

# Benzotrifluoromethyl Group-Substituted Poly(*p*-phenylenevinylene): Effect on Solubility, Optical, and Electronic Properties

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**ABSTRACT:** A new organosoluble benzotrifluoromethyl group containing poly(*p*-phenylenevinylene) (BTFM-PPV) has been synthesized via Gilch polymerization. The polymer is soluble in common organic solvents such as tetrahydrofuran, chloroform, dichloromethane, toluene, and xylene. BTFM-PPV exhibited fluorescence emission peak with a very high blue shift at 474 nm with an excitation wavelength at 420 nm compared with many other PPV derivatives reported earlier. Incorporation of fluorated bezotrifluoromethyl pendent group in the PPV backbone lowers the HOMO and LUMO energy levels of BTFM-PPV (2.48 eV) which retarded the hole

injection and increase the electron injection in the device. The current–voltage (I–V) characteristic of the polymer was measured by fabricating the polymer as ITO/BTFM-PPV/Al diode. The device performance was markedly improved by incorporation of 4-fluoro-3trifluoromethyl-phenyl units into the polymer main chain. The turn on voltage of the device observed from the I–V measurements was 7 V. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1603–1610, 2010

**Key words:** MEH-PPV derivative; benzotrifluoromethyl group; photoluminescence

## INTRODUCTION

Designing and synthesis of new light emitting polymers has been attracting a significant interest since the discovery of electroluminescence (EL) in 1990.<sup>1</sup> A large number of reports are available on poly(*p*-phenylenevinylene) (PPV) derivatives containing electron withdrawing group such as cyano,<sup>2,3</sup> oxadiazole,<sup>4–6</sup> fluoroaryl,<sup>7</sup> and quinoline<sup>8</sup> in the main chain or side chain as electron transporting material. The unsubstituted PPV is insoluble, intractable, and infusible. An extensive research has been done to make the PPV derivatives processable. The entire concept behind the design of soluble PPV is the use of side chain such as alkoxy,<sup>9</sup> alkyl-silyl,<sup>10</sup> and fluorenyl<sup>11</sup> at 2 or 5 position to improve solubility and suppress molecular aggregation. Recently, fluorated- and trifluoromethyl-substituted PPV derivatives have also been reported with a good processability along with good opto-electronic properties.<sup>12,13</sup> Intro-

duction of –F and –CF<sub>3</sub> group make the PPVs good electron acceptors and of low LUMO energy. The imbalance of charge injection occurs due to high LUMO energy. To overcome the imbalance of charge carrier injection and for adjusting the energy band of the polymer, electron withdrawing group were incorporated into the polymer backbone. Substituents with electron capturing unit are of great interest for optical study, whereas side chain causes steric hindrance along the polymer backbone which in turn controls the color of the polymers.<sup>14–17</sup> Here, we report the synthesis and characterization of a stable, highly soluble, and high-molecular-weight PPV derivative. High solubility and higher stability of this polymer is due to the flexible side chain with –F and –CF<sub>3</sub> substituted phenyl ring. Generally, electron withdrawing –CF<sub>3</sub> group makes the –F atom present at the ortho position more labile toward substitution reaction. Various aromatic or aliphatic hydroxy compounds containing different electron withdrawing or electron donating substituents can substitute these –F atoms easily. This will, in turn, lead to further optimization of opto-electronic properties of this BTFM-PPV derivative. The diodes are fabricated by spin coating of BTFM-PPV on ITO and Al was finally evaporated on the organic layer as a cathode. The I–V characteristics were measured at room temperature.

Additional Supporting Information may be found in the online version of this article.

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## EXPERIMENTAL

### Measurements

FTIR spectra were recorded using a NEXUS 870 FTIR (Thermo Nicolet) spectrophotometer at room temperature and humid free atmosphere by making KBr pellets.  $^1\text{H-NMR}$  and proton decoupled  $^{13}\text{C-NMR}$  were recorded on a Bruker 200 MHz and 500 MHz instrument (Switzerland), respectively.  $\text{CDCl}_3$  was used as solvent and TMS as reference. Elemental carbon, hydrogen, and nitrogen of the compounds were analyzed by pyrolysis method using Euro EA elemental analyzer. Gel permeation chromatography was performed using a Waters 2414 instrument. THF was used as eluent (flow rate, 0.5 mL/min), polystyrene was used as standard, and RI detector was used to record the signal. Glass transition temperature ( $T_g$ ) of the polymer were analyzed by differential scanning calorimetry (DSC) using NETZSCH DSC 200PC differential scanning calorimeter at a heating rate of  $20^\circ\text{C min}^{-1}$  under nitrogen atmosphere. Glass transition temperature ( $T_g$ ) were taken at the center of the step transition in the second heating run. Thermal decomposition behavior of these polymers was measured on a NETZSCH TG 209 F1 thermal analyzer at a heating rate of  $10^\circ\text{C/min}$  under nitrogen atmosphere. The absorption and fluorescence spectra of the polymer solutions were measured using Mikropack UV-VIS-NIR, DH2000 spectrophotometer and a Spex—Fluorolog-3 (model no: FL3-11) spectrofluorimeter. Molecular weight of the repeat unit (392.43 g/mol) was used to calculate the concentration of the polymer solutions. Current density–voltage was measured using Keithley 2400 source measure unit. The cyclic voltammetry was performed by a computer control potentiostat and galvanostat system from Gamry instrument.

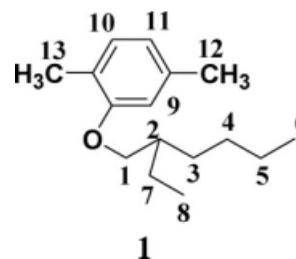
### Starting materials

All reagents were purchased from Aldrich and used as received unless otherwise noted. 2,5-Dimethylphenol was purchased from Spectrochem, India. Anhydrous  $\text{K}_2\text{CO}_3$  (E Merck, India) were further dried before use. Toluene and tetrahydrofuran (THF) were dried by refluxing with sodium metal using benzophenone as indicator. Carbontetrachloride was dried by distillation over anhydrous phosphorus pentoxide.

### Preparation of BTFM-PPV

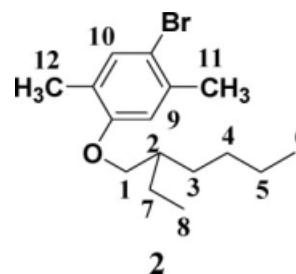
BTFM-PPV was prepared in five steps starting from 2,5-dimethylphenol and is shown in Scheme 1. The detailed synthetic procedure for each intermediate and their characterizations is shown below.

### Preparation of 2-(2'-ethylhexyloxy)-p-xylene (1)

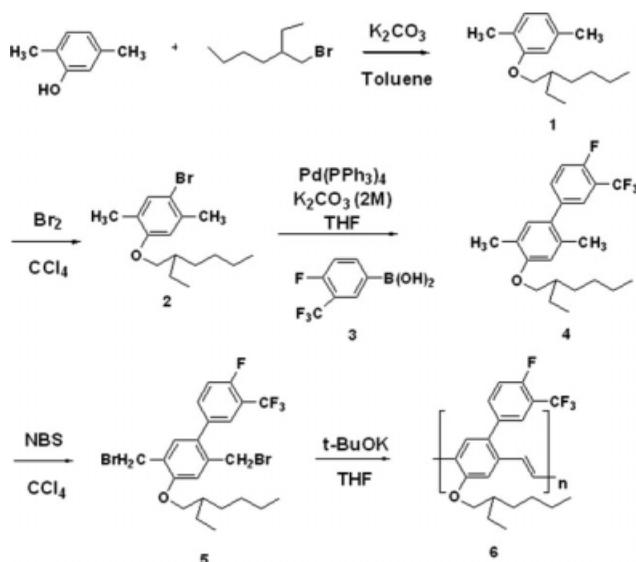


2,5-Dimethylphenol (10 g, 81.9 mmol), 1-Bromo-2-ethylhexane (17.4 g, 90.1 mmol), and  $\text{K}_2\text{CO}_3$  (14.7 g, 106.4 mmol) was mixed into dry *N,N*-dimethylformamide (DMF) and toluene (1 : 1). The mixture was heated to reflux for 4 h with constant stirring. After completion of reaction (monitored by TLC), the reaction mixture was diluted with water and extracted with dichloromethane (50 mL  $\times$  3). The organic layer was again washed with water (20 mL  $\times$  2), dried with anhydrous  $\text{MgSO}_4$  and concentrated under vacuo to get 17.1 g (90%) as colorless oil. Anal. Calcd. for  $\text{C}_{16}\text{H}_{26}\text{O}$  (234.38 g/mol): C, 81.99; H, 11.18; O, 6.83. Found: C, 81.46; H, 12.13; O, 6.67. FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 3049, 3022, 2958, 2921, 2865, 2731, 1615, 1586, 1507, 1460, 1414, 1378, 1307, 1263, 1156, 1128, 1038, 931, 844, 802, 778, 725, 591.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz,  $\delta$  ppm): 7.04 (d,  $J = 7.2$  Hz, 1H,  $\text{H}^{10}$ ), 6.69 (d,  $J = 7.6$  Hz, 1H,  $\text{H}^{11}$ ), 6.68 (s, 1H,  $\text{H}^9$ ), 3.87 (d,  $J = 4$  Hz, 2H,  $\text{H}^1$ ), 2.35 (s, 3H,  $\text{H}^{12}$ ), 2.22 (s, 3H,  $\text{H}^{13}$ ), 1.79–0.90 (m, 15H,  $\text{H}^1$ ,  $\text{H}^2$ ,  $\text{H}^3$ ,  $\text{H}^4$ ,  $\text{H}^5$ ,  $\text{H}^6$ ,  $\text{H}^7$ ,  $\text{H}^8$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125 MHz,  $\delta$  ppm): 157.36, 136.31, 130.25, 123.64, 120.51, 111.69, 69.97, 39.76, 31.71, 29.25, 24.24, 23.16, 15.78, 14.07, 11.25.

### Preparation of 2-bromo-5-(2'-ethylhexyloxy)-p-xylene (2)



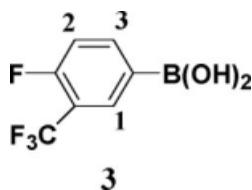
In a 250-mL three necked round bottom flask equipped with a dropping funnel compound 1 (10 g, 42.7 mmol) and iron (III) chloride (116 mg, 0.72 mmol) were mixed into carbon tetrachloride (40 mL). Bromine (6.91 g, 43.26 mmol) was added dropwise to the ice-cooled mixture. The mixture was left for stirring for 8 h at room temperature. After the



Scheme 1 Synthetic scheme for BTFM-PPV.

completion of the reaction, the reaction mixture was washed with sodium hydroxide solution (5–10%), dried with anhydrous magnesium sulfate, and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography using hexane as eluent. 2-Bromo-5-(2'-ethylhexyloxy)-*p*-xylene (**2**) (11.2 g, 84%) was obtained as colorless oil. Anal. Calcd. for  $C_{16}H_{25}BrO$  (313.27 g/mol): C, 61.34; H, 8.04; O, 5.11. Found: C, 60.03; H, 8.86; O, 5.13. FTIR (KBr pellet,  $cm^{-1}$ ): 3049, 2958, 2921, 2864, 2731, 1744, 1605, 1566, 1495, 1459, 1386, 1365, 1300, 1250, 1161, 1040, 960, 873, 835.  $^1H$ -NMR ( $CDCl_3$ , 200 MHz,  $\delta$  ppm): 7.26 (s, 1H,  $H^{10}$ ), 6.64 (s, 1H,  $H^9$ ), 3.81 (d,  $J = 3.9$  Hz, 2H,  $H^1$ ), 2.35 (s, 3H,  $H^{11}$ ), 2.16 (s, 3H,  $H^{12}$ ), 1.76–0.87 (m, 15H,  $H^1, H^2, H^3, H^4, H^5, H^6, H^7, H^8$ ).  $^{13}C$ -NMR ( $CDCl_3$ , 125 MHz,  $\delta$  ppm): 156.50, 135.35, 133.45, 126.15, 114.26, 113.12, 70.29, 39.63, 30.70, 29.12, 24.15, 23.06, 22.73, 15.39, 14.00, 11.15.

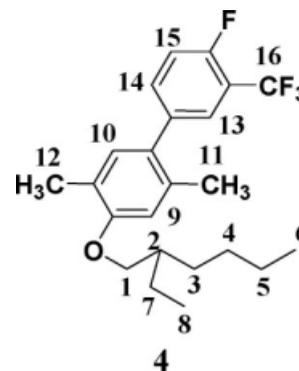
Preparation of 4-fluoro-3-trifluoromethylphenylboronic acid (**3**)



A solution of 5-bromo-2-fluoro-benzotrifluoride (10 g, 41.2 mmol) in 50 mL of anhydrous THF was added slowly to a stirred mixture of magnesium turnings (1.1 g, 45.3 mmol) and 150 mL of dry THF under nitrogen atmosphere. The reaction was initiated by the addition of a trace of iodine. The resulting mixture was stirred at 25°C for 4–5 h, until consumption of

almost all magnesium turnings. The resulting mixture was added dropwise to a cold ( $-78^\circ C$ ) solution of trimethylborate (23.06 mL, 205.8 mmol) in dry ether (200 mL). After complete addition, the mixture was allowed to warm to room temperature and stirred overnight at 25°C. Subsequently, 3M HCl (150 mL) was added. The organic layer was separated, and the aqueous layer was extracted with ether ( $2 \times 150$  mL). The combined organic phases were washed with water ( $2 \times 200$  mL) and dried (anhy.  $MgSO_4$ ). The extract was evaporated and the boronic acid derivative was washed several times with *n*-hexane to remove any impurity to get 7.4 g (86%) as light brown powder. Anal. Calcd. for  $C_7H_5BF_4O_2$  (207.92 g/mol): C, 40.44; H, 2.42. Found: C, 39.82; H, 2.25. FTIR (KBr  $cm^{-1}$ ): 1671, 1593, 1507, 1364, 1305, 1278, 1242, 1226, 1058, 844, 753, 725, 658, 540.  $^1H$ -NMR ( $CDCl_3/DMSO-d_6$  1 : 1, 200 MHz,  $\delta$  ppm): 8.2–7.9 (m, 1H,  $H^1$ ); 7.5–7.4 (m, 2H,  $H^2, H^3$ ).  $^{13}C$ -NMR ( $CDCl_3/DMSO-d_6$  1 : 1,  $\delta$  ppm): 115.4, 116.2, 122.2, 127.7, 133.9, 139.0, 159.9.

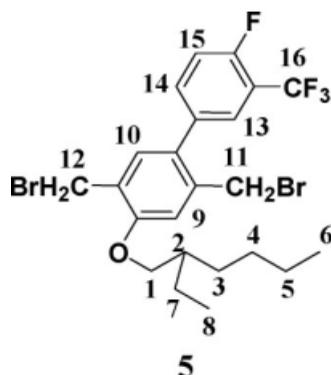
Preparation of 1,4-dimethyl-2-(2'-ethylhexyloxy)-5-(4-fluoro-3-trifluoromethyl benzyl) benzene (**4**)



2-Bromo-5-(2'-ethylhexyloxy)-*p*-xylene (**2**) (8 g, 25.5 mmol), 4-fluoro-3-trifluoromethylbenzylboronic acid (**2**) (6.37 g, 30.6 mmol),  $K_2CO_3$  (13.82 g, 0.1 mol) were mixed into of in 50 mL of THF,  $Pd(PPh_3)_4$  (0.14 g, 0.6 mol %) was added as catalyst. The reaction mixture was refluxed for 3 days under nitrogen atmosphere. After the completion of the reaction (monitored by TLC), organic layer was separated from the reaction mixture and passed through neutral alumina to remove the dissolved catalyst. The organic layer was then dried over anhydrous magnesium sulfate, concentrated under reduced pressure to get viscous oil. Further purification by silica gel column chromatography (with *n*-hexane as an eluent) leads to 8 g (79%) of colorless oil. Anal. Calcd. for  $C_{23}H_{28}F_4O$  (396.46 g/mol): C, 69.68; H, 7.12; O, 4.04. Found: C, 69.76; H, 7.68; O, 6.89. FTIR (KBr pellet,  $cm^{-1}$ ): 3051, 3027, 2958, 2930, 2864, 2737, 1614, 1572, 1498, 1464, 1382, 1334, 1262, 1237, 1166, 1140, 1055, 1047, 1004, 965, 910, 888, 835, 803, 768, 737, 688, 573.  $^1H$ -NMR ( $CDCl_3$ , 200

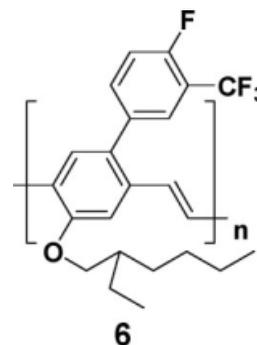
MHz,  $\delta$  ppm): 7.52 (d,  $J = 3.4$  Hz, 1H, H<sup>13</sup>), 7.48–7.44 (m, 1H, H<sup>14</sup>), 7.21 (t,  $J = 4.8$  Hz, 1H, H<sup>15</sup>), 6.97 (s, 1H, H<sup>10</sup>), 6.73 (s, 1H, H<sup>9</sup>), 3.89 (d,  $J = 2.8$  Hz, 2H, H<sup>1</sup>), 2.22 (s, 6H, H<sup>11</sup>, H<sup>12</sup>), 1.78–1.75 (m, 1H, H<sup>2</sup>), 1.55–1.44 (m, 4H, H<sup>7</sup>, H<sup>3</sup>), 1.39–1.33 (m, 4H, H<sup>4</sup>, H<sup>5</sup>), 0.98–0.90 (m, 6H, H<sup>8</sup>, H<sup>6</sup>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz,  $\delta$  ppm): 157.30, 138.47, 134.75 (C–F coupling, <sup>3</sup> $J = 8$  Hz), 133.61, 131.91, 131.08, 127.94, 124.64, 122.87 (C–F coupling, <sup>1</sup> $J = 270.8$  Hz), 118.02 (C–F coupling, <sup>2</sup> $J = 32.63$  Hz), 116.53, 116.37, 112.85, 70.37, 39.76, 30.88, 29.26, 24.26, 23.17, 20.27, 15.66, 14.05, 11.23.

Preparation of 1,4-bis(bromomethyl)-2-(2'-ethylhexyloxy)-5-(4-fluoro-3-trifluoromethylbenzyl)benzene (5)



1,4-Dimethyl-2-(2'-ethylhexyloxy)-5-(4-fluoro-3-trifluoromethylbenzyl)benzene (4) (5 g, 12.6 mmol), *N*-bromo succinimide (NBS) (4.48 g, 25.2 mmol) and catalytic amount of benzoyl peroxide (BPO) were taken into dry CCl<sub>4</sub> (50 mL). The mixture was refluxed for 8 h under nitrogen. The side product appeared as floating solid was filtered off. The crude product was further purified by silica gel column chromatography using *n*-hexane as eluent to give 1.8 g (26%) of white solid 1,4-bis(bromomethyl)-2-(2'-ethylhexyloxy)-5-(4-fluoro-3-trifluoromethyl benzyl)benzene (5) Anal. Calcd. for C<sub>23</sub>H<sub>26</sub>Br<sub>2</sub>F<sub>4</sub>O (554.25 g/mol): C, 49.84; H, 4.73; O, 2.89. Found: C, 49.67; H, 4.59; O, 2.78. FTIR (KBr pellet, cm<sup>-1</sup>): 3058, 3020, 2958, 2927, 2867, 2737, 1614, 1575, 1498, 1466, 1415, 1384, 1330, 1267, 1257, 1237, 1166, 1140, 1058, 1048, 1004, 965, 912, 890, 838, 801, 768, 737, 689, 571. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz,  $\delta$  ppm): 7.63 (d,  $J = 7.7$  Hz, 1H, H<sup>15</sup>), 7.54 (s, 1H, H<sup>13</sup>), 7.53 (s, 1H, H<sup>10</sup>), 7.34 (d,  $J = 9.6$  Hz, 1H, H<sup>14</sup>), 7.09 (s, 1H, H<sup>9</sup>), 6.47 (s, 2H, H<sup>11</sup>), 4.52 (s, 2H, H<sup>12</sup>), 4.08 (d,  $J = 5.2$  Hz, 2H, H<sup>1</sup>), 1.88–1.82 (m, 1H, H<sup>2</sup>), 1.58 (s, 6H, H<sup>6</sup>, H<sup>8</sup>), 1.42–1.36 (m, 4H, H<sup>3</sup>, H<sup>7</sup>), 1.04–0.86 (m, 4H, H<sup>4</sup>, H<sup>5</sup>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz,  $\delta$  ppm): 157.18, 138.31, 134.71 (C–F coupling, <sup>3</sup> $J = 8$  Hz), 133.58, 131.87, 131.01, 127.95, 124.6, 122.75 (C–F coupling, <sup>1</sup> $J = 270.3$  Hz), 118.02 (C–F coupling, <sup>2</sup> $J = 32.6$  Hz), 116.56, 116.4, 112.80, 70.37, 39.65, 30.79, 29.19, 24.18, 23.11, 20.37, 15.69, 14.10, 11.28.

Preparation of poly(2-(2'-ethylhexyloxy)-5-(4-fluoro-3-trifluoromethyl benzyl)-1,4-phenylene vinylene) (6)



A stirred solution of 1,4-bis(bromomethyl)-2-(2'-ethylhexyloxy)-5-(4-fluoro-3-trifluoromethylbenzyl)benzene (5) (1.6 g, 2.88 mmol) in dry THF (200 mL) was heated to reflux. Potassium *tert*-butoxide (0.97 g, 8.65 mmol) in THF (1.0M) was added dropwise through a dropping funnel. The resulting mixture was refluxed for another 6 h and cooled to room temperature. The fibrous solid was obtained after precipitation in large excess of methanol and water (10 : 1). The polymer was filtered off and washed with methanol after that the polymer was dried under high vacuum to get 1.2 g of polymer. Anal. Calcd. for (C<sub>23</sub>H<sub>24</sub>F<sub>4</sub>O)<sub>*n*</sub> (392.43)<sub>*n*</sub> g/mol: C, 70.39; H, 6.16; O, 4.08. Found: C, 69.98; H, 6.43; O, 4.16. FTIR (KBr pellet, cm<sup>-1</sup>): 3047, 2965, 2931, 2868, 1661, 1502, 1473, 1426, 1376, 1334, 1246, 1099, 987, 911, 760, 626. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz,  $\delta$  ppm): 7.6–6.7 (m, 7H, aromatic C–H and vinylic C–H), 4.16–3.91 (m, 2H, O–CH<sub>2</sub>), 1.8–0.9 (m, 17H, aliphatic C–H).

### Device fabrication

Electroluminescent device was fabricated using ITO glass as anode and Al as cathode. The ITO substrate was cleaned in an ultrasonic bath of acetone for few minutes and rinsing over isopropyl alcohol at room temperature. The polymer film was spin coated from the solution of THF (10 mg/mL, 1800 rpm), and the thickness was optimized up to 20 nm after that the film was dried under vacuum for 2 h. Aluminum was deposited on the surface of the polymer film via vacuum evaporation under a vacuum pressure below 10<sup>-5</sup> Torr. The active area of the device was 5 mm<sup>2</sup>.

## RESULTS AND DISCUSSION

### Synthesis

The synthetic scheme for the preparation of the monomer and the polymer is outlined in Scheme 1.

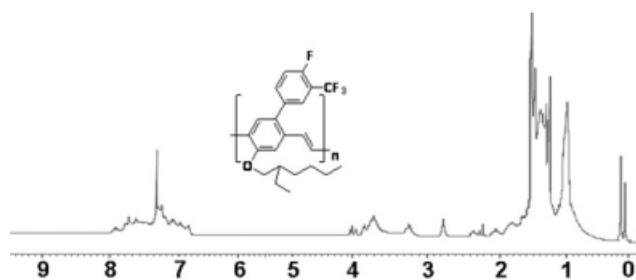


Figure 1  $^1\text{H-NMR}$  spectrum of polymer.

2,5-Dimethylphenol was first *O*-alkylated with 2-ethylhexyl bromide in presence of  $\text{K}_2\text{CO}_3$  to give compound **1**, which was further reacted with bromine under catalytic condition to give 2-bromo-5-(2'-ethylhexyloxy)-*p*-xylene (**2**). Suzuki coupling of 2-bromo-5-(2'-ethylhexyloxy)-*p*-xylene (**2**) with 4-fluoro-3-trifluoromethylphenylboronic acid (**3**) in THF produced 1,4-dimethyl-2-(2'-ethylhexyloxy)-5-(4-fluoro-3-trifluoromethyl benzyl)benzene (**4**). Finally, bromination of compound **4** by *N*-bromo succinimide (NBS) gave monomer [1,4-bis (bromomethyl)-2-(2'-ethylhexyloxy)-5-(4-fluoro-3-trifluoromethyl benzyl)benzene (**5**). The polymer (BTFM-PPV) was synthesized by Gilch process of polydehydrohalogenation polymerization of compound **5** with potassium *tert*-butoxide after refluxing in THF. To avoid formation of any side product, potassium *tert*-butoxide was added dropwise to the reaction mixture. A yellow powder of polymer was obtained after repeated precipitation in methanol. The polymer is soluble in common organic solvents such as tetrahydrofuran, chloroform, dichloromethane, toluene, and xylene. The number average molecular weight ( $M_n$ ) and weight average molecular weight ( $M_w$ ) of the BTFM-PPV were 29,900 and 154,000, respectively, with polydispersity index of 5.2 as determined by gel permeation chromatography (GPC) using THF as eluent and calibrated with polystyrene standards at  $30^\circ\text{C}$ . The polymer was well characterized by NMR, FTIR, and elemental analysis (Fig. 1).

### Thermal properties

It is well known that materials with a high-glass-transition temperature ( $T_g$ ) can provide device longevity.<sup>18</sup> Usually, highly soluble PPV derivatives show low  $T_g$  because they possess flexible long alkyl or alkoxy groups, e.g., MEH-PPV shows  $T_g$  at about  $65^\circ\text{C}$ .<sup>19</sup> DSC curve of BTFM-PPV shows the glass transition temperature at  $122^\circ\text{C}$  which is higher compared with MEH-PPV (Fig. 2) and almost same with other reported PPV derivative like BDMCyS-PPV, BDMPS-PPV, TEH-PPV, and TAA-PPV.<sup>12,19,20</sup> BTFM-PPV showed good thermal stability under nitrogen with 5% weight loss at  $210^\circ\text{C}$ . Low thermal stability

of this polymer compared with PPV is probably due to the presence of large alkoxy group in BTFM-PPV polymer similar to  $\text{CF}_3\text{F}_4$ -PPV and  $\text{P-CF}_3\text{F}_4\text{P}$ -PPV, respectively.<sup>12</sup>

### Optical properties

Optical properties of dilute solutions of this polymer in THF was measured by UV-Vis and fluorescence spectroscopy. The absorbance peaks were in the range of 418–422 nm and emission peaks were at 474–480 nm for three different concentrations in THF, e.g., 0.000625M, 0.00125M, and 0.0025M. A large blue shift for fluorescence emission was observed in respect to PPV (540 nm), MEH-PPV (595 nm) and many other PPV derivatives.<sup>21</sup>

The UV-Vis absorption for 0.0025M solution exhibit two major absorptions, at 309 nm and 422 nm (Fig. 3). The absorption at shorter wavelength (309 nm) is due to  $\pi$  to  $\pi^*$  transition from 4-fluoro-3-trifluoromethylphenyl substituent, whereas the absorption band maximum at 422 nm corresponds to  $\pi$  to  $\pi^*$  transition due to the main chain.<sup>18</sup> The optical band gap energy calculated from the absorption band edge of UV-Vis spectra is 2.48 eV. The  $\pi$  to  $\pi^*$  absorption maximum from the main chain of BTFM-PPV appeared at a shorter wavelength than that of MEH-PPV ( $\lambda_{\text{max}} = 501$  nm). Thus the substituent, 4-fluoro-3-trifluoromethylphenyl ( $-\text{F}$  and  $-\text{CF}_3$  attached with a phenyl ring), has a great influence on the absorption and emission spectra of this polymer. The electron density of the conjugated main chain in BTFM-PPV is diminished by electron withdrawing 4-fluoro-3-trifluoromethyl phenyl pendent group.<sup>22</sup> The absorption and emission maximum steadily blue shifted as the polymer solution

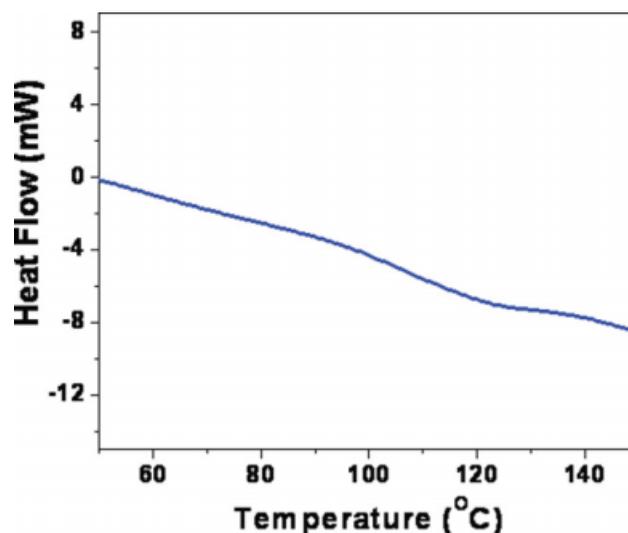
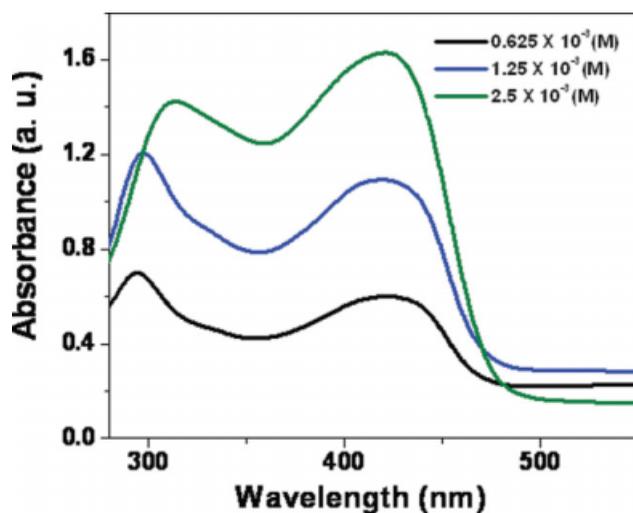


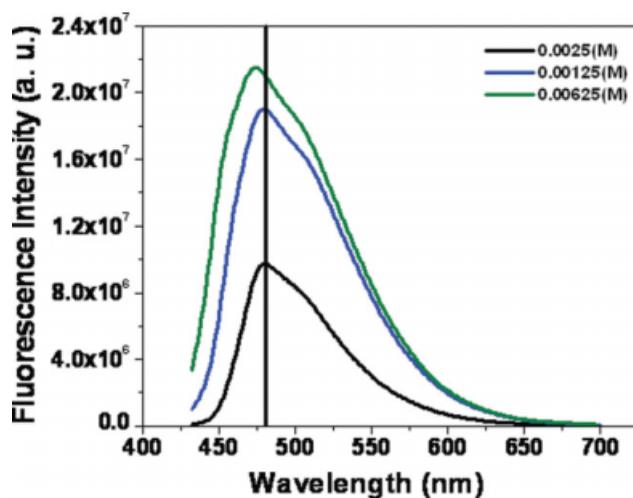
Figure 2 DSC thermogram of polymer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



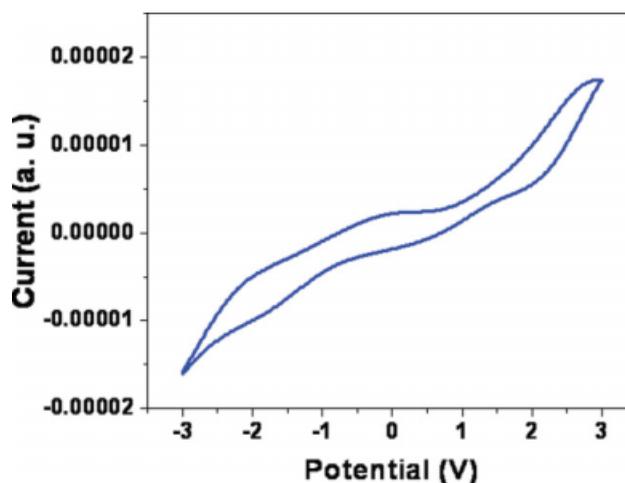
**Figure 3** UV-Vis spectra of BTFM-PPV in different dilute solutions. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

becomes diluted (Figs. 3 and 4). As we see from Figure 6, the broadening of the fluorescence emission becomes less with increase in the dilution of the solutions. This is probably due to the significant reduction of the aggregation of the polymer chains.<sup>23,24</sup>

Recently, Shim et al. described the electron withdrawing effect of fluorine attached directly to the PPV and the effect of perfluorinated moieties. Trifluoromethyl moiety attached to aromatic ring give slight blue shift, on the other hand when two  $-\text{CF}_3$  moiety attach on the aromatic ring give absorption and emission in the range of 361 nm and 489 nm.<sup>18,25</sup> Perfluorinated biphenyl unit as substituent in PPV exhibits absorption at 400 nm and emission at 520 nm. This perfluorinated biphenyl is an



**Figure 4** Fluorescence spectra of BTFM-PPV in different concentrations in THF. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

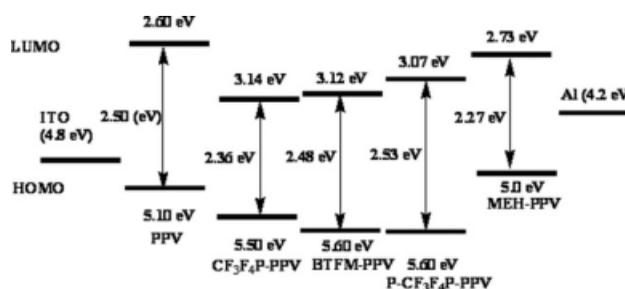


**Figure 5** Cyclic voltammogram of BTFM-PPV film coated on platinum plate electrode in acetonitrile solution. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

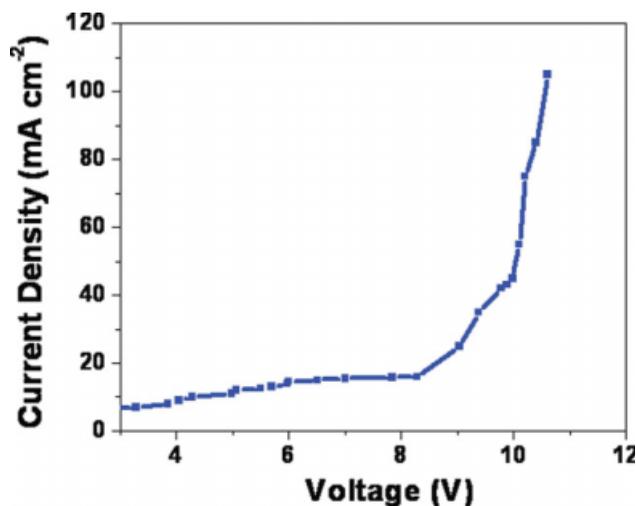
efficient electron withdrawing moiety and it was used as chromophore blocking unit.<sup>26,27</sup> So from above discussion it is clear that presence of electron withdrawing group shifted the fluorescence maximum in blue region.<sup>28</sup> Interestingly, in case of this newly synthesized BTFM-PPV, the fluorescence emission was shifted toward more to the blue region (upto 474 nm) in comparison to any other electron withdrawing group containing PPV derivatives.<sup>29,30</sup> This is most probably due to the inclusion of an extra phenyl ring between the electron withdrawing  $-\text{F}$  and  $-\text{CF}_3$  groups.

### Electrochemical Properties

The energy band diagram of the polymer was determined from the absorption edges and cyclic voltammetry (CV) method. The CV was performed with a solution of tetrabutylammonium perchlorate (0.10M) in acetonitrile solution at a scan rate of 50 mV/s at room temperature under inert atmosphere (Fig. 5). A platinum electrode ( $0.05 \text{ cm}^2$ ) coated with a thin



**Figure 6** Band diagram of BTFM-PPV polymer with respect to reported polymers.



**Figure 7** Current density–voltage characteristics of OLED of BTFM-PPV with the configuration of ITO/polymer/Al. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

polymer film was used as the working electrode. Pt wire and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. The onset potential of p- and n-doping are used to determine the IP (HOMO) and EA (LUMO) level through the relationship IP ( $E_{\text{HOMO}}$ ) =  $-(E_{\text{ox}} + 4.39)$  (eV) and EA ( $E_{\text{LUMO}}$ ) =  $-(E_{\text{red}} + 4.39)$  (eV).<sup>31</sup> The oxidation onset of the polymer was estimated to be 1.21 eV for BTFM-PPV. This corresponds to HOMO energy level of 5.60 eV. LUMO energy level is calculated by subtracting optical band gap value from HOMO energy level. The calculated LUMO energy level of the polymer is 3.12 eV. The extent of lowering of HOMO and LUMO energy level of BTFM-PPV polymer has been compared with other reported polymers in the energy band gap diagram (Fig. 6). This fluorated benzotrifluoromethyl group substituted PPV has much more negative HOMO and LUMO values in comparison to many other PPV derivatives. Lower HOMO level inhibit the hole injection and low energy band of the LUMO level facilitate electron injection that allow the construction of efficient single layer device.<sup>12,13,19</sup>

### I–V characteristics

Figure 7 shows the current–voltage (I–V) characteristic of the ITO/BTFM-PPV/Al diode.<sup>32</sup> The turn on voltage of the device was 7 Volt.<sup>33,34</sup> Such high value of the turn on voltage is due to the higher energy barrier for electron injection compared with holes, since the work function of ITO is  $-4.8$  eV and that of Al is 4.2 eV. The device performance can be markedly improved by incorporation of 4-fluoro-3-trifluoromethylphenyl units into the polymer main chain. All the measurements were performed under

ambient atmosphere at room temperature using unoptimized devices, so further improvements could be expected after optimization of the device fabrication.

### CONCLUSIONS

In conclusion, a new soluble PPV derivative (BTFM-PPV) has been synthesized successfully by the Gilch polymerization. BTFM-PPV exhibits good thermal and optical property along with high solubility. Introduction of pendent fluorated bezotrifluoromethyl group in PPV backbone causes a large blue shift making it a promising candidate for electroluminescence studies. BTFM-PPV has higher  $T_g$  in comparison to other common PPV which is essential for device longevity. The polymer has lower HOMO and LUMO energy. Lower HOMO level inhibit the hole injection and low energy band of the LUMO level facilitate electron injection that allow the construction of efficient single layer device. The further optimization of opto-electronic properties by substituting the  $-F$  atom present in the benzotrifluoromethyl group with various aromatic hydroxy containing different electronwithdrawing/electron-donating group is under investigation.

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