



Benzo crown ether functionalized conjugated polyfluorenes with anthracene fragment for sustainable light-emitting device technology

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Abstract

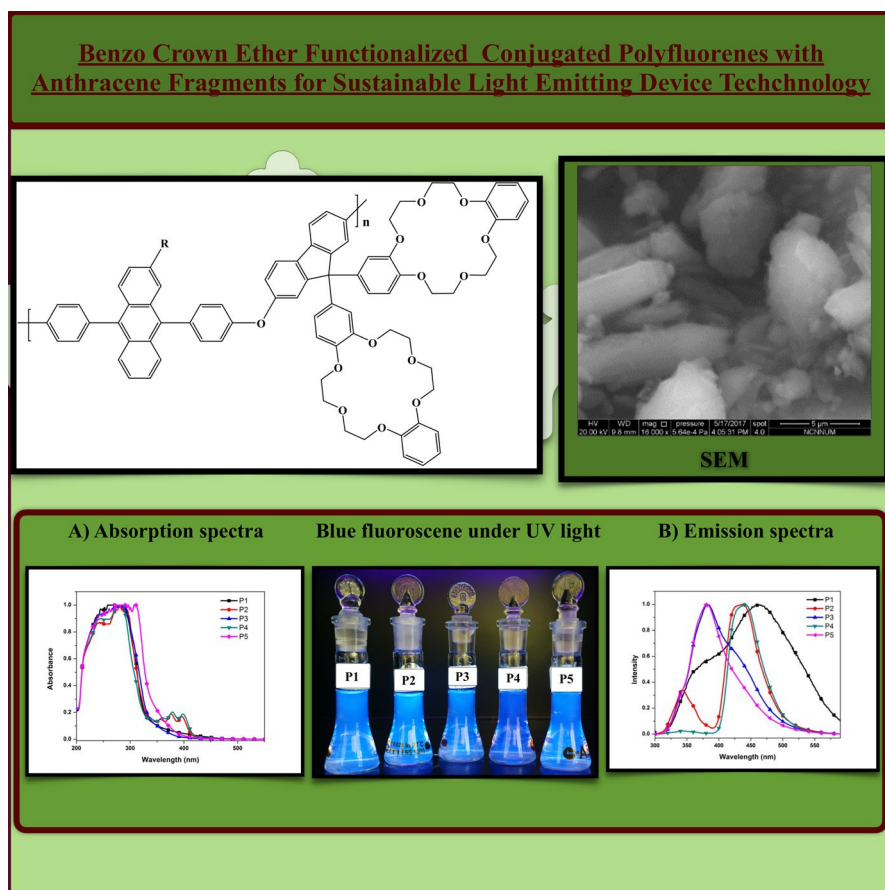
Dibenzo crown ether-substituted units of fluorene and acene-bearing copolymers have been successfully synthesized. FTIR, ¹H and ¹³C NMR spectroscopy, DSC, TGA and GPC were used to characterize the resulting copolymers (P1–P5). With fascinating quantum yield, the polymers showed large band gaps. With a polydispersity index of 1.58–2.21, these polymers showed a higher molecular weight (16,080–20,480). Strong thermal stability was indicated by DSC and TGA studies. The cyclic voltammetry analysis found that these polyfluorenes were stable in the range of 0.43–0.53 eV under redox conditions with HOMO and LUMO. For light-emitting materials, thermal stability and emission studies display strong results that are desirable.

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Graphic abstract



Keywords Dibenzo crown ether: acene units · Polyfluorenes · Photoluminescence · Cyclic voltammetry

Introduction

For academic and industrial research aimed at sustainable light-emitting system technology, improvement in light-emitting polymers is an extremely important goal [1]. Since the revolutionary 1987 study by Tang and VanSlyke of an operational organic light-emitting diode (OLED) device [2], several researchers from both academia and industry have been involved in achieving sustainable light-emitting displays. Conjugated light-emitting polymers became promising materials for device technology shortly after the discovery of polymer light-emitting diodes (PLEDs) in 1990 [3]. In order to improve PLED quality, the connection between the polymer

structure and the performance of the fabricated system is extremely significant. There are two significant factors that need to be addressed when applying polymers to PLED depending on the structure. One is the conjugated backbone from one repeating unit to another with the ability to delocalize π -electrons. Another factor is the conjugated backbone comprising charge transport and/or emission moieties that can also be tailored to achieve desired properties with certain electro active group [4–6]. Due to the capacity of charge transfer, quantum performance, thermal behavior and color tenability achieved by integrating low-band-gap organic moieties, interest in conjugated polyfluorenes has been steadily increased. As a result, polyfluorene research has increased due to its possible use in OLED tuning [7–9]. In addition, researchers are seeking to reduce polyfluorene-related disadvantages. Fluorene copolymerization with anthracene [10, 11] or donor–acceptor units [12, 13] or end capping with organic moieties that are sterically damaged [14–16] or sterically impaired use suppresses the undesirable emission of long wavelengths. The feature of acene shows high emission intensities and is one of the most assured blue-emitting materials. Anthracene and its derivatives for thermal stability and electroluminescence efficiency [19–22] have recently been tested by Shi [17] and Tang et al. [18].

As an electron transport part in polyfluorenes, Chen and co-workers grafted ether to improve electroluminescence desirable for solar cells. The emission properties of conjugated fluorine copolymers have also been stated to be further enhanced by alkyl modification with aryl groups or by incorporation of the acene moiety into the main chain [23]. The introduction of crown ether as a side group also decreases the levels of LUMO and HOMO, which are efficient in improving electron injection and the efficiency of organic electroluminescence devices [24–33].

The analysis of the properties of conjugated polyfluorenes based on dibenzo crown ether substituted fluorene and acene fragment has been demonstrated in this paper. The aggregate/excimer suppressed polymers with high PL quantum efficiencies desirable for LEDs [34] were these crown ether-based conjugated polyfluorenes.

Experimental methods

Materials

A.R. grade chemicals required were purchased from Sigma-Aldrich. Only THF was distilled using sodium–benzophenone ketyl. Crown ether and dibromofluorene were ordered from S D Fine Chem-Limited India and Sigma-Aldrich, respectively. Nitrogen atmosphere was employed while conducting all synthetic processes.

Instrumentation

Euro Vector EA-3000 instrument was used for elemental analysis of M1 and M2. PerkinElmer 1600 series FTIR instrument was used for infrared analysis. Bruker AMX-300 NMR spectrometer was used for ^1H and ^{13}C analysis. Star system Mettler

Toledo TGA instrument with N₂ atmosphere was used for thermal stability study. PL analysis was done on Shimadzu spectrofluorophotometer RF-5310. Shimadzu UV-2100 spectrophotometer was used to record UV–Visible spectra. Morphology was studied on Cameca (France) model SU-30 SEM instrument. The X-Ray diffractograms were recorded on Shimadzu XRD-7000. PerkinElmer series 200 GPC was used for molecular weight determination.

Synthesis of monomers

Synthesis of monomer M1

In the mixture of 2, 7 dibromofluorene (0.972 g, 0.0030 mmol) and 50% aq NaOH (5 mL), tetrabutylammonium iodide (0.046 g, 10 mol %) was added. This mixture was transferred into a flask maintaining with nitrogen environment. A bromo dibenzo crown (0.971 g, 0.0028 mmol) was slowly added in this mixture which was then heated to 100–110 °C for 5 h. The obtained product was isolated and purified in pet ether (Yield 65%) (Fig. 1) [34].

M. P. 123–125 °C.

FTIR (KBr) cm⁻¹: 2960, 1448, 3070, 1499, 2860.84.

¹H NMR (300 MHz, CDCl₃, δ ppm): 3.79 (t, 8H) 4.11 (t, 4H), (7.2–6.68 (m, 20H); ¹³C NMR (75 MHz, CDCl₃, δ ppm): 113.00–149.49 (aromatic carbon); 69.59–69.92 (–OCH₂). Anal calcd for: C₅₃H₅₂O₁₂Br₂: C, 61.15; H 5.0%. Found: C 60.81, H 4.96 %.

General synthesis of monomer M2

This monomer was synthesized and characterized by the method reported in our previous investigation [32–34]. By using various quinones, five different acene monomers were (M2a, M2b, M2c, M2d and M2e) obtained. (Fig. S₁ and Fig. S₂ supporting information).

General polymerization

Monomer M1, and M2 were mixed in a bottom flask. Few milligrams of potassium carbonate were added into this mixture. Then, toluene and dioxane in 1:2 were added in the flask and refluxed for 12 hours. Excess of M1 was added after polymerization.

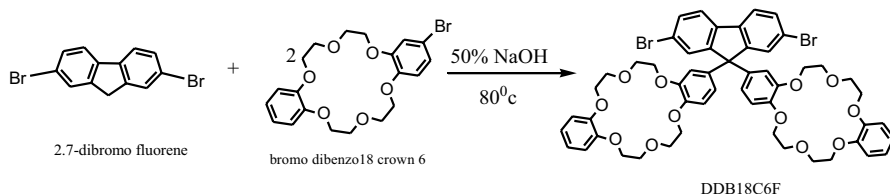


Fig. 1 Synthesis of 2, 7-Dibromo-9, 9-di (dibenzo 18crown 6)—fluorene monomer

Then water was added to the flask. The solvent was evaporated to precipitate the polymer and was further extracted using dichloromethane [34–39]. Changing monomers M2a, M2b, M2c, M2d and M2e, polymers P1–P5 were prepared (Fig. 2).

All these polyfluorenes were well characterized by various techniques (Data included in supporting information).

Results and discussion

The polymers (P1–P5) were characterized by ^1H (Fig. S₃), ^{13}C NMR (Fig. S₄), and FTIR (Fig. S₅) spectroscopy. Benzo crown ether functionalized conjugated polyfluorenes prepared in the present investigation are having good solubility in various organic solvents.

Optical study of the polymers

The solution (THF, 10 ppm) of benzo crown ether functionalized conjugated polyfluorenes exhibited a deep absorption in 345 to 405 nm wavelength due to the over transition of fluorene moiety [40–42]. The PL analysis showed that the maximum emission for these polymers was between 300 and 600 nm (Fig. 3), consisting of two maximums of approximately 341–365 nm and 435–465 nm, both regions were elongated to blue emission [32, 33]. The band gap observed was 2.65–3.63 eV [34, 43,

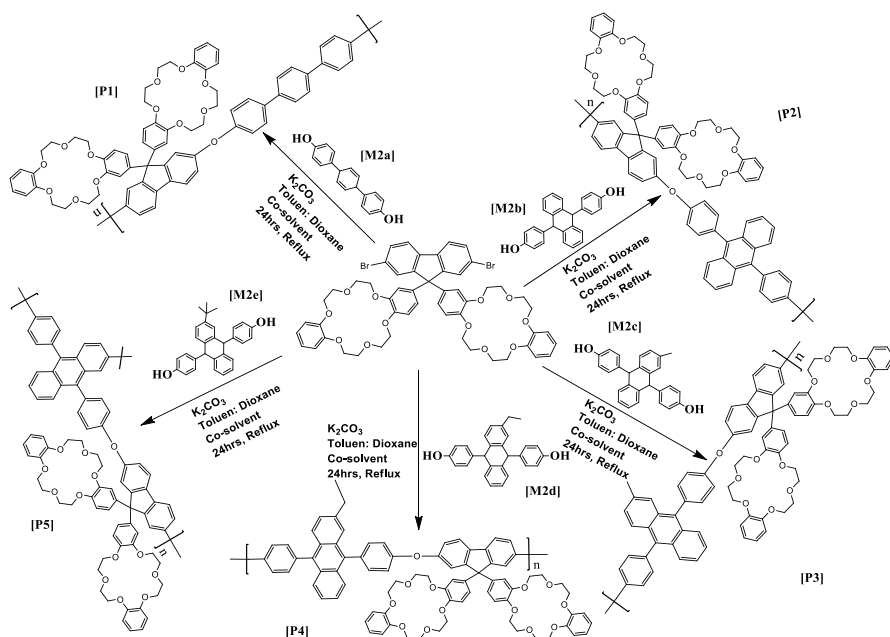


Fig. 2 Synthesis of polymers

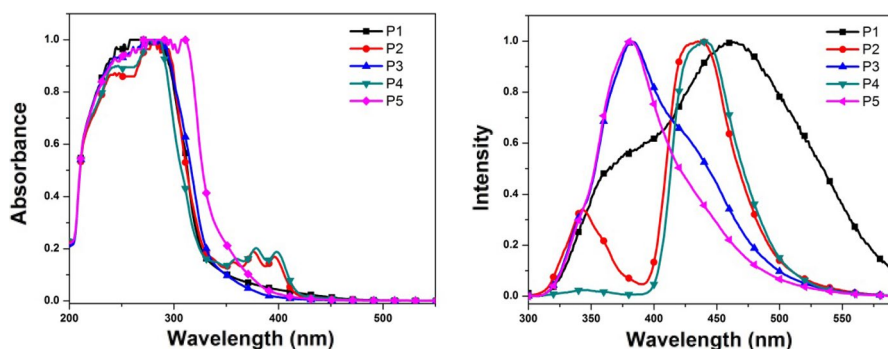


Fig. 3 Normalized overlay Absorption and Emission spectra

44]. The higher quantum efficiencies of these polymers were observed in the range 0.28–0.60 (Table 1). Higher values of band gaps and PL quantum yield have meant that these blue light-emitting conjugate polymers can be of use in sustainable light-emitting system technology [45].

Thermal study

Thermograms of benzo crown ether functionalized conjugated polyfluorenes show that these polymers have excellent thermal stability. Weight loss was observed due to polymer degradation [46–48]. No weight was observed below 100 °C suggesting the absence of water moisture in the polymer chain (Fig. 4, Table 2).

The observed onset temperature was between 200 and 800 °C while the onset of the decomposition temperature was observed after 200 °C. It also suggested that these polymers were thermally stable up to 200 °C. Almost 80% of the decomposition takes place around 400 °C. Maximum decomposition of P1 was observed to be about 365 °C, while for other polymers, maximum decomposition was observed to be between 360 and 380 °C. TG of the polymers also suggested that their higher decomposition temperature would mean their rigidity.

Table 1 Photo-physical data of polyfluorenes

Polymer	λ_{Abs} (nm) ^a (nm) ^a	λ_{em} (nm) ^b	E_g (eV) ^c	Quantum yield (ϕ_{PL}) ^{d,e}
P1	285	463	2.79	0.29
P2	284	435	3.10	0.47
P3	285	424	2.82	0.32
P4	287	441	3.08	0.67
P5	283	430	3.04	0.38

^aAbsorption wavelength, ^bemission wavelength, ^coptical band gap calculated from the emission and excitation band, ^dmeasured in THF, ^emeasured using 9, 10-DPA as standard

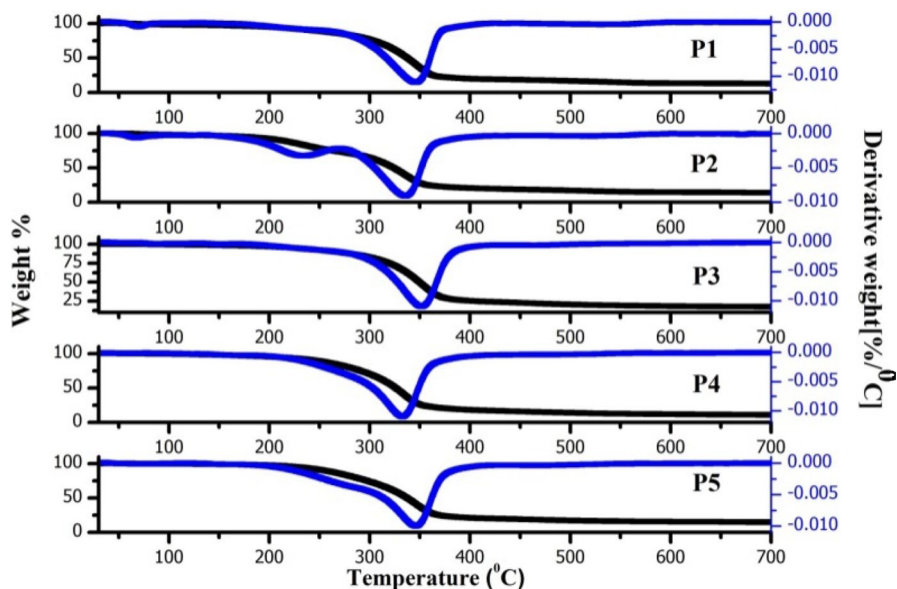


Fig. 4 Thermograms of polyfluorenes

Table 2 Molecular weight and thermal analysis data of polyfluorenes

Polymer	M_n^a	M_w	M_w/M_n Đ	Td ^b (°C)	DTA Peak Temp (°C)	Tg ^c (°C)
P1	16,080	28,140	1.75	190–700	276	114
P2	18,360	40,576	2.21	200–700	248	108
P3	17,332	27,385	1.58	210–700	278	128
P4	20,032	43,069	2.15	220–700	368	135
P5	20,480	40,550	1.98	220–700	298	127

^aDetermined by GPC by eluting with THF, by comparison with polystyrene standard, ^btemperature at which a 5% weight loss occurred was determined at a heating rate of 10 °C/min under a nitrogen atmosphere

^cThe value of Tg was determined at a heating rate of 20 °C/min under a nitrogen atmosphere

DSC research indicated that glass transition temperatures (T_g) were observed between 120 and 140 °C. No crystallization or melting point peaks were observed in TG. These T_g values were comparatively higher than the polyfluorene value of 55 °C [49, 50] which means that the insertion of crown ether moiety and aromatic feature increased thermal stability [34]. Organic light-emitting diodes must be built from materials with reasonably high T_g value in order to prevent problems associated with the formation of aggregates and excimers after exposure to heat [49, 50]. Higher T_g value is of enormous importance for polymer processing in advanced optical and electronic products based on conjugated polymers. Thermal analysis

has also established that these dibenzo crown ether functionalized conjugated polymers may play an important role in the technology of sustainable light-emitting devices.

Molecular weights of the polymers

GPC analysis showed that, average molecular weights M_n and M_w of polymers were in the range of 16080–20480 and 28140–43069, respectively, whereas PDI calculated from these molecular weights was in the range of indices M_w/M_n of 1.58–2.21. (Table 2) [32, 51–55].

X-ray diffraction study

The nature of polyfluorenes and its crystallinity can be in terms of their crystallite size. The data indicated their semi-crystalline nature (Fig. 5). For polymers P1 and P3, area under the peak shown was slightly broad as compared to polymer P2, P4 and P5. Therefore, these polymers were considered to be more crystalline (3.2–10.33 Å) than P1 and P3 (0.93–1.12 Å). The corresponding data of polymer is summarized in Table S₁.

Surface morphology

The SEM images of benzo crown ether functionalized conjugated polyfluorenes are shown in Fig. 6. In some cases, large intermittent crystals were observed. The

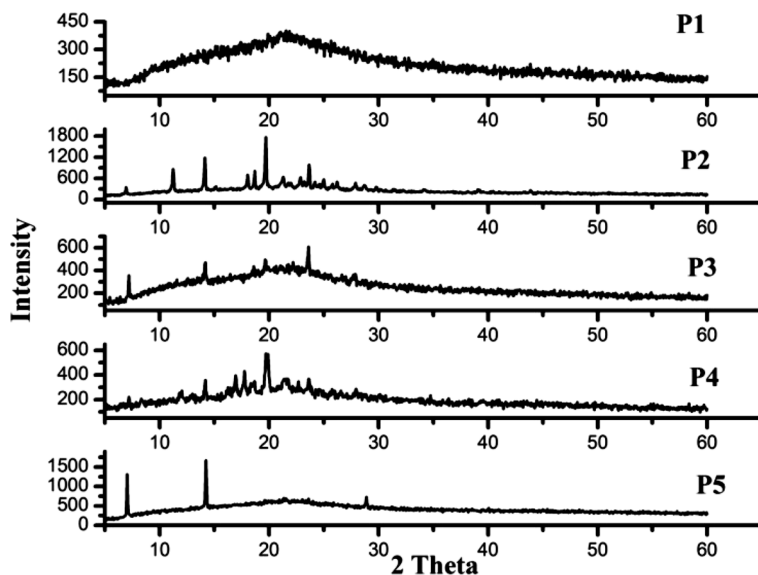


Fig. 5 X-ray diffractograms of polyfluorenes

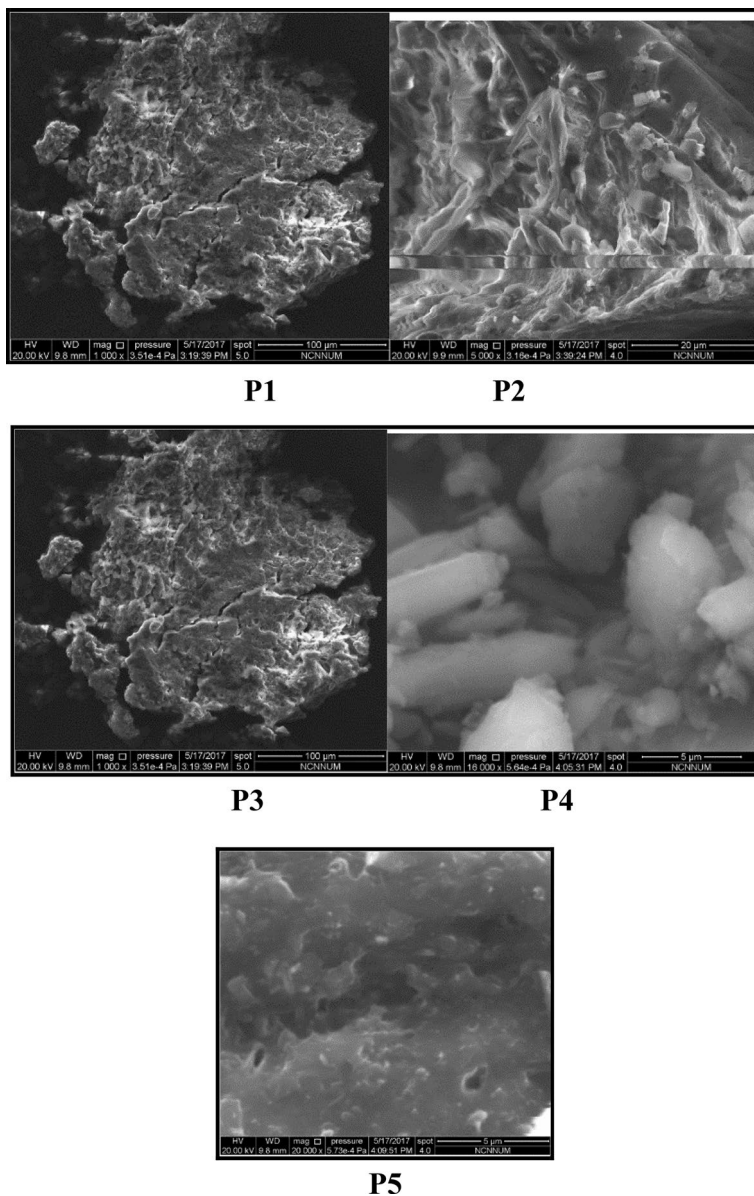


Fig. 6 SEM images of polyfluorenes

morphology also exhibited disheveled, irregular globoid and rough shaped structure. Further, SEM study established crystalline in nature of P2, P4 and P5 polyfluorenes, whereas polyfluorenes P1, P3 were semi-crystalline in nature.

Electrochemical study of the polymers

Cyclic measurement of benzo crown ether functionalized conjugated polyfluorides was performed on a glass carbon electrode of 0.1 M tertiary butyl ammonium hexafluorophosphate (TBAPF₆) in anhydrous DCM using standard ferrocene using a scan rate of 50 mV s⁻¹ at room temperature. Platinum wire and silver/silver chloride counter and reference electrode were used, respectively.

A cyclic voltammetry analysis of the synthesized polymers was performed to analyze their redox behavior. The oxidation half potential (Fig. 7) of the synthesized polymers observed against the reference electrode and the corresponding data are summarized in Table S2. The energy levels of HOMO and LUMO were determined in relation to the onset potential of oxidation and the observed reductions [56–61]. The band gaps for these polyfluorenes ranged from 2.79 to 3.10 eV [62, 63].

As shown in Fig. 7, polyfluorenes exhibited halfway reversibility in both n and p-doping processes in this sample. High EHOMO values confirm that synthesized polymers are suitable for high voltage device applications and sustainable light-emitting devices technology [64].

Conclusion

Benzo crown ether functionalized conjugated polyfluorins with alkyl substituted acetate fragments have been successfully synthesized and investigated as emissive materials suitable for PLEDs. TGA has shown that polymers demonstrate excellent thermal stability. The introduction of dibenzo crown feature along with ace moiety into polymer decreases the intermolecular forces due to fluorene, achieves a good

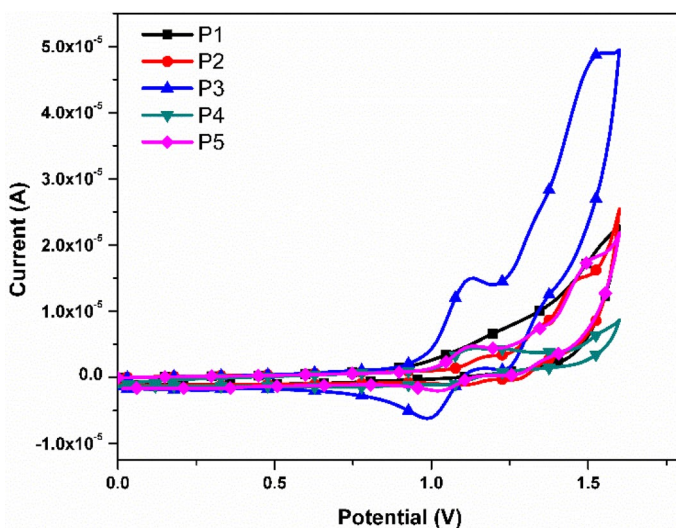


Fig. 7 Cyclic voltammograms of polyfluorenes

quality hole injection and increases the emission properties. We assume that these polymers have the potential to achieve the objective of light-emitting device technology that is viable for solid state lighting and displays.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00289-021-03617-w>.

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