coating technique sequentially, and LiF/Al were deposited thermally to complete the device structure. Application of electric field shows electroluminescence with λ_{max} at 600 nm having CIE color co-ordinates $x = 0.45$, $y = 0.53$ which are in well agreement with CIE co-ordinates ($x = 0.44$, $y = 0.53$) calculated for PL in film. Current–voltage characteristics of the device were also recorded and found that the device shows well-behaved diode like characteristic with threshold voltage around 6 V. The electroluminescence spectrum and current–voltage characteristics of the device are shown in Fig. 8. Further optimization of device parameters and insertion of other hole-blocking or electron-transporting layers can improve the device performances.

Conclusions

In summary, we have investigated the synthesis and characterization of a series of conjugated poly(arylene ethynylene)s consisting of different heteroaromatic groups and 9,9-bis(2-ethylhexyl)-9H-fluorene. Tunable electro-optical properties have been achieved from these fluorene-based PAEs. The synthesized PAEs possess high molecular weight, good solubility, and thermal stability. These polymers are also found to be optically active and fluorescent in nature. The combination of excellent solubility in common organic solvents, appropriate HOMO/LUMO energy level, and narrow band gap of these copolymers renders as promising active materials for polymer optoelectronic device applications. The fabricated bi-layer PLED using polymer (**PAE2**) having highest M_n value as emissive material with device configuration ITO/PEDOT:PSS/**PAE2**/LiF/Al shows EL maxima at 600 nm (CIE color co-ordinates: $x = 0.45$, $y = 0.53$) and well-behaved diode like characteristic (threshold voltage around 6 V).

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