## Controlled Synthesis of *ortho*, *para*-alternating linked polyarenes via Catalyst-Transfer Suzuki coupling polymerization

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## **Supporting Information**

**General**: NMR spectra were recorded at 23 °C on a Varian VNMRS 500 MHz NMR spectrometer, operating at 499.7 MHz for proton, in CDCl<sub>3</sub> unless otherwise noted. Chemical shifts were determined relative to residual CHCl<sub>3</sub> (7.26 ppm) for proton, and to the CDCl<sub>3</sub> "triplet" at 77.23 ppm for carbon. All yields reported refer to isolated yields unless otherwise indicated. *M*n and *Mw/M*n (PDI) value of polymers were measured with gel permeation chromatography (Waters Alliance 2695 separations module equipped with three polymer labs PLgel 5 µm mixed C columns) using THF as eluent (1 mL/min) at 40 °C, which were calibrated with polystyrene standards. Electronic absorption spectra were recorded using a quartz cell of 10 mm path length on a Cary 5000 UV-vis-NIR spectrophotometer. MALDI-TOF mass spectra were recorded on a Bruker Reflex III in the reflection mode with a laser ( $\lambda = 337$  nm) using 1,1,4,4-tetraphenyl-1,3-butadiene as a matrix. Thermal properties were measured by a TA Instruments Q-2000 differential scanning calorimeter (DSC). All the solvents were degassed for 2 h before use. All the reagents were purchased from commercial sources and used as received. 2,3-Dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**s3**) was prepared according to the reported procedure.<sup>1</sup>

Synthetic route to monomer 1



**Preparation of compound s2 from compound s1:** 1-bromododecane (37.5 g, 150 mmol) was added to a vigorously stirred solution of 4-bromocatechol (9.45 g, 50 mmol) and potassium carbonate (27.6 g, 200 mmol) in ethanol (250 mL). The reaction mixture was stirred under reflux for 24 h and filtered with copious washings of ethanol. The filtrate was concentrated via evaporation. The crude product was purified via column chromatography (silica gel, hexane:CH<sub>2</sub>Cl<sub>2</sub> = 1 : 1 v/v).



Br s2: Yield: 85% white solid. <sup>1</sup>H NMR:  $\delta$  6.98 ~ 7.00 (m, 2 H), 6.74 (d, J = 9.0 Hz, 1 H), 3.95 ~ 3.98 (m, 4 H), 1.78 ~ 1.83 (m, 4 H), 1.44 ~ 1.46 (m, 4 H), 1.27 ~ 1.36 (m, 30 H), 0.88 ~ 0.91 (m, 6 H); <sup>13</sup>C NMR:  $\delta$  150.14, 148.46, 123.48, 117.13, 115.35, 112.84, 69.61, 69.45, 33.90, 32.85, 31.90, 29.66, 29.34, 29.25, 29.16, 28.75, 28.17, 25.97, 22.66, 14.06.

**Preparation of compound s4 from compound s2:** In an argon glovebox, to 100 mL roundbottom flask containing  $Pd_2(dba)_3$  (196 mg, 0.24 mmol), *t*-Bu<sub>3</sub>P (96 mg, 0.48 mmol), K<sub>3</sub>PO<sub>4</sub> (3.84 g, 18 mmol), compound **s2** (3.15 g, 6 mmol) and compound **s3** (2.22 g, 6 mmol) was added 1,4-dioxane (30 mL) and water (3 mL). Then, the reaction was performed at 80 °C overnight. The reaction was quenched with saturated NH<sub>4</sub>Cl solution. The product was extracted with dichloromethane (3 x 15 mL). The combined organic layer was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of solvents under vacuum, the crude product was purified via column chromatography (silica gel, hexane:CH<sub>2</sub>Cl<sub>2</sub> = 1 : 1, v/v).



**s4**: Yield: 70% brown solid. <sup>1</sup>H NMR: δ 7.68 (dd,  $J_I = 8.0$  Hz,  $J_2 = 33.5$  Hz, 4 H), 7.15 ~ 7.19 (m, 4 H), 7.07 (d, J = 8.0 Hz, 2 H), 6.97 (d, J = 9.0 Hz, 1 H), 6.45 (d, J = 8.0 Hz, 2 H), 6.08 (s, 2 H), 4.05 ~ 4.10 (m, 4 H), 1.84 ~ 1.88 (m, 4 H), 1.49 ~ 1.52 (m, 4 H), 1.28 ~ 1.39 (m, 30 H), 0.88 ~ 0.91 (m, 6 H); <sup>13</sup>C NMR: δ 149.4, 149.3, 142.9, 141.0, 137.8, 136.3, 133.7, 131.8, 127.6, 126.5, 119.7, 117.8, 114.2, 113.2, 106.0, 69.6, 69.4, 31.9, 29.6, 29.6, 29.4, 29.3, 26.0, 22.6, 14.0.

**Preparation of compound s5 from compound s4:** Hydrochloride acid (6 N, 3.6 mL) was added to a vigorously stirred solution of compound s4 (2.8 g, 4 mmol) in THF (45 mL). The reaction mixture was stirred at room temperature for 16 h. The product was extracted with dichloromethane (3 x 40 mL). The combined organic layer was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of solvents under vacuum, the crude product was directly added to the solution of pinacol (590 mg, 5 mmol) in THF (50 mL). The mixture was stirred under reflux for 12 h. The product was extracted with dichloromethane (3 x 40 mL). The combined organic layer was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of solvents under vacuum, the crude product was extracted with dichloromethane (3 x 40 mL). The combined organic layer was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of solvents under vacuum, the crude product was purified via column chromatography (silica gel, hexane:CH<sub>2</sub>Cl<sub>2</sub> = 1 : 1 v/v).



**s5 s5:** Yield: 70% brown solid. <sup>1</sup>H NMR: δ 7.83 (d, J = 8.5 Hz, 2 H), 7.53 (d, J = 9.0 Hz, 2 H), 7.12 ~ 7.13 (m, 2 H), 6.91 (d, J = 9.0 Hz, 1 H), 4.00 ~ 4.05 (m, 4 H), 1.80 ~ 1.83 (m, 4 H), 1.45 ~ 1.47 (m, 4 H), 1.24 ~ 1.34 (m, 44 H), 0.86 (t, J = 7.5 Hz, 6 H); <sup>13</sup>C NMR: δ 149.4, 149.2, 143.7, 135.1, 134.0, 126.0, 119.8, 114.2, 113.4, 83.7, 69.5, 69.4, 31.9, 29.6, 29.6, 29.4, 29.3, 26.0, 24.8, 22.6, 14.0.

**Preparation of monomer 1 from compound s5:** NBS (594 mg, 3.3 mmol) was added to a vigorously stirred solution of compound **s5** (2 g, 3 mmol) in  $CH_2Cl_2$  (15 mL). The reaction mixture was stirred at room temperature for 16 h. The reaction was quenched by  $Na_2S_2O_3$  solution and then extracted with dichloromethane (3 x 40 mL). The combined organic layer was washed with brine and dried over  $Na_2SO_4$ . After removal of solvents under vacuum, the crude product was purified via column chromatography (silica gel, hexane: $CH_2Cl_2 = 1 : 1 v/v$ ).



**1**: Yield: 70% brown solid. <sup>1</sup>H NMR:  $\delta$  7.86 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 9.7 Hz, 2H), 7.13 (s, 1H), 6.83 (s, 1H), 4.09 – 3.83 (m, 4H), 1.95 – 1.68 (m, 4H), 1.52 – 1.15 (m, 54H), 0.88 (dd, J = 6.7, 5.5 Hz, 6H). <sup>13</sup>C NMR:  $\delta$  149.1, 148.4, 143.9, 134.7, 134.3, 128.8, 118.1, 116.4, 112.3, 83.8, 69.6, 31.9, 31.4, 30.2, 29.5, 29.3, 29.2, 29.1, 25.9, 24.8, 22.6, 14.0.

Polymerization of monomer 1 with  $Pd_2(dba)_3/t$ -Bu<sub>3</sub>P/4-BrC<sub>6</sub>H<sub>4</sub>COPh as initiator: In a drybox under N<sub>2</sub> atmosphere, to 5-mL vial containing  $Pd_2(dba)_3$  (5.5 mg, 0.006 mmol), THF (0.4 mL) and *t*-Bu<sub>3</sub>P (48 µL, 0.5 M solution in THF) was added 4-bromobenzophenone (40 µL, 0.25 M solution in THF). The mixture was stirred for 1 hour at room temperature to generate the initiator. To another vial containing monomer 1 (0.1 mmol) and THF (5.4 mL) was added 0.5 mL of K<sub>3</sub>PO<sub>4</sub> (2 M solution in water) and the mixture was cooled to 0 °C. The solution of the in situ generated initiator was quickly injected into the solution of monomer and the resulting mixture was stirred for 30 min at 0 °C. The reaction was quenched by pouring the mixture into 12 N HCl. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL). The organic layer was combined, washed by brine and dried with Na<sub>2</sub>SO<sub>4</sub>. The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was dissolved in a minimum amount of THF and the solution was added dropwise to methanol with stirring. The precipitate was collected by filtration, washed with methanol and water and dried under vacuum to get target polymer 2.



Polymer **2**: 83% yield. Brown solid. GPC: Mn = 7000 (PDI = 1.16). <sup>1</sup>H NMR:  $\delta$  6.94 (s, 4 H), 6.85 (s, 2 H), 3.95 (s, 4 H), 1.76 (s, 4 H), 1.22 ~ 1.41 (m, 36 H), 0.84 (t, J = 7.2 Hz, 6 H); <sup>13</sup>C NMR:  $\delta$  145.8, 136.8, 130.2, 126.8, 113.4, 74.6, 74.6, 74.4, 74.1, 66.8, 29.3, 27.1, 27.1, 26.9, 26.8, 26.8, 23.5, 20.1, 11.5.

Molecular Weight–Conversion Relationship Study for Polymerization with  $Pd_2(dba)_3/t$ -Bu<sub>3</sub>P/4-BrC<sub>6</sub>H<sub>4</sub>COPh as the Initiator: In a glovebox under N<sub>2</sub> atmosphere, to a 5-mL vial containing Pd<sub>2</sub>(dba)<sub>3</sub> (5.5 mg, 0.003 mmol), THF (0.4 mL), *t*-Bu<sub>3</sub>P (24 µL, 0.5 M solution in THF) was added 4-bromobenzophenone (20 µL, 0.25 M solution in THF). The mixture was stirred for 1 hour at room temperature to in situ generate the initiator. In another vial containing monomer 1 (72.7 mg, 0.1 mmol) and THF (5.4 mL) was added 0.5 mL of K<sub>3</sub>PO<sub>4</sub> (2 M solution in water). The mixture was cooled to 0 °C. The solution of initiator was quickly injected into the solution of monomer and the resulting mixture was stirred at 0 °C. A small aliquot (0.3 mL) of the organic phase of the reaction mixture was sampled at 10, 15, 20, 30, 60 min. Each aliquot was quenched with 12 N HCl and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The separated organic layer was evaporated under reduced pressure to get a residue. Half of the residue was dissolved in CDCl<sub>3</sub> to determine the conversion of monomer by <sup>1</sup>H NMR (conversions of 39%, 80%, 85%, 96% and 99% were observed for 10, 15, 20, 30 and 60 min, respectively). The other half of the residue was dissolved in THF and the solution was filtered. The filtrate was analyzed by GPC to determine the *M*n and *M*w/*M*n values of the polymers. The *M*n (*M*w/*M*n) values of each polymer initiated by  $Pd_2(dba)_3/t$ -Bu<sub>3</sub>P/4-BrC<sub>6</sub>H<sub>4</sub>COPh for 10, 15, 20, 30 and 60 min were 5100 (1.23), 9800 (1.23), 11000 (1.26), 12400 (1.25) and 12700 (1.27) respectively.



Figure S1: GPC traces and molecular weight–conversion relationship for Pd<sub>2</sub>(dba)<sub>3</sub>/*t*-Bu<sub>3</sub>P/4-BrC<sub>6</sub>H<sub>4</sub>COPh initiated polymerization of monomer 1

The polymerization of polymer **2** with different amounts of initiator  $(Pd_2(dba)_3/t-Bu_3P/4-BrC_6H_4COPh, 3, 6 and 9 mol % loading for Pd_2(dba)_3, with the ratio of Pd_2(dba)_3 : t-Bu_3P: 4-BrC_6H_4COPh to be 1 : 4 : 1.67) was performed in a manner similar to the general procedure described in the [General Procedure for the polymerization of monomers 1 initiated by Pd_2(dba)_3/t-Bu_3P/4-BrC_6H_4COPh] except different initiator loadings. The polymer yields were 76%, 80% and 83%, respectively and$ *M*n (PDI) were found to be 13500 (1.22), 7000 (1.16) and 5000 (1.19), respectively. (Figure S2, shown below).



Figure S2: GPC traces and relationship of polymerization with different catalyst loading



Figure S3: MALDI-TOF spectrum of Pd<sub>2</sub>(dba)<sub>3</sub>/t-Bu<sub>3</sub>P/4-BrC<sub>6</sub>H<sub>4</sub>COPh catalyzed polymerization of monomer 1 quenching with phenylboronic acid



Figure S4. (a) UV-vis absorption of polymer 2a and 2b in CHCl<sub>3</sub>. (b) fluorescence spectra of polymer 2a and 2b in CHCl<sub>3</sub> at different concentrations.



**Figure S5: DSC spectrum of polymer 2a and 2b**. (The samples were first heated at a rate of  $10^{\circ}$ C/min to  $280^{\circ}$ C and held for 5 minutes. Subsequently the samples were cooled to  $0^{\circ}$ C at  $2^{\circ}$ C/min and held for 5 minutes. Then the samples were subjected to the aforementioned process again.)



**Figure S6: XRD profiles of polymer 2a and 2b**. (X-ray diffractometer (Smartlab, Rigaku) with CuKa radiation, the wavelength of Ka radiation as 1.5409, scan speed 2 degree/min, step 0.02 degree)

General procedure for synthesis of block copolymer: In a drybox under N<sub>2</sub> atmosphere, to 5mL vial containing Pd<sub>2</sub>(dba)<sub>3</sub> (5.5 mg, 0.006 mmol), THF (0.4 mL) and t-Bu<sub>3</sub>P (48 µL, 0.5 M solution in THF) was added 4-bromobenzophenone (40 µL, 0.25 M solution in THF). The mixture was stirred for 1 hour at room temperature to generate the initiator. To another vial containing 2-(7-Bromo-9,9-dihexyl-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane  $(0.1 \text{ mmol})^2$  and THF (5.4 mL) was added 0.5 mL of K<sub>3</sub>PO<sub>4</sub> (2 M solution in water) and the mixture was cooled to 0 °C. The solution of the in situ generated initiator was quickly injected into the solution of monomer and the resulting mixture was stirred for 30 min at 0 °C. A small aliquot (0.3 mL) of the organic phase of the reaction mixture was sampled and analyzed by GPC (conversion: 99%; Mn = 9500; PDI = 1.22). Then, a solution of monomer 1 (0.1 mmol) in THF was injected, the resulted mixture was stirred for 40 min. The reaction was quenched by pouring the mixture into 12 N HCl. The product was extracted with  $CH_2Cl_2$  (3 x 20 mL). The organic layer was combined, washed by brine and dried with Na<sub>2</sub>SO<sub>4</sub>. The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was dissolved in a minimum amount of THF and the solution was added dropwise to methanol with stirring. The precipitate was collected by filtration, washed with methanol and water and dried under vacuum to get target polymer 3. The product was analyzed by GPC to determine the Mn and PDI values of the polymers as Mn = 15500 and PDI = 1.20.



Polymer **3**: 72% yield. Brown solid. GPC: Mn = 15500 (PDI = 1.20). <sup>1</sup>H NMR:  $\delta$  7.67 ~ 7.86 (m, 6 H), 6.95 (s, 4 H), 6.86 (s, 2 H), 3.97 (s, 4 H), 2.11 (s, 4 H), 1.79 (s, 4 H), 1.14 ~ 1.55 (m, 54 H), 0.80 ~ 0.86 (m, 16 H); <sup>13</sup>C NMR:  $\delta$  151.8, 148.4, 140.5, 140.0, 139.3, 129.5, 128.9, 128.4, 126.2, 121.5, 119.9, 69.5, 55.3, 40.3, 32.1, 31.9, 31.4, 29.7, 29.5, 29.4, 26.1, 23.5, 22.7, 22.5, 14.1



Figure S7: GPC profiles of PFO and copolymer 3



Figure S8: comparation of <sup>1</sup>H NMR spectrum of PFO, polymer 2 and copolymer 3

## **Reference:**

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## Proton and Carbon NMR Spectra:

















