

Electronic Supplementary Information

Unusual cyclic polymerization through Suzuki-Miyaura coupling of polyphenylene bearing diboronate at both ends with excess dibromophenylene

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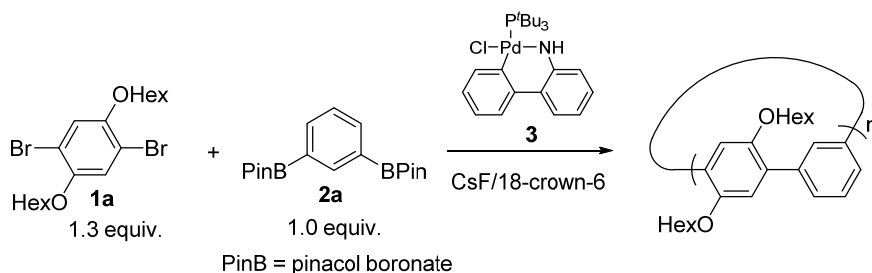
1. Materials

All starting materials were purchased from commercial suppliers (TCI, Aldrich, Wako and Kanto) and used without further purification. Commercially available dehydrated tetrahydrofuran (THF, stabilizer-free, Kanto) were used as a dry solvent.

2. General

^1H and ^{13}C NMR spectra were obtained on JEOL ECA-500 and ECA-600 spectrometers. The internal standard for ^1H NMR spectra in CDCl_3 was tetramethylsilane (0.00 ppm) and the internal standard for ^{13}C NMR spectra in CDCl_3 was the midpoint of CDCl_3 (77.0 ppm). IR spectra were recorded on a JASCO FT/IR-410. All melting points were measured with a Yanagimoto hot stage melting point apparatus without correction. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, Merck) with a specified solvent. Purification of polymer was carried out by LC908-C60 recycling preparative HPLC (eluent, CHCl_3) with two JAIGEL columns (1H-40 and 2H-40). The M_n and M_w/M_n values of polyphenylenes were measured on a Tosoh HLC-8020 gel permeation chromatography (GPC) unit (eluent, THF; calibration, polystyrene standards) with two TSK-gel columns ($2 \times$ Multipore $\text{H}_{\text{XL}}\text{-M}$). MALDI-TOF mass spectra were recorded on a Shimadzu/Kratos AXIMA-CFR plus in the reflectron ion mode by use of a laser ($\lambda = 337 \text{ nm}$). DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as the matrix for the MALDI-TOF mass measurements.

3. General procedure for cyclic polymerization of **1a** and **2a**



All glass apparatus was dried prior to use. Addition of reagents into a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. **1a** 0.0566 g (0.130 mmol), **2a** 0.0328 g (0.0994 mmol), CsF 0.0672 g (0.442 mmol), 18-crown-6 0.219 g (0.829 mmol), and **3** 0.00230 g (0.00449 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (3.0 mL) and distilled water (0.1 mL) were added to the flask via a syringe. The mixture was degassed with argon and stirred at room temperature for 24 h. 1 M Hydrochloric acid was added, and the mixture was extracted with CHCl_3 . The combined organic layers were dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residual product was purified

by HPLC (CHCl_3) to give 0.0341 g (97%) of poly(2,5-dihexyloxy-1,4-phenylene-*alt*-1,3-phenylene).

^1H NMR (600 MHz, CDCl_3) δ 7.82-7.71 (m, 1 H), 7.63-7.59 (m, 2 H), 7.49-7.42 (m, 1 H), 7.08-7.02 (m, 2 H), 3.95-3.90 (m, 4 H), 1.72-1.69 (m, 4 H), 1.35-1.20 (m, 12 H), 0.89-0.80 (m, 3 H); ^{13}C NMR (150 MHz, CDCl_3) δ 150.37, 138.13, 130.85, 130.37, 128.32, 127.26, 116.37, 69.65, 31.48, 29.40, 25.79, 22.54, 13.99; IR (KBr) 2930, 1509, 1467, 1377, 1206, 798 cm^{-1} .

4. Effect of excess amount of dibromophenylene **1a**

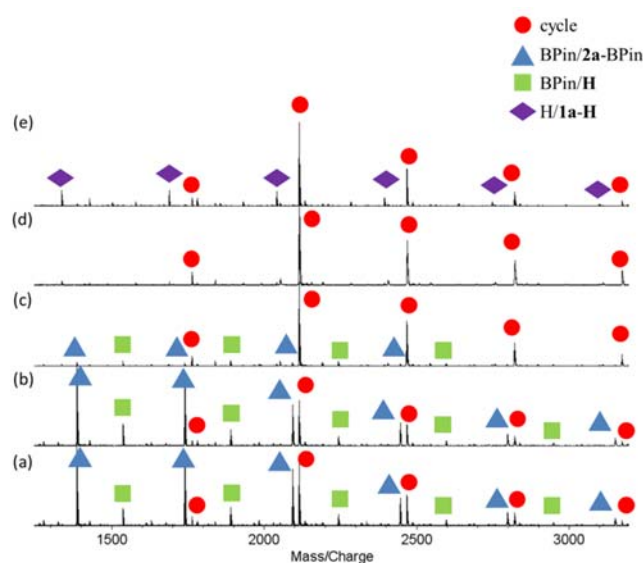


Fig. S1 MALDI-TOF mass spectra of the products obtained by the polymerization of **1a** and **2a** with 5.0 mol % of **3**, CsF (4 equiv.), and 18-crown-6 (8 equiv.) in THF ($[\mathbf{2a}]_0 = 16.6 \times 10^{-3} \text{ M}$) and water (THF/water = 3.0/0.1, v/v) at rt for 24 h, followed by quenching with 1 M hydrochloric acid: equivalent of **1a** is (a) 1.05, (b) 1.10, (c) 1.15, (d) 1.20, and (e) 10.

5. Polymerization with other catalysts

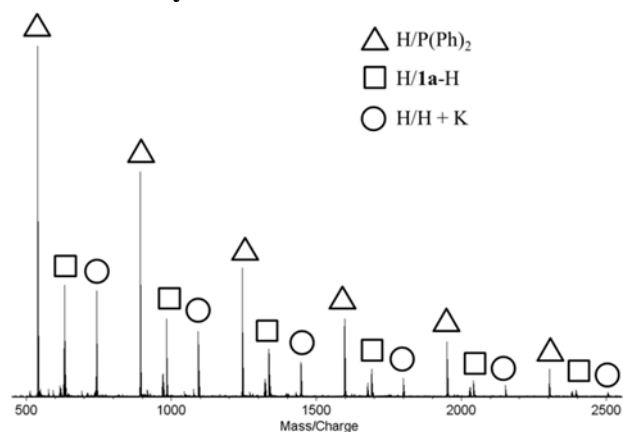


Fig. S2 MALDI-TOF mass spectra of the products obtained by the polymerization of 1.3 equiv.

of **1a** and 1.0 equiv. of **2a** with 11.0 mol % of $(\text{PPh}_3)_4\text{Pd}$, CsF (4 equiv.), and 18-crown-6 (8 equiv.) in THF ($[\mathbf{2a}]_0 = 16.6 \times 10^{-3} \text{ M}$) and water (THF/water = 3.0/0.3, v/v) was refluxed for 96 h, followed by quenching with 1 M hydrochloric acid.

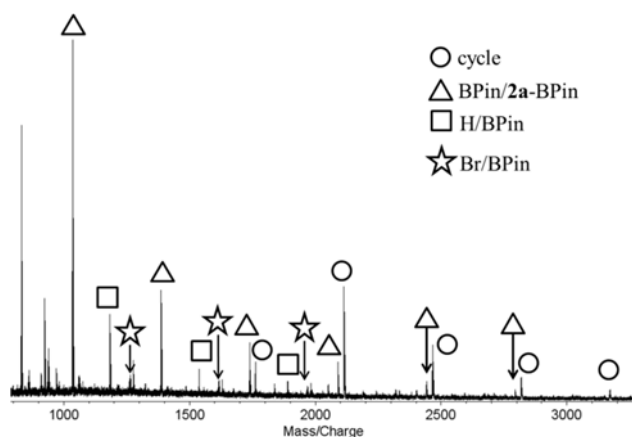
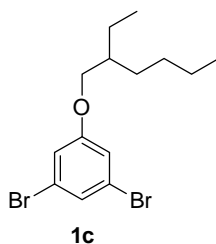


Fig. S3 MALDI-TOF mass spectra of the products obtained by the polymerization of 1.3 equiv. of **1a** and 1.0 equiv. of **2a** with 5.0 mol % of (XPhos)Pd G2, CsF (4 equiv.), and 18-crown-6 (8 equiv.) in THF ($[\mathbf{2a}]_0 = 8.2 \times 10^{-3} \text{ M}$) and water (THF/water = 3.0/0.1, v/v) at 40 °C for 144 h, followed by quenching with 1 M hydrochloric acid.

6. Synthesis of a variety of cyclic polyphenylenes

6-1. Synthesis of 1-(2-ethylhexyloxy)-3,5-dibromobenzene (**1c**)

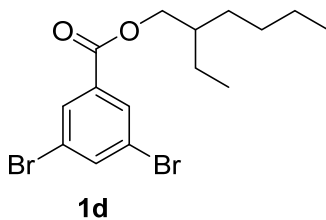
All glass apparatus was dried prior to use. Addition of reagents into a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. 3,5-Dibromophenol 2.482 g (9.853 mmol), potassium carbonate 1.900 g (13.748 mmol), and 18-crown-6 0.212 g (0.802 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry 2-butanone (27.0 mL) and 1-bromo-2-ethylhexane 5.5 mL (25.382 mmol) were added to the flask via a syringe. The mixture was refluxed for 7 h. Water was added, and the mixture was extracted with CH_2Cl_2 . The combined organic layers were dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was purified by means of column chromatography on silica gel (hexane) to give 1-(2-ethylhexyloxy)-3,5-dibromobenzene as a colorless liquid (3.365 g, 94%).



^1H NMR (600MHz, CDCl_3) δ 7.22 (s, 1 H), 6.99 (s, 2 H), 3.82-3.78 (m, 2 H), 1.71-1.67 (m, 2 H), 1.48-1.25 (m, 8 H), 0.93-0.89 (m, 3H); IR (neat) 2927, 1584, 1557, 1437, 1297, 1254, 829, 744 cm^{-1} .

6-2. Synthesis of 2-ethylhexyl 3,5-dibromobenzoate (1d)

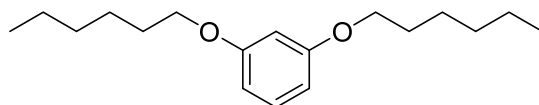
All glass apparatus was dried prior to use. Addition of reagents into a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. 3,5-Dibromobenzoic acid 1.381 g (4.934 mmol), 2-ethyl-1-hexanol 1.6 mL (10.222 mmol), 4-dimethylaminopyridine (DMAP) 0.7945 g (6.503 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDCI) 0.9930 g (6.396 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry DMF (20.0 mL) were added to the flask via a syringe, and the mixture was stirred at room temperature for 7 h. Water was added, and the mixture was extracted with CH_2Cl_2 . The combined organic layers were dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residue was purified by means of column chromatography on silica gel (CH_2Cl_2) to give 2-ethylhexyl 3,5-dibromobenzoate as a yellow liquid (1.499 g, 77%).



^1H NMR (600 MHz, CDCl_3) δ 8.08 (d, $J = 2.1$ Hz, 2 H), 7.85 (t, $J = 1.7$ Hz, 1 H), 4.27-4.22 (m, 2 H), 1.75-1.69 (m, 1 H), 1.48-1.33 (m, 8 H), 0.96-0.90 (m, 6 H); IR (neat) 1727, 1559, 1463, 1424, 1378, 1261, 1132, 960, 870, 763 cm^{-1} .

6-3. Synthesis of 1,3-dihexyloxybenzene

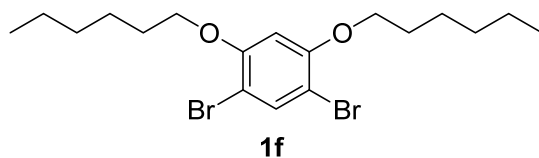
All glass apparatus was dried prior to use. Addition of reagents into a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. Resorcinol 5.051 g (45.876 mmol) and KOH 6.874 g (122.519 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry MeOH (50 mL) and 1-bromohexane 26.0 mL (184.285 mmol) were added to the flask via a syringe. The mixture was refluxed for 37 h. Water was added, and the mixture was extracted with CH_2Cl_2 . The combined organic layers were dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residue was purified by means of column chromatography on silica gel twice (CH_2Cl_2 , hexane/ $\text{CH}_2\text{Cl}_2 = 3/1$) to give 1,3-dihexyloxybenzene as a pale yellow liquid (4.686 g, 37%).



^1H NMR (500 MHz, CDCl_3) δ 7.15 (t, $J = 8.2$ Hz, 1 H), 6.90-6.45 (m, 3 H), 3.93 (t, $J = 6.6$ Hz, 2 H), 1.79-1.74 (m, 2 H), 1.40-1.30 (m, 8 H), 0.90 (t, $J = 7.0$ Hz, 6 H); IR (neat) 2932, 2859, 1590, 1493, 1469, 1386, 1334, 1287, 1263, 1182, 1154, 1045, 836, 760, 722 cm^{-1} .

6-4. Synthesis of 1,3-dibromo-4,6-dihexyloxybenzene (**1f**)¹

All glass apparatus was dried prior to use. Addition of reagents into a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. 1,3-Dihexyloxybenzene 2.380 g (8.548 mmol), CaCO_3 1.759 g (17.575 mmol), and benzyltrimethylammonium tribromide (BTMABr_3) 6.626 g (16.991 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Mixed solvent ($\text{CH}_2\text{Cl}_2/\text{MeOH} = 5/2$) 40 mL was added to the flask via a syringe. The mixture was stirred at room temperature for 64 h. The reaction mixture was filtered, and the filtrate was diluted by CH_2Cl_2 and washed with water. The organic layers were dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residue was recrystallized from MeOH to give 1,3-dibromo-4,6-dihexyloxybenzene as a white crystal (2.557 g, 69%); mp 52.0-52.2 $^\circ\text{C}$. (lit.² 52.5 $^\circ\text{C}$)

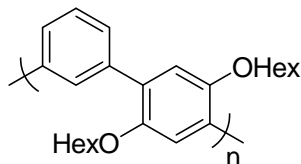


^1H NMR (500 MHz, CDCl_3) δ 7.64 (s, 1 H), 6.46 (s, 1 H), 3.99 (t, $J = 6.5$ Hz, 2 H), 1.86-1.80 (m, 4 H), 1.37-1.33 (m, 8 H), 0.90 (t, $J = 7.0$ Hz, 6 H); IR (KBr) 2940, 1580, 1488, 1458, 1375, 1288, 1201, 1182, 1058, 803, 701 cm^{-1} .

6-5. Cyclic polymerization of **1b** and **2b**

All glass apparatus was dried prior to use. Addition of reagents into a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. **2b** 0.0265 g (0.0500 mmol), CsF 0.0324 g (0.213 mmol), 18-crown-6 0.118 g (0.447 mmol), and **3** 0.00120 g (0.00234 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (3.0 mL), distilled water (0.1 mL) and **1b** 0.0154 g (0.0653 mmol) were added to the flask via a syringe. The mixture was degassed with argon and stirred at room temperature for 24 h. 1 M Hydrochloric acid was added, and the mixture was extracted with CHCl_3 . The combined organic layers were dried over

anhydrous MgSO_4 , and concentrated under reduced pressure. The residual product was purified by HPLC (CHCl_3) to give 0.0147 g (83%) of cyclic poly(2,5-dihexyloxy-1,4-phenylene-*alt*-1,3-phenylene).



^1H NMR (600 MHz, CDCl_3) δ 7.82 (s, 1 H), 7.64-7.59 (m, 2 H), 7.47-7.49 (m, 1 H), 7.08-7.05 (m, 2 H), 3.96-3.91 (m, 4 H), 1.72-1.69 (m, 4 H), 1.34-1.20 (m, 12H), 0.89-0.80 (m, 6H); IR (KBr) 2924, 1600, 1509, 1467, 1378, 1207, 1031 cm^{-1} .

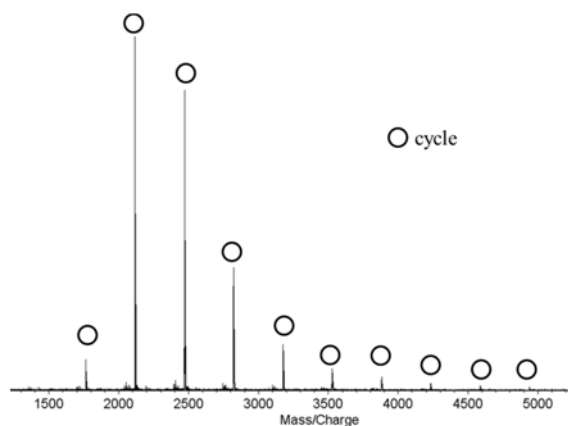
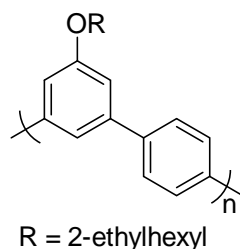


Fig. S4 MALDI-TOF mass spectrum of cyclic poly(2,5-dihexyloxy-1,4-phenylene-*alt*-1,3-phenylene) obtained by polymerization of **1b** and **2b**.

6-6. Cyclic polymerization of **1c** and **2c**

All glass apparatus was dried prior to use. Addition of reagents into a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. **1c** 0.0237 g (0.0651 mmol), **2c** 0.0164 g (0.0497 mmol), CsF 0.0347 g (0.228 mmol), 18-crown-6 0.109 g (0.413 mmol), and **3** 0.00120 g (0.00234 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (3.0 mL) and distilled water (0.1 mL) were added to the flask via a syringe. The mixture was degassed with argon and stirred at room temperature for 24 h. 1 M Hydrogen chloride was added, and the mixture was extracted with CHCl_3 . The combined organic layers were dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residual product was purified by HPLC (CHCl_3) to give 0.0129 g (93%) of cyclic poly 5-(2-ethylhexyloxy)-1,3-phenylene-*alt*-1,4-phenylene.



^1H NMR (600 MHz, CDCl_3) δ 7.80-7.73 (m, 4 H), 7.50-7.46 (m, 1 H), 7.19-7.18 (m, 2 H), 400 (s, 2 H), 1.82-1.79 (m, 1 H), 1.60-1.25 (m, 8 H), 1.01-0.87 (m, 6 H); IR (KBr) 2923, 1588, 1517, 1449, 1343, 1262, 1195, 1033, 822 cm^{-1} .

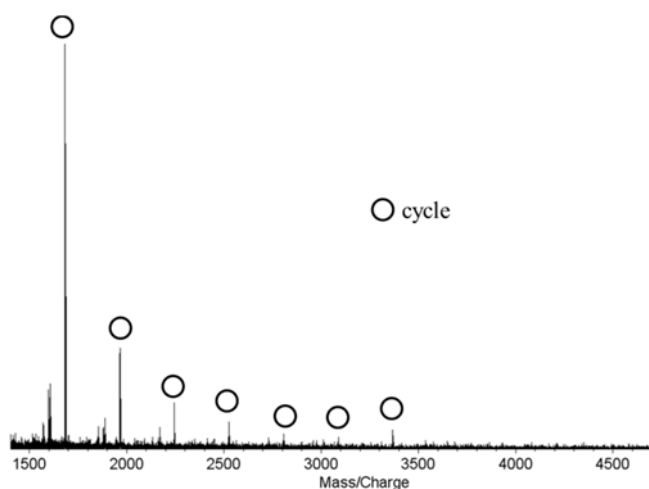
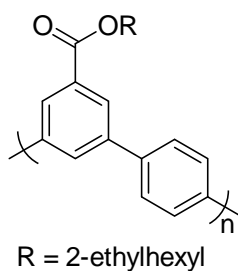


Fig. S5 MALDI-TOF mass spectrum of cyclic poly[5-(2-ethylhexyloxy)-1,3-phenylene-*alt*-1,4-phenylene] obtained by polymerization of **1c** and **2c**.

6-7. Cyclic polymerization of **1d** and **2c**

All glass apparatus was dried prior to use. Addition of reagents into a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. **1d** 0.0500 g (0.128 mmol), **2c** 0.0327 g (0.0990 mmol), CsF 0.0632 g (0.416 mmol), 18-crown-6 0.216 g (0.818 mmol), and **3** 0.00240 g (0.00468 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (6.0 mL) and distilled water (0.2 mL) were added to the flask via a syringe. The mixture was degassed with argon and stirred at room temperature for 24 h. 1 M Hydrochloric acid was added, and the mixture was extracted with CHCl_3 . The combined organic layers were dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residual product was purified by HPLC (CHCl_3) to give 0.0274 g (90%) of cyclic poly[5-(2-ethylhexyloxycarbonyl)-1,3-phenylene-*alt*-1,4-phenylene].



$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.39-8.35 (m, 2 H), 8.16-8.06 (m, 1 H), 7.88-7.82 (m, 4 H), 4.34-4.34 (m, 2 H), 1.80-1.79 (m, 1 H), 1.68-1.26 (m, 8 H), 1.03-0.87 (m, 6 H); IR (KBr) 2959, 1719, 1599, 1459, 1341, 1234, 1116, 892, 767 cm^{-1} .

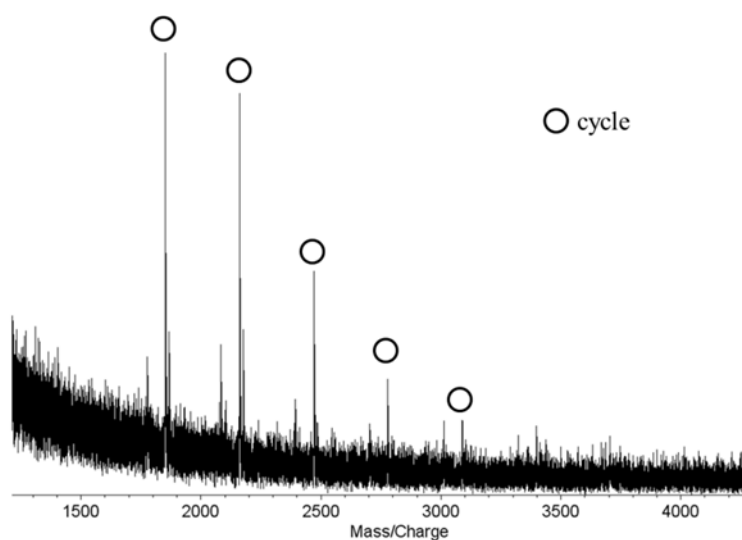
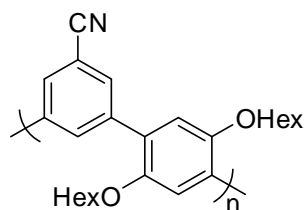


Fig. S6 MALDI-TOF mass spectrum of cyclic poly[5-(2-ethylhexyloxy)-1,3-phenylene-*alt*-1,4-phenylene] obtained by polymerization of **1d** and **2c**.

6-8. Cyclic polymerization of **1e** and **2b**

All glass apparatus was dried prior to use. Addition of reagents into a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. **1e** 0.0170 g (0.0652 mmol), **2b** 0.0265 g (0.0500 mmol), CsF 0.0328 g (0.216 mmol), 18-crown-6 0.108 g (0.409 mmol), and **3** 0.00130 g (0.00254 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (3.0 mL) and distilled water (0.1 mL) were added to the flask via a syringe. The mixture was degassed with argon and stirred at room temperature for 24 h. 1 M Hydrochloric acid was added, and the mixture was extracted with CHCl_3 . The combined organic layers were dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residual product was purified by HPLC (CHCl_3) to give 0.0166 g (88%) of cyclic poly(5-cyano-1,3-phenylene-*alt*-2,5-dihexyloxy-1,4-phenylene).



^1H NMR (600 MHz, CDCl_3) δ 8.06-7.98 (m, 1 H), 7.93-7.86 (m, 2 H), 7.05-7.00 (m, 2 H), 4.04-3.91 (m, 4 H), 1.75-1.70 (m, 4 H), 1.43-1.23 (m, 12 H), 0.91-0.80 (m, 6H); IR (KBr) 2928, 2228, 1591, 1509, 1446, 1377, 1209, 1020, 865 cm^{-1} .

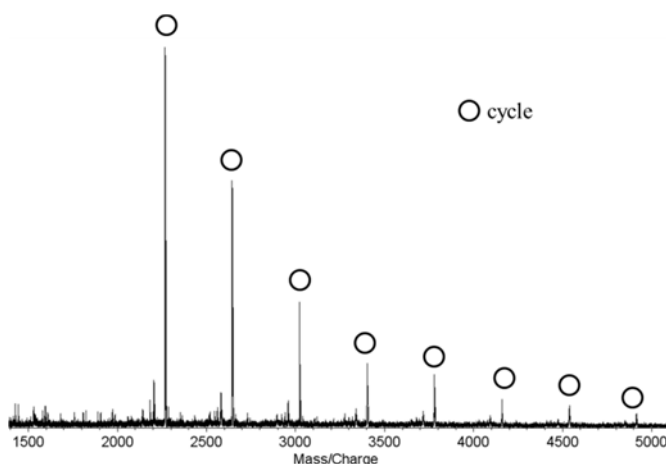
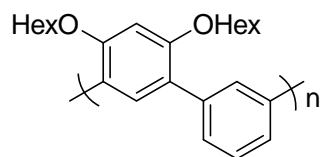


Fig. S7 MALDI-TOF mass spectrum of cyclic poly(5-cyano-1,3-phenylene-*alt*-2,5-dihexyloxy-1,4-phenylene) obtained by polymerization of **1e** and **2b**.

6-9. Cyclic polymerization of **1f** and **2a**

All glass apparatus was dried prior to use. Addition of reagents into a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. **1f** 0.0284 g (0.0651 mmol), **2a** 0.0164 g (0.0497 mmol), CsF 0.0335 g (0.221 mmol), 18-crown-6 0.112 g (0.462 mmol), and **3** 0.00140 g (0.00273 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (3.0 mL) and distilled water (0.1 mL) were added to the flask via a syringe. The mixture was degassed with argon and stirred at room temperature for 24 h. 1 M Hydrochloric acid was added, and the mixture was extracted with CHCl_3 . The combined organic layers were dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residual product was purified by HPLC (CHCl_3) to give 0.0164 g (94%) of cyclic poly(2,4-dihexyloxy-1,5-phenylene-*alt*-1,3-phenylene).



$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.78-7.67 (m, 1 H), 7.53-7.28 (m, 4 H), 6.66-6.51 (m, 1 H), 4.06-3.85 (m, 4 H), 1.71-1.61 (m, 4 H), 1.36-1.15 (m, 12 H), 0.93-0.77 (m, 6 H); IR (KBr) 2958, 1608, 1509, 1467, 1261, 1173, 1022, 890, 801, 705 cm^{-1} .

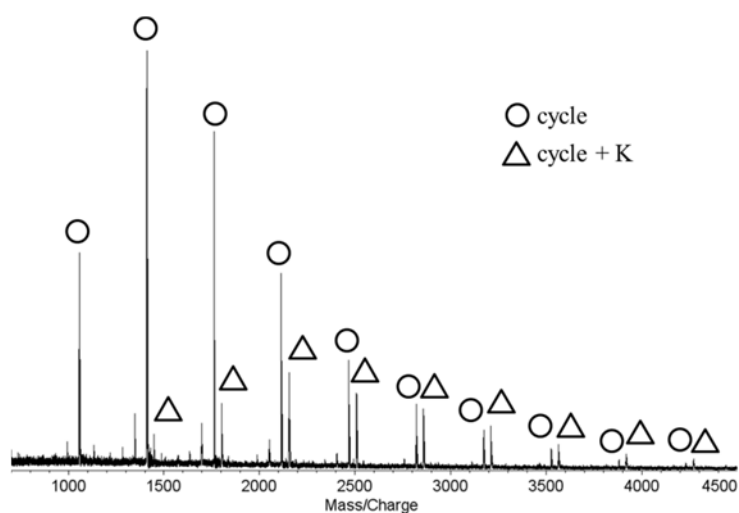
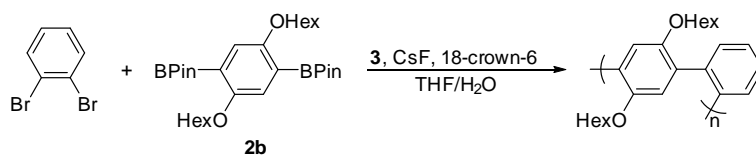


Fig. S8 MALDI-TOF mass spectrum of cyclic poly(2,4-dihexyloxy-1,5-phenylene-*alt*-1,3-phenylene) obtained by polymerization of **1f** and **2a**.

7. Attempt to synthesize cyclic polyphenylenes using *ortho*-monomers



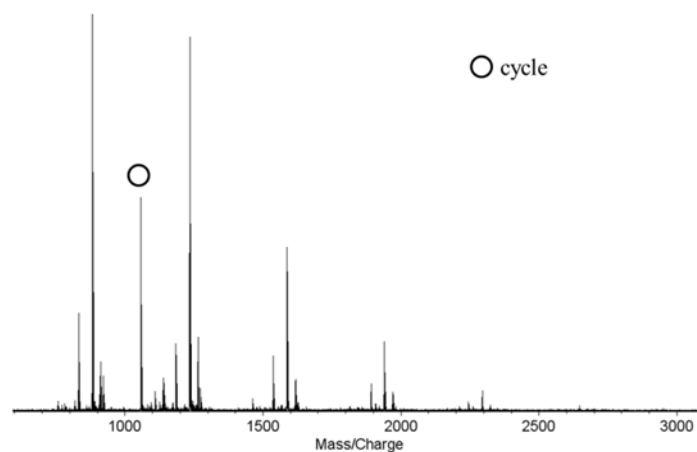


Fig. S9 MALDI-TOF mass spectrum of products obtained by polymerization of *ortho*-dibromophenylene and **2b**.

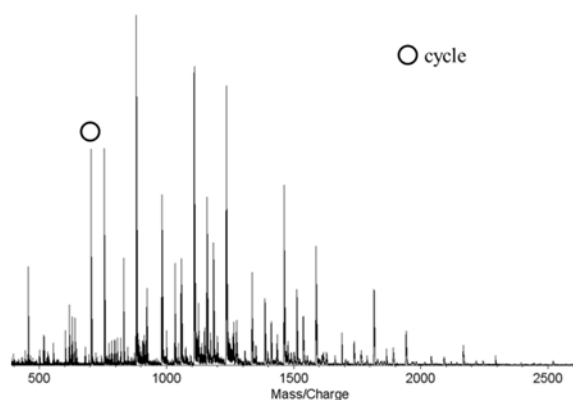
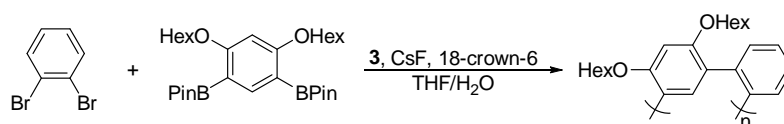
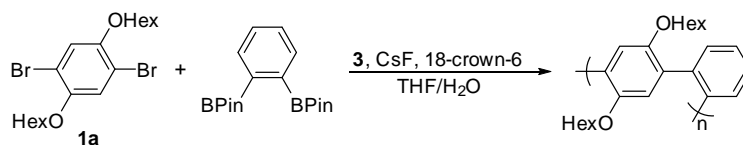


Fig. S10 MALDI-TOF mass spectrum of products obtained by polymerization of *ortho*-dibromophenylene and 2,4-dihexyloxy-1,5-phenyenediboronic acid pinacol ester.



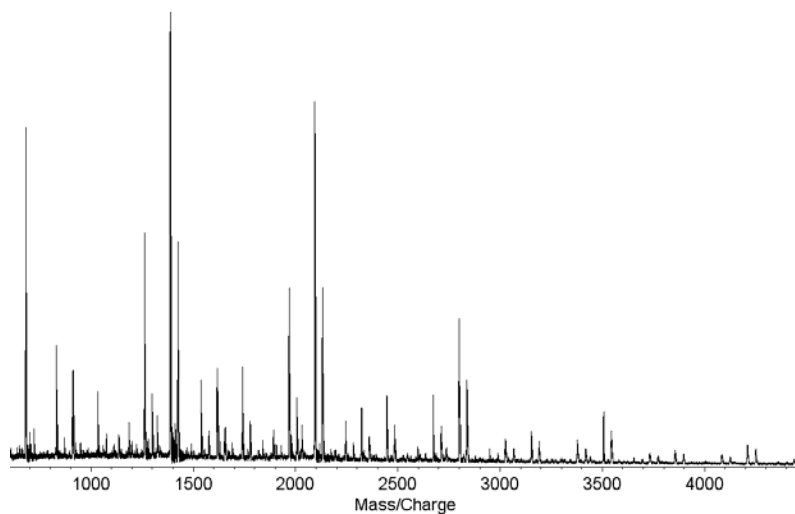


Fig. S11 MALDI-TOF mass spectrum of products obtained by polymerization of **1a** and *ortho*-phenyenediboronic acid pinacol ester.

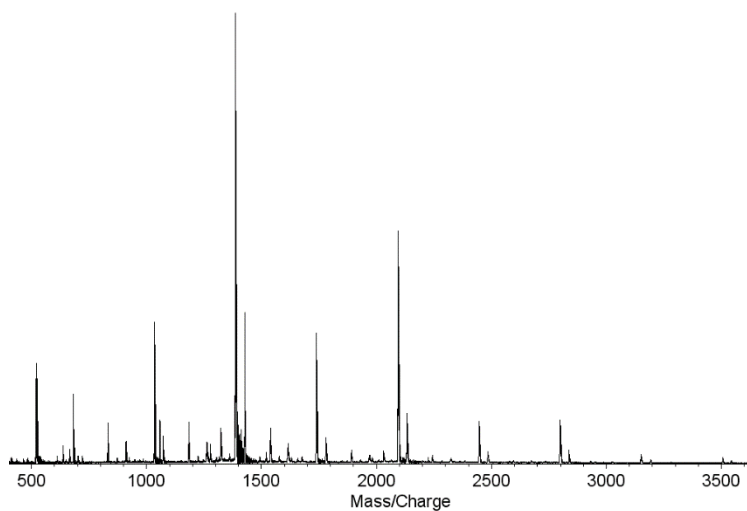
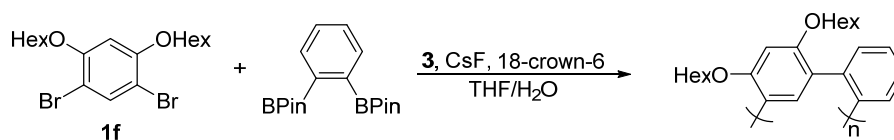


Fig. S12 MALDI-TOF mass spectrum of products obtained by polymerization of **1f** and *ortho*-phenyenediboronic acid pinacol ester.

8. References

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