



# Recent development of crown-substituted polyfluorenes for blue light-emitting devices in organic electronics

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## Abstract

The efficient photoluminescent polymers containing crown-substituted fluorene and diphenyl anthracene units were synthesized by aromatic nucleophilic substitution reaction. The light-emitting polymers contain benzo-15-crown-5 groups at the C-9 position of fluorene and diphenyl anthracene-emitting segments in the main chain. Introduction of a crown ether group in polymer backbone leads to its high thermal stability at varying temperature ranges and good solubility in common organic solvents such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , THF, and toluene. The novel combination of pendant crown ether and anthracene moiety enhanced the electroluminescence of polymers. The synthesized polymers were effectively characterized by elemental analyses, GPC, TGA, FTIR,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectroscopy and UV–Visible spectroscopy. The electrochemical measurements and optical properties of the polymers were also studied. The obtained polymers showed good photoluminescence and electroluminescence properties with blue fluorescence.

**Keywords** Photoluminescence · Crown-substituted fluorene · Diphenyl anthracene units · Light-emitting polymers · Thermal stability

## Introduction

Within the last century electronic devices have largely enhanced the standard of living. Organic light-emitting diodes (OLEDs) have been renowned as one of the most encouraging candidates for flat-panel displays, solid-state lighting, and

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polymer solar cells because of their high efficiency, low fabrication cost, ease of fabricating large-area devices, and wide range of emission colours [1–8].

Among the light-emitting polymers, fluorene-based polymers have stimulated special interest in electronic devices [9–12], especially in OLEDs because of their good efficiencies both in photoluminescence (PL) and in electroluminescence (EL) [13–15]. For full colour OLEDs display, it is very important to develop wide band gap materials for achieving high colour, pure and efficient blue emission. The use of electroluminescent materials has many advantages over inorganic materials and small organic molecules for large-area display applications. This led to the development of polyacetylenes, polythiophenes, polyanilines, polyfluorenes, etc. Excellent photophysical and electrical properties have been observed for these polymers [16–22].

Fluorene-based conjugated oligomers represent an emerging class of light-emitting materials in the field of optoelectronics. These polymers can be designed from highly crystalline to morphologically stable amorphous materials [23]. These polymers have shown high solid and solution state fluorescence quantum yields (0.6–0.8) [24–28]. Due to high luminescence efficiency, high charge mobility, thermal stability, and good film-forming properties, polyfluorenes have stimulated tremendous research activity in the development of OLEDs for display applications [29–31]. The functional properties of the polyfluorenes can be readily modified by attaching various moieties at the C-9 position of fluorene monomers. The emission colour of this polymer can be easily tailored by modifying the molecular design of an organic material used in the polymer structures. These characteristics are especially suitable for large-area display devices fabricated by spin-coating or printing methods.

Nearly all polyfluorenes exploited side-chain substituents that improved solution processing as well as conversed new functionality. Thermal cycling of polyfluorenes results in distinct backbone and side-chain conformations that lead to improved optical and electronic properties. Numerous polyfluorenes with various comonomers have been developed with a view to obtaining stable, highly efficient, red, green, and blue emitters. However, traditional fluorene-based polymer shows poor thermal and chemical stabilities, excimer interchain aggregates formation, and keto defects [32, 33], which finally leads to shortening in the lifetime of OLED device.

The conjugated blue-emitting organic polymers suffer from the problem of intrinsic wide band gaps, and the insolubility of the polymers may cause the difficulties in the processing of polymer. Device lifetime, especially for blue light-emitting devices, is a key concern.

In addition to excellent luminescent properties, OLEDs also need adequate and balanced transport of both injection of electrons and holes to allow an efficient recombination of these electrical charges in the luminescent chromophores [17, 34]. Due to their wide energy gaps, blue luminescent polymers usually have high oxidation potentials and low electron affinities. Because of these features, polymeric blue light-emitting devices usually face charge injection difficulties for both types of charge carries with the currently available anode and cathode materials. Many ways have been used to modulate the ionization potential (IP), electron affinity (EA), and band gap of polyfluorene derivatives [35]. An introduction of alkoxy and oxadiazole units in polymeric

chain will lead to better injections of holes from anode and electrons from cathode, enhancing the performance of device [36].

During the last 25 years the macrocyclic polyethers, crown ethers and cryptands, in particular, have relished a considerable interest because of their prospective applications. Crown-substituted fluorene has been selected for the backbone of LEPs. Chen and co-workers reported a water/methanol-soluble polyfluorenes grafted with 18-crown-6 ether as electron injection/transport materials, which were applied for enhancement of electroluminescence and solar cell efficiency. Because of its polar characteristic, crown ether-containing fluorene is beneficial in reducing barrier height of electron injection when used as emitting layer or electron injection layer. The emission stability of fluorene copolymers was improved by the replacement of alkyl groups on the C-9 carbon of fluorene with aryl groups or by the integration of anthracene units into the copolymer main chain [37]. Linna Zhu and co-workers reported the synthesis of novel fluorene-based copolymer with pendant crown ether in 2008 [38]. Luminescence properties of copolymers, which combine moieties carrying a crown ether side group 15-crown-5 (15C5) with monomers of highly luminescent polymers, showed high PL efficiencies [39–42]. The introduction of crown ether also lowered the HOMO and LUMO energy states, effective in enhancing electron injection and device performance [43, 44].

In this article, we focus the synthesis and investigation of physical and optical properties of fluorene-substituted benzo crown ethers and acene moiety. Literature survey reveals that blue light-emitting materials based on acene moiety are of great interest and were first pioneered by Pope [45]. Acenes anthracene and pentacene are having aromatic rigid structure and can be substituted with various groups at different position offering colour purity, efficiency, and stable thermal and electrochemical properties [46]. Recently, blue light-emitting polymers based on methoxy-substituted spirobifluorene containing alkyl-substituted acene moiety were synthesized. The connecting monomers via 2, 2', 7, 7' positions of spirobifluorene significantly restricted the inter-chain interaction and controlled the conjugation length. The polymers exhibited blue emission with good quantum yield and excellent colour stability [47].

Therefore, it was worthwhile to synthesize the LEPs where these two areas could be combined in novel way. Hence, the LEPs containing crown ether-substituted fluorene and diphenyl anthracene segments in the backbone were synthesized. In the present study, series of crown-substituted fluorene with anthracene moiety with ether linkages were developed to provide high blue fluorescent host material. The good thermal, morphological stability and enhanced solubility in different organic solvents for solution process ability and electroluminescence are reported. The investigated polymers may result in the formation of some valuable polyether desirable in electronic devices such as light-emitting diodes.

## Experimental

### Materials and methods

All reagents and solvents of analytical grade were commercially purchased. Benzo-15-crown-5, *N*-bromosuccinimide and fluorene were purchased from S D Fine Chem-Limited India and Sigma-Aldrich and used as received. All glass wares were properly washed with double distilled water and dried in an oven. All reactions were carried out in nitrogen atmosphere.

### Instrumentation

All the monomers were analysed for C, H, O, and N using Euro Vector EA-3000 elemental analyser. IR spectra were recorded on a PerkinElmer 1600 series FTIR spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AMX-300 spectrometer in  $\text{CDCl}_3$ . The molecular weight determination was done by gel permeation chromatograms (GPC) measured on a PerkinElmer series 200 GPC equipped with an isocratic pump, a solvent degasser, a column oven, a refractive index (RI) detector, and Chromatographic Column PLgel 10 m Mixed-B, 300  $\mu$  7.5 mm [tetrahydrofuran (THF) 40 °C, flow rate of 1 mL min $^{-1}$  and polystyrene was used for calibration]. The thermal stability of PFs was studied with Star system Mettler Toledo TGA assembly using 10 °C min $^{-1}$  heating rate and  $\text{N}_2$  atmosphere. UV–Visible spectra were recorded by Shimadzu UV-2100 spectrophotometer. Fluorescence spectra were recorded on Shimadzu spectrofluorophotometer RF-5310. The morphology of the polymers was studied by scanning electron microscopy (SEM). Electron micrographs were obtained on Cameca (France) model SU-30 Scanning Electron Microscope. Samples were prepared for SEM by freeze fracturing them in liquid nitrogen and applying gold coating of approximately 200 Å units by ion sputtering method. The gold-coated samples were mounted on the SEM stubs with silver adhesive paste. The X-ray diffraction analyses were carried out using Shimadzu XRD-7000 X-Ray Diffractometer.

### Synthesis of monomers

#### Synthesis of 2, 7-dibromo-9, 9-di (benzo 15-crown-5)—fluorene (DB15C5-F) (M1)

2, 7 Dibromofluorene (0.972 g, 0.0030 mmol), 50% aq NaOH (5 mL), and a catalytic amount of tetrabutylammonium iodide (0.046 g, 10 mol%) were added to a flask maintained under nitrogen environment. Bromobenzo crown (0.971 g, 0.0028 mmol) was added in the flask, and the mixture was heated at about 100–110 °C continuously for 5 h. The reaction mixture was cooled to room temperature and poured in water and then extracted with chloroform. The organic layer was washed with water and dried over anhydrous sodium sulphate. The solvent was removed under vacuum, and the crude product was purified in pet ether.

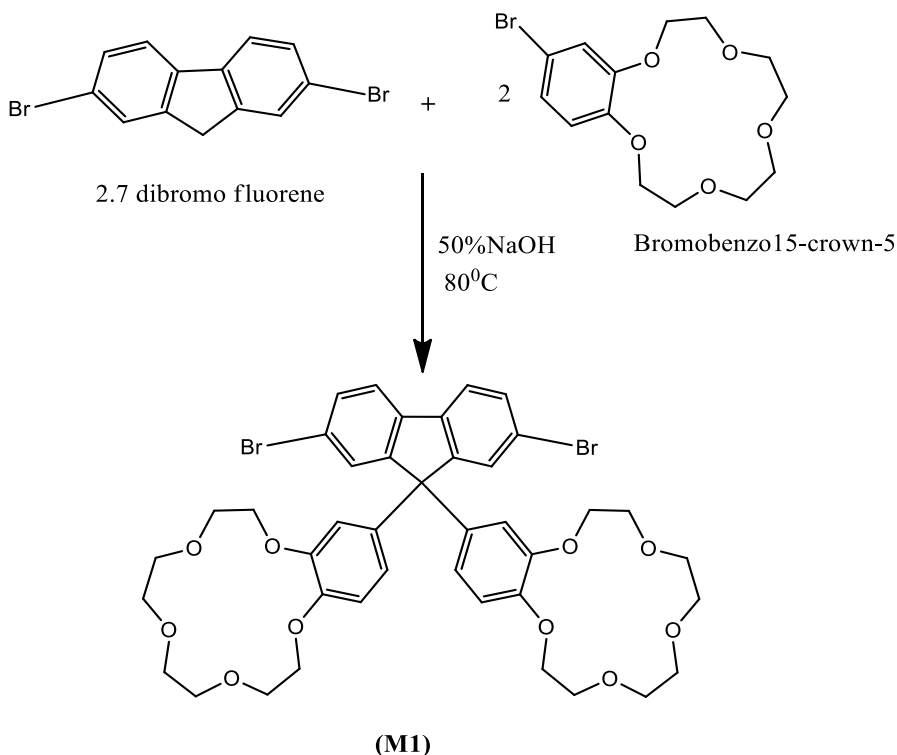
(Yield 50%): MP:90–93 °C.

IR (KBr)  $\text{cm}^{-1}$ : 2960, 1448, 3070, 1499, 2860.84.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 3.7 (t, 8H) 3.8 (t, 4H), 4.06–4.1 (t, 4H), 6.70–6.72, (d, 3H), (7.00–7.34 (d, 3H), 7.48–7.57 (m, 3H), 7.55–7.72 (d, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm):149.97, 148.41, 144.76, 142.196, 139.64, .22, 130.11, 128.265, 120.91, 118.43, 115.40, 113.156, 71.04, 70, 70.47, 70.41, 69.34, 69.11 Anal calcd for:  $\text{C}_{41}\text{H}_{44}\text{O}_{10}\text{Br}_2$  : C, 57.61; H 5.15%. Found: C, 56.89; H 5.05% (Fig. 1).

### Synthesis of di (p-hydroxyphenyl) anthracene monomer (M2) comprises of two steps

**General synthesis di (p-methoxyphenyl) anthracene (4)** The solution of 32 mmol of p-bromo anisole in THF was mixed to nitrogen purged solution of Mg (32 mmol) in THF at room temperature to produce the Grignard reagent. The mixture was stirred for 30 min. The suspension of different quinones (anthraquinone/methyl anthraquinone/ethyl anthraquinone and tertbutyl anthraquinone) of 3.2 mmol in THF was added dropwise to the mixture in round-bottom flask, and the whole mixture was



**Fig. 1** Synthesis of 2, 7-dibromo-9, 9-di (benzo-15-crown-5)—fluorene monomer

cooled with ice. The mixture was then heated at 60 °C for 2 h. The reaction flask was cooled with ice to lower the temperature, and then a mixture of 30 mL 20% HCl and 3 g  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was added. The mixture was heated at 60 °C for extra 1 h. After the reaction, product obtained was collected via filtration and then thoroughly washed with water and solvents like ethanol and diethyl ether [46].

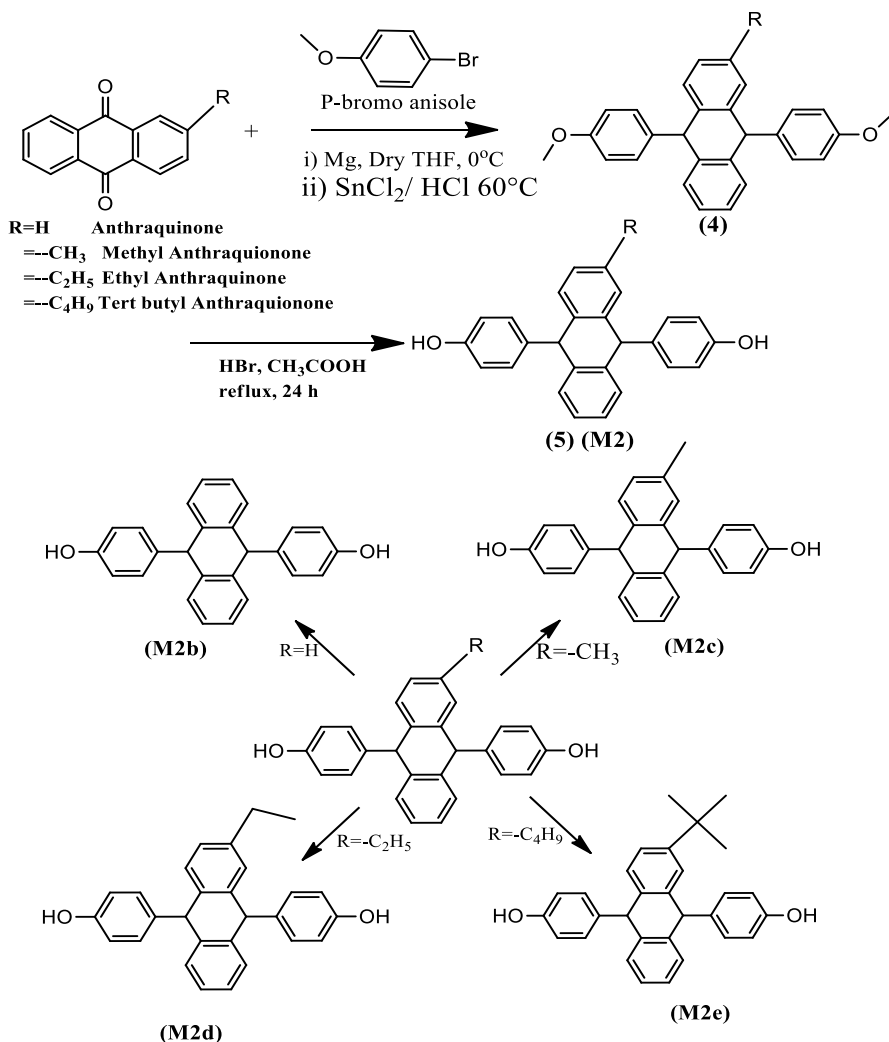
**General synthesis of di(p-hydroxyphenyl) anthracene (M2)** A solution of (p-methoxyphenyl) acene completely dissolved in acetic acid was taken in three-necked round-bottom flask equipped with  $\text{N}_2$  atm. to obtain inert atmosphere, and hydrobromic acid (48%) was added drop wise for nearly one hour. The resulting reaction mixture was refluxed at 120 °C for 24 h with spirited stirring. The reaction mixture was cooled to room temperature. The crude product obtained was filtered and washed with water and acetic acid; the product was recrystallized in toluene/ethanol (80/20) to produce the product in powder form [46]. By following similar reaction scheme, series of di (p-hydroxyphenyl) acene monomers (**M2b**, **M2c**, **M2d**, and **M2e**) were synthesized using various quinones as shown in Fig. 2.

**1,4-di(p-hydroxyphenyl)benzene-M2a** Yield: 80%, M.P.: 98 °C, IR (KBr pellet,  $\text{cm}^{-1}$ ): 3402 (–OH), 2956 (C–H stretch), 1607–1382 (C=C stretch), 810–876 (–phenyl group),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  in ppm): 6.951–7.617, (m, 12 H, Ar–H), 3.870 (s, 2 H, –OH),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 44.5–155.4 (aromatic carbon); Mass spectrum:  $m/z$  262 (M+), Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{O}_2$ : C, 82.44, H, 5.34% Found: C, 82.63, H 5.59% (Fig. 3).

**9,10-di(p-hydroxyphenyl)anthracene-M2b** Yield 81%; M.P.: 184 °C; IR (KBr pellet,  $\text{cm}^{-1}$ ): 3421 (s) [–OH, aromatic], 2955 (s) [C–H, aromatic], 1606–1390 (s) [C=C, aromatic], 809–880 (b) [phenyl group]  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 6.921–7.80 (m, 16H, Ar–H), 3.962 (s, 2H, –OH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 116.4–157.4 (aromatic carbon); MS ( $m/z$ ) 362, Anal. Calcd for  $\text{C}_{26}\text{H}_{18}\text{O}_2$ : C 86.17, H 4.98%; Found: C, 86.11, H 4.90%.

**2-methyl-9,10-di(p-hydroxyphenyl)anthracene-M2c** Yield 79%; M.P.: 198 °C; IR (KBr pellet,  $\text{cm}^{-1}$ ): 3422 (s) [–OH, aromatic], 2995 (s) [C–H, aromatic], 1616–1390 (s) [C=C, aromatic], 804–889 (b) [phenyl group]  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz  $\text{CDCl}_3$ ,  $\delta$  ppm): 6.937–8.328 (m, 15H, Ar–H), 3.969 (s, 2H, –OH), 2.537 (s, 3H, – $\text{CH}_3$ );  $^{13}\text{C}$  NMR: (75 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 116.4–157.4 (aromatic carbon), 24.7 (– $\text{CH}_3$ ); MS ( $m/z$ ) 376, Anal. Calcd for  $\text{C}_{27}\text{H}_{20}\text{O}_2$ : C, 86.17; H, 5.31%; Found: C, 86.13; H, 5.53%.

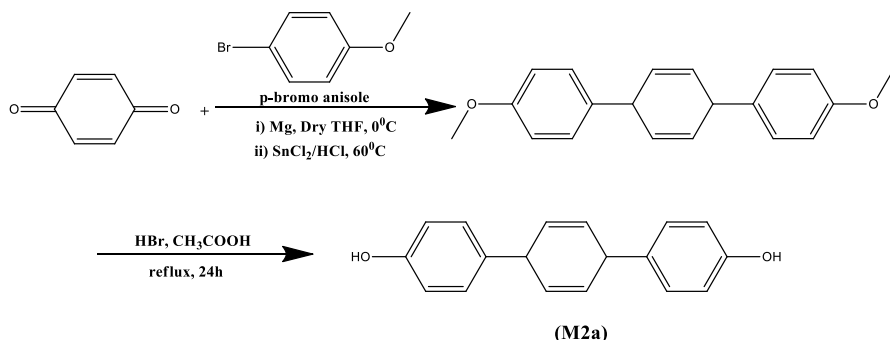
**2-ethyl-9,10-di(p-hydroxyphenyl)anthracene-M2d** Yield 72%; M.P.: 180 °C; IR (KBr, pellet,  $\text{cm}^{-1}$ ): 3426 (s) [–OH, aromatic], 2969 (s) [C–H, aromatic], 1596–1400 [C=C, aromatic], 809–880 (b) [phenyl group]  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 6.938–8.324 (m, 15H, Ar–H), 3.969 (s, 2H, –OH), 2.847 (q, 2H, methylene proton), 1.306 (t, 3H, – $\text{CH}_3$ );  $^{13}\text{C}$  NMR: (75 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 116.4–157.4



**Fig. 2** General synthesis of di (p-hydroxyphenyl) anthracene monomers

(aromatic carbon), 32.8 (–CH<sub>2</sub>–), 14.6 (–CH<sub>3</sub>); MS (m/z) 390, Anal. Calcd for C<sub>28</sub>H<sub>22</sub>O<sub>2</sub>: C, 86.15; H, 5.64%; Found: C, 86.71; H, 5.27%.

**2-tertbutyl-9,10-di(p-hydroxyphenyl)anthracene-M2e** Yield 86%; M.P.: 196 °C; IR (KBr pellet, cm<sup>–1</sup>): 3426 (s) [–OH, aromatic], 3059 (s) [C–H, aromatic], 1608–1399 [C=C, aromatic], 809–880 (b) [phenyl group] cm<sup>–1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ ppm): 6.939–7.670 (m, 13H, Ar–H), 3.971 (s, 2H, –OH), 1.269 (s, 9H, 3–CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ ppm) 116.4–157.4 (aromatic carbon), 41.1 (tert carbon), 31.4 (–CH<sub>3</sub>); MS (m/z) 418, Anal. Calcd for C<sub>30</sub>H<sub>26</sub>O<sub>2</sub>: C, 86.12; H, 6.22%; Found: C, 86.33; H, 6.08%.



**Fig. 3** Synthesis of di (p-hydroxyphenyl) benzene monomer (DPB) (**M2a**)

### General polymerization

Our synthetic strategy includes the synthesis of desired polymers (**P1–P5**) using monomers (**M1**) and (**M2**).

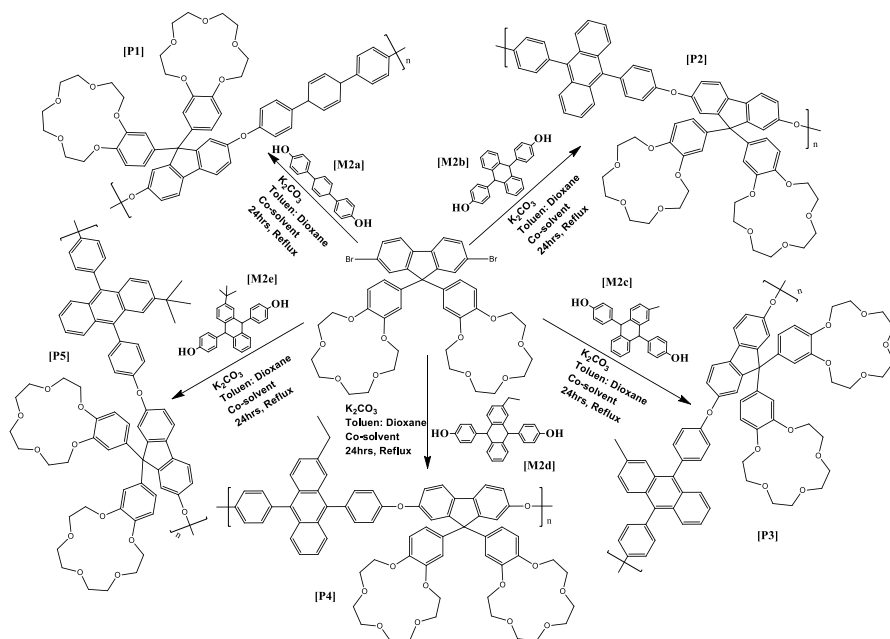
The mixture of 2,7-dibromo-9, 9-di(benzo-15-crown-5) fluorene monomer (**M1**) and di(p-hydroxyphenyl) acene (**M2**) monomer was taken in a three-necked round-bottom flask and pinch of potassium carbonate added as a base. Mixture of solvents toluene and dioxane (1:2) was added and refluxed for 12 h. After the polymerization was completed, excess (**M1**) monomer was added for end capping of hydroxyl groups. The reaction temperature was then reduced to room temperature and was added to water. The polymer was precipitated in methanol once the toluene solvent was evaporated and was further extracted using dichloromethane. The polymer obtained was dried in oven [17, 34–40].

Using the similar reaction scheme synthesis of series of (**P1–P5**) polymers was achieved (Fig. 4).

**P1** IR (KBr, pellet,  $\text{cm}^{-1}$ ): 3062 (s) [C–H, aromatic], 1590 (s) [C=C, aromatic], 2923 (s) [aliphatic C–H], 1470 (b) [aliphatic C–H], 1047 (s) [aromatic ether C–O–C], 1284 (s) [C–O–C, ether linkage]  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 3.72–4.09 (s, 3H, C–O–C), 6.70–7.65 (m, 24H, Ar–H);  $^{13}\text{C}$  NMR: (75 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 68.70 (carbon of C–O–C), 113.16–149.90 (aromatic Carbon).

**P2** IR (KBr, pellet,  $\text{cm}^{-1}$ ) : 3008 (s) [C–H, aromatic], 1587 (s) [C=C, aromatic], 2927 (s) [C–H, aliphatic], 1458 (b) [C–H, aliphatic], 1042 (s) [C–O–C, aromatic ether], 1276 (s) [C–O–C, ether linkage];  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 3.49–4.04 (t, 32H, C–O–C), 6.68–8.29 (m, 28H, Ar–H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 68.20 (carbon of –O–CH<sub>2</sub>), 123.33–159.25 (aromatic Carbon).

**P3** IR (KBr, pellet,  $\text{cm}^{-1}$ ): 2988 (s) [C–H, aromatic], 1590 (s) [C=C, aromatic], 2953 (s) [C–H, aliphatic], 1455 (b) [C–H, aliphatic], 1033 (s) [C–O–C, aromatic ether], 1278 (s) [C–O–C, ether linkage],  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 3.73–4.09 (t, 32H, C–O–C), 6.93–7.79 (m, 74H, Ar–H), 2.53 (s, 3H, –CH<sub>3</sub>);  $^{13}\text{C}$



**Fig. 4** Synthesis of polymers

NMR (75 MHz,  $CDCl_3$ ,  $\delta$  ppm): 24.7 (carbon of  $-CH_3$ ), 68.70 (carbon of  $C-O-C$ ), 134.135–160.00 (aromatic carbon).

**P4** IR (KBr, pellet,  $cm^{-1}$ ): 3072 (s) [C–H, aromatic], 1592 (s) [C=C, aromatic], 2968 (s) [aliphatic C–H], 1452 (b) [C–H, aliphatic], 1031 (s) [C–O–C, aromatic ether], 1268 (s) [C–O–C], ether linkage]  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $\delta$  ppm): 3.72 (t, 32H, C–O–C), 6.70–7.72 (m, 27H, Ar–H), 2.69 (q, 2H,  $-CH_2-$ ), 1.31 (t, 3H,  $-CH_3$ );  $^{13}C$  NMR: (75 MHz,  $CDCl_3$ ,  $\delta$  ppm): 14.50 (carbon of  $-CH_3$ ), 21.30 (carbon of  $-CH_2-$ ), 68.20 (carbon of  $C-O-C$ ), 134.10–160.00 (aromatic carbon).

**P5** IR (KBr, pellet,  $cm^{-1}$ ): 3008 (s) [C–H, aromatic], 1594 (s) [C=C, aromatic], 2943 (s) [aliphatic C–H], 1465 (b) [C–H, aliphatic], 1040 (s) [C–O–C, aromatic ether], 1287 (s) [C–O–C], ether linkage]  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $\delta$  ppm): 3.72–4.09 (s, 32H, C–O–C), 6.70–7.62 (m, 27H, Ar–H), 1.25 (s, 9H,  $-CH_3$ );  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ,  $\delta$  ppm): 30.99 (carbon of  $-CH_3$ ), 34.78 (tertiary carbon, 69.02 (carbon of  $C-O-C$ ), 113.16–158.69 (aromatic carbon).

## Results and discussion

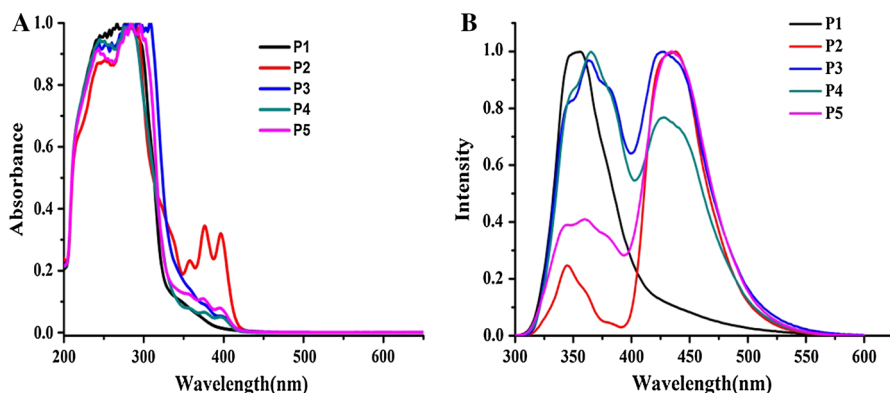
The series of fluorene-based crown-containing polymers were characterized by  $^1H$  NMR (Fig. S<sub>1</sub>),  $^{13}C$  NMR (Fig. S<sub>2</sub>), and IR spectroscopy (Fig. S<sub>3</sub>). The polymers obtained were studied for their photoluminescence, electroluminescence

and thermal properties, and their surface morphology was studied. Polymers with good solubility in common organic solvents, thermal stability and excellent emission properties were obtained.

### Photoluminescence studies

The absorption spectra of the polymers were recorded in THF solvent with the solutions of 10 ppm concentration. The polymers in the solution showed the intense absorption maxima in the range of 245–295 nm. Absorption spectra of all the derivatives were mainly comprised of the broad  $\pi-\pi^*$  transition band originating from the conjugation in the molecule. Figure 5 shows the normalized overlay absorption spectrum of the polymers in solution. A strong emission in the range from 300 to 600 nm with two maxima at about 341–365 and 435–440 nm was observed. The literature survey revealed that the region 380–500 nm reported for blue light emission of polymers **P1**, **P3** and **P4** showed higher intensity of emission maxima as compared to **P2** and **P5** in the same range of 341–365 and 435–440 nm (Fig. 5). For **P1** single maxima was observed and can be explained by increase in conjugation by benzene rings in the polymeric network **P3** and **P4** showed both maxima with higher intensity compared to **P2** and **P5**, which shows the effect of presence of alkyl group in the anthracene moiety.

The emission spectrum of the polymers obtained showed that the polymers were highly fluorescent. The optical band gaps of the polymers obtained from the emission and excitation spectra of the polymers were found in the range of 2.85–3.32 eV. The photoluminescence data of the polymers are shown in Table 1. All the polymers showed high quantum efficiencies in the range of 0.28–0.60. The optical band gap and fluorescence quantum yield suggested that polymer emits light in the blue region of the spectrum and can be used as desirable blue emitters for commercial applications in optoelectronics.



**Fig. 5** Normalized overlay **a** absorption **b** emission spectra of polymer in solution

**Table 1** Photophysical data of polymers

| Polymer   | $\lambda_{\text{Abs}}$ (nm) <sup>a</sup> | $\lambda_{\text{em}}$ (nm) <sup>b</sup> | $E_g$ (eV) <sup>c</sup> | Quantum yield ( $\phi_{\text{PL}}$ ) <sup>d,e</sup> |
|-----------|------------------------------------------|-----------------------------------------|-------------------------|-----------------------------------------------------|
| <b>P1</b> | 284                                      | 435                                     | 3.29                    | 0.29                                                |
| <b>P2</b> | 290                                      | 437                                     | 2.64                    | 0.47                                                |
| <b>P3</b> | 295                                      | 434                                     | 2.98                    | 0.32                                                |
| <b>P4</b> | 287                                      | 433                                     | 3.07                    | 0.67                                                |
| <b>P5</b> | 285                                      | 439                                     | 2.87                    | 0.38                                                |

<sup>a</sup>Absorption wavelength<sup>b</sup>Emission wavelength<sup>c</sup>Optical band gap calculated from the emission and excitation band<sup>d</sup>Measured in THF<sup>e</sup>Measured using 9, 10-DPA as standard

## Thermal studies

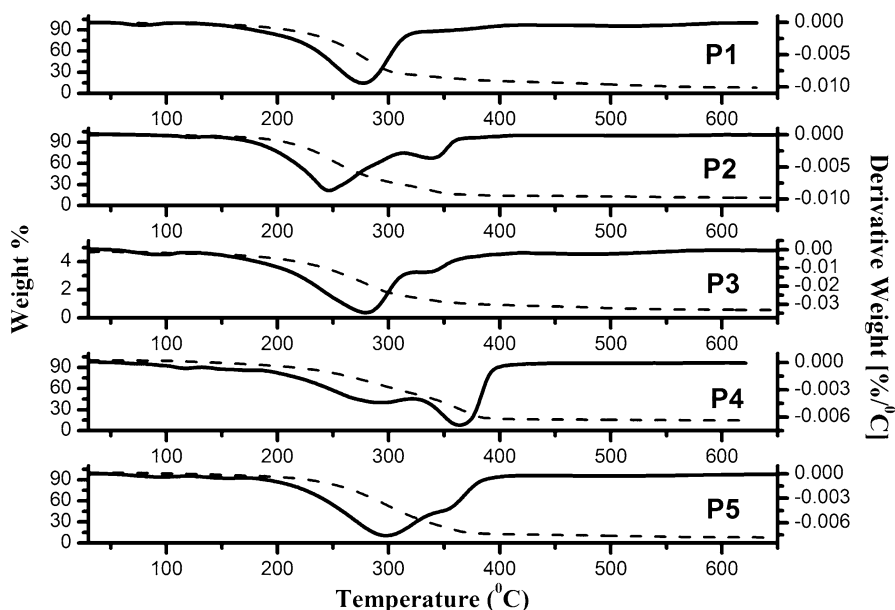
Thermal behaviour being one of the physical property of any material, it gives fair approximation of constituents and nature of material. The thermal properties of all polymers were investigated by TGA and DSC.

The TG study revealed that the polymers were thermally extra stable to varying degree. Gradual loss in weight due to decomposition of polymer by fragmentation with increase in temperature was observed in the thermogram of polymers. Polymers did not show significant weight loss below 100 °C indicating absences of moisture content (free moisture or bound moisture) in the polymer chain (Fig. 6).

In nitrogen atmosphere they exhibit decomposition onset temperature in the range of 200–800 °C (Table 2). This indicated that polymers were stable up to 200 °C and the onset of decomposition starts after 200 °C. Almost 80% decomposition of compounds takes place till 400 °C. It has been observed that **P1** undergoes loss in mass at about 305 °C, whereas **P2**, **P3**, **P4**, and **P5** undergo loss in mass in between 360 and 390 °C. As alkyl chain length increases, molecular weight increases and decomposition curve shifts to higher temperature. TG of the polymers also suggested that these polymers decomposed at higher temperature indicating their rigid and strong nature.

All the polymers showed glass transition temperatures (T<sub>g</sub>) ranging from 108 to 135 °C. This T<sub>g</sub> was relatively higher than that of typical polyfluorene 55 °C [49], signifying that the incorporation of the benzo crown ether and acene moiety enhances the thermal stability of fluorene-based polymers. Higher T<sub>g</sub> value has great importance for polymer functioning in LED applications.

The number average molecular weight (M<sub>n</sub>) and weight average molecular weight (M<sub>w</sub>) of polymers ranged from 4700 to 6576 and 4790 to 6588 respectively with polydispersity indices M<sub>w</sub>/M<sub>n</sub> of 1.00–1.01 [45]. The GPC data suggested that the average molecular weights of the polymers were low which might be due to non-accelerating polymerization reactions (Table 2) [46, 48–50].



**Fig. 6** Thermograms of polymers

**Table 2** Molecular weight and thermal analysis data of polymers

| Polymer   | Mn <sup>a</sup> | Mw   | Mw/Mn<br><b>D</b> | Td <sup>b</sup> (°C) | DTA peak<br>temp (°C) | Tg <sup>c</sup> (°C) |
|-----------|-----------------|------|-------------------|----------------------|-----------------------|----------------------|
| <b>P1</b> | 4700            | 4790 | 1.01              | 190–700              | 276                   | 114                  |
| <b>P2</b> | 5200            | 5228 | 1.00              | 200–700              | 248                   | 108                  |
| <b>P3</b> | 6398            | 6398 | 1.01              | 210–700              | 278                   | 128                  |
| <b>P4</b> | 5145            | 5145 | 1.00              | 220–700              | 368                   | 135                  |
| <b>P5</b> | 6576            | 6588 | 1.00              | 220–700              | 298                   | 127                  |

<sup>a</sup>Determined by GPC by eluting with THF, in comparison with polystyrene standard

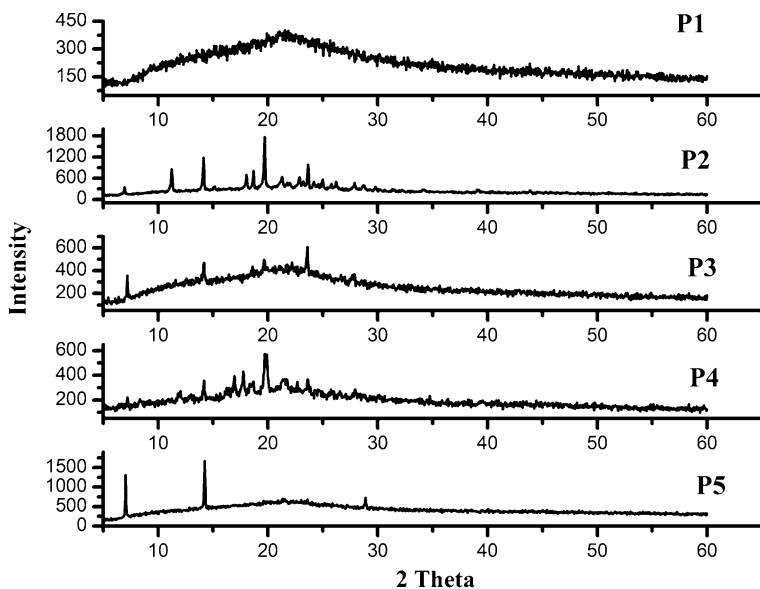
<sup>b</sup>Temperature at which a 5% weight loss occurred was determined at a heating rate of 10 °C/min under a nitrogen atmosphere

<sup>c</sup>The value of Tg was determined at a heating rate of 20 °C/min under a nitrogen atmosphere

## X-ray diffraction studies

Polymer crystallinity is one of the important properties of all polymers. Polymer exists in both crystalline and amorphous forms.

X-ray diffraction studies of the polymers were done to study the nature of polymer as crystalline or amorphous and to interpret the crystallite size of the new polymers. The compounds obtained were semi-crystalline in nature which was evident from the diffractograms shown in Fig. 7. Crystallite size of the polymer is



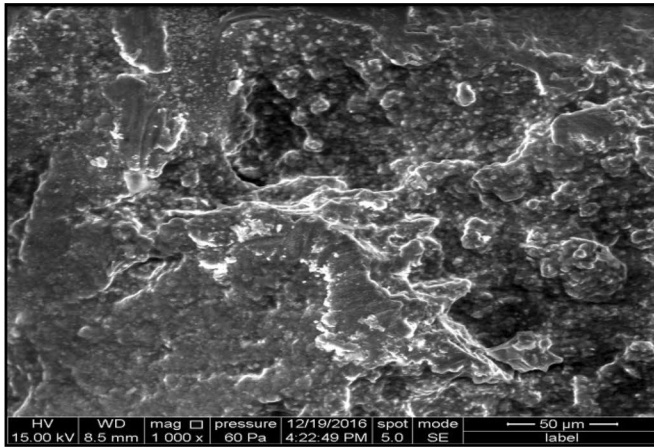
**Fig. 7** X-ray diffractograms of polymers

a significant factor in describing the nature of polymer and extent of crystallinity present in the polymer sample.

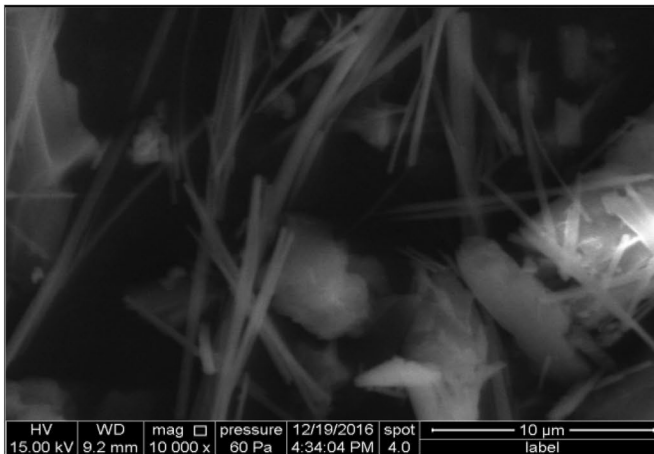
For polymers **P2**, **P3**, and **P5** the crystallite size was in the range from 3.3 to 10.3 Å (Table 2). The X-ray diffractograms of these polymers showed sharp, well-resolved peaks with varying intensity. Crystallite size calculated was less than 11 Å but greater than zero. For these polymers some of the peaks obtained were slightly higher in intensity with no noticeable broadening under the peaks being observed, suggesting crystalline nature of polymers. For polymers **P1**, **P4** crystallite size was in the range from 0.93 to 1.12 Å (Table 2). The X-ray diffractograms of these polymers showed broad, poorly resolved peaks with varying intensity, crystallite size calculated was less than 2 Å but greater than zero suggesting partial crystalline and amorphous nature of polymers.

## Surface morphology

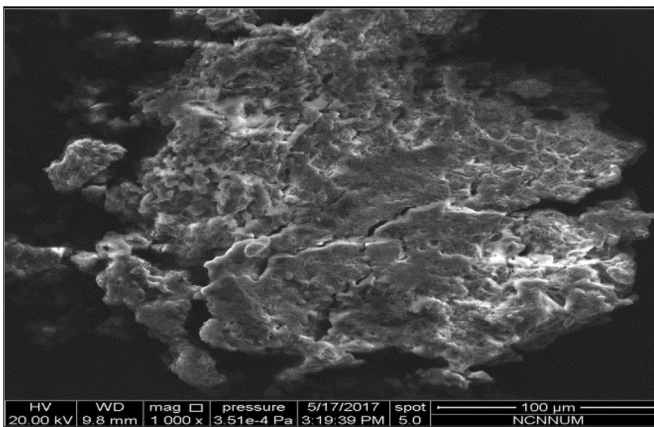
The surface morphology of crown-containing polymers was scrutinized by scanning electron microscopy (SEM) using Carl Zeiss supra-55VP with an operating voltage of 5.00 kV. The samples for SEM analysis were prepared by gold layer coating on the surface of the film by sputtering. The SEM microphotographs of synthesized new polymers are shown in Fig. 8. The images consisted of some large irregular crystals with coarse particles. The SEM photomicrographs of macro crystals showed platy rough structure, amorphous globular structure, and rock-shaped structure. The microscopic or macroscopic phase separation was not



P1



P2



P3

Fig. 8 SEM images of polymers

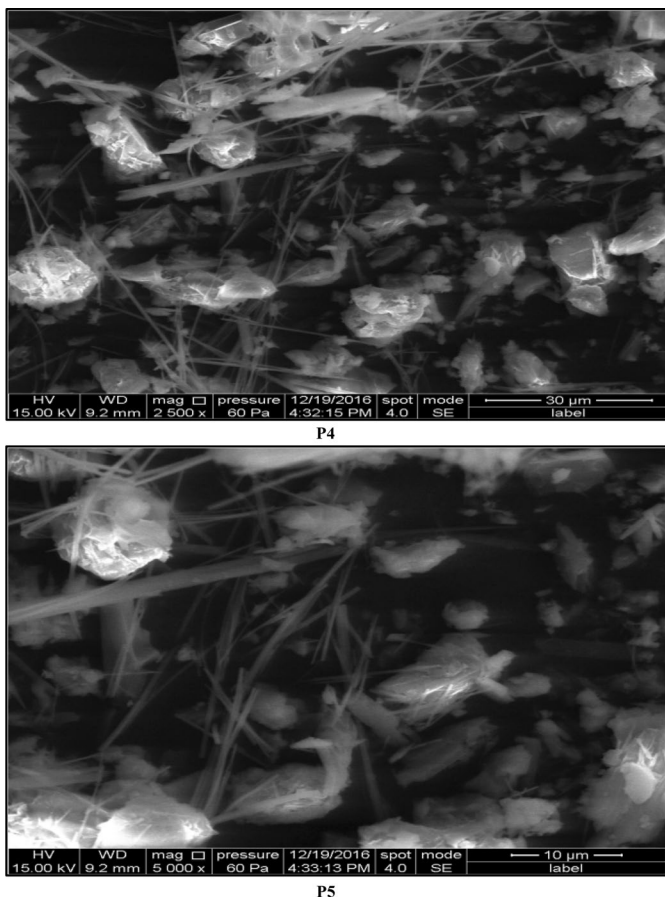


Fig. 8 (continued)

observed in the images. SEM study also showed that the **P2**, **P4**, and **P5** were crystalline in nature, whereas **P1** and **P3** were partially crystalline.

## Conclusion

Highly stable blue light-emitting conjugated polymers with pendant crown-substituted fluorene- and alkyl-substituted acene moiety were synthesized. Introduced benzo crown and acene into the polymer structure restricted the intermolecular interactions of fluorene moieties, rendered a better injection of holes by low oxidation potential and provided an improved polymer backbone emission. The resulting polymers displayed good PL and EL properties with blue emission, due to its combinations of good quantum yield, thermal stability and excellent colour stability.

We believe that these polymers are good aspirant in organic optoelectronics for blue light emission.

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