




Blue light-emitting fluorene–dendron hybridized polymers: optophysical features

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Abstract

In this manuscript, we have demonstrated an efficient and rapid synthetic strategy for preparation of new fluorene–dendron-hybridized blue light-emitting polymers P1–P7 by the reaction of 9,9 long-chain dialkylated fluorenes M2–M8 with dendronized monomer (M1) under microwave-assisted reaction condition. These fluorene–dendron-hybridized polymers P1–P7 were characterized using different spectroscopic techniques. Furthermore, the optophysical properties of these polymers P1–P7 were studied which revealed that these synthesized polymers P1–P7 have potential to emerge as capable materials in the development of diodes, particularly for blue light emission. In the future, similar approaches would be utilized for preparation of light-emitting polymer composite.

Keywords Polyphenylene · Fluorene · Dendron · Blue light-emitting polymers

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Introduction

Conjugated polymers can be incorporated in various electronic materials like composites, diodes, transistors, light-emitting diodes [1, 2]. Similar approaches for light-emitting polymers are associated with epoxy materials and its nanocomposites [1–5]. Light-emitting polymers find major applications in large and small area devices such as displays, thin and flat light sources, cloth-type PLEDs, PLEDs in wearable electronics [6].

In the context of ample applications of polymeric materials in diverse fields, the development in the field of polymers is continually progressing [7–12]. In the family of conjugated polymers, “dendronized polymers” have embraced reputed space where they are explored as an efficient light-emitting material because of their unique structural features and properties [13–18]. There are reports on biopolymer showing good diffraction, absorption, light-emitting properties in the presence and absence of metal nanoparticles [19–22]. However, they have limited application due to low stability at ambient conditions [23–26]. Dendronized polymers have compact spherical geometry with three-dimensional tree-like branching arrangement. In the same way, fluorene-based polymers have also emerged as an obvious aspirant in optoelectronics due to their excellent thermal and optical stability. Fluorene-based polymers also possess high fluorescence quantum efficiency, photoluminescence (PL), and electroluminescence efficiency [27–29]. Literature review has revealed number of examples of such materials exhibiting hopeful results in electrochromic devices [30–40]. To be particular, the 9,9 long-chain dialkylated fluorenes are very potential candidates in the exploration of blue-emitting materials for PLEDs [41, 42]. Our exhaustive literature study of polymer framework exposed that their properties can be tuned through incorporating electron releasing or withdrawing groups in parent fluorene molecule using electrophilic or nucleophilic substitution reactions [43]. In addition to this, fluorene molecule can be structurally modified at 9th position by changing substituent on methylene carbon of fluorene. This fact provides an additional scope for synthesis of fluorene-based molecular framework by substitution on methylene group of the fluorene molecule.

Nowadays, demands for conjugated polymers are increasing drastically due to their potential applications in optoelectronic materials. Hence, there is an essential need to develop the new and rapid method for polymer production enabling its utilization in OLED's [44, 45]. Literature search showed that Kenneth et al. [46] have developed method for the synthesis of homopolymers of fluorene with 9,9 dialkyl substitution (Fig. 1A). Similarly, Setayesh et al. have also reported a method for preparation of 9,9 di(polyphenylene)-benzyl)-substituted fluorene homopolymers (Fig. 1B). Due to significant importance of both of these structural units in polymeric framework, it is highly desirable to prepare a new polymer containing both of these units. In this context and continuation of our research work in the synthesis of macromolecular framework [47–52], we herein report the nickel (0)-mediated, microwave-assisted polymerization process for synthesis of new fluorene–dendron-hybridized polymers containing 9,9 long-chain

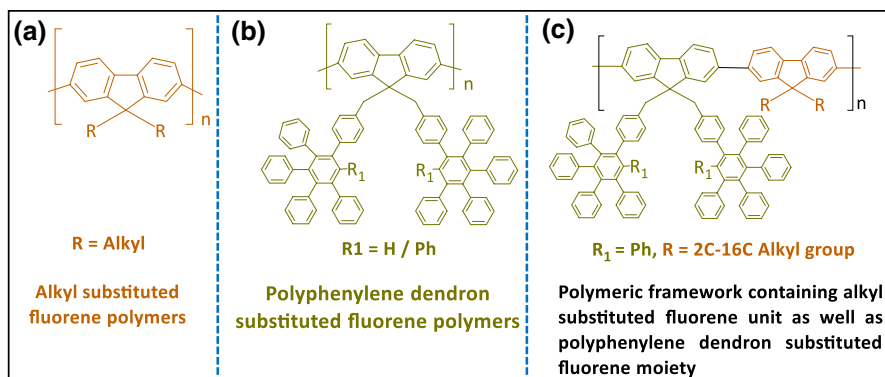


Fig.1 Envisioned polymeric framework

dialkylated fluorenes M2–M8 and dendronized monomer (M1) (Fig. 1C). Additionally, we also report the characterization and optophysical study of these newly synthesized polymers.

Experimental

All chemicals were procured from Sigma-Aldrich and S D Fine-Chem, Mumbai. All chemicals were of A.R. grade and used without further treatment. Glasswares were properly washed with deionized water and dried in oven.

Synthesis of polymers

Prepared 20 ml of *N,N*,dimethyl formamide: toluene (1:4) solvent system to that 0.5 g of bis(1,5-cyclooctadiene)nickel (0), 0.35 g 2,2'-bipyridine, and 0.25 ml cyclooctadiene was added under inert atmosphere. After stirring this mixture, addition of dendronized monomer (M1) 0.250 g and 2,7-dibromo-9,9-diethylfluorene (M2) 0.250 g was accomplished. Then, the reaction vessel was sealed and kept in microwave reactor assembly for 20 min irradiation at 130 °C temperature using 300 W power. The end capping was done by addition of 5 ml of bromobenzene to the reaction mixture. Heating was continued for another 5 min. under identical condition. The above reaction mixture was cooled and diluted by adding 20 ml of dichloromethane and washed with sufficient quantity of deionized water to collect dichloromethane phase which was dried over anhydrous magnesium sulphate (MgSO_4) and subjected to evaporation. Before complete drying, it was treated with 20 ml 0.5 M methanolic HCl solution to afford precipitate of the desired fluorene–dendron-hybridized polymers (P1–P7), respectively (all name of polymers are mentioned in supporting information section).

Instrumentation and characterization of synthesized polymers

UV–visible spectroscopic analysis was performed using LAB UV3000plus at ambient temperature with quartz cuvette of 1 cm path-length as a sample holder (200–800 nm). Fluorescence emissions measurement were carried out by RF-5301PC SHIMADZU at ambient temperature with quartz cuvette of 1 × 1 cm path-length (emission at 200 to 800 nm). All cyclic voltametric measurements have been performed using three electrode cell on Electrochemical Work Station, model Autolab PGSTAT 30. Gel permeation chromatograms (GPC) were 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 lm mixed-B, 300 × 7.5. Thermal analysis of polymers was performed with PerkinElmer assembly using 10 °C/min heating rate and nitrogen atmosphere. The X-ray diffraction pattern of the polymers was recorded using Shimadzu maxima 7000 X-ray diffractometer with CuK α radiation ($\lambda = 0.154060$ nm) with the scanning range between 5° and 80° to determine its nature (crystalline/amorphous). The surface morphology of polymers was analyzed by SEM. The ^1H NMR spectra of the polymers were recorded at 500 MHz using Bruker (Advance) NMR instrument in CDCl_3 solvent. Chemical shifts were reported in δ (ppm) values relative to the internal standard tetramethyl silane (TMS). FT-IR spectrum was recorded in the transmittance range of 4000 to 400 cm^{-1} on PerkinElmer FT-IR spectrometer using Frontier using ATR, and transmittances are reported in cm^{-1} .

Polymer P1 Nature: solid, Color: Green, Yield: 93.10%. ^1H NMR (ppm): δ 0.50–1.53 (m, 50H), 3.18 (s, 20H), 6.83–7.82 (m, 360H of aromatic proton) ppm. FT-IR: 2917 cm^{-1} C–H stretching, 1441 cm^{-1} C–H bending, 1600 cm^{-1} aromatic C=C stretching, 3023 cm^{-1} aromatic C–H stretching, 1495 cm^{-1} C–C stretching.

Polymer P2 Nature: solid, Color: Brown, Yield: 94.3%. ^1H NMR (ppm): δ 0.64–1.93 (m, 84H), 3.14 (s, 24H), 6.81–7.52 (m, 432H of aromatic proton) ppm. FT-IR: (cm^{-1})=2927 cm^{-1} C–H stretching, 1440 cm^{-1} C–H bending, 1599 cm^{-1} aromatic C=C stretching, 3024 cm^{-1} aromatic C–H stretching, 1496 cm^{-1} C–C stretching.

Polymer P3 Nature: solid, Color: Brown, Yield:95.4%. ^1H NMR (ppm): δ 0.58–1.94 (m, 90H), 3.14 (s, 20H), 6.81–7.52 (m, 360H of aromatic proton) ppm. FT-IR: 2926 cm^{-1} C–H stretching, 1442 cm^{-1} C–H bending, 1599 cm^{-1} aromatic C=C stretching, 2980 cm^{-1} aromatic C–H stretching, 1495 cm^{-1} C–C stretching.

Polymer P4 Nature: solid, Color: Brown, Yield: 94.3%. ^1H NMR (ppm): δ 0.75–1.93 (m, 132H), 3.14 (s, 24H), 6.81–7.49 (m, 432H of aromatic proton) ppm. FT-IR: 2925 cm^{-1} C–H stretching, 1442 cm^{-1} C–H bending, 1599 cm^{-1} aromatic C=C stretching, 3016 cm^{-1} aromatic C–H stretching, 1496 cm^{-1} C–C stretching.

Polymer P5 Nature: solid, Color: Light yellow, Yield: 96.7%. ^1H NMR (ppm): δ 0.58–1.93 (m, 180H), 3.14 (s, 24H), 6.81–7.53 (m, 432H of aromatic proton) ppm. FT-IR: 2926 cm^{-1} C–H stretching, 1441 cm^{-1} C–H bending, 1600 cm^{-1} aromatic C=C stretching, 3025 cm^{-1} aromatic C–H stretching, 1497 cm^{-1} C–C stretching.

Polymer P6 Nature: solid, Color: Brown, Yield: 96.4%. ^1H NMR (ppm): δ 0.57–1.93 (m, 204H), 3.39 (s, 24H), 7.25–8.36 (m, 432H of aromatic proton) ppm.

FT-IR: 2922 cm^{-1} C–H stretching, 1441 cm^{-1} C–H bending, 1599 cm^{-1} aromatic C=C stretching, 3025 cm^{-1} aromatic C–H stretching, 1495 cm^{-1} C–C stretching.

Polymer P7 Nature: solid, Color: Brown, Yield: 93.3%. ^1H NMR (ppm): δ 0.89–1.95 (m, 330H of alkyl group), 3.35 (s, 20H of benzyl group), 6.73–7.25 (m, 360H of aromatic proton) ppm. FT-IR: 2921 cm^{-1} C–H stretching, 1441 cm^{-1} C–H bending, 1577 cm^{-1} aromatic C=C stretching, 3024 cm^{-1} aromatic C–H stretching, 1496 cm^{-1} C–C stretching.

Results and discussion

Synthesis of fluorene–dendron-hybridized polymers P1–P7

This synthetic approach utilizes microwave as microwave-assisted synthesis methods are rapid and provide uniform heating. This process is also an energy savings with higher yield and cost-effective. Compared to the conventional methods, this method gives small narrow particle size distribution and high purity. The synthesis of 2,7-dibromo-9,9-di(4-pentaphenylphenyl)-benzyl fluorene (M1) monomer was achieved by using previously published work [47–52], and 9,9 long-chain dialkylated fluorene monomers (M2–M8) were synthesized by using method reported by Saikia et al. [39]. The method involves the nucleophilic substitution reaction of 2,7-dibromofluorene with various alkyl bromides under aqueous–organic medium in the presence of TBAI at 100–110 $^{\circ}\text{C}$ for 5 h. Thus, we decided to investigate microwave-assisted polymerization process for the synthesis of fluorene–dendron-hybridized polymers containing 9,9 long-chain dialkylated fluorenes M2–M8 and dendronized monomer (M1) [53–55]. We have taken 20 ml of *N,N*,dimethyl formamide: toluene (1:4) solvent system in which 0.5 g of bis(1,5-cyclooctadiene)nickel (0), 0.35 g 2,2'-bipyridine, and 0.25 ml cyclooctadiene were added under inert atmosphere. After stirring this mixture, addition of dendronized monomer (M1) 0.250 g and 2,7-dibromo-9,9-diethylfluorene (M2) 0.250 g was accomplished. Then, the reaction vessel was sealed and kept in microwave reactor assembly for 20 min, irradiation at 130 $^{\circ}\text{C}$ temperature using 300 W power. The end capping was done by the addition of 5 ml of bromobenzene to reaction mixture and continued the heating for another 5 min under identical parameters. The above mixture was cooled and diluted by adding 20 ml dichloromethane and washed with H_2O to collect dichloromethane phase which was dried over anhydrous MgSO_4 and evaporated. Before complete drying, it was treated with 20 ml 0.5 M methanolic HCl solution to afford 93.1% yield of green color solid product. The obtained product was extensively characterized by different spectroscopic techniques and gel permeation chromatography (GPC). The characterization data confirmed the formation of desired polymer P1. Further this reaction condition was also tested for polymerization of other monomers M3, M4, M5, M6, M7, M8 and found equally efficient. In this way, we have synthesized fluorene–dendron-hybridized polymers P1–P7 using microwave irradiation with bis(1,5-cyclooctadiene) nickel (0), 2,2'-bipyridyl, cyclooctadiene, in *N,N*,dimethyl formamide: toluene (1:4) solvent system at 300 W power at 130 $^{\circ}\text{C}$ for 20 min

under inert atmosphere (Fig. 2). Formation of all synthesized polymers P1–P7 was confirmed by various characterization techniques.

Optophysical study of the polymers

Table 1 contains the optophysical study data of fluorene–dendron-hybridized polymers P1–P7 recorded using tetrahydrofuran. Figure 3a, b shows the absorption and photoluminescence spectrums, respectively. In this study, the fluorene–dendron-hybridized polymers P1–P7 exhibited an absorption peak at 344–385 nm that can be assigned to the $\pi \rightarrow \pi^*$ transition due to presence of fluorene unit. Furthermore, the observed emission peaks in the range of 436–444 nm in photoluminescence spectrums are a characteristics peak of polymers framework. This optophysical study of the polymers revealed that synthesized series of fluorene–dendron-hybridized

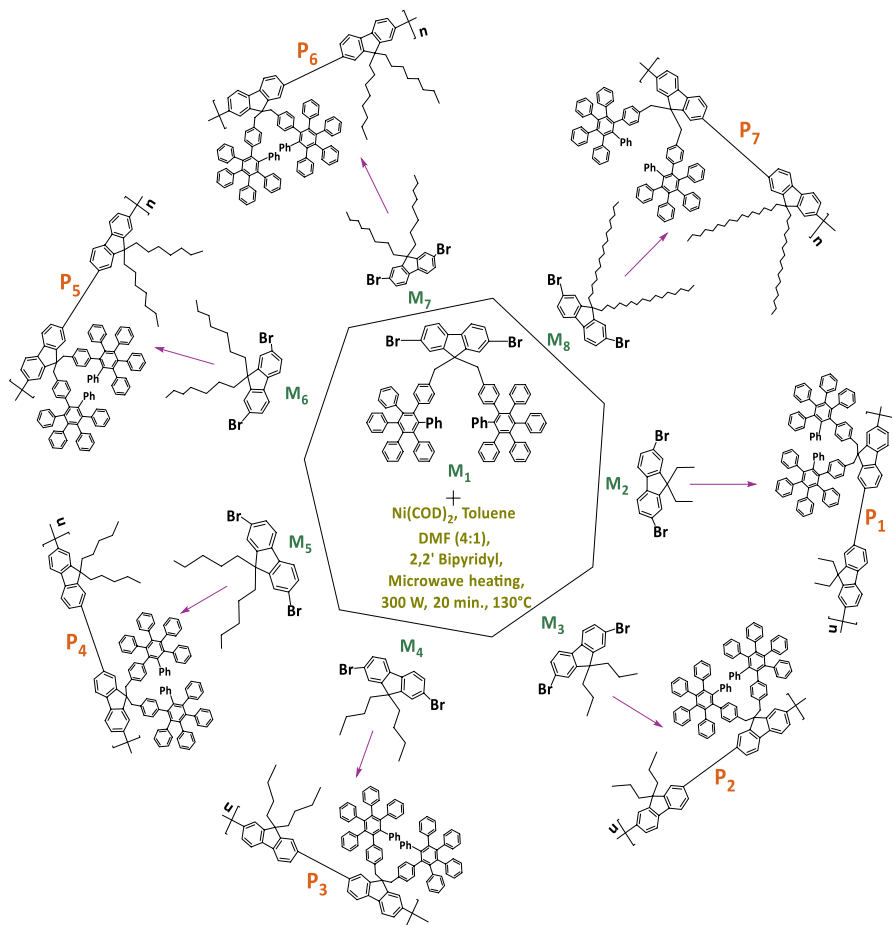
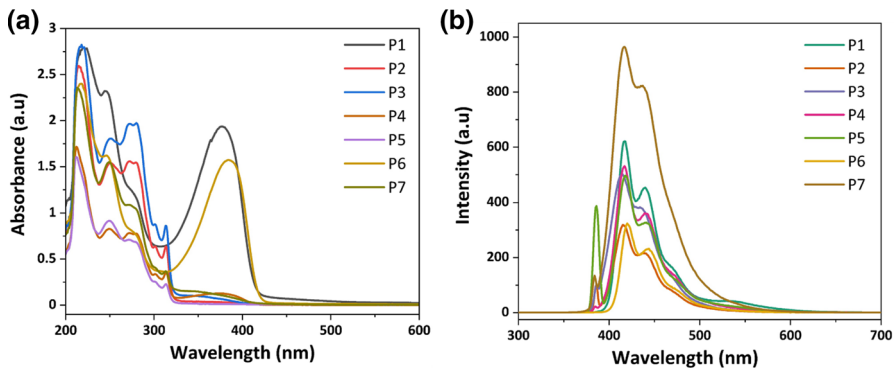


Fig. 2 Synthesis of fluorene–dendron-hybridized polymers P1–P7

Table 1 Data of absorption and photoluminescence spectroscopy study

Polymer	λ_{abs} (nm)	Band gap (eV)	λ_{PL} (nm)	Stoke shift (nm)	ϕ_{PL}
P1	376	2.99	440	64	0.44
P2	371	3.00	440	69	0.52
P3	364	3.01	436	72	0.46
P4	373	3.00	439	66	0.43
P5	344	3.01	440	96	0.53
P6	385	2.99	444	59	0.46
P7	368	3.00	434	66	0.43

**Fig. 3** **a** UV–Vis. absorption spectra of fluorene–dendron-hybridized polymers and **b** photoluminescence spectra of fluorene–dendron-hybridized polymers

polymers, P1–P7, displayed excellent light-emitting property selectively for blue color.

Furthermore, the optical band gap for P1–P7 polymers was derived from the corresponding absorption spectrums and found in 2.99–3.01 eV range, which was in accordance with the reported data related to emission of blue color light [9]. Images of P1–P7 polymers in CHCl_3 under visible light and UV light are shown in Fig. 4a, b, respectively. The diluted solutions of the polymer emitted strong blue light under UV excitation compared to visible light. The fluorene–dendron-hybridized P1–P7 polymers not only exhibited good quantum yields but also showed good stoke shift value in 59–96 nm range.

Thermogravimetric analysis (TGA) of synthesized fluorene–dendron-hybridized polymers

We have conducted the thermogravimetric analysis of synthesized fluorene–dendron-hybridized polymers. We have observed the steady weight loss which can be attributed to the decomposition of polymeric framework caused by fragmentation

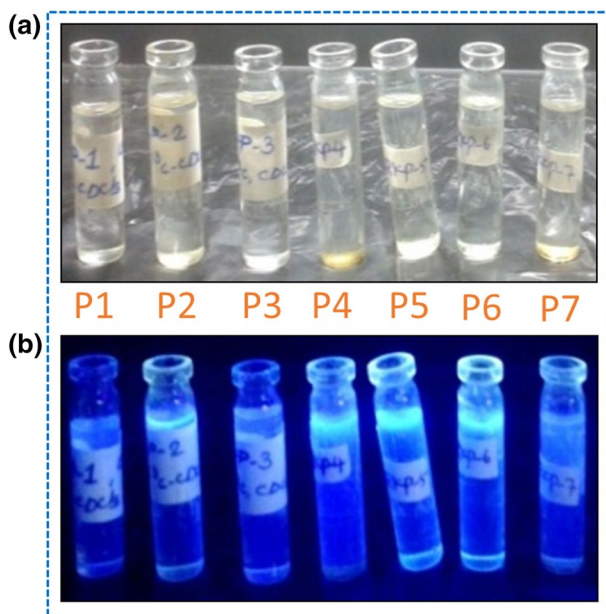


Fig. 4 **a** Polymer solutions in CHCl_3 under visible light and **b** polymer solutions in CHCl_3 under UV light

of molecules with breaking of chemical bonds as an effect of increasing temperature [16, 17]. Mentioned in the electronic supplementary information file, displays the thermogram of the thermogravimetric analysis of synthesized fluorene–dendron-hybridized polymers P1–P7 it indicates these polymers underwent multistep decomposition. Specifically, P2, P4, and P5 polymers underwent two-step decomposition, whereas P3, P6, and P7 polymers adapted three step decomposition and P1 polymer followed four-step decomposition process. This thermogravimetric analysis of synthesized fluorene–dendron-hybridized polymers P1–P7 has confirmed the thermal stability with negligible weight loss up to 200 °C.

Cyclic voltammetry (CV) study of the polymers

We have investigated CV studies of the synthesized fluorene–dendron-hybridized polymers P1–P7 in which we observed the irreversible oxidation wave in the range of 0.85–0.98 V of P1–P7 polymers. The obtained data are summarized in Table S1. On the basis of observed onset oxidation potential for the polymers P1–P7, we have approximated the HOMO energy level in -5.55 to -5.68 eV range and LUMO energy level in -2.55 to -2.67 eV range. In general, all polymers undergo a reversible oxidation process originating from dendron substituted fluorene molecule followed by alkyl substituted fluorene moiety. This study confirms the stability of all polymers in an electrolytic solution (mentioned in the electronic supplementary information file for CV spectrums of polymers P1–P7).

Gel permeation chromatography (GPC) study

GPC is a prominent technique used to establish average molar mass of the copolymers and attests formation of a link between the two constituting blocks. The data obtained from this GPC analysis give molar masses of polymers. GPC analysis was used to obtain the polydispersity index (PDI), degree of polymerization (DP) as well as number average molecular weight (M_n), weight average molecular weight (M_w), size average molecular weight (M_z) of fluorene–dendron-hybridized polymers P1–P7 which are mentioned in Table 2. The data of this study have given PDI values for the polymers in 1.084–4.500 range (Table 2). It is noteworthy to mention that, among the P1–P7 polymers, the polymer which was substituted with dioctyl group (P6) showed higher DP values and the polymer with dipropyl group (P2) showed lower DP values.

Scanning electron microscopy of the polymers

The SEM images showed that the fluorene–dendron-hybridized polymers are microcrystals which have platy rough, rock-shaped, and slightly amorphous globular structure (Fig. 5 mentioned in the electronic supplementary information file). Furthermore, the SEM images do not reveal the separation of phases in polymeric structures. These images confirmed the slight crystalline and amorphous nature of polymers (P1–P7). It was consistent with reported literature data which showed similar platy rough morphology for some blue light-emitting polymers.

X-Ray diffraction study of fluorene–dendron-hybridized polymers P1–P7

Different peak diffraction intensities were observed in obtained XRD diffractograms of fluorene–dendron-hybridized polymers P1–P7 (Fig. 6 and mentioned in the electronic supplementary information file). The range of crystallite size for these polymers was from 0.2 to 6.33 Å (Table S2). The synthesized P2 polymer showed crystallite size of 6.333 Å and 0.215 Å for P6 polymer. Besides this, the rest of the polymers showed crystallite size range from 0.314 to 4.616 Å. The diffractograms showed sharp as well as broad peaks; hence, this observation suggested that polymers were slightly crystalline in nature. In the diffractograms of these polymers,

Table 2 GPC study of fluorene–dendron-hybridized polymers

Polymer	M_n	M_w	M_z	M_w/M_n (PDI)	DP
P1	14,156	26,746	49,315	1.880	7.87
P2	4973	5389	6020	1.084	2.72
P3	3333	3969	4947	1.190	1.80
P4	3330	4134	5348	1.240	1.77
P5	3510	3936	4433	1.210	1.81
P6	93,160	420,666	1,167,388	4.500	47.38
P7	7106	9409	12,890	1.320	3.24

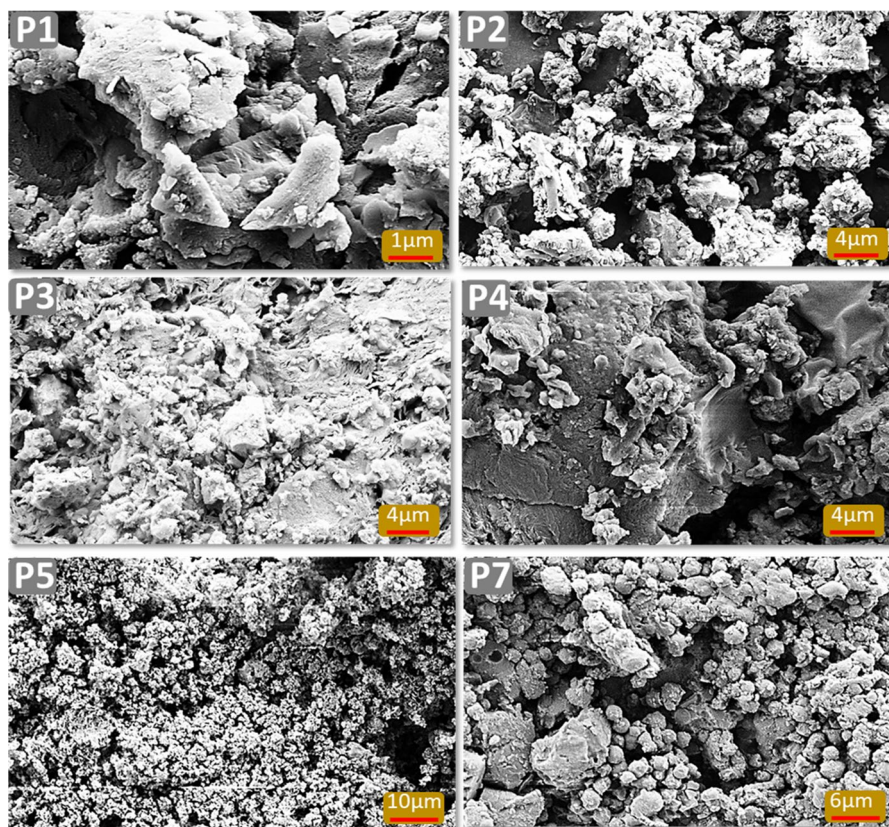


Fig. 5 SEM images of fluorene–dendron-hybridized polymers P1–P5 and P7

broad diffraction peaks were observed which indicated the presence of amorphous content in the polymer chain.

Conclusions

We have developed an efficient synthetic strategy for fluorene–dendron-hybridized polymers P1–P7. Synthesis of these fluorene–dendron-hybridized polymers was achieved by reacting 9,9 long-chain dialkylated fluorenes monomers (M2–M8) with dendronized monomer (M1) under microwave-assisted reaction condition. The structure elucidation and various optoelectronic, thermal, chromatographic, and spectroscopic studies of these polymers were performed by NMR, FT-IR, UV–Vis., GPC, TGA, XRD, and SEM techniques. The optophysical study of these polymers showed well-resolved transitions in the UV–Vis., attributing to the presence of non-breakable polymer linkage, and was found to be stable in THF solvent. The UV–Vis. spectral data were used to calculate direct band gaps of polymers which were observed in 2.99–3.01 eV range. The CV study of fluorene–dendron-hybridized

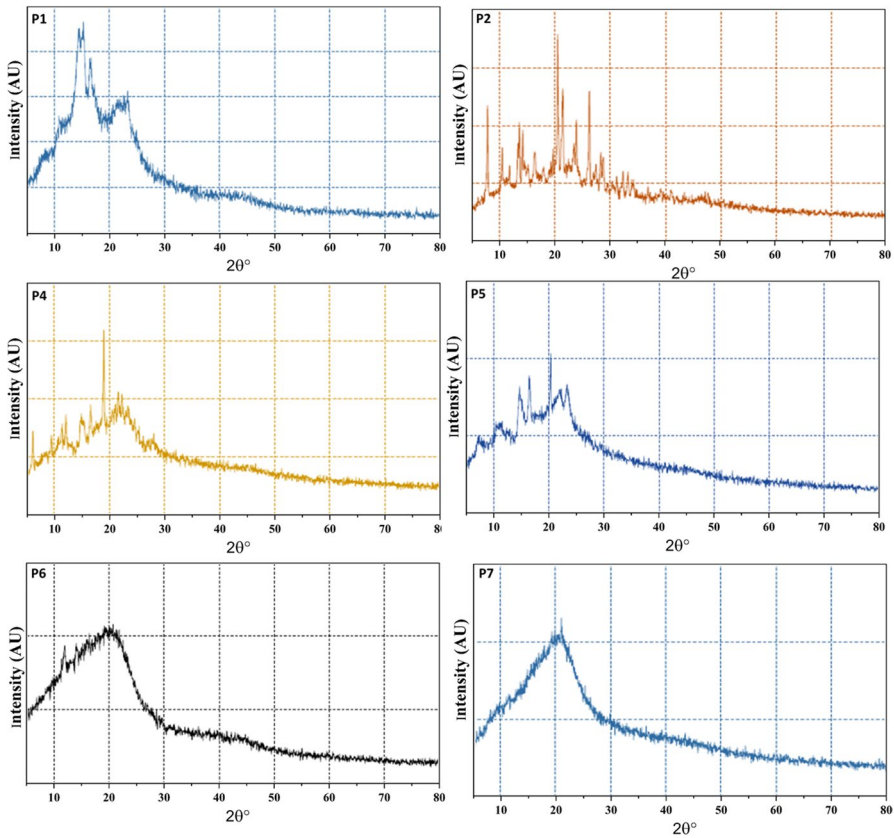


Fig. 6 XRD diffractograms of polymers P1, P2, and P4–P7

polymers was also performed to get HOMO and LUMO energy-level values. Furthermore, gel permeation chromatography (GPC) study is used to obtain PDI, DP as well as M_n , M_w , M_z for these fluorene–dendron-hybridized polymers P1–P7. Through SEM and X-Ray diffraction study, slight crystalline and amorphous nature of polymers was confirmed. Synthesized polymers have potential to emerge as capable materials in the development of diodes, particularly for blue light emission. In future, we might require use of such polymeric material for preparing light-emitting polymer composites.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00289-022-04571-x>.

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Declarations

Conflicts of interest There are no conflicts to declare.

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