Synthesis of porphyrin-appended poly(fluorene-alt-carbazole): photoluminescent and electrochemical studies

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ABSTRACT

Poly(fluorene-alt-carbazole) appended with meso-tetraphenylporphyrin (MTPPC) linked through oxyethylene spacer and the parent poly(N-hexyl-2,7-carbazole-alt-9,9-di-n-hexyl fluorene) (P1) were synthesized and characterized. Optical absorption properties of the polymers containing 5% of MTPPC (P2) and 10% of MTPPC (P3) in the polymer backbone show extended optical absorption toward long wavelength compared to the parent polymer P1. Optical absorption studies of the polymers showed that polymer P1 has absorption at 384 nm in solution, whereas polymers P2 and P3 have absorption at 384 nm corresponding to polymer backbone and soret band at 421 nm with Q bands at around 518 and 554 nm in solution. P1 shows photoluminescence emission around 417 nm, whereas P2 and P3 fall around 656 nm. Thermal, electrochemical, and quenching studies of the polymers have been studied and the details are reported.

1. Introduction

Synthesis of conjugated polymers has received great attention due to their potential applications in polymer light emitting diodes (PLED),[1] transistors,[2] non-linear optical devices [3], and polymer solar cells (PSC).[4] Among the conjugated polymers, polyfluorene have good solubility in organic solvents and good film-forming ability. Their optical and physical properties can be controlled by facile substitution at position 9. Polyfluorenes are promising polymers in PLED due to their carrier-transporting ability and high photoluminescent properties. Variety of polyfluorenes have been synthesized and characterized for polymer light emitting applications.[5,6] In PSC, fluorene moiety acts as a weak donor that has low-lying HOMO levels and enhances the open-circuit voltages and hole mobility. Co-polymers of fluorene with different monomers and different substitution at 9-position were synthesized and good power conversion efficiencies have been reported.[7,8]

Carbazole is analogous to fluorene, in which the 9-position replaced by –NH group. Carbazoles, has good thermal stability, good solubility in common organic solvents and exhibits optical properties. A variety of polycarbazoles have been synthesized and characterized for light emitting applications, because they have no color tailoring in the longer wavelength like polyfluorenes.[9–12] In PSC, carbazoles are also used as weak donor blocks due to their higher thermal stability and hole-transporting ability. Polycarbazoles with electron-deficient blocks have been synthesized, characterized and their power-conversion efficiencies have been evaluated.[13,14] Polyfluorenes and polycarbazoles have absorption around 350 nm and emission around 420 nm. Morin and Leclerc synthesized poly(N-octyl-2,7-carbazole-alt-9,9-di-n-octyl-2,7-fluorene) and observed an absorption at 380 nm and emission at 417 nm in solution.[9] PLED and PSC applications of these polymers are limited due to their absorption and emission in lower wavelength region. To enhance the absorption and emission properties of poly(m fluorene at higher wavelength without changing the polymer backbone is to incorporate organic moieties that absorb in visible range as side chains. Porphyrins are tetrapyrrolic pigments that have highly delocalized π electrons and high absorption coefficient in the range of 400–700 nm, and can be used as an appended group. Porphyrin has been incorporated as side chain in thiophene polymers and the optical properties of the appended polymers were studied by Angiolini et al. and Arce et al. [15–17].

In this article, we report the synthesis of poly(fluorene-alt-carbazole) appended with 5 and 10% porphyrin. The optical, physical, and electrochemical properties of the synthesized polymers have been studied and the results are presented.
2. Experimental

2.1. Materials

The starting materials such as biphenyl, pyrrole and bromobenzene, tetrabutylammonium bromide were purchased from Merk India Pvt. Ltd., India, 9,9-di-n-hexylfluorene-2,7-diboronic acid, triethylphosphite, phenylboronic acid, [6,6]-phenyl C_{61} butyric acid methyl ester (PC_{60}BM), 1,8-dioctooctane (DIO) and Pd(PPh_{3})_{4} were obtained from Sigma–Aldrich India Pvt. Ltd., India and used as received. 1-Bromohexane, propionic acid, potassium carbonate, cesium carbonate and all solvents were purchased from Sisco Research Laboratories Pvt. Ltd., India. All solvents were purified prior to use by standard reported procedures. 4,4'-Dibromobiphenyl was prepared from biphenyl by standard procedure. [18] Monomer 2,7-dibromo-N-hexyl (M1) was synthesized according to reported literature,[19] whereas 5-(4'-hydroxyphenyl)-10,15,20-triphenylporphyrin (D2) was synthesized by modified procedure reported by Jeyakumar and Krishnan and presented in Supplementary information (SI-1).[20]

2.2. Characterization

Thermogravimetric analysis (TGA) of alternating copolymers was carried out using TA instrument SDT Q600 V8-3 Build 101 at heating rate of 20 °C/min in nitrogen atmosphere. Micro-analytical measurements of the monomers were carried out using CHNS Elemental Analyzer-elementar Model Vario EL-III (Elementar Analysensysteme GmbH, Germany). FT-IR spectra of the monomers and polymers were measured by Bruker spectrophotometer (Model Tensor 27, Germany). UV–vis spectra of the polymers in chloroform and polymer films coated on a quartz plate were recorded in Agilent diode array UV–vis Spectrophotometer (Agilent-8453, USA). The photoluminescence spectra (PL) of the alternating copolymers in chloroform and polymer films coated on a quartz plate were recorded using Jasco spectrophotometer (FP-8500, Japan). \(^{1}H\) NMR and \(^{13}C\) NMR spectra for monomers and polymers were recorded in CDCl\(_{3}\) as solution with TMS as internal reference using BRUKER-400-MHz multiprobe NMR spectrophotometer (Switzerland). Molecular weights of the synthesized polymers were measured by gel permeation chromatography (GPC) using HPLC-GPC systems (Shimadzu model No LC-20 A, Japan). Electrochemical properties of the polymers were studied by cyclic voltammetry (Autolab Potentiostat Galvanostat Model PGSTAT-30). Surface studies of the polymer with PC_{60}BM were studied by using atomic force microscopy (Molecular Imaging, Model: PicoSPM – Picoscan 2100, USA).

2.3. Synthesis of monomers

2.3.1. 2,7-Dibromo-N-hexylcarbazole was synthesized in four steps by following the reported procedures [18,19]

2.3.1.1. Synthesis of 4,4'-dibromobiphenyl. White solid with 75% yield. Melting point: 161–163 °C. \(^{1}H\) NMR (400 MHz, CDCl\(_{3}\)) \(\delta\) : 7.50–7.52 (d, 4H, \(J = 8.4\) Hz), 7.36–7.38 (d, 4H, \(J = 8.4\) Hz). \(^{13}C\) NMR (400 MHz, CDCl\(_{3}\)) \(\delta\) : 138.9, 132.0, 128.5, 121.9.

2.3.1.2. Synthesis of 4,4'-dibromo-2-nitrobiphenyl. Yellow solid with 77% yield. Melting point: 123–124 °C. \(^{1}H\) NMR (400 MHz, CDCl\(_{3}\)) \(\delta\) : 8.05–8.06 (d, 1H, \(J = 2\) Hz), 7.77–7.97 (d, 1H, \(J = 8.4\) Hz), 7.58–7.60 (d, 2H, \(J = 8.0\) Hz), 7.30–7.32 (d, 1H, \(J = 8.0\) Hz), 7.17–7.19 (d, 2H, \(J = 8.0\) Hz). \(^{13}C\) NMR (400 MHz, CDCl\(_{3}\)) \(\delta\) : 135.6, 135.3, 134.1, 133.0, 132.1, 129.4, 127.3, 123.1, 121.8.

2.3.1.3. Synthesis of 2,7-dibromocarbazole. White powder with 60% yield. Melting point: 234–236 °C. \(^{1}H\) NMR (400 MHz, CDCl\(_{3}\)) \(\delta\) : 8.14 (s, 1H, NH), 7.90–7.92 (d, 2H, \(J = 8.4\) Hz), 7.61 (s, 2H), 7.37–7.39 (d, 2H, \(J = 8.4\) Hz). \(^{13}C\) NMR (400 MHz, CDCl\(_{3}\)) \(\delta\) : 140.2, 123.2, 121.2, 121.7, 121.4, 119.7, 113.8. Anal. Calcd for C_{12}H_{7}Br_{2}N: C, 44.35%; H, 2.17%; N, 4.31% Found: C, 44.55%; H, 2.20%; N, 4.32%. MS-ESI (m/z): 323.93 [M–1].

2.3.1.4. Synthesis of 2,7-dibromo-N-hexylcarbazole (M1). White fiber-like solid with 75% yield. Melting point: 72–74 °C. \(^{1}H\) NMR (400 MHz, CDCl\(_{3}\)) \(\delta\) : 7.90–7.92 (d, 2H, \(J = 8.4\) Hz), 7.55 (s, 2H), 7.35–7.37 (dd, 2H, \(J = 8.4\) Hz), 4.19–4.23 (t, 2H, \(J = 8.4\) Hz), 1.82–1.90 (m, 2H), 1.33–1.39 (m, 6H), 0.89–0.92 (t, 3H, \(J = 8.14\) Hz). \(^{13}C\) NMR (400 MHz, CDCl\(_{3}\)) \(\delta\) : 141.34, 122.50, 121.47, 121.26, 119.68, 111.99, 43.35, 31.51, 28.77, 26.86, 22.56, 14.02. FT-IR (cm\(^{-1}\)) : 3072, 2925, 2859, 1583, 1440, 1322, 1230, 1125, 1046, 995, 918, 794, 726, 653, 586. Anal. Calcd for C_{12}H_{7}Br_{2}N: C, 52.84%; H, 4.68%; N, 3.42% Found: C, 52.71%; H, 4.70%; N, 3.42%.

2.3.2. Synthesis of 2,7-dibromo-N-(2-bromoethyl)carbazole (D1)

A 250-mL round-bottomed flask (RB) was charged with 3.24 g (10 mmol) of 2,7-dibromocarbazole, 50 mL of anhydrous DMF and stirred to get a clear solution to which 3.25 g (10 mmol) of anhydrous Cs_{2}CO_{3} was added. The resulting mixture was stirred for 30 min at room temperature under argon atmosphere, then 1 mL of 1,2-dibromomethane (116 mmol) was added to the mixture and stirring was continued at 80 °C for 12 h under argon atmosphere. The reaction mixture was quenched with 20 mL of distilled water and extracted with CHCl\(_{3}\) (3 × 100 mL). The
combined organic layers were washed with water and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, followed by recrystallization which afforded the title product as a fiber-like solid in 70% (3.02 g) yield. ¹H NMR (400 MHz, CDCl₃) δ: 7.91–7.93 (d, 2H, J = 8.4 Hz), 7.60 (s, 2H), 7.39–7.41 (d, 2H, J = 8.4 Hz), 4.62–4.66 (t, 2H, J = 7.2 Hz), 3.67–3.71 (t, 2H, J = 7.2 Hz).

2.3.3. Synthesis of monomer Carbazole linked with meso-tetraphenylporphyrin (MTPPC)

In a 250-mL RB flask, 4.31 g (10 mmol) of 5-(4'-hydroxyphenyl) 10, 15, 20-trisphenylporphyrin were dissolved in 100 mL of anhydrous DMF. The solution was purged in an argon atmosphere and 1.38 g (10 mmol) of anhydrous K₂CO₃ were added to the solution and to this solution 2.4. Synthesis of polymers

2.4.1. Synthesis of polymer P1

9,9-Dihexyfluorene-2,7-diboronic acid (1.013 g, 2.4 mmol), MTPPC (0.235 g, 0.24 mmol), and tetracetylammonium bromide (200 mg) were charged. Anhydrous THF was added to the mixture and stirred for 30 min under argon atmosphere. 2,7-Dibromo-N-hexyl carbazole (0.882 g, 2.16 mmol) was added to the solution and stirred to get a red-colored clear solution. 2.0 M solution of K₂CO₃ (10 mL) was added to the above-stirred solution and stirring was continued for 10 min. Pd(PPh₃)₄ (0.110 g) was then added to the stirred solution and heated at 80 °C for 24 h, under argon atmosphere. After 24 h, phenylboronic acid (0.0146 g, 0.12 mmol), bromobenzene (0.0188 g, 0.12 mmol) with small amount (0.006 g) of catalyst were added to the stirred solution for end-capping. After 3 h, the reaction mixture was cooled to room temperature, concentrated, and poured in methanol to give polymer P1 as green powder. Purification of the polymer was achieved by Soxhlet extraction with water, methanol, and acetone. Then, the remaining material was extracted with chloroform and the extract was evaporated under reduced pressure and precipitated using methanol. The precipitate was filtered and dried under vacuum to obtain a greenish violet solid. ¹H-NMR (400 MHz, CDCl₃) δ: 8.14–8.16 (m, 7.80–7.82 (m), 7.63 (s), 7.67–7.71 (m), 4.41 (m, N–CH₃), 1.95 2.06 (m), 1.52–1.45 (m), 1.28–1.35 (m), 1.06 (m), 0.70–0.74 (m, –CH₃). FT-IR (cm⁻¹): 3028, 2927, 2856, 1602, 1450, 1329, 1239, 1135, 995, 804, 740, 446.

2.4.2. Synthesis of polymer P2

In a 100-mL RB flask 9,9-dihexyfluorene-2,7-diboronic acid (1.013 g, 2.4 mmol), MTPPC (0.235 g, 0.24 mmol), and tetracetylammonium bromide (200 mg) were charged. Anhydrous THF was added to the mixture and stirred for 30 min under argon atmosphere. 2,7-Dibromo-N-hexyl carbazole (0.882 g, 2.16 mmol) was added to the solution and stirred to get a red-colored clear solution. 2.0 M solution of K₂CO₃ (10 mL) was added to the above-stirred solution and stirring was continued for 10 min. Pd(PPh₃)₄ (0.110 g) was then added to the stirred solution and heated at 80 °C for 24 h, under argon atmosphere. After 24 h, phenylboronic acid (0.0146 g, 0.12 mmol), bromobenzene (0.0188 g, 0.12 mmol) with small amount (0.006 g) of catalyst were added to the stirred solution for end-capping for 3 h. Then the reaction was allowed to cool to room temperature and the reaction mixture was poured drop-wise to 200 mL of methanol to give crude polymer as greenish violet powder. The crude polymer was then subjected to Soxhlet extraction with distilled water, methanol, acetone, and chloroform subsequently. The chloroform fraction was evaporated under reduced pressure and then precipitated using methanol. The powder was dried under vacuum to obtain greenish violet solid. ¹H-NMR (400 MHz, CDCl₃) δ: 8.86 (m, pyrrole protons), 8.76–8.74 (m, phenyl protons), 8.12–8.18 (m, 7.80–7.81 (m), 7.63–7.67 (m), 7.53–7.54 (m), 7.40–7.44 (m), 5.0 (m, O–CH₂ protons), 4.75 (m, N–CH₂ protons in hexyl carbazole), 4.42 (m, N–CH₂ protons in hexyl carbazole), 1.95–2.06 (m), 1.44–1.48 (m), 1.28–1.35 (m), 1.06 (m), 0.70–0.74 (m, –CH₃). FT-IR (cm⁻¹): 3317, 3038, 2854, 1713, 1603, 1451, 1327, 1234, 1187, 1135, 995, 804, 740, 446.

2.4.3. Synthesis of polymer P3

Polymer 3 was synthesized by the same procedure followed for polymer 2 using 9,9-dihexyfluorene-2,7-diboronic acid (1.013 g, 2.4 mmol), MTPPC (0.473 g, 0.48 mmol),
3. Results and discussion

3.1. Synthesis and characterization of polymers

Monomer M1 has been synthesized by following the reported procedures and the purity of the compounds were checked by $^1$H NMR, $^{13}$C NMR, and analytical methods. Scheme 1 depicts the synthesis of monomers. Precursor D1 was synthesized by the N-alkylation of 2,7-dibromocarbazole with 1,2-dibromoethane in the presence of anhydrous Cs$_2$CO$_3$. Reaction completion was checked by TLC as free carbazole has lower $R_f$ value than 2,7-dibromo-N(2-bromoethyl) carbazole. The formation and purity of the compound have been studied by analytical methods, $^1$H NMR and $^{13}$C NMR spectroscopy. The $^1$H NMR and $^{13}$C NMR spectra of the precursors D1 are provided in Supplementary information (SI-2 and SI-3). 5-(4'-Hydroxyphenyl)-10, 15, 20-triphenylporphyrin [D2] was synthesized by the reaction of four equivalent pyrrole with three equivalent benzaldehyde and 1.0 equivalent 3-hydroxy benzaldehyde in propionic acid medium. Synthetic scheme of D2, $^1$H NMR, UV–vis absorption and photoluminescence emission spectra of D2 was presented as Supplementary information (SI-4 and SI-5). Monomer MTTPPC has been synthesized via etherification of precursor D1 and precursor 5-(4'-hydroxyphenyl)-10,15,20-triphenylporphyrin (D2) in the presence of anhydrous K$_2$CO$_3$ as base. The formation of the compound was checked by TLC during the reaction after the confirmation of completion of product formation, the reaction was stopped and processed. The formation of the monomer was confirmed by $^1$H NMR, 13C NMr studies and mass spectroscopy. 1H NMr spectra of the monomer MTTPPC is shown in Figure 1. In NMr spectra, peaks at 4.6 and 4.8 ppm obtained from N–CH$_2$ and O–CH$_2$ protons indicates the formation of O–CH$_2$ bond in addition, proton resonance of the carbazole peaks were observed. Peaks at around 8.8 and −2.7 ppm corresponds to pyrrolic and –NH protons of porphyrin ring. All the polymers were synthesized by Suzuki coupling reaction of diboronic acid with dibromo derivative and are depicted in Scheme 2. Polymer 1 has been synthesized and reported by Leclerc et al. [9]. Polymer P2 and P3 have been synthesized by following the same method using MTTPPC as 10 and 20% equivalent with respect to 2,7-dibromo-N-hexylcarbazole (0.783 g, 1.92 mmol) equivalents to yield greenish violet powder. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.85 (m, pyrrole protons), 8.72–8.75 (m, phenyl protons), 8.10–8.16 (m), 7.97–8.02 (m), 7.89–7.92 (m), 7.78–7.75 (m), 7.62–7.66 (m), 7.52–7.54 (m), 7.39–7.43 (m), 7.29–7.33 (m), 5.03 (m, O–CH$_3$ protons), 4.70 (m, N–CH$_2$ protons in porphyrin carbazole), 4.40 (m, N–CH$_2$ protons in hexyl carbazole), 1.95–2.06 (m), 1.41–1.50 (m), 1.25–1.34 (m), 1.03–1.05 (m), 0.76–0.84 (−CH$_3$ end protons), −2.87 (s, porphyrin NH protons). FT-IR (cm$^{-1}$): 3316, 3034, 2924, 2854, 1723, 1601, 1451, 1329, 1235, 1060, 986, 804, 738, 522.

Table 1. Molecular weight of the polymers.

| Polymer | $M_0$ (Dalton)$^a$ | $M_n$ (Dalton)$^a$ | PDI |
|---------|-------------------|-------------------|-----|
| P1      | 6743              | 11,356            | 1.68|
| P2      | 7070              | 15,664            | 2.22|
| P3      | 4866              | 9890              | 2.03|

$^a$Measured using polystyrene as standard.
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Symmetric and asymmetric stretching, respectively, whereas peak at 3032 cm\(^{-1}\) corresponds to aromatic C–H stretching frequencies.

Figure 1. \(^1\)H NMR spectrum of MTPPC in CDCl\(_3\) using TMS as internal standard.

Scheme 2. Synthesis of polymers P1–P3.

KBr pellets. FT-IR spectra of polymers P1–P3 are shown as Supplementary information (SI-6). From the FT-IR spectra, peaks at 2920 and 2858 cm\(^{-1}\) correspond to aliphatic symmetric and asymmetric stretching, respectively, whereas peak at 3032 cm\(^{-1}\) corresponds to aromatic C–H stretching frequencies.
polymers are thermally stable up to 400 °C. Thermogram of polymers P1–P3 is shown in Figure 4. Analysis of thermogram indicates all the polymers are thermally stable and 5% of weight loss occurs less than 150 °C due to absorbed solvent.

3.3. Electrochemical properties of the polymers

Electrochemical properties of the polymers were studied by cyclic voltametry with polymer film coated on Pt electrode as working electrode, platinum wire as counter electrode and Ag wire as quasi reference electrode in 0.1 M tetrabutylammonium hexafluorophosphate (C$_4$H$_9$)$_4$NPF$_6$ in anhydrous acetonitrile medium with a scan rate of 10 mV/s. Figure 5 shows the cyclic voltamograms of polymers P1–P3. Polymer P1 has an oxidation potential at 1.199 V, whereas polymers P2 and P3 have an oxidation potential at 1.151 and 1.091 V, respectively. HOMO levels of the synthesized polymers were estimated from the onset of oxidation potentials of the polymers. Ferrocene/ferrocenium redox couple was used as standard and the $E_{1/2}$ appears at around 0.40 V vs. Ag wire reference electrode. [21,22] The value of −4.8 eV is used as an absolute energy level of our electrochemical system. The oxidation onset of polymers was used to calculate the HOMO levels of polymers using the following equation.[21,22]

$$E_{\text{HOMO}}(eV) = -e (\Phi_{\text{ox}}, \text{Ag} + 4.8 - E_{1/2}, \text{Fc/Fc}^+)$$

The reduction potential of the polymers was not clearly observed. So, the energy of the LUMO levels of the polymers were calculated using the optical band gap of the polymer in film and the HOMO values of the polymers using the following equation [23]:
\[ E_{\text{LUMO}}(\text{eV}) = E_{\text{HOMO}} + E_{\text{opt}}(\text{eV}). \]

HOMO, LUMO energy states of the polymers P1–P3 and their optical band gaps are shown in Table 2.

3.4. Optical properties of the polymers in solution and as thin films

Optical properties of the polymers were studied in solution as well as thin film (Figure 6–13 and Table 3). Figure 6 shows the optical absorption spectra of polymers P1–P3 in chloroform solution. Leclerc et al. and Tirapattur et al. have synthesized poly(N-octyl-2,7-carbazole-alt-9,9-di-n-octyl-2,7-fluorene) and reported its optical absorption and emission properties.[9,10] Absorption of P1 synthesized in this work has absorption maximum of 384 nm and is same as absorption of poly(N-octyl-2,7-carbazole-alt-9,9-di-n-octyl-2,7-fluorene) in chloroform solution. Polymers P2 and P3 have absorption from 300 to 600 nm with absorption maxima at around 380 and 422 nm with additional bands around 522, 555, and 595 nm. The absorption maxima at around 422 nm and other visible bands are originated from porphyrin moiety. Absorption maxima at 422 nm

| Polymer | Optical onset (nm) | \( E_{\text{g}}(\text{eV}) \) | HOMO (eV) | LUMO (eV) |
|---------|--------------------|-----------------|-----------|-----------|
| P1      | 467                | 2.655           | −5.599    | −2.944    |
| P2      | 575                | 2.156           | −5.551    | −3.395    |
| P3      | 575                | 2.156           | −5.491    | −3.335    |

Table 2. Electrochemical properties of the polymers.
was called Soret band due to $S_0 \rightarrow S_2$ transition, whereas all other Q bands were from $S_0 \rightarrow S_1$ transition. Polymer P2 has 5% equivalent of porphyrin moiety in the polymer chain exhibiting low absorption peaks at 422 nm; whereas P3, that has 10% equivalent porphyrin moiety in polymer chain, gives strong absorption at 422 nm, compared to P1 & P2. The presence of peaks at 422 nm with additional bands around 522, 555 and 595 nm indicates the presence of porphyrin onto the polymer backbone and well supported by absorption at 328, 422, 519, 555, 594, 674 nm for polythiophene having side chain porphyrin reported by Arce et al. [15]. For comparison, the optical properties

![Figure 10](image1.png)

**Figure 10.** Photoluminescence excitation and emission spectra of monomer MTPPC.  
Notes: Dark line: emission at 650 nm, dashed line: excited at 309 nm, and dotted line: excited at 418 nm.

![Figure 11](image2.png)

**Figure 11.** Photoluminescence excitation and emission spectra of pristine films of the polymers P1–P3.

![Figure 12](image3.png)

**Figure 12.** Optical absorption spectra of polymer P3 quenched with PCBM as thin film, P3, P3: PCBM (1: 0.25), P3: PCBM (1: 0.50), P3: PCBM (1: 1).

![Figure 13](image4.png)

**Figure 13.** Photoluminescence spectra of polymer P3 quenched with PCBM as thin film, P3, P3: PCBM (1: 0.25), P3: PCBM (1: 0.50), P3: PCBM (1: 1).

| Polymer | Absorption in solution (nm)$^a$ | Absorption in film (nm)$^b$ | Emission in solution (nm)$^c$ | Emission in film (nm)$^d$ |
|---------|---------------------------------|-----------------------------|-------------------------------|-----------------------------|
| P1      | 384                             | 393                         | 417, 442                      | 431, 455, 528              |
| P2      | 384, 421, 554                   | 389, 424, 520, 556, 601, 650| 416, 442, 602, 651            | 605, 656, 718              |
| P3      | 383, 422, 554                   | 385, 427, 520, 556, 601, 650| 416, 442, 602, 651            | 605, 656, 718              |

$^a$Maximum wavelength of absorption in chloroform.  
$^b$Maximum wavelength of absorption in polymer film coated on quartz plate.  
$^c$Maximum wavelength of photoluminescence in chloroform with shoulder peak.  
$^d$Maximum wavelength of photoluminescence in polymer film coated on quartz plate.
of monomer 2,7-dibromo-N-hexylcarbazole (M1) and monomer MTPPC have been studied. 2,7-Dibromo-N-hexylcarbazole has absorption from 290 to 350 nm with absorption maxima at 306 nm and with shoulder at 340 and 350 nm (SI-7), while monomer MTPPC has absorption from 280 nm with absorption maxima at 304 nm, intense soret band at 418 nm and Q bands at 513, 548, 593, and 649 nm. From the absorption studies of monomer M1 and MTPPC, we can conclude that the monomer MTPPC has absorption of both carbazole and porphyrin moiety. Figure 7 shows the absorption spectra of monomer MTPPC in chloroform solution.

Optical absorption studies of the polymers as thin films coated on quartz plates were studied. Figure 8 shows the absorption spectra of polymers P1–P3 as thin films. Polymer P1 has absorption from 320 to 450 nm with absorption maxima at 393 nm (reported absorption maxima for thin film of poly(N-octyl-2,7-carbazole-alt-9,9-di-n-octyl-2,7-fluorene) is at 387). In polymer P1, bathochromic shift (10 nm) was observed from solution state to thin film state due to aggregation in solid state. Polymers P2 and P3 have absorption from 320 to 600 nm with absorption maxima at 390 and 428 nm. The absorption maximum at 390 nm corresponds to polymer backbone and absorption maximum at 428 nm corresponds to porphyrin Soret band. The Q bands of the porphyrin are also observed in the absorption spectra. Figure 9 shows the photoluminescence excitation and emission spectra of the polymers P1–P3 in chloroform solution. Polymer P1 has emission from 400 to 500 nm with emission maxima at 417 nm and a shoulder at 442 nm, whereas polymers P2 and P3 have emission from 400 to 500 nm with emission maxima at 416 nm when excited at 380 nm. When excited at 422 nm, polymers P2 and P3 have emission maxima at 656 nm with small peaks at 605 and 718 nm. The emission peaks from 605 to 718 nm arise from the porphyrin moiety in MTPPC. It may be noted that emission intensities of porphyrin group are lowered by more than 100 times than carbazole unit. The excitation spectra were recorded at 650 nm emission and the corresponding absorbances at 422, 380 and 306 nm were observed indicating that, there is a weak energy transfer in P2 and P3 from the backbone to the porphyrin. For a comparative study, the photoluminescence emission properties of monomers, 2,7-dibromo-N-hexylcarbazole (M1) and MTPPC, have been measured in solution. Monomer M1 has emission from 350 to 600 nm with an emission maxima at 371 nm when excited at 306 nm (SI-8), whereas monomer MTPPC shows emissions at around 387 (shoulder at 425 nm) and 654 nm (shoulders at 603 and 717 nm). The excitation spectra recorded at 654 nm show peaks corresponding to porphyrin at 422, 520, 550, and 595 nm and absorption at 306 nm due to carbazole unit. Figure 10 shows excitation and emission spectra of monomer MTPPC. From this figure it can be concluded that there was energy transfer from carbazole moiety to the appended porphyrin moiety. However, the extent of energy transfer is not 100% as the emission corresponding to carbazole has also been observed.

Photoluminescence emission properties of the polymers as thin films on quartz plates were studied (Figure 11 and Table 3). Polymer P1 has emission from 420 to 600 nm with emission maxima at 432 nm with a shoulder peak at 455 nm. For polymer P1, the minimum (10 nm) shift of emission maxima from solution state to solid state would reveal that polymer P1 has less aggregation in solid state. Polymers P2 and P3 have emission from 600 to 750 nm with an emission maxima at 655 nm and low-intensity peaks at around 608 and 718 nm. The peaks

![Figure 14](image-url). (a) AFM images of polymer P2 blend with PCBM (1:1) and (b) polymer P2 blend with PCBM (1:1) with 2 wt% DIO as additive.
4. Conclusions

We have synthesized two polymers possessing appended porphyrins with alkyl spacer. Grafting porphyrin onto the polymer backbone enhanced the optical absorption of the polymer from 300–450 to 300–600 nm. The synthesized polymers were thermally stable up to 400 °C and their electrochemical studies showed that they have very deep HOMO energy levels. Photoluminescence and quenching studies of the polymer as thin films showed that the appended porphyrin changed the photoluminescence emission from 431 to 656 nm and there was an energy transfer from polymer backbone to the porphyrin unit. Furthermore, quenching of PL emission in thin films of polymer: PC_{60}BM indicated effective charge transfer from polymer to PC_{60}BM. Fabrication of polymer solar cell using the synthesized polymers and measuring the photovoltaic properties is in progress.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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