# Synthesis, Characterization, and Structure–Property Investigation of Conformationally Rigid Regioisomers of Poly(*p*-phenylene ethynylene)s

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**ABSTRACT:** A series of rigid poly(*p*-phenylene ethynylene)s (**PPE1-PPE4**) with biphenyl- (**M1–M3**) and phenyl- (**M4**) side groups is prepared from appropriately functionalized monomers. Herein, the solution and solid state absorption studies show the polymers have adopted twisted and rigid conformations, as supported by deep HOMO energy levels (-5.76 to -5.81 eV). The absorption maxima of **PPE1-PPE3** are shifted to shorter wavelength ( $\lambda_{max} = 375-381$  nm) as compared to linear poly(*p*-phenylene ethynylene)s (446 nm), implying a nonplanar conformation. The self-assembly of polymers into fibers is

**INTRODUCTION** Chiral-conjugated polymers have been considered as a useful material owing to interesting electrical and electronic properties, flexibility and processability, ability to form supramolecular structures and unique chiroptical properties. For example, they could be used as circular polarized luminescent materials,<sup>1,2</sup> chiral catalyst for asymmetric synthesis,<sup>3,4</sup> chiral sensor,<sup>5</sup> and nonlinear optics.<sup>6</sup> The general approaches for inducing chirality in conjugated polymers include introducing a chiral group on the side chain,  $^{7\mbox{-}9}$  chiral building blocks incorporated on the polymer backbone,<sup>10,11</sup> or helical macrostructure assembly induced by interaction between functionalized polymers with metal ions.<sup>12,13</sup> Majority of the studies were focused on polythiophenes, and poly(p-phenylene ethynylene)s incorporated with chiral functional groups.<sup>14</sup> Supramolecular helical structures are induced inside the polymer lattice by chiral alkoxy side group on polymer backbone,<sup>14</sup> or by the "sergeant-and-soldiers" co-assembly method,<sup>15-18</sup> where the chiral moieties (sergeant) decide the overall chirality of the polymer conformation mediated through nonchiral (soldiers) moieties. Other approaches were used to enhance the overall chirality of poly(phenylene ethynylene)s via structural modifications, including polymerization through meta-positions of benzene rings,<sup>19</sup> or introduction of branching on polymer backbone.<sup>20</sup> It has been demonstrated that poly(*m*phenylene ethynylene)s or oligo(*m*-phenylene ethynylene)s thermodynamically fold into helical conformation due to

examined using scanning electron microscopy. The fibers are not observed in **PPE4** with short phenyl side group, suggesting the important role of the interplay between rigidity, position, and size of the side chains toward the formation of fibers. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *00*, 000–000

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structural rigidity, and solvophobic effects.<sup>21,22</sup> On the other hand, the conformation of a rigid-conjugated polymer backbone can be frozen in helix architecture by incorporating bulky substituents on every repeating units, which prevents relaxation or free rotation along the chain.<sup>23,24</sup>

Herein, we report the synthesis and characterization of a series of conformationally rigid poly(*p*-phenylene ethynylene)s (**PPEs**) and comparison of their properties in detail (Fig. 1). The **PPE** backbone is designed to investigate the role of steric hindrance of the biphenyl side chains incorporated on every repeating units on polymer properties. Moreover, the rotations along polymer backbone are restricted depending on the position of the alkoxy biphenyl side chains. The effect of regioregularity of the polymer backbone on chiroptical properties is investigated by synthesizing regioirregular **PPE1**, **PPE2**, and regioregular **PPE3**. Symmetrical **PPE4** with shorter phenyl side groups is also synthesized and properties are compared with unsymmetrical polymers, **PPE1-PPE3**. Incorporation of alkyl chain on the biphenyl group helps to improve solubility of the target polymers.

#### **EXPERIMENTAL**

## Materials

All chemicals and reagents were purchased from commercial sources (Sigma Aldrich, Strem Chemical, Alfa Aesar and TCI)

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**FIGURE 1** Schematic representation and molecular structures of different poly(*p*-phenylene ethynylene) (**PPE1–PPE4**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and used without further purification. All reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates. Preparative separations were performed by column chromatography on a silica gel grade 60 (0.040–0.063 mm) from Silicycle.

#### Instrumentation

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance AV300 (300 MHz), a Bruker Avance AV400 (400 MHz), or a Bruker Avance AV500 (500 MHz) NMR instruments using appropriate deuterated solvents from Cambridge Isotope Laboratories. The chemical shifts were reported in part per million or ppm and referenced to the residual solvent peak: s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad. Electron Impact mass spectroscopy (EI-MS) mass spectra were obtained on a Finnigan TSQ7000. Atmospheric-pressure chemical ionization (APCI) mass spectra (APCI-MS) were obtained on Bruker MicroTOF-QII. UV-visible spectra were measured on a UV-1800 Shimadzu UV-VIS spectrophotometer with an optical filter that is calibrated at a bandwidth of 1 nm using a quartz cuvette with 10 mm light path. Emission spectra were measured on an Agilent Cary Eclipse Fluorescence Spectrophotometer with respective analytical grade solvents. Cyclic voltammograms were recorded with a computer controlled CHI electrochemical analyzer at a constant scan rate of 100 mV/s. The potentials were calibrated using ferrocene/ferocenium ion redox couple as internal reference. The onset of oxidation ( $E_{ox}^{onset}$ ) and reduction ( $E_{red}^{onset}$ ) were used to estimate HOMO ( $E_{HOMO}$ ) and LUMO ( $E_{LUMO}$ ) energy levels of polymers  $E_{\rm HOMO} = -(4.8 + E_{\rm ox}^{\rm onset})$ using equation the and  $E_{\rm LUMO} = -(4.8 + E_{\rm red}^{\rm onset})$ . Thermogravimetric analysis (TGA) was recorded under nitrogen atmosphere at heating rate of 10 °C/min on a TA Instruments 2960. All samples (3 mg) were dried at 50 °C under vacuum for 24 h to remove residual moisture prior to thermal analysis. Scanning electron micrograph was recorded on a JEOL JSM-6701F field emission scanning electron microscope. Optical rotations were acquired on a ADP 440 Polarimeter using a 10-cm polarimeter tube at 589 nm at 20 °C. Circular dichroism (CD) spectra

were acquired on a Jasco J-810 CD spectropolarimeter using a quartz cuvette with 1 mm light path.

# Synthesis of Monomers and Polymers 1-(2-Ethylhexyloxy)-4-Iodobenzene (3a)

A stirred solution of 4-iodophenol (2.56 g, 11.6 mmol), 2ethylhexyl bromide (2.70 g, 14.0 mmol), and potassium carbonate (3.30 g, 23.9 mmol) in DMF (80 mL) were added and heated to 90 °C for 18 h.25 The reaction mixture was cooled, diluted with water (50 mL) and extracted with diethyl ether  $(2 \times 100 \text{ mL})$ . The combined organic fractions were washed with water (2  $\times$  50 mL), followed by brine solution and water, dried over anhydrous sodium sulfate, filtered, and organic filtrate was concentrated under reduced pressure. The crude liquid was purified on a silica gel column using a mixture of 5% ethyl acetate in hexane as eluent to afford a colorless liquid. Yield = 2.78 g (72%), <sup>1</sup>H NMR (300 MHz,  $CDCl_3$ ,  $\delta$  ppm) 7.54 (d, 2H, J = 6.81 Hz), 6.67 (d, 2H, J = 6.81Hz), 3.79 (d, 2H, J = 5.71 Hz), 1.70 (m, 1H), 1.51-1.28 (m, 8H), 0.94–0.88 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 159.26, 138.10, 116.96, 82.26, 70.61, 39.27, 30.46, 29.03, 23.80, 23.01, 14.05, 11.06. MS (EI): M<sup>+</sup> (C<sub>14</sub>H<sub>21</sub>IO) Calculated m/z = 332.0, Found m/z = 332.1.

#### 4-Bromo-4'-(2-Ethylhexyloxy)Biphenyl (4a)

Compound 3a (1.70 g, 5.11 mmol), 4-bromophenylboronic acid (1.24 g, 5.60 mmol), and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.18 g, 0.25 mmol) were added to a predegassed solution mixture of THF (12 mL)/ethanol (3 mL)/2M aqueous K2CO3 solution (10 mL) under nitrogen atmosphere. The reaction mixture was heated to reflux for 20 h, cooled, concentrated, diluted with water (25 mL), and extracted with ethyl acetate (2  $\times$ 50 mL). The combined organic fractions were washed with water (2  $\times$  15 mL), followed by brine solution and water, dried over anhydrous sodium sulfate, filtered, and organic filtrate was concentrated under reduced pressure. The crude product was purified on silica gel column using a mixture of 5% ethyl acetate in hexane as eluent to afford a colorless liguid. Yield = 1.16 g (63%), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.52 (d, 2H, J = 8.68 Hz), 7.47 (d, 2H, J = 8.85 Hz), 7.40 (d, 2H, J = 8.68 Hz), 6.96 (d, 2H, J = 8.85 Hz), 3.88 (d, 2H, *I* = 5.78 Hz), 1.75 (m, 1H), 1.50–1.30 (m, 8H), 0.96–0.85 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 159.25, 139.84, 132.16, 131.75, 128.26, 127.89, 120.67, 114.90, 70.59, 39.37, 30.52, 29.69, 29.07, 23.85, 23.05, 14.08, 11.10. HR-MS (EI):  $M^+$  (C<sub>20</sub>H<sub>25</sub>BrO) Calculated m/z = 360.1083, Found m/zz = 360.1090. Anal. Calcd. for C<sub>20</sub>H<sub>25</sub>BrO: C, 66.48; H, 6.97. Found: C, 66.37; H, 7.01%.

# 2-(4'-(2-Ethylhexyloxy)-Biphenyl-4-Yl)-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolane (5a)

Compound **4a** (1.56 g, 4.31 mmol), bis(pinacolato)diboron (3.30 g, 13.00 mmol), Pd(dppf)Cl<sub>2</sub> (0.15 g, 0.18 mmol), and KOAc (2.55 g, 25.96 mmol) were added to a round bottom flask under nitrogen atmosphere. 1,4-Dioxane (35 mL) was added to the mixture via syringe and stirred at 80 °C for 20 h, cooled, concentrated, diluted with water (25 mL) and extracted with ethyl acetate (2  $\times$  50 mL). The combined

organic fractions were washed with water (2  $\times$  20 mL), followed by brine solution and water, dried over anhydrous sodium sulfate, filtered, and organic filtrate was concentrated under reduced pressure. The crude product was purified on a silica gel column using a mixture of 5% ethyl acetate in hexane as eluent to afford a colorless sticky liquid. (1.29 g, yield 73%) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.85 (d, 2H, J = 8.20 Hz), 7.57 (d, 2H, J = 8.21 Hz), 7.54 (d, 2H, J = 8.77 Hz), 6.97 (d, 2H, J = 8.77 Hz), 3.89 (d, 2H, J = 5.64 Hz), 1,75 (m, 1H), 1.51-1.26 (m, 8H), 1.36 (s, 12H), 0.96-0.90 (m, 6H).  $^{13}\text{C}$  NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 159.19, 143.51, 135.16, 133.11, 128.09, 125.87, 114.74, 83.66, 70.52, 39.33, 30.47, 29.01, 24.80, 23.81, 22.98, 14.00, 11.04. HR-MS (EI): M<sup>+</sup>  $(C_{26}H_{37}BO_3)$  Calculated m/z = 408.2830, Found m/zz = 408.2836. Anal. Calcd. for C<sub>26</sub>H<sub>37</sub>BO<sub>3</sub>: C, 76.47; H, 9.13. Found: C, 75.99; H, 9.03%.

## 1-[(S)-3,7-Dimethyl-Oct-6-Enyloxy]-4-Iodobenzene (3b)

A stirred solution of 4-iodophenol (4.86 g, 22.1 mmol), (S)-(+)-citronellyl bromide (5.80 g, 26.5 mmol) and potassium carbonate (6.10 g, 44.1 mmol) in DMF (40 mL) was heated to 90 °C for 18 h, cooled, concentrated, diluted with water (50 mL) and extracted with diethyl ether (50 mL x 2). The combined organic fractions were washed with water (20 mL x 2), followed by brine solution and water, dried over anhydrous sodium sulfate, filtered and organic filtrate was concentrated under reduced pressure. The crude liquid was purified on a silica gel column using a mixture of 5% ethyl acetate in hexane as eluent to give a colorless liquid. Yield = 5.86 g (74%), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.53 (d, 2H, J = 8.99 Hz), 6.68 (d, 2H, J = 8.99 Hz), 5.10 (t, 1H, J = 7.11 Hz), 3.94 (t, 2H, J = 6.81 Hz), 2.03 (m, 2H), 1.81 (m, 1H), 1.69 (s, 3H), 1.68-1.65 (m, 1H), 1.60 (s, 3H), 1.37 (m, 1H), 1.23 (m, 2H), 0.95 (d, 3H, J = 6.46 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 158.97, 138.11, 131.31, 124.58, 116.92, 82.37, 66.38, 37.07, 35.96, 29.46, 25.69, 25.41, 19.50, 17.64. HR-MS (EI):  $M^+$  ( $C_{16}H_{23}IO$ ) Calculated m/z=358.0794, Found m/z = 358.0788. Anal. Calcd. for C<sub>16</sub>H<sub>23</sub>IO: C, 53.64; H, 6.47. Found: C, 53.73; H, 6.41%.

4-Bromo-4'-[(S)-3,7-Dimethyl-Oct-6-Enyloxy]Biphenyl (4b) Compound 3b (3.84 g, 10.72 mmol), 4-bromophenylboronic acid (2.80 g, 13.94 mmol) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.49 g, 0.70 mmol) were added to a predegassed solution of THF (20 mL)/ethanol (5 mL)/2M aqueous K<sub>2</sub>CO<sub>3</sub> solution (15 mL) under nitrogen atmosphere. The reaction mixture was refluxed for 20 h, cooled, concentrated, diluted with water (25 mL), and extracted with ethyl acetate (50 mL  $\times$ 2). The combined organic fractions were washed with water (50 mL), followed by brine solution and water, dried over anhydrous sodium sulfate, filtered and organic filtrate was concentrated under reduced pressure. The crude product was purified on a silica gel column using a mixture of 5% ethyl acetate in hexane as eluent to afford a white solid. Yield = 2.11 g (51%), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.53 (d, 2H, J = 8.62 Hz), 7.48 (d, 2H, J = 8.81 Hz), 7.42 (d, 2H, J = 8.62 Hz), 6.97 (d, 2H, J = 8.81 Hz), 5.12 (t, 1H, J = 7.1 Hz), 4.03 (t, 2H, J = 6.83 Hz), 2.03 (m, 2H), 1.85 (m, 1H),

1.70 (s, 3H), 1.65 (m, 1H), 1.62 (s, 3H), 1.40 (m, 1H), 1.26 (m, 2H), 0.98 (d, 3H, J = 6.45 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 158.98, 139.81, 132.26, 131.75, 131.30, 128.25, 127.91, 124.65, 120.69, 114.91, 66.41, 37.12, 36.12, 29.55, 25.69, 25.45, 19.55, 17.65. HR-MS (EI): M<sup>+</sup> (C<sub>22</sub>H<sub>27</sub>BrO) Calculated m/z = 386.1245, Found m/z = 386.1244. Anal. Calcd. for C<sub>22</sub>H<sub>27</sub>BrO: C, 68.22; H, 7.03. Found: C, 68.32; H, 6.93%.

# 2-(4'-[(S)-3,7-Dimethyl-Oct-6-Enyloxy]-Biphenyl-4-Yl)-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolane (5b)

Compound 4b (1.33 g, 3.43 mmol), bis(pinacolato)diboron (3.50 g, 13.78 mmol), Pd(dppf)Cl<sub>2</sub> (0.17 g, 0.21 mmol) and KOAc (2.00 g, 20.37 mmol) were added to a round bottom flask under nitrogen atmosphere. 1,4-Dioxane (12 mL) was added via syringe and the reaction mixture was stirred at 80 °C for 20 h. The reaction mixture was cooled, concentrated, diluted with water (50 mL) and extracted with ethyl acetate (50 mL  $\times$  2). The combined organic layers were washed with water twice (25 mL  $\times$  2), followed by brine solution and water, dried over anhydrous sodium sulfate, filtered, and organic filtrate was concentrated under reduced pressure. The crude product was purified on a silica gel column using a mixture of 5% ethyl acetate in hexane as eluent to afford a pale-yellowish sticky liquid. Yield = 0.98 g (66%), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.86 (d, 2H, J = 8.28 Hz), 7.56 (d, 2H, J = 8.28 Hz), 7.55 (d, 2H, J = 8.83 Hz), 6.97 (d, 2H, J = 8.83 Hz), 5.12 (t, 1H, J = 7.11 Hz), 4.03 (t, 2H, J = 6.83Hz), 2.00 (m, 2H), 1.85 (m, 1H), 1.69 (s, 3H), 1.65 (m, 1H), 1.61 (s, 3H), 1.42 (m, 1H), 1.35 (s, 12H), 1.26 (m, 2H), 0.97 (d, 3H, I = 6.45 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 158.96, 143.53, 135.22, 133.26, 131.28, 128.18, 125.93, 124.66, 114.80, 83.73, 66.36, 37.12, 36.13, 29.53, 25.70, 25.45, 24.85, 19.55, 17.65. HR-MS (EI): M<sup>+</sup> (C<sub>28</sub>H<sub>39</sub>BO<sub>3</sub>) Calculated m/z = 434.2992, Found m/z = 434.3006. Anal. Calcd. for C<sub>28</sub>H<sub>39</sub>BO<sub>3</sub>: C, 77.41; H, 9.05. Found: C, 77.46; H, 8.94%.

## 1-(Octyloxy)-4-Iodobenzene (6)

A stirred solution of 4-iodophenol (1.32 g, 6.0 mmol), 1bromooctane (1.61 g, 8.3 mmol), and potassium carbonate (1.65 g, 11.9 mmol) in DMF (15 mL) was heated to 90 °C for 18 h.<sup>26</sup> The reaction mixture was cooled, concentrated, diluted with water (25 mL), and extracted with diethyl ether (30 mL  $\times$  2). The combined organic layers were washed with water (20 mL  $\times$  2), followed by brine solution and water, dried over anhydrous sodium sulfate, filtered, and organic filtrate was concentrated under reduced pressure. The crude liquid was purified on a silica gel column using hexane as eluent to afford a colorless liquid. Yield = 1.45 g, (73%), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 (d, 2H, *J* = 9.00 Hz), 6.66 (d, 2H, *J* = 9.00 Hz), 3.91 (t, 2H, *J* = 6.58 Hz), 1.74 (m, 2H), 1.43 (m, 2H), 1.30 (m, 8H), 0.89 (t, 3H, *J* = 6.80 Hz).

# 2-(4-Octyloxyphenyl) – 4,4,5,5-Tetramethyl-1,3,2-Dioxaborolane (7)

Compound **6** (0.89 g, 2.68 mmol), bis(pinacolato)diboron (1.02 g, 4.00 mmol), Pd(dppf)Cl<sub>2</sub> (0.10 g, 0.12 mmol), and KOAc (1.57 g, 15.99 mmol) were added to a round bottom flask under nitrogen atmosphere. 1,4-Dioxane (20 mL) was



added via syringe and the reaction mixture was stirred at 80 °C for 20 h. The reaction mixture was cooled, concentrated, diluted with water (15 mL) and extracted with ethyl acetate (25 mL  $\times$  2). The combined organic layers were washed with water (15 mL  $\times$  2), followed by brine solution, dried over anhydrous sodium sulfate, filtered and organic filtrate was concentrated under reduced pressure. The crude product was purified on a silica gel column using a mixture of 15% DCM in hexane as eluent to afford a pale-yellowish sticky liquid. Yield = 0.71 g (80%), <sup>1</sup>H NMR (300 MHz,  $CDCl_3$ ,  $\delta$  ppm) 7.73 (d, 2H, I = 8.68 Hz), 6.88 (d, 2H, I = 8.68Hz), 3.97 (t, 2H, J = 6.61 Hz), 1.78 (m, 2H), 1.55 (m, 2H), 1.33 (s, 12H), 1.31 (m, 8H), 0.88 (t, 3H, J = 6.95 Hz). HR-MS (EI):  $M^+$  (C<sub>20</sub>H<sub>33</sub>BO<sub>3</sub>) Calculated m/z = 332.2522, Found m/z = 332.2z = 332.2531. Anal. Calcd. for C<sub>20</sub>H<sub>33</sub>BO<sub>3</sub>: C, 72.29; H, 10.01. Found: C, 72.25; H, 9.94%.

#### **Compound 8a**

Compound 5a (0.79 g, 1.93 mmol), compound 1 (0.70 g, 1.93 mmol), Aliquat® 336 (3 mL), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.06 g, 0.05 mmol) were added to a predegassed mixture of THF (22 mL) and 2M aqueous K<sub>2</sub>CO<sub>3</sub> solution (18 mL) under nitrogen atmosphere. The reaction mixture was refluxed for 24 h, cooled, concentrated, diluted with water (15 mL) and extracted with ethyl acetate (20 mL  $\times$  2). The combined organic fractions were washed with water (15 mL), followed by brine solution, dried over anhydrous sodium sulfate, filtered and organic filtrate was concentrated under reduced pressure. The crude product was purified on a silica gel column using hexane as eluent to afford a colorless sticky liquid. Yield = 0.71 g (72%), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.62 (d, 2H, J = 8.48 Hz), 7.56 (d, 2H, J = 8.9 Hz), 7.54 (d, 1H, J = 8.51 Hz), 7.52 (d, 1H, J = 2.41 Hz), 7.43 (d, 2H, *J* = 8.48 Hz), 7.33 (dd, 1H, *J* = 8.51, 2.45 Hz), 7.00 (d, 2H, J = 8.9 Hz), 3.90 (d, 2H, J = 5.68 Hz), 1.76 (m, 1H), 1.51-1.28 (m, 8H), 0.98–0.92 (m, 6H).  $^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ppm) 159.23, 144.12, 140.64, 137.96, 134.49, 133.99, 132.65, 131.57, 129.59, 128.08, 126.31, 121.34, 121.18, 114.87, 77.42, 77.00, 76.58, 70.60, 39.41, 30.55, 29.09, 23.89, 23.05, 14.08, 11.12. HR-MS (EI): M<sup>+</sup> (C<sub>26</sub>H<sub>28</sub>Br<sub>2</sub>O) Calculated m/z = 514.0501, Found m/z = 514.0502. Anal. Calcd. for C<sub>26</sub>H<sub>28</sub>Br<sub>2</sub>O: C, 60.48; H, 5.47. Found: C, 60.19; H, 5.53%.

#### **Compound 8b**

Compound **5b** (0.31 g, 0.71 mmol), compound **1** (0.23 g, 0.64 mmol), Aliquat<sup>®</sup> 336 (1 mL), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.02 g, 0.017 mmol) were added to a predegassed mixture of THF (10 mL) and 2M aqueous K<sub>2</sub>CO<sub>3</sub> solution (5 mL) under nitrogen atmosphere. The reaction mixture was refluxed for 24 h. The work up procedure is same as described for **8a**. The crude product was purified on a silica gel column using a mixture of 5% DCM in hexane as eluent to afford a colorless sticky liquid. Yield = 0.24 g, (63%), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.62 (d, 2H, *J* = 8.49 Hz), 7.58 (d, 2H, *J* = 8.82 Hz), 7.54 (d, 1H, *J* = 8.48 Hz), 7.52 (d, 1H, *J* = 2.45 Hz), 7.44 (d, 2H, *J* = 8.49 Hz), 7.33 (dd, 1H, *J* = 8.48, 2.45 Hz), 7.00 (d, 2H, 8.82 Hz), 5.12 (t, 1H, *J* = 7.11 Hz), 4.05 (t, 2H, *J* = 6.83

Hz), 2.03 (m, 2H), 1.86 (m, 1H), 1.70 (s, 3H), 1.66 (m, 1H), 1.62 (s, 3H), 1.42 (m, 1H), 1.26 (m, 1H), 0.98 (d, 3H, J = 6.44Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 158.95, 144.13, 140.61, 138.00, 134.49, 133.99, 132.74, 131.57, 131.29, 129.59, 128.10, 126.30, 124.67, 121.34, 121.18, 114.88, 66.40, 37.14, 36.16, 29.57, 25.70, 25.46, 19.57, 17.66. HR-MS (EI): M<sup>+</sup> (C<sub>28</sub>H<sub>30</sub>Br<sub>2</sub>O) Calculated m/z = 540.0663, Found m/z = 540.0667. Anal. Calcd. for C<sub>28</sub>H<sub>30</sub>Br<sub>2</sub>O: C, 62.01; H, 5.58. Found: C, 61.93; H, 5.51%.

#### **Compound 8c**

Compound 7 (0.38 g, 1.14 mmol), compound 2 (0.24 g, 0.49 mmol), Aliquat<sup>®</sup> 336 (2 mL), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.03 g, 0.025 mmol) were added to a predegassed mixture of THF (8 mL) and 2 M aqueous  $K_2CO_3$  solution (3 mL) under nitrogen atmosphere. The reaction mixture was refluxed for 24 h. The work up procedure is same as described for 8a. The crude product was purified on a silica gel column using hexane as eluent to afford a colorless sticky liquid. Yield = 0.45 g (61%), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (s, 2H), 7.36 (d, 4H, *I* = 8.79 Hz), 6.96 (d, 4H, *I* = 8.79 Hz), 4.01 (t, 4H, J = 6.55 Hz), 1.82 (m, 4H), 1.48 (m, 4H), 1.33 (m, 16H), 0.90 (t, 6H, J = 6.91 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  159.05, 142.24, 135.19, 131.66, 130.48, 121.53, 114.05, 68.07, 31.83, 29.37, 29.25, 26.08, 22.67, 14.11. HR-MS (EI): M<sup>+</sup>  $(C_{34}H_{44}Br_2O_2)$  Calculated m/z = 642.1708, Found m/zz = 642.1703. Anal. Calcd. for  $C_{34}H_{44}Br_2O_2$ : C, 63.36; H, 6.88. Found: C, 63.38; H, 6.82%.

## **Monomer M1**

Compound 8a (0.33 g, 0.64 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.06 g, 0.05 mmol), and CuI (0.01 g, 0.06 mmol) were dissolved in a predegassed solution of THF (3 mL) and diisopropylamine (3 mL) under nitrogen atmosphere, followed by addition of ethynyltrimethylsilane (0.31 g, 3.19 mmol) via syringe. The reaction mixture was stirred at 80 °C for 24 h, cooled and concentrated under reduced pressure. The crude product was purified on a silica gel column using a mixture of 5% DCM in hexane as eluent to afford a colorless sticky liquid (0.31 g, yield 89%), which was dissolved in DCM/MeOH (10 + 10 mL) followed by addition of K<sub>2</sub>CO<sub>3</sub> (0.31 g, 2.25) mmol). The reaction mixture was stirred overnight at room temperature, diluted with DCM (20 mL), washed with water (15 mL), followed by brine solution and water, dried over anhydrous sodium sulfate, filtered and organic filtrate was concentrated under reduced pressure. The crude product was purified on a silica gel column using 5% DCM in hexane as eluent to afford a colorless sticky liquid. Yield = 0.21 g (92%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.67 (d, I = 1.3 Hz, 4H), 7.64-7.59 (m, 4H), 7.45 (dd, J = 7.9, 1.7 Hz, 1H), 7.04 (d, J = 8.7 Hz, 2H), 3.94 (d, J = 5.8, 2H), 3.22 (s, 1H), 3.20 (s, 1H), 1.81 (m, 1H), 1.63–1.36 (m, 8H), 0.99 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, δ ppm) 159.22, 144.18, 140.46, 137.50, 133.99, 133.19, 132.87, 130.43, 129.57, 128.12, 126.36, 122.85, 120.96, 114.93, 83.08, 82.76, 82.15, 79.23, 70.65, 39.49, 30.63, 29.18, 23.97, 23.14, 14.18, 11.22. MS (APCI, +ve):  $[M + H]^+$  (C<sub>30</sub>H<sub>31</sub>O) Calculated m/z = 407.24, Found

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m/z = 407.33. Anal. Calcd. for C<sub>30</sub>H<sub>30</sub>O: C, 88.63; H, 7.44. Found: C, 85.49; H, 7.21%.

## **Monomer M2**

Compound 8b (0.19 g, 0.35 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.03 g, 0.028 mmol), and CuI (6.7 mg, 0.035 mmol) were dissolved in a predegassed solution of THF (3 mL) and diisopropylamine (3 mL) under nitrogen atmosphere, followed by addition of ethynyltrimethylsilane (0.17 g, 1.75 mmol) via syringe. The reaction mixture was stirred at 80 °C for 24 h, cooled and concentrated under reduced pressure. The crude product was purified on a silica gel column using a mixture of 10% DCM in hexane as eluent to afford a colorless sticky liquid (0.14 g, yield 71%), which was dissolved in DCM/MeOH (5+5 mL) followed by addition of K<sub>2</sub>CO<sub>3</sub> (0.13 g, 0.94 mmol). The reaction mixture was stirred overnight at room temperature, diluted with DCM (10 mL), washed with water (15 mL), followed by brine solution and water, dried over anhydrous sodium sulfate, filtered and organic filtrate was concentrated under reduced pressure. The crude product was purified on a silica gel column using 10% DCM in hexane as eluent to afford a colorless sticky liquid. Yield = 0.09 g (86%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.66 (m, 4H), 7.63–7.58 (m, 4H), 7.44 (dd, J = 7.9, 1.7 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 2H), 5.17 (t, *J* = 7.1 Hz, 1H), 4.08 (m, *J* = 9.3 Hz, 2H), 3.21 (s, 1H), 3.19 (s, 1H), 2.15–2.01 (m, 2H), 1.95-1.86 (m, 2H), 1.74 (s, 3H), 1.68 (s, 3H), 1.51-1.42 (m, 1H), 1.34–1.24 (m, 2H), 1.02 (d, I = 6.6 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, δ ppm) 158.84, 144.07, 140.32, 137.43, 133.88, 133.08, 132.85, 131.24, 130.33, 129.47, 128.03, 126.25, 124.67, 122.74, 120.86, 114.82, 82.98, 82.65, 82.03, 79.12, 66.33, 37.12, 36.14, 29.53, 25.70, 25.45, 19.55, 17.65. MS (APCI, +ve):  $[M + H]^+$  (C<sub>32</sub>H<sub>33</sub>O) Calculated m/z=433.25, Found m/z = 433.42. Anal. Calcd. for C<sub>32</sub>H<sub>32</sub>O: C, 88.85; H, 7.46. Found: C, 89.92; H, 7.19%.

## **Monomer M3**

Compound 8a (0.30 g, 0.58 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.03 g, 0.02 mmol), and CuI (9 mg, 0.05 mmol) were dissolved in a predegassed solution of THF (6 mL) and diisopropylamine (6 mL) under nitrogen atmosphere, followed by addition of ethynyltrimethylsilane (0.06 g, 0.61 mmol) via syringe. The reaction mixture was stirred at 80  $^\circ\!C$  for 24 h, cooled and concentrated under reduced pressure. The crude product was purified on a silica gel column using a mixture of 5% DCM in hexane as eluent to afford a colorless sticky liquid (0.16 g, yield 52%), which was dissolved in DCM/MeOH (5+5 mL) followed by addition of  $K_2CO_3$  (0.12 g, 0.86 mmol). The reaction mixture was stirred overnight at room temperature, diluted with DCM (10 mL), washed with water (15 mL), followed by brine solution and water, dried over anhydrous sodium sulfate, filtered, and organic filtrate was concentrated under reduced pressure. The crude product was purified on a silica gel column using hexane as eluent to afford a colorless sticky liquid. Yield = 0.11 g (80%),  $^{1}$ H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.65 (d, 1H, J = 8.20 Hz), 7.63 (d, 2H, J = 8.46 Hz), 7.58 (d, 2H, J = 8.81 Hz), 7.50 (d, 1H, J = 2.07 Hz), 7.46 (d, 2H, J = 8.46 Hz), 7.32 (dd, 1H,

*J* = 8.25, 2.07 Hz), 7.00 (d, 2H, *J* = 8.81 Hz), 3.91 (d, 2H), 3.14 (s, 1H), 1.79–1.73 (m, 1H), 1.58–1.34 (m, 8H), 0.99– 0.89 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 159.17, 142.49, 140.45, 138.31, 134.68, 133.26, 132.71, 131.91, 129.64, 128.06, 126.25, 123.39, 121.53, 114.85, 82.46, 78.39, 70.58, 39.40, 30.54, 29.68, 29.08, 23.87, 23.05, 14.08, 11.11. HR-MS (EI): M<sup>+</sup> (C<sub>28</sub>H<sub>29</sub>BrO) Calculated *m/z* = 460.1396, Found *m/z* = 460.1402. Anal. Calcd. for C<sub>28</sub>H<sub>29</sub>BrO: C, 72.88; H, 6.33. Found: C, 72.59; H, 6.30%.

## **Monomer M4**

Compound 8c (0.56 g, 0.87 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.08 g, 0.07 mmol), and CuI (0.016 g, 0.087 mmol) were dissolved in a predegassed solution of THF (8 mL) and diisopropylamine (8 mL) under nitrogen atmosphere, followed by addition of ethynyltrimethylsilane (0.43 g, 4.35 mmol) via syringe. The reaction mixture was stirred at 80 °C for 24 h, cooled and concentrated under reduced pressure. The crude product was purified on a silica gel column using a mixture of 5% DCM in hexane as eluent to afford a white solid (0.49 g, yield 84%). The white solid (0.16 g, 0.24 mmol) was dissolved in DCM/MeOH (5 + 5 mL) followed by addition of  $K_2CO_3$ (0.13 g, 0.94 mmol). The reaction mixture was stirred overnight at room temperature, diluted with DCM (10 mL), washed with water (15 mL), followed by brine solution and water, dried over anhydrous sodium sulfate, filtered and organic filtrate was concentrated under reduced pressure. The crude product was purified on a silica gel column using hexane as eluent to afford a white solid. Yield = 0.10 g (79%), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.60 (s, 2H), 7.55 (d, J = 8.7 Hz, 4H), 6.96 (d, J = 8.7 Hz, 4H), 4.01 (t, J = 6.5Hz, 4H), 3.14 (s, 2H), 1.87-1.77 (m, 4H), 1.47 (m, 4H), 1.32 (m, 16H), 0.90 (t, J = 6.7 Hz, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 158.99, 142.09, 134.78, 131.11, 130.25, 120.85, 114.05, 82.89, 81.48, 68.01, 31.82, 29.37, 29.30, 29.25, 26.08, 22.66, 14.10. HR-MS (EI): M<sup>+</sup> (C<sub>38</sub>H<sub>46</sub>O<sub>2</sub>) Calculated m/z = 534.3498, Found m/z = 534.3496. Anal. Calcd. for C<sub>38</sub>H<sub>46</sub>O<sub>2</sub>: C, 85.35; H, 8.67. Found: C, 85.46; H, 8.71%.

## General Polymerization Procedures for PPEs Sonogashira polymerization

Monomers,  $Pd(PPh_3)_4$  and CuI were added into a sealed Schlenk tube under nitrogen atmosphere.<sup>27</sup> A solution of tetrahydrofuran/triethylamine (2:1) was degassed with nitrogen for 30 min, transferred into the sealed Schlenk tube under nitrogen atmosphere. The reaction mixture was refluxed for 48 h under darkness, cooled and concentrated under reduced pressure. The resulting sticky solid was dissolved in minimal amount of chloroform and precipitated from excess MeOH to afford the crude polymer.

## **Purification of Polymers**

The crude polymer was purified using Soxhlet extraction with various organic solvents. MeOH was used to remove unreacted monomers and catalyst. Acetone was used to remove small molecules and oligomers. Chloroform was used to extract the polymers, concentrated, and precipitated from excess MeOH to yield the target polymer.



# **Polymer PPE1**

The polymerization of **M1** (0.06 g, 0.15 mmol), and compound **8a** (0.08 g, 0.15 mmol) in presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (17 mg, 0.015 mmol) and CuI (4 mg, 0.021 mmol) in THF (6 mL) and triethylamine (3 mL) was carried out according to the Sonogashira polymerization procedure. The purification of polymer was done according to the general procedure to yield the yellow powder. Yield = 0.08 g (72%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.65 (br, 2H), 7.61–7.51 (br, 3H), 7.51–7.44 (br, 2H), 7.44–7.31 (br, 2H), 7.03–6.87 (br, 2H), 3.94–3.73 (br, 2H), 1.81–1.66 (br, 1H), 1.63–1.23 (br, 8H), 0.95 (br, 6H). IR (KBr, cm<sup>-1</sup>): 3030, 2957, 2926, 2858, 1606, 1501, 1467, 1382, 1286, 1246, 1178, 1113, 1036, 900, 824, 793, 691. GPC (THF, polystyrene standard),  $M_n$ : 7500 g/mol;  $M_w$ : 13,600 g/mol; PDI: 1.81.

## **Polymer PPE2**

The polymerization of **M2** (0.06 g, 0.14 mmol), and compound **8b** (0.076 g, 0.14 mmol) in presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (16 mg, 0.014 mmol) and CuI (4 mg, 0.021 mmol) in THF (6 mL) and triethylamine (3 mL) was carried out according to the Sonogashira polymerization procedure. The purification of polymer was done according to the general procedure to yield the yellow powder. Yield = 0.075 g (66%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.76-7.66 (br, 1H), 7.66-7.52 (br, 4H), 7.51-7.44 (br, 2H), 7.38 (br, 2H), 7.02-6.88 (br, 2H), 5.16-5.05 (m, 1H), 4.09-3.87 (br, 2H), 2.02 (br, 2H), 1.93-1.73 (br, 2H), 1.70 (br, 3H), 1.62 (br, 3H), 1.48-1.36 (br, 1H), 1.24 (br, 2H), 1.02-0.87 (br, 3H). IR (KBr, cm<sup>-1</sup>): 3036, 2923, 2853, 1608, 1519, 1468, 1390, 1290, 1246, 1176, 1094, 1024, 831, 804. GPC (THF, polystyrene standard),  $M_n$ : 8650 g/mol;  $M_w$ : 13,300 g/mol; PDI: 1.54.

#### **Polymer PPE3**

The polymerization of **M3** (0.21 g, 0.45 mmol) in presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.04 g, 0.03 mmol) and CuI (0.01 g, 0.05 mmol) in THF (15 mL) and triethylamine (7 mL) was carried out according to the Sonogashira polymerization procedure. The purification of polymer was done according to the general procedure to yield the yellow powder. Yield = 0.12 g (68%), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.79–7.30 (br, 6H), 7.24–6.54 (br, 5H), 3.97–3.53 (br, 2H), 1.83–1.25 (br, 9H), 1.04–0.69 (br, 6H). IR (KBr, cm<sup>-1</sup>): 3031, 2957, 2926, 2858, 1607, 1498, 1463, 1379, 1287, 1246, 1175, 1033, 821, 692, 518. GPC (THF, polystyrene standard), *M*<sub>n</sub>: 7950 g/mol; *M*<sub>w</sub>: 8660 g/mol; PDI: 1.09.

## **Polymer PPE4**

The polymerization of **M4** (0.034 g, 0.06 mmol), and compound **8c** (0.041 g, 0.06 mmol) in presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (6.9 mg, 0.006 mmol) and CuI (1.7 mg, 0.009 mmol) in THF (3 mL) and triethylamine (1.5 mL) was carried out according to the Sonogashira polymerization procedure. The purification of polymer was done according to the general procedure to yield the yellow powder. Yield = 0.049 g (75%), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 7.53 (br, 6H), 6.96 (br, 4H), 4.01 (br, 4H), 1.81 (br, 4H), 1.48–1.30 (br, 20 H), 0.89 (br, 6H). IR (KBr, cm<sup>-1</sup>): 3035, 2924, 2853, 1607, 1519, 1467, 1393,



**SCHEME 1** Synthetic routes for borylated phenyl compounds **5a**, **5b**, and **7**. (i) R-Br,  $K_2CO_3$ , DMF, 90 °C, 18 h; (ii) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, THF/EtOH/2M aqueous  $K_2CO_3$  solution, reflux, 20 h; (iii) bis(pinacolato)diboron, Pd(dppf)Cl<sub>2</sub>, KOAc, 1,4-dioxane, 80 °C, 20 h.

1250, 1179, 1094, 1029, 832, 803. GPC (THF, polystyrene standard), *M*<sub>n</sub>: 3800 g/mol; *M*<sub>w</sub>: 4800 g/mol; PDI: 1.24.

#### **RESULTS AND DISCUSSION**

#### Synthesis and Characterization

The syntheses of functionalized phenyl and biphenyl starting materials are shown in Scheme 1.

Commercially available 4-iodophenol was alkylated with three different alkyl bromides (2-ethylhexyl bromide, (S)-(+)-citronellyl bromide, and octyl bromide) using potassium carbonate as base to afford **3a** (72%), **3b** (74%), and **6** (73%) in good yields. The iodo groups on **3a** and **3b** were used for selective Suzuki-Miyaura coupling<sup>28</sup> with 4bromophenylboronic acid in presence of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as catalyst to afford biphenyl derivatives, **4a** and **4b** in 63 and 51% yields. Subsequently, Miyaura borylation<sup>29</sup> of **4a**, **4b**, and **6** with bis(pinacolato)diboron using Pd(dppf)Cl<sub>2</sub> as the catalyst and KOAc as the base gave borylated compounds, **5a** (73%), **5b** (66%), and **7** (80%), which were used for further coupling as described in Scheme 2.

The Suzuki-Miyaura coupling of 1,4-dibromo-2-iodobenzene with one equivalent of **5a** or **5b** gave the corresponding compounds **8a** or **8b** with achiral and chiral alkyl groups in 72 and 63% yields, respectively. Similarly, the symmetric compound **8c** was synthesized using Suzuki coupling of 1,4-diiodo-2,5-dibromobenzene (**2**) with **7** in 61% yield. All compounds were characterized fully using NMR spectroscopy, mass spectrometry and elemental analysis (Supporting Information, Figs. S1–S22).

The bi-functionalized monomers **M1**, **M2**, and **M4** were prepared by using Sonogashira coupling reactions of compounds **8a**, **8b**, and **8c** with ethynyltrimethylsilane, followed by deprotection of trimethylsilyl group with potassium carbonate in DCM/MeOH (Scheme 2, yields 61–81%). The



SCHEME 2 Synthetic approaches to the monomers (M1-M4); (i) Pd(PPh<sub>3</sub>)<sub>4</sub>, THF/2M aqueous K<sub>2</sub>CO<sub>3</sub> solution, Aliquat<sup>®</sup> 336, 80 °C, 24 h; (ii) (a) ethynyltrimethylsilane, Pd(PPh<sub>3</sub>)<sub>4</sub>, Cul, THF/ DIPA, 80 °C, 24 h; (b) K<sub>2</sub>CO<sub>3</sub>, DCM/MeOH, r.t, 18 h.

copolymerization of bifunctionalized monomers, such as, M1 and 8a, gave regioirregular polymer PPE1 as a result of nonregioselective step growth polymerization (Scheme 3).

In order to prepare regioregular polymer, the monoacetylene functionalized monomer (M3) was synthesized using Sonogashira coupling reaction of 8a with one equivalent of ethynyltrimethylsilane, followed by deprotection of trimethylsilyl group in an overall yield of 42%. The polymerization of M3 is expected to proceed in a regioselective manner compared to the nonregioselective polymerization of bi-functionalized monomers (M1 and M2).

<sup>1</sup>H NMR spectrum of isolated product was used to establish the regioisomer of M3. It is conceivable that the Sonogashira reaction between compound 8a and ethynyltrimethylsilane will result in two regioisomers of M3 as shown in Scheme S1. The <sup>1</sup>H NMR data of **M3** showed that it is not a mixture of both regioisomers. If it is a mixture of both regioisomers, the two different acetylene protons (f) peaks on NMR spectrum (Supporting Information, Fig. S27) should be observed owing to the nonsymmetrical structures between isomer 1 and isomer 2. In addition, proton 1, 2, and 3 of the benzene ring would have different chemical shifts for both isomer 1 and isomer 2, resulting in a complex NMR spectrum. However, the NMR spectrum of isolated product showed relatively simple and clear peaks.

All aromatic protons of M3 were assigned based on their chemical shifts and couplings (splitting and coupling constant) (Supporting Information, Fig. S29). It is observed that chemical shift of proton 1 shifts to downfield (from 7.54 to 7.65 ppm) upon substitution with acetylene group. On the other hand, the chemical shifts of proton 2 and proton 3 showed little changes. Similar changes were also observed for model compounds (Supporting Information, Scheme S2).<sup>30,31</sup> Hence we propose that **M3-isomer 1** is obtained based on the NMR spectrum of the molecule.

The monomers were polymerized via Sonogashira polymerization to afford PPEs in good yields (66-75%, Scheme 3). The crude polymers were purified by using Soxhlet extraction with a few organic solvents. Methanol extraction (12 h) was used to remove any unreacted monomers and catalysts. Acetone extraction (24 h) was used to remove low molecular weight oligomers. Chloroform extraction (24 h) was used to extract the target polymers, followed by precipitation from excess methanol to afford yellow polymers. All polymers are soluble in common organic solvents such as chloroform, THF, and toluene. The structures of PPE1-PPE4 were confirmed using <sup>1</sup>H NMR (Supporting Information, Fig. S32-S35) and molecular weights were estimated using gel permeation chromatography (GPC) with polystyrene as standards



PPE4 (R = R3), 75%

SCHEME 3 Polymerization route to afford PPE1-PPE4. (i) Pd(PPh<sub>3</sub>)<sub>4</sub>, Cul, THF/TEA, 80 °C, 48 h.

Polymer	<i>M</i> <sub>n</sub> a (g/mol)	<i>M</i> <sub>w</sub> a (g/mol)	Polydispersity Index <sup>a</sup>	Decomposition Temperature <sup>b</sup> (°C)
PPE1	7 500	13 600	1.81	403
PPE2	8 650	13 300	1.54	390
PPE3	7 950	8 660	1.09	360
PPE4	3 800	4 800	1.24	340

TABLE 1 Summary of molecular weights and decomposition temperatures of PPEs

<sup>a</sup>  $M_n$ ,  $M_w$ , and polydispersity indexes were determined using GPC with polystyrene as standard in THF. <sup>b</sup>Measured at 5% weight loss of polymer under nitrogen atmosphere with a heating rate of 10 °C/min from TGA thermograms.

(Table 1). TGAs were done using a heating rate of 10  $^{\circ}$ C/min up to 700  $^{\circ}$ C under nitrogen atmosphere (Fig. 2). All polymers showed good thermal stability up to 340  $^{\circ}$ C.

## **Photophysical Properties of PPEs**

The solution state absorption spectra of PPEs showed an absorption maximum at 290 nm in chloroform (Fig. 3), which corresponds to the absorption of terphenyl group, as compared to the spectra of monomers in chloroform (Supporting Information, Fig. S48). In addition, PPE1, PPE2, and PPE3 showed shoulder peaks at 380 nm, which are attributed to the absorption of poly(p-phenylene ethynylene)s polymer backbone. PPE1 and PPE2 exhibited similar absorption  $(\lambda_{max} = 292 \text{ nm}; 378-380 \text{ nm})$  and emission maxima  $(\lambda_{\rm ems} = 443-451 \text{ nm})$ , indicating a negligible effect of different alkoxy chains on photophysical property. PPE3 showed an absorption maximum at 380 nm, and emission maximum at 448 nm in chloroform. In contrast, PPE4 showed absorption and emission maxima at longer wavelength ( $\lambda_{max} = 460$  nm,  $\lambda_{ems} = 480$  nm) in chloroform. It is conceivable that the observed red-shifts in absorption and emission maxima of **PPE4** are originated from a better  $\pi$ -conjugation along the polymer backbone of PPE4.

In comparison to the maximum wavelengths of 446 nm and 390 nm reported in poly(*p*-phenylene ethynylene)s with alkoxy<sup>32</sup> and alkyl substituents,<sup>33</sup> **PPEs** showed blue-shifts in the absorption maxima. This suggests that presence of



FIGURE 2 Thermogravimetric analysis (TGA) curves of PPE1, PPE2, PPE3, and PPE4 at a heating rate of 10 °C/min under nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

biphenyl side groups on the **PPEs** induces high degree of twisting and freezing of conformation of the polymer backbone, resulting in poor  $\pi$ -orbital overlapping and blue-shift in absorption maxima. In general, red-shifts in absorption maxima are explained by better conjugation length along polymer backbone with higher molecular weight. However, the red-shifts in absorption maxima are limited according to the concept of effective conjugation length. The theoretical calculation showed that the effective conjugation length of linear poly(*p*-phenylene ethynylene)s is around 10 repeating units, however, this number decreases to less than 5 for the twisted poly(*p*-phenylene ethynylene)s backbones.<sup>34</sup> Such blue-shift in absorption maximum was reported for similar poly(*p*-phenylene ethynylene)s with bulky and extended side groups.<sup>35–37</sup>

It is known that planarization and  $\pi$ -stacking of poly(*p*-phenylene ethynylene) chains lead to strong red shift of absorption maximum in solid state.<sup>38</sup> All polymer thin films were examined by spectroscopies on quartz plates (Supporting Information, Fig. S49). **PPE1** and **PPE2** thin films showed red shifts in absorption peak edges by 25–30 nm but with no significant red shift in absorption maxima as compared to solution states. On the other hand, thin film of regioregular polymer, **PPE3** showed larger red shift (40 nm) in absorption edge than the regioirregular polymers, **PPE1** and **PPE2**.

The higher red shift in **PPE3** is attributed to its regioregular arrangement of biphenyl arms along the polymer backbone which allows better packing and planarization. **PPE4** did not show significant red shift in absorption edge in thin film,



**FIGURE 3** Absorption spectra (a) and photoluminescence spectra (b) of **PPE1** (-**-**), **PPE2** (-•), **PPE3** (-**-**), and **PPE4** (-**-**) in chloroform. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 2 Summary	of option	al properties	s of PPEs in	chloroform	and thin	ı films
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	Absorption					Fluorescence	
	C	CHCI3		Thin Film		CHCl <sub>3</sub>	Thin Film
Polymer	$\lambda_{\max}$ (nm)	$\epsilon^{a} 10^{4} (cm^{-1} M^{-1})$	$\lambda_{\max}$ (nm)	$\lambda_{onset}$ <sup>b</sup> (nm)	E <sup>c</sup> <sub>g solid</sub> (eV)	λ (nm)	$\lambda$ (nm)
PPE1	292, 378	50, 20	290	465	2.66	443	501
PPE2	292, 380	67, 28	290	460	2.69	451	504
PPE3	290, 381	39, 7	300	470	2.64	448	518
PPE4	280, 420, 460	13, 8, 8	278, 420, 450	485	2.56	450, 480	520

<sup>a</sup>  $\varepsilon$  extinction coefficient was calculated by dividing absorbance with concentration (M) and cuvette path length (1 cm). <sup>b</sup> $\lambda_{onset}$  was calculated from the intersection of the tangent lines drawn to the lowest energy absorption edge to the baseline. <sup>c</sup> $E_g = 1240/\lambda_{onset}$ . The concentrations (molarity on monomer basis) of **PPE1**, **PPE2**, **PPE3**, and **PPE4** are 2.4, 2.0, 2.3, and 3.1  $\mu$ M, respectively.

which suggests that the **PPE4** has adopted similar conformation in solution and in solid state. The effect of interchain  $\pi$ stacking in **PPE4** is minimized with two phenyl side groups. On the other hand, the interchain  $\pi$ -interaction is more pronounced in **PPE1-PPE3**. All photophysical properties of polymers are summarized in (Table 2).

#### **Electrochemical Properties of PPEs**

Cyclic voltammetry was carried out to probe the electrochemical properties of **PPEs** thin films. The HOMO energy levels of **PPEs** were estimated from the onset oxidation potential as summarized in Figure 4 and Table 3. In our studies, the HOMO energy levels of **PPE1-PPE4** were estimated under same conditions (solvent, electrolyte, and electrodes) for comparison. All **PPEs** showed irreversible oxidation waves at a significantly higher potential of 1.59–1.70 V (vs. Ag<sup>+</sup>/Ag) as compared to that reported in poly(*p*-phenylene ethynylene) (1.10 V vs. Ag<sup>+</sup>/Ag) with alkoxy side chains.<sup>39</sup>

The phenyl substituents and low degree of conjugation in our polymers are responsible for high oxidation potentials as compared to alkoxy **PPEs**. The high onset oxidation potential is accompanied with a deep HOMO energy level (-5.77 to -5.81 eV) in **PPEs**, which is lower than the HOMO energy



**FIGURE 4** Cyclic voltammograms of **PPE1** (-**I**-), **PPE2** (-•-), **PPE3** (-**A**-), and **PPE4** (-**V**-) thin films measured with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile at the scan rate of 100 mV s<sup>-1</sup> using Ag/AgCl as reference electrode. The **PPE** films were prepared by drop casting chloroform solution of **PPEs** on platinum disk electrode.

level (0.45 V vs. Fc/Fc<sup>+</sup>, thus a -5.25 eV for HOMO) reported for alkoxy poly(*p*-phenylene ethynylene)s.<sup>40</sup> No significant differences in HOMO energy levels of **PPE1-PPE4** were observed. It is conceivable that the highly twisted and rigid polymer conformations lead to poorly overlapped  $\pi$ -electron wave function along **PPEs** backbone, which results in the deep HOMO energy level.

## **Chiroptical Properties of PPEs**

The effects of bulky substituents on the chiral properties of the **PPEs** were studied. Optical rotation and CD spectroscopy has been widely used to study the chiroptical properties of polypyrroles, polythiophenes, and poly(aryleneethynylene)s to provide useful information about the variations in polymer conformation under different environments.<sup>14,24,41</sup> It is reported that the conjugated polymers such as polythiophene, showed chiroptical CD signals when their backbone aggregates into chiral conformation in the presence of a poor solvent.<sup>8,42</sup>

The optical activities of the **PPEs** in chloroform were first examined using a polarimeter at 589 nm under ambient conditions. **PPE1** and **PPE3** showed no specific rotations (0.5 mg/mL, chloroform). On the other hand, the **PPE2** with chiral (S)-(+)-citronellyl group showed a specific rotation  $[\alpha]_D$  of +23. Similarly, no specific optical rotation was observed from symmetric **PPE4** with a shorter phenyl side group in chloroform.

TABLE 3 Summar	y of electrochemical	properties of PPEs

Polymer	E <sub>ox</sub> a (V vs. Ag/AgCl)	E <sup>b</sup> <sub>oxonset</sub> (V vs. Ag/AgCl)	HOMO <sup>c</sup> (eV)
PPE1	1.65	1.40	-5.77
PPE2	1.60	1.39	-5.76
PPE3	1.59	1.42	-5.80
PPE4	1.70	1.43	-5.81

<sup>a</sup> Determined from the potential where maximum oxidation occurred <sup>b</sup>Determined from the onset oxidation potential. <sup>c</sup>Electrochemical HOMO =  $-(E^{\text{ox calibrated}} + 4.8)$  eV, where  $E^{\text{ox calibrated}}$  were determined from the onset potentials of first oxidation peak calibrated with ferrocene/ferocenium ion redox couple.

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FIGURE 5 SEM images of fibers obtained by dropcasting the chloroform/methanol (2:1) solution of PPEs on glass substrates. The solvent was allowed to evaporate slowly inside a desiccator over 24 h at room temperature. The concentration of all polymer solutions was kept at 0.05 mg/mL.

In order to investigate the effect of substituents on chiral conformation of PPEs, the CD spectra of the polymers were recorded in chloroform and chloroform/methanol solution. Only weak CD signals were observed for all PPEs (Supporting Information, Figs. S50-S53). This suggests the formation of single-handed helical macrostructures for PPEs in presence of poor solvent may not be strong with a small side chain. It is known that the interaction of chiral alkyl chains between adjacent polymer backbones leads to highly ordered helical aggregates.<sup>8</sup> However, **PPE2** incorporated with chiral alkyl substituents showed no recognizable CD signals in presence of methanol. The absence of helical aggregates for PPE2 is attributed to the short biphenyl side groups, which may not facilitate chiral  $\pi$ -stacking of polymer chains. We are currently developing other substituents to test such a hypothesis.

#### **Morphology Studies of PPEs**

The morphology of the **PPEs** film was examined by fieldemission scanning electron microscopy (SEM). The polymer solution in chloroform/methanol (0.05 mg/mL) was dropcasted on a glass substrate, which was kept inside a desiccator. The solvent was allowed to evaporate slowly over 24 h at room temperature prior to SEM examination. The scanning electron micrographs of **PPE1** and **PPE3** dropcasted from chloroform/ methanol (2:1) solution showed fibers with a diameter of 150– 200 nm (Fig. 5). On the other hand, fibers with a diameter of 200 nm were formed from **PPE2** under similar conditions. In contrast, **PPE4** with shorter side arms only showed random aggregates under similar conditions. This suggests the shorter phenyl side arm and symmetric nature of the backbone in **PPE4** do not allow formation of ordered macrostructures.

#### CONCLUSIONS

In summary, a series of rigid poly(*p*-phenylene ethynylene)s (**PPE1-PPE3**) with biphenyl side chains was synthesized. Photophysical studies in solution and solid states showed that **PPE1-PPE3** adopted a twisted conformation of the backbone with significant blue shifts in absorption maxima, and supported by the deep HOMO energy levels (-5.76 to -5.81 eV). Helical aggregates were not confirmed for **PPEs** with short biphenyl side groups, which may not be sufficient to stabilize chiral aggregations. Scanning electron micrographs showed the formation of twisted fibers after slow evaporation of **PPE1-PPE3** polymer solutions on glass substrates. Overall, this article highlights the substituent induced structural and property changes on the **PPE** backbone.

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