Efficient blue light-emitting polydibenzofluorenes through the integration of an anthracene unit

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ABSTRACT

Series of light emitting polymers based on dibenzofluorene-acene have been synthesized through aromatic nucleophilic substitution reaction. The polymer displayed strong solubility in specific organic solvents with a polydispersity index of 1.5–2.0 and weight average molecular weight within the range from 25000 to 34000. At 420 nm the highest photoluminescence of the polymer solution was observed. The temperature of the thermal decomposition was determined by TGA and ranged from 300 to 446 °C while the value of Tg was between 120 and 140 °C. Cyclic voltammetry tests of polydibezofluorenes show that the compounds with HOMO and LUMO in the range 2.23–5.26 eV is stable under redox condition. The optical properties of these polydibenzofluorenes showed significant blue emissions in the polymers obtained.

1. Introduction

Organic unsaturated polymers and crystals are electro-driven due to the π-electron delocalization, which can conjugate the whole species. The π-conjugated backbones of most polymers employed in organic photovoltaic cell and in the first effective organic light diode (OLEDs) [1]. Conjugated polymer-based devices like OLED are a modern light emission medium in which organic, so called an organic light emitting (OLED), emitting layer content for light emitting diode (LED) is used [2–14].

Research into the conductive polymer is in its growth stage. In several ways, such as enhancing processability, adjusting color and color purity, increasing system performance and brightness, remarkable progress has been made over the past seven years. The molecular nature of these materials makes changes to their chemical structure especially sensitive to their properties, either by design or as a result of the process of degradation. Several parameters for the design of multifunctional molecules, such as high temperatures of the glass transition, matching HOMO and LUMO with anode and cathode energy rates, high fluorescence of quantum yield and amorphous film type, were suggested.

Blue OELDs are typically less efficient than green or red OLEDs due to poor transportation injections into the emitters [15] so blue devices need to improve their Electroluminescent (EL) properties, particularly in terms of EL efficiency and purity of color. Therefore, one area of ongoing research in this field is the discovery of a stable, blue-emitting material [4].

In this work we have developed and synthesized a dibenzofluorene-acene based derivative which was not previously studied in OLEDs as a continuous effort to develop an effective blue emitter.

Anthracene was used as a building block for the manufacture of a number of emissive materials because of its special chemical and electron-rich structure, low electronic band gap and blueish fluorescence [16,17]. It was also reported that the establishment of anthracene and its 9,10 substituted derivatives in or linked to the main polymer chain [18] as pending groups [19] helped to solve the problem of preparing or suppressing good optical quality excimer films. Therefore, polyacene-based light-emitting diodes must be more photoluminescent, efficient in blue emission, and strong device properties [20,21].

Harvey R. G., et al. first reported a synthesis of dibenzofluorene [22] with high melting points, glass transition temperatures relative to fluorene moiety. Organic materials based on dibenzofluorenes are demonstrated to have excellent properties for use in luminescent devices, including high stability and efficiency, and low excimer formation. In addition to emissive properties, the products may be advantageously designed to have the capability to transport hole or electron.

In addition, previous studies stated that the problem of low EL and color stability due to PF-associated aggregation was solved with the use

of substituted dibenzofluorene monomer instead of fluorene. Owing to the broad steric group substitution, the crystallinity of synthesized polymers decreases which can make them suitable for display applications. This research investigates the thermal, photophysical, and electrochemical properties of these polymers.

2. Experimental section

2.1. Materials and methods

A.R. grade chemicals required were purchased from SD fine and Sigma Aldrich. Nitrogen atmosphere was employed while conducting all synthetic processes. Only THF was distilled using sodiumbenzophenoneketyl. The diphenol monomers 4,4'-(anthracene-9,10-diyl)diphenol (DPA), 4,4'-(2- methylanthracene-9,10-diyl)diphenol (MDPA), 4,4'-(2-ethylanthracene-9,10-diyl)diphenol (EDPA) and 4,4'-(2-(tertbutyl) anthracene-9,10-diyl)diphenol (TBDPA) were prepared and characterized previously [25–29].

2.2. Instrumentation-

The elemental analysis of **M1**, **M2** and polymers **(P1–P4)** was performed on Euro Vector EA 3000 instrument using microanalytical technique. Bruker AMX-300 NMR spectrometer was used for ^{1}H and ^{13}C analysis of all synthesized compounds. GC-MS Shimadzu GCMS/QP 2010 was used to determine molecular weights of the compounds. Thin Layer Chromatography analyses were performed to confirm the purity of compound on plates coated with silica gel G (Merck). The X-Ray diffractograms were recorded on Shimadzu XRD-7000. Shimadzu UV-2100 spectrophotometer were used to record UV spectra. PerkinElmer Instruments LS55 Luminescence Spectrometer of wavelength range 200–800 nm were use to study photoluminescence behaviour of compounds. PerkinElmer series 200 GPC was used for molecular weight determination. Morphology was studied on Hitachi S-4800 field emission scanning electron microscope (Japan) SEM instrument.

2.3. Synthesis of monomers

2.3.1. Synthesis of dibenzofluorene (DBF)

Bis-(naphthalyl-1-yl)methanol (3.66 mg, 10 mmol) was heated in H_3PO_4 (85% water; 30 ml) in an oil bath for 3 h at 180 °C. Chloroform and water were added after the reaction was completed, and organic layers separated and washed by saturated Na_2CO_3, saturated NaCl, and dried over Na_2SO_4. Light yellow white solid was obtained after purification with chromatographic columns (silica gel, PET: CHCl$_3$, 10:2 v/v). The product yield was 85%.

IR (KBr cm^{-1}): 3131(S); 1589(S); ^{1}H NMR (300 MHz, CDCl$_3$) 4.41 (S, 2H); 6.99–7.94 (m, 12H, Ar-ring); ^{13}C NMR (75 MHz, CDCl$_3$): 34.41; 124.48; 125.40; 125.53; 125.86; 126.92; 128.56; 130.75; 132.21; 132.70; 137.49; MS (*m/z*) 266; Anal. Calcd for C$_{21}$H$_{16}$: C, 94.03%; H, 5.97% Found: C, 93.87%; H, 6.13%.

2.3.2. 13,13-Dipropyl-13H-dibenzo[a,i]fluorene

In a flask, dibenzofluorene (1 g, 0.004 mmol), 50% aqueous NaOH and a catalytic quantity of tertiary butyl ammonium iodide (TBAI) (0.14 g, 0.004 mmol) were added under nitrogen atmosphere. 1-Bromo propane (3.5 ml, 0.02 mmol) was added slowly to the flask and then heated for 5 h at 100–110 °C. The reaction mixture was cooled and extracted chloroform then organic layer was washed twice with water and dried over anhydrous Na_2SO_4. Product purification was done by chromatography of the silica gel column using PET ether as a solvent to provide light yellow solid with a yield of 80% [23,24].

IR (KBr cm^{-1}): 2949(S); 2926.75 (S); 1590(S);; M.P-190-191 °C; ^{1}H NMR (300 MHz, CDCl$_3$) 0.28 (t, 6H,-CH$_3$); 0.44 (m, 2H,-CH$_2$); 2.72 (m, 2H, –CH$_2$); 8.33 (d, 2H); 7.9 1 (m, 2H); 7.55 (m, 2H); 7.43 (m, 2H); 7.24 (d, 2H); 7.68 (d, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) 14.28; 17.11; 42.30;

60.42; 118.201; 128.25; 124.58; 126.05; 128.44; 129.81; 129.91; 133.62; 139.13; 145.63; MS (*m/z*) 368; Anal. Calcd for C$_{27}$H$_{24}$: C, 93.10%; H, 6.89% Found: C, 92.64%; H, 7.36%.

2.3.3. Synthesis of 5,8- dibromo-13,13-dipropyl-13H-dibenzo[a,i]fluorene (M1)

A mixture of 13,13-dipropyl-13H-dibenzo [a, i]fluorene (1 g, 0.003 mmol) and NBS (1,3 g, 0.007 mmol) in DMF was stirred at room temperature for 24 h and then extracted with chloroform. Separated organic layer, washed with brine, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, crude product obtained was purified using column chromatography (eluent: petroleum ether: chloroform 9:1 v/v) to afford a light brown solid (Fig. 1).

IR (KBrcm^{-1}): 3047 (s), 2952 (s), 2926 (w), 1583 (s), 1459 (m), 908 (s), 816 (m), 754 (s), M.P.: 215–218 °C, ^{1}H NMR (300 MHz, CDCl$_3$): 0.24 (t, 6H, –CH$_3$), 0.46 (m, 4H, –CH$_2$CH$_3$), 2.67 (m, 4H, –CH$_2$CH$_2$CH$_3$), 7.25–8.56 (10H, Ar–H), ^{13}C NMR (75 MHz, CDCl$_3$): 14.2, 17.1, 42.4, 60.4, 119.3, 127.7, 124.8, 128.1, 129.2, 129.5, 129.9, 134.9, 139.2, 145.8, MS (*m/z*): 508; Anal. Calcd for C$_{27}$H$_{24}$Br$_2$: C, 63.77%; H, 4.72% Found: C, 63.64%; H, 4.55%.

2.3.4. Synthesis of 9,10-di(p-hydroxyphenyl)anthracene (M2)

This monomer was synthesized and characterized by the method reported in our previous investigation [25–30]. By using various quinones five different acene monomers were (**M2a, M2b, M2c** and **M2d**) obtained. Detail scheme for the synthesis and its characterization included in supporting file. (Figure S$_1$ and Figure S$_2$ supporting information).

2.4. General polymerization

A mixture of **M1** [5,8- dibromo-13,13-dipropyl-13H-dibenzo [a,i] fluorene]and **M2** [4,4'-(2-R-anthracene-9,10-diyl)diphenol monomer (R = H (DPA), methyl (MDPA), ethyl (EDPA) or tert-butyl (TBDPA)]; 0.001 mol) were taken in a three necked round bottom flask and added potassium carbonate as a base. Then toluene and dioxane in 1:2 were added in the flask and refluxed for 12 h. Excess **M1** was added for end capping of hydroxyl groups after polymerization. Water was added to the reaction mixture. The solvent was evaporated to precipitate the polymer and was further extracted using dichloromethane [20,23]. The brown coloured polymers with a yield of 75–79% were obtained.

Changing monomers **M2a, M2b, M2c,** and **M2d,** polymers **P1–P4** were prepared (Fig. 2).

2.4.1. NMR and FTIR signals, elemental analysis, molecular weight of polymers [Poly(DBF)s]

Poly [4,4'-(anthracene-9,10- diyl)diphenyloxy-co-13,13-dipropyl-13H-dibenzo [a,i] fluorenyl-5,8-diyl] [P1]: ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 0.34 (t, 6H, –CH$_3$), 2.66 (m, 4H, –CH$_2$CH$_2$CH$_3$), 0.50 (m, 4H, –CH$_2$CH$_3$), 7.55–8.31 (m, 26H, Ar–H), ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 14.19 (CH$_3$), 17.06 (-CH$_2$CH$_3$), 46.93 (-CH$_2$CH$_2$CH$_3$), 60.40 (C(Pr)2), 118.68–145.78 (C arom.)- IR (KBr,cm^{-1}): 3055 (s) [H–C arom.], 1607 (s) [C=C], 2930 (s) [H–C aliph.], 1504 (b), [C–C arom.], 1042 (s) [C–O–C]; Mw/Mn: (25711/15985) = 1.60; Anal. Calcd for C$_{1219}$H$_{966}$O$_{23}$: C, 91.51%; H, 6.19%; O, 2.30%. Found: C, 91.48%; H, 6.12%; O, 2.40%.

Poly [4,4'-(2-methylanthracene-9,10-diyl)diphenyloxy-co-13,13-dipropyl 13H-dibenzo [a,i] fluorenyl-5,8-diyl] [P2]: ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 0.20 (t, 6H, CH$_2$CH$_3$) 0.41 (m, 2H, CH$_2$CH$_3$) 2.55 (m, 2H, CH$_2$CH$_2$CH$_3$), 2.94 (s, 3H, Ar-CH$_3$) 6.93–8.35 (m, 25H, Ar–H); ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 14.29 (CH$_2$CH$_3$), 17.56 (CH$_2$CH$_3$), 42.98 (CH$_2$CH$_2$CH$_3$), 58.34 (C(Pr)$_2$), 24.75(Ar-CH$_3$), 119.61–155.78 (C arom.), IR (KBr, cm^{-1}): 3059 (s) [H–C arom.], 1602 (s) [C=C], 2932 (s) [H–C aliph.], 1508 (b) [C–C], 1034 (s) [C–O–C]; Mw/Mn: (27313/16992) = 1.60; Anal. Calcd for C$_{1296}$H$_{1056}$O$_{24}$: C, 91.52%; H, 6.21%; O, 2.27%. Found: C, 91.60%; H, 6.17%; O 2.23%.

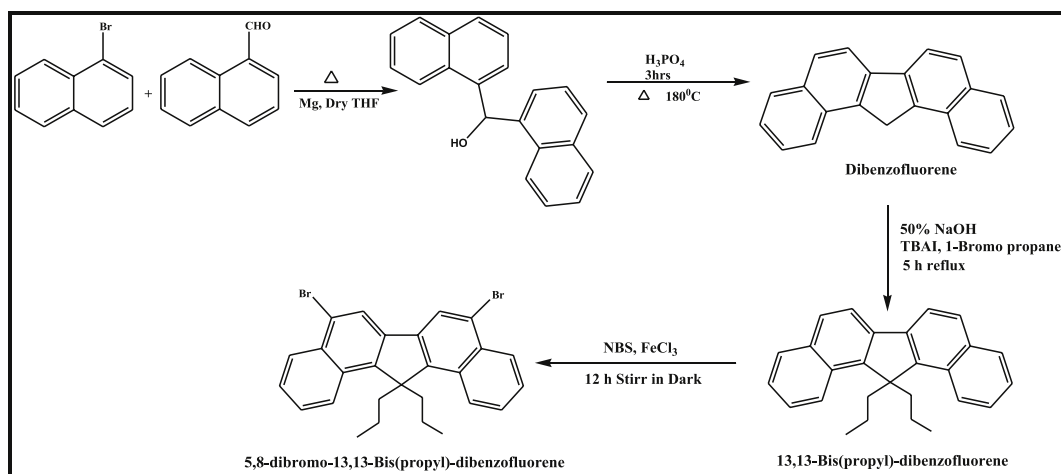**Poly [4,4'-(2-ethylanthracene-9,10-diyl)diphenyloxy-co-13,13-**

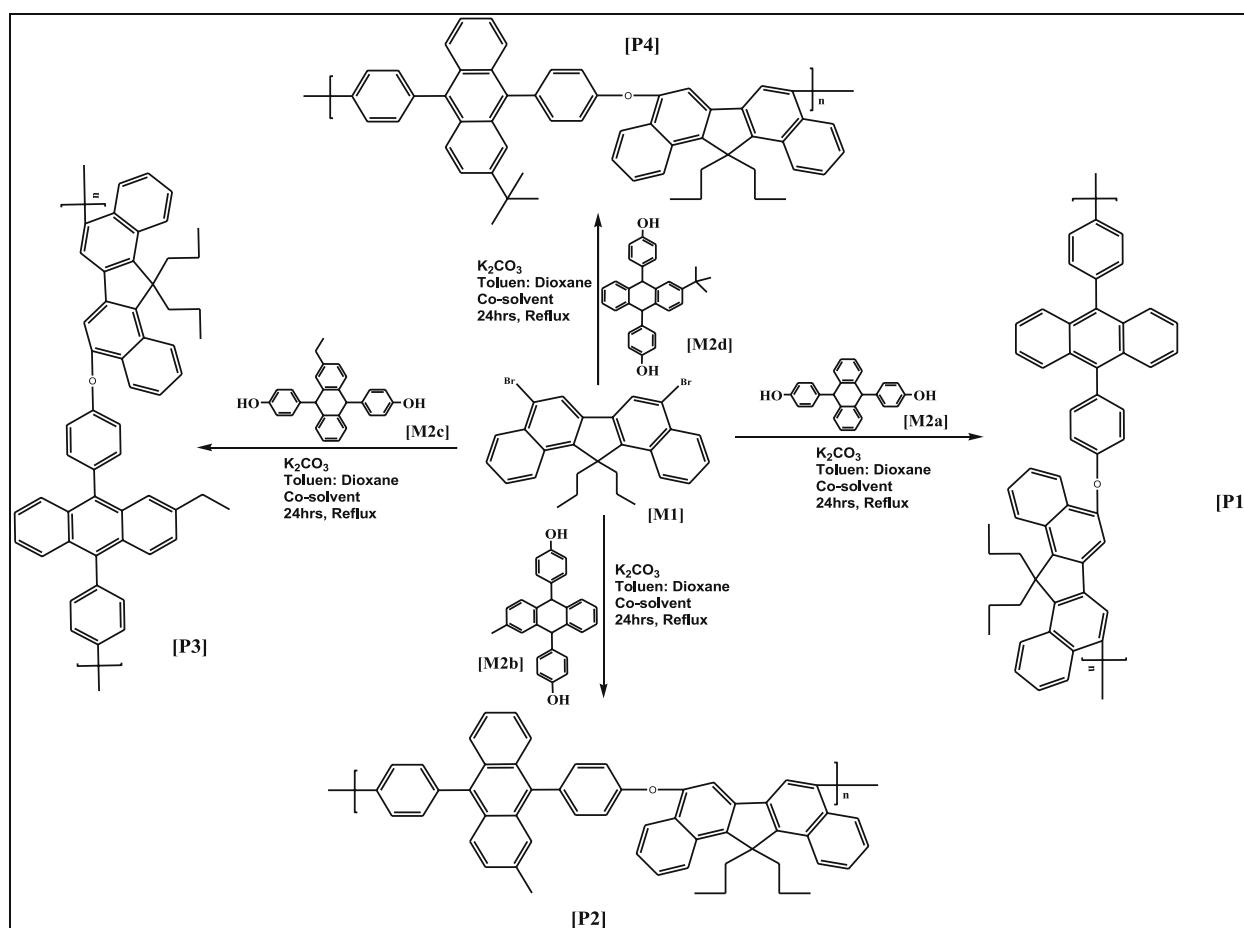**Fig. 1.** Synthesis of 5,8- dibromo-13,13-dipropyl-13H-dibenzo[a,i]fluorene.

Fig. 2. Synthesis of polymers.

dipropyl-13H-dibenzo [a,i] fluo-renyl-5,8-diyl] [P3] :^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 0.31 (t, 6H, CH$_2$CH$_2$CH$_3$), 0.42 (m, 4H, CH$_2$CH$_2$CH$_3$), 1.47 (t, 3H, Ar-CH$_2$CH$_3$), 2.07 (m, 4H, CH$_2$CH$_2$CH$_3$), 2.47 (q, 2H, Ar-CH$_2$CH$_3$), 7.28–8.45 (m, 25H, Ar–H); ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 14.75(Ar-CH$_2$CH$_3$), 15.19 (CH$_2$CH$_2$CH$_3$), 18.16 (CH$_2$CH$_2$CH$_3$), 34.83 (Ar-CH$_2$CH$_3$), 44.96(CH$_2$CH$_2$CH$_3$), 61.76 (C(Pr)2), 112.46–151.18 (C arom.); IR (KBr, cm^{-1}): 3049 (s) [H–C arom.], 1589 (s) [C═C], 2956 (s) [H–C aliph.], 1492 (b) [C–C arom.], 1034 (s) [C–O–C]; Mw/Mn: (29736/17352) = 1.71; Anal. Calcd for

C$_{1320}$H$_{1104}$O$_{24}$: C, 91.28%; H, 6.46%; O, 2.26%. Found: C, 91.16%; H, 6.51%; O, 2.33%.

Poly [4,4'-(2-tert-butylanthracene-9,10-diyl)diphenyloxy-co-13,13-dipropyl-13H-dibenzo [a,i] fluorenyl-5,8-diyl] [P4] :^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 1.29 (s, 9H, C(CH$_3$)$_3$), 0.21 (t, 6H, CH$_2$CH$_2$CH$_3$), 0.53 (m, 4H, CH$_2$CH$_2$CH$_3$), 2.97 (m, 4H, CH$_2$CH$_2$CH$_3$), 7.12–8.75 (m, 25H, Ar–H); ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 14.13 (CH$_2$CH$_3$), 20.16 (CH$_2$CH$_3$), 43.19 (CH$_2$CH$_2$CH$_3$), 60.06 (C(Pr)$_2$) 31.77 (C(CH$_3$)$_3$), 40.12 (C(CH$_3$)$_3$), 115.16–160.28 (C arom.); IR (KBr, cm^{-1}):

3039 (s) [H–C arom.], 1604 (s) [C=C], 2934 (s) [H–C aliph.], 1511 (b) [C–C arom.], 1042 (s) [C–O–C], Mw/Mn: (33753/18775) = 1.79; Anal. Calcd for $C_{1425}H_{1250}O_{25}$: C, 91.07%; H, 6.65%; O, 2.28%. Found: C, 91.25%; H, 6.55%; O, 2.20%.

3. Results and discussion

A series of luminescent poly (DBF)s were obtained that had good emission properties and excellent solubility in common organic solvents (). Poly (DBF) solubility in common organic solvents such as chloroform, dichloromethane, acetonitrile, ethanol, tetrahydrofuran, dimethylsulphoxide, and other solvents was quite higher than monomer solubility. The obtained Poly (DBF)s were studied according to their optical and thermal behavior. Additionally, X-ray diffraction and electrochemical studies were carried out and the surface morphology was established.

3.1. Structural characterization

Poly (DBF)s obtained have also been studied for their optical, thermal, X-ray diffraction, electrochemical and surface morphology studies. The significant feature of polymer infrared spectra was the absence of a band at 697 cm^{-1}, indicating the removal of dialkyl substituted dibenzofluorene monomer Br atoms and the absence of 3400 cm^{-1} absorption peaks, indicating polymerization is complete. The high absorption peak in the range 1038–1045 cm^{-1} was observed inside the spectra due to the C–O–C stretching of the ether linkage on the main polymer backbone indicating the formation of polymers by eliminating the HBr molecule.

3.2. Solubility test

Poly (DBF) derivatives are important as they have a rigidly planar biphenyl structure and easy replacement at the remote C-13 site provides an opportunity to improve the solubility and processability of polymers without significantly increasing the steric interactions in the polymer backbone. The solubility of polymers in 1 ml solvent was qualitatively tested on a sample of 1 mg. The polymers showed significant solubility in common organic solvents. The data of solubility of polymers is reported in Table 1.

3.3. X-ray diffraction studies

Studies on X-Ray diffraction can be used to evaluate the strain, desired orientation, crystallographic structure and grain size of crystalline materials [20,21,23]. Figure S$_3$ displays the XRD patterns of the polymers. The polymers' crystallite sizes were determined using the Deby-Scherrer relation. The crystallite sizes were found in the range of 0.2838–0.5554 Å for polymer **P2**, **P3** and **P4** as shown in Table 2. Polymer X-ray diffractogram showed small, large and poorly resolved peaks. The crystallite size for polymer **P1** was found to be 4.4906 Å as

shown in Table 2. **P1** showed sharp, well-resolved peaks of varying intensity than **P2**, **P3** and **P4**. It suggested that, the synthesized polymer **P1** was more crystalline in nature than others.

3.4. Optical studies

Fig. 3 and Fig. 4 display the UV–visible absorption and photoluminescence (PL) spectra of polymers respectively. At room temperature, absorption and emission spectra have been reported in dilute THF solution. The standard absorption spectrum of dilute solution of poly (9,9-dialkyl fluorene) was shown at around 370 nm with maximum absorption [31–33,45,46]. The maximum absorption of synthesized polydibenzofluorenes showed a blue shift to 333 nm compared with typical poly (9,9-dialkyl fluorene), due to the presence of dibenzofluorene moiety. Even now, the polymers have shown the highest absorption in the range of 264–290 nm due to the contribution of the conjugated segments of the transition from π-π*.

The polymers' optical band gaps from the absorption onsets were estimated to be 3 eV, which was consistent with previous electrochemically measured Eg's.

Polymers' emission spectrum has shown that the polymers are extremely fluorescent in nature. As shown in Fig. 4, all of these polymers display a strong blue fluorescence of approximately 428–437 nm upon photoexcitation. Compared to poly (9,9-dialkyl fluorene) (πPLmax = 447 nm) [34] due to the enhanced steric effect of the dibenzofluorene group the maximum PL was shifted blue by around 10 nm. The torsional angle between the units is greater than dibenzofluorene, reducing the effective length of the conjugation along the main polymer chain, resulting in a blue shift. The higher quantum efficiencies of these polymers were observed range 0.43–0.47 (Table 3). The higher values of band gaps and PL quantum yield signified that these blue light emitting conjugated polymers can be useful in sustainable light emitting device technology.

3.5. Thermal studies

The polymer TGA and DTA curves are shown in Fig. 5 and the details are summarized in Table 4. Both polymers demonstrated excellent thermal stability under the atmosphere of nitrogen with a weight loss of 10% between 300 and 357 °C. Such values describe the polymers were synthesized as thermally stable material. In all cases, material degradation requires the removal of volatile components such as oxygen, carbon monoxide, methane and carbon dioxide [35]. Fig. 5 showed that **P3** and **P4** had only one thermal decomposition peak centered at 300 and 383 °C, while **P1** and **P2** showed the main decomposition peak at 402 and 446 °C, followed by another secondary peak. For **P1** and **P2**, the type of the curve evidence was more complex thermal mechanism, [DTA analysis (Figure S$_5$a-S$_5$d) can better explain this fact].

For the determination of the Tg value of synthesized polymers, DSC analysis was performed. The results are shown in Table 4, and selected thermal curve intervals are shown in Figure S$_6$ (Supplementary data). DSC analysis suggested that, glass transition temperatures (Tg) was observed in between 120 to 140 °C, and no other crystallization and melting peaks were detected.

The Tg values were relatively high in all situations. The alkyl

Table 1
Solubility of polymers in different solvents.

Polymer				
Solvent	P1	P2	P3	P4
Hexane	–	–	–	–
Pet Ether	–	–	–	–
Toluene	++	++	++	++
DCM	++	++	++	++
Chloroform	++	++	++	++
Acetone	++	++	++	++
Ethanol	+	+	+	+
Acetonitrile	+	+	+	++

++ Soluble at room temperature.
+ Soluble on heating.
- Partial soluble on heating.

Table 2
X-Ray Diffraction Data of polymers.

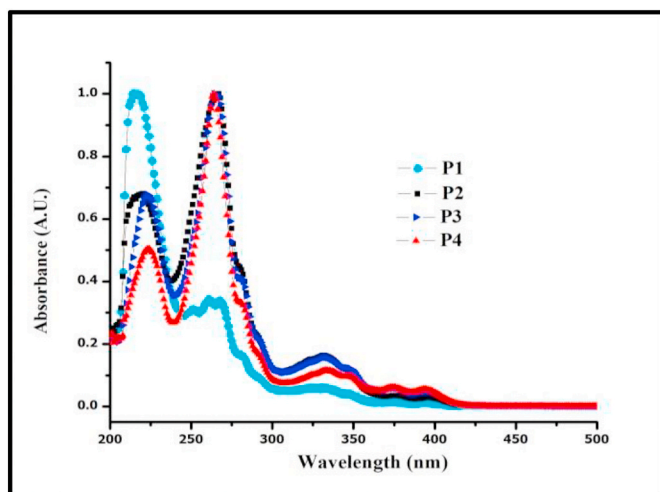| Polymer	2θ of max. int. peak (Degrees)	θ Degrees	cosθ	β	Bragg spacing (d) (Å)	Crystallite size (Å)
P1	11.4432	5.7216	0.9950	0.3106	7.7266	4.4906
P2	20.1000	10.0500	0.9847	2.5376	4.4141	0.5554
P3	20.9975	10.4988	0.9833	3.3550	4.2275	0.4207
P4	20.1166	10.0583	0.9846	4.9667	4.4105	0.2838

Fig. 3. Normalised overlay absorption spectra of polymers (P1–P4) in THF.
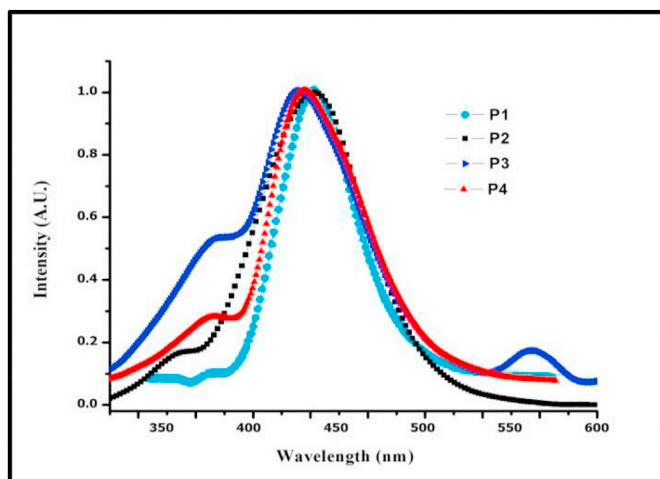

Fig. 4. Normalised overlay emission spectra of polymers (P1–P4) in THF.

Table 3
Photo-physical and Electrochemical Data of polymers.

Polymer	$\lambda_{max}^{abs,}$ THF (nm)	$\lambda_{max}^{PL,}$ THF (nm)	Eg (eV)[a]	Quantum Yield (ΦPL)[b,c]	$E_{ox}^{peak[d]}$	HOMO[e]	LUMO[f]
P1	328	437	3.02	0.46	0.85	5.25	223
P2	333	436	2.98	0.43	0.83	5.23	2.25
P3	335	428	2.95	0.44	0.86	5.26	2.31
P4	331	432	2.95	0.47	0.82	5.22	2.27

[a] Optical band gap calculated from the emission and excitation band.
[b] Measured in THF.
[c] Measured using 9,10-DPA as standard.
[d] Peak oxidation potential.
[e] HOMO = E_{ox}^{peak} + 4.4 eV.
[f] LUMO = E_g^{opt} – HOMO.

moieties and quasi-planarity of dibenzofluorene fragments are likely to increase chain rigidity, which may be responsible for reported high value. The increased values of Tg may be due to the existence of a rigid dibenzofluorene unit which rigidly enhances the molecularity of polymers and restricts their segmental mobility. The high thermal stability of amorphous-nature polymers prevents morphological deformation and polymer degradation in light emitting products. Therefore, it is important to develop organic light emitting diodes from materials with

relatively high Tg value to avoid issues associated with aggregation formation and excimers during heat exposure [36].

GPC analysis showed that, average molecular weights Mn and Mw of polymers were in the range of 15985–18775 and 25711 to 33753 respectively (Table 4) whereas PDI calculated from these molecular weights was in the range of indices *Mw/Mn* of 1.60–1.79 [28,44].

3.6. Electrochemical studies

Electrochemical studies of the synthesized Poly [DBF]s were carried out to analyze their redox behaviour. For determined energy band structure of OLEDs unit, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were used. Cyclic measurement of synthesized Poly [DBF]s were coated on a glassy carbon electrode have been carried out in 0.1 m tertiary butyl ammonium hexafluorophospate (TBAPF$_6$) in anhydrous DCM using standard ferrocene at a scan rate of 50 mV^{-1} at room temperature. Platinum wire and silver/silver chloride were used counter and reference electrode respectively. On the surface of the electrode oxidation (reduction) occurs when applied potential has reached some voltage and therefore anodic (cathodic) current has been observed [37].

The half-potential oxidation of synthesized polymers against the reference Ag/AgCl electrode is shown in Fig. 6, and the corresponding information is summarized in Table 3. Based on the onset potential of oxidation and reductions, the energy levels of HOMO and LUMO were calculated in relation to ferrocene energy level. The onset oxidation potentials were determined from the intersection of the two tangents drawn at the rising current and baseline charging current of the CV traces. According to the empirical relationship proposed by Leeuw et al., E$_{HOMO}$ = -(Eonset, ox + 4.8) was calculated, [where, Eonset, ox were the onset potentials of oxidation].

According to the peak oxidation potential, the E$_{HOMO}$ values were determined to be 5.22–5.26 eV; and, based on the E$_{LUMO}$ = E$_{HOMO}$-Eg [opt.] relationship, the energy level of LUMO was estimated [38,39]. The LUMO values were in the range of 2.23–2.31eV. (supplementary information Figure S$_8$a to S$_8$d). The high E$_{HOMO}$ values confirmed that the synthesized polymers were a suitable material for the application of high voltage devices [40–46].

3.7. Surface morphology

The SEM microphotographs of Poly [DBF]s are shown in Figure S$_9$ (Supporting information). In some cases large intermittent crystals were observed. The morphology also exhibited disheveled, irregular globoid and bouldered shaped structure. Further SEM study established crystalline in nature of polymer **P1**, whereas Poly [DBF]s **P2, P3** and **P4** were semi crystalline in nature.

4. Conclusion

A series of dibenzofluorenes based light emitting polymers, poly [4,4'-(2-R anthracene-9,10-diyl)diphenyloxy-co-13,13- dipropyl-13H-dibenzo [a,i]fluorenyl-5,8-diyl] (R = H, methyl, ethyl, tert-butyl) were synthesized and explored as emissive materials for polymer light emitting diodes. The glass transition temperature for Poly [DBF]s were in the range of 120–140 °C. For synthesized Poly [DBF]s, UV–Visible intense absorption peaks were observed between 264 and 290 nm and PL maximum at 432–437 nm. The polymer solutions display a PL quantum yield within 0.43–0.47 range. The optical band gap was in the 2.95–3.02 eV range. From the electrochemical study of polymers **P1–P4,** The HOMO levels were estimated in the range of −5.22 to −5.26 eV and LUMO of −2.23 to −2.31 eV. This polymers showed simple reversible electrochemical reductions with 2.95–3.02 eV electron affinities. We believe that, these polymers have sufficient potential in achieving the goal of light emitting device technology that is sustainable for solid state lightning and displays.
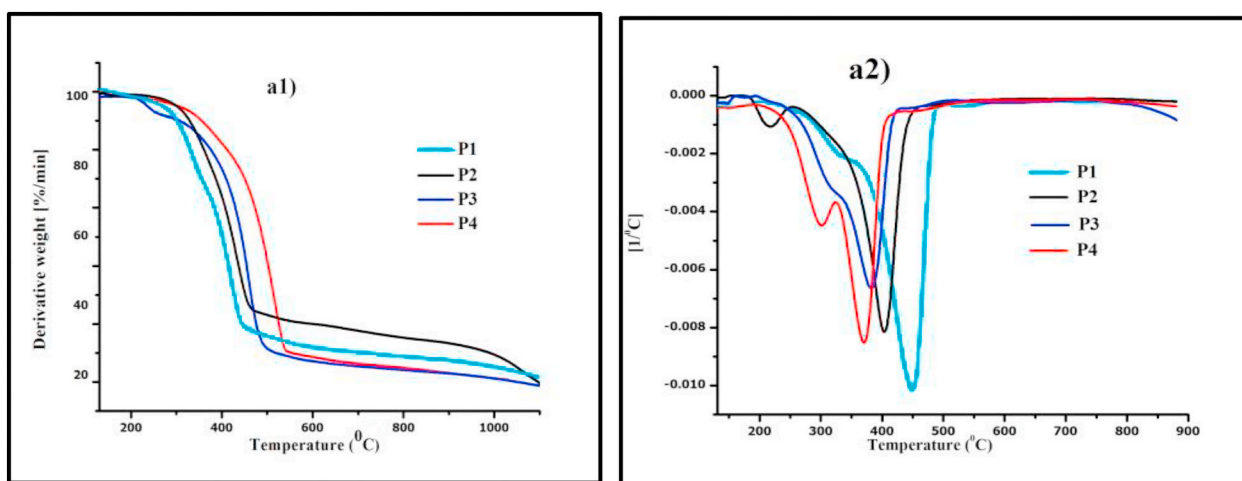
Fig. 5. Thermal behavior of the polymers: **a1)** TGA curves, **a2)** DTA curves (20 °C/min in N₂ atmosphere).

Table 4
Molecular weights and thermal analysis data of polymers.

Polymer	Mn[a]	Mw[a]	Mw/Mn Đ	DTA peak Temp (°C)[b]	Tg[c] (°C)
P1	15985	25711	1.608	446	120
P2	16992	27313	1.607	402	128
P3	17352	29736	1.713	383	136
P4	18775	33753	1.797	300, 371	140

[a] Determined by GPC by eluting with THF, by comparison with polystyrene slandered.

[b] Temperature at which a 5% weight loss occurred was determined at a heating rate of 10 °C/min under a nitrogen atmosphere.

[c] The value of Tg was determined at a heating rate of 20 °C/min under a nitrogen atmosphere.
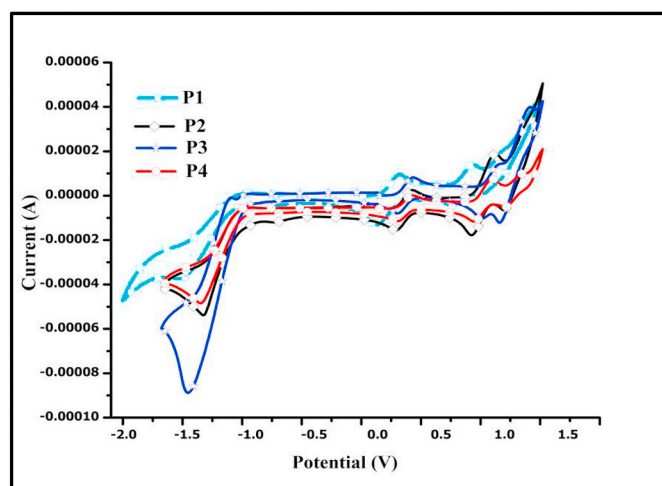

Fig. 6. Cyclic voltammogramms of Polymers (P1–P4) in DCM using Ag/Ag + electrode calibrated with fc/fc+ and TBAPF6 [tertiary butyl ammonium hexafluorophospate (0.1 m)] as an electrolyte. The scan rate used was 50 mV S⁻¹.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2020.122947.

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