Electronic Supplementary Information for

Unstoichiometric Suzuki-Miyaura cyclic polymerization of extensively conjugated monomers

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1. Materials

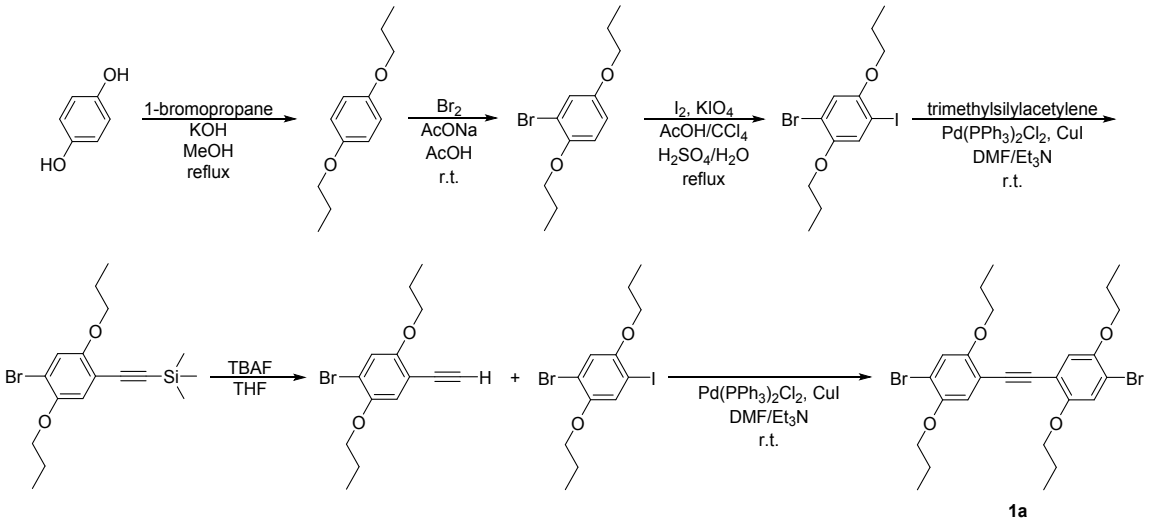
All starting materials were purchased from commercial suppliers (TCI, Aldrich, Wako and Kanto) and used without further purification. Commercially available dehydrated tetrahydrofuran (THF, stabilizer-free, Kanto) was used as a dry solvent. *n*-Butyllithium (1.60 M, 1.66 M, and 2.66 M solution in hexane, Kanto) were used as received. 9,9-Di-(2'-ethylhexyl)-2,7-dibromofluorene (**1e**) and *t*-Bu_3PPd G2 precatalyst **5** were purchased from Aldrich Inc. 3,5-Dibromobiphenyl (**3c**), 2,7-dibromonaphthalene (**3d**), CsF, and 18-crown-6 were purchased from TCI, and were used as received. 1,3-Benzenedibronic acid bis(pinacol)ester (**2**) was purchased from Wako, and was used as received.

2. General

^{1}H and ^{13}C NMR spectra were obtained on JEOL ECA-500 and ECA-600 spectrometers. The internal standard for ^{1}H 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) and LC-908 recycling preparative HPLC (eluent, $CHCl_3$) with two TSKgel ($G3000H_{HR}$ and $G4000H_{HR}$). The M_n and M_w/M_n values of polymers were measured on a Tosoh HLC-8020 gel permeation chromatography (GPC) unit (eluent, THF; calibration, polystyrene standards) with two TSK-gel columns (2 × Multipore H_{XL}-M). MALDI-TOF mass spectra were recorded on a Shimadzu/Kratos AXIMA-CFR plus and Shimazu/Biotech AXIMA-Confidence in the reflectron ion mode and linear ion mode by use of a laser (λ = 337 nm). DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as the matrix for the MALDI-TOF mass measurements.

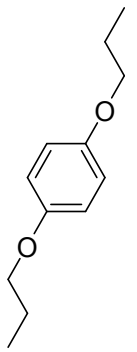
3. Synthesis of dibromo monomers 1

1,2-bis(4-bromo-2,5-dipropoxyphenyl)ethyne (**1a**)



1,4-dipropoxybenzene[S1]

Hydroquinone (60.02 g, 0.53 mol) and KOH (73.65 g, 1.38 mol) were placed in a flask, and the atmosphere in the flask was replaced with argon. MeOH (500 mL) was added to the flask under a stream of nitrogen, and the mixture was refluxed for 20 min. 1-Bromopropane (190 mL, 2.12 mol) was added under a stream of nitrogen, and the reaction mixture was refluxed for 2 h. After concentration of the reaction mixture under reduced pressure, the residue was dissolved in CH_2Cl_2. Organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by recrystallization from MeOH to afford 1,4-dipropoxybenzene as a colorless crystal (77.56 g, 73%).

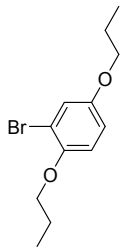


^{1}H NMR (600 MHz, $CDCl_3$) δ 6.82 (s, 4 H), 3.86 (t, J = 6.5 Hz, 4 H), 1.81-1.75 (m, 4 H), 1.02 (t, J = 7.6 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.1, 115.4, 70.1, 22.7, 10.5.

2-bromo-1,4-dipropoxybenzene[S1)]

To a solution of 1,4-dipropoxybenzene (28.61 g, 147 mmol) and sodium acetate (11.76 g, 143 mmol)

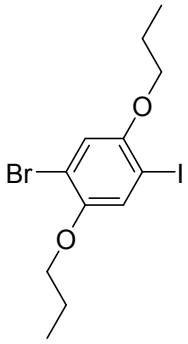
in acetic acid (88 mL) at 0 °C, Br_2 (7.9 mL, 150 mmol) was added dropwise over 7 h, and the mixture was stirred at room temperature for 14 h. The reaction was quenched with water, and the mixture was extracted with $CHCl_3$. Combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by distillation under reduced pressure (0.08 mmHg, 117-126 °C) to afford 2-bromo-1,4-dipropoxybenzene as a pale yellow oil (24.78 g, 62%).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (d, J = 2.7 Hz, 1 H), 6.82 (d, J = 8.9 Hz, 1 H), 6.79 (dd, J = 8.9 and 2.7 Hz, 1 H), 3.92 (t, J = 6.4 Hz, 2 H), 3.85 (t, J = 6.7 Hz, 2 H), 1.85-1.74 (m, 4 H), 1.06 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.6, 149.7, 119.5, 114.7, 114.4, 112.8, 71.7, 70.3, 22.63, 22.56, 10.54, 10.45.

1-bromo-4-iodo-2,5-dipropoxybenzene[S1)]

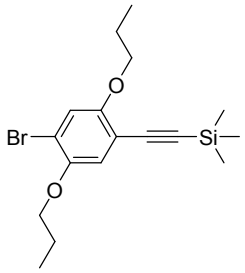
To a solution of 2-bromo-1,4-dipropoxybenzene (23.21 g, 23.2 mmol) in acetic acid (55 mL) and CCl_4 (13.5 mL) was added KIO_4 (7.25 g, 33.9 mmol), I_2 (20.70 g, 81.6 mmol), 96% H_2SO_4 (7.0 mL), and water (2.5 mL), and the mixture was refluxed for 16 h. Reaction was quenched with saturated aqueous $Na_2S_2O_3$, and the mixture was poured into ice water and extracted with $CHCl_3$. Combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by recrystallization from $CHCl_3$/MeOH to afford 1-bromo-4-iodo-2,5-dipropoxybenzene as a colorless crystal (19.4 g, 57%).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (s, 1 H), 6.99 (s, 1 H), 3.92 (t, J = 6.2 Hz, 2 H), 3.91 (t, J = 6.2 Hz, 2 H), 1.86-1.54 (m, 4 H), 1.09-1.05 (m, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.5, 150.4, 124.3, 117.6, 112.5, 84.8, 71.81, 71.76, 22.5, 10.7, 10.5.

[(4-bromo-2,5-dipropoxyphenyl)ethynyl]trimethylsilane

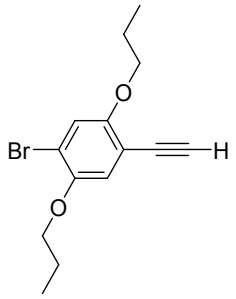
1-Bromo-4-iodo-2,5-dipropoxybenzene (7.89 g, 19.78 mmol), $Pd(PPh_3)Cl_2$ (0.71 g, 1.00 mmol), CuI (0.39 g, 2.03 mmol) were placed in a flask, and the atmosphere in the flask was replaced with argon. Dry DMF (60 mL), Et_3N (6 mL), and trimethylsilylacetylene (3.2 mL, 23.16 mmol) were added under a stream of nitrogen, and the mixture was stirred at room temperature for 3 h. The reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with CH_2Cl_2. Combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/$CHCl_3$ = 9/1) to afford [(4-bromo-2,5-dipropoxyphenyl)ethylnyl]trimethylsilane as a yellow solid (4.45 g, 61%).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 (s, 1 H), 6.94 (s, 1 H), 3.93-3.90 (m, 4 H), 1.83-1.81 (m, 4 H), 1.08-1.04 (m, 6 H), 0.25 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.7, 149.3, 118.0, 117.9, 113.6, 112.5, 100.6, 99.2, 71.5, 71.3, 22.63, 22.56, 10.51, 10.45, -0.09.

1-bromo-4-ethynyl-2,5-dipropoxybenzene

To a solution of [(4-bromo-2,5-dipropoxyphenyl)ethylnyl]trimethylsilane (4.09 g, 11.07 mmol) in dry THF (95 mL) was added 1.0 M tetrabutylammonium fluoride THF solution (12.0 mL, 12 mmol), and the mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with hexane, washed with saturated aqueous NH_4Cl, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 3/1) to afford 1-bromo-4-ethynyl-2,5-dipropoxybenzene as a white solid (3.09 g, 94%).

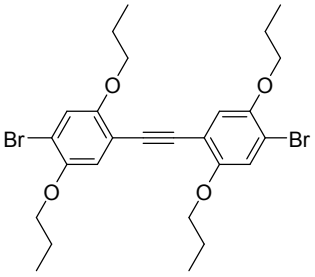


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (s, 1 H), 6.98 (s, 1 H), 3.95-3.91 (m, 4 H), 3.23 (s, 1 H), 1.85-

1.80 (m, 4 H), 1.07-1.04 (m, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.7, 149.3, 118.4, 118.0, 114.0, 111.3, 81.6, 79.5, 71.6, 71.3, 22.53, 22.48, 10.5, 10.4.

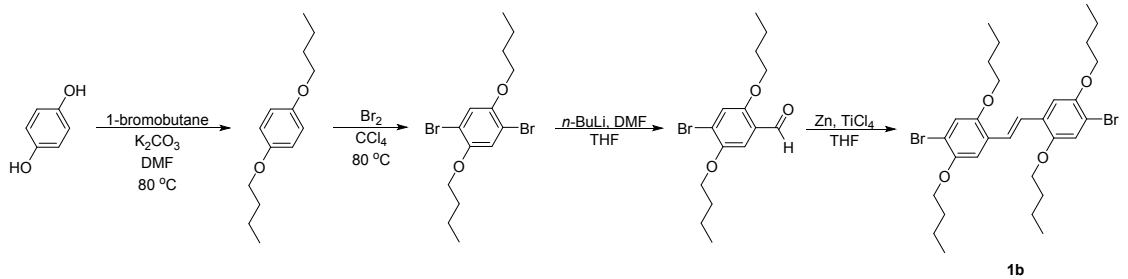
1,2-bis(4-bromo-2,5-dipropoxyphenyl)ethyne (**1a**)

1-bromo-4-iodo-2,5-dipropoxybenzene (99.7 mg, 0.25 mmol), $Pd(PPh_3)_2Cl_2$ (8.7 mg, 0.01 mmol), CuI (5.2 mg, 0.03 mmol) were placed in a flask, and the atmosphere in the flask was replaced with argon. Dry DMF (0.75 mL) and Et_3N (0.1 mL) were added under a stream of nitrogen. A solution of 1-bromo-4-ethynyl-2,5-dipropoxybenzene (78.6 mg, 0.26 mmol) in dry DMF (0.5 mL) was added to the flask under a stream of nitrogen, and the mixture was stirred at room temperature for 3 h. The reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with CH_2Cl_2. Combined organic layers were washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/$CHCl_3$ = 4/1) to afford 1,2-bis(4-bromo-2,5-dipropoxyphenyl)ethyne (**1a**) as a yellow solid (123.1 mg, 87%).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (s, 2 H), 7.01 (s, 2 H), 3.97 (t, *J* = 6.2 Hz, 4 H), 3.94 (t, *J* = 6.2 Hz, 4 H), 1.88-1.81 (m, 8 H), 1.08-1.05 (m, 12 H), ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.0, 149.4, 118.2, 117.8, 113.3, 112.9, 89.9, 71.5, 71.4, 22.59, 22.56, 10.51, 10.49.

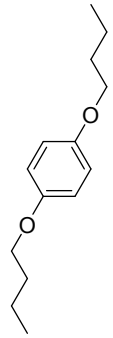
(*E*)-1,2-bis(4-bromo-2,5-dibutoxyphenyl)ethene (**1b**)



1,4-dibutoxybenzene

Hydroquinone (40.12 g, 0.36 mol) and K_2CO_3 (125.85 g, 0.91 mol) was placed in a flask, and the atmosphere in the flask was replaced with argon. Dry DMF (240 mL) and 1-bromobutane (96 mL, 0.91 mol) were added under a stream of nitrogen, and the reaction mixture was stirred at 80 °C for 3 days. The reaction was quenched with water, and the mixture was extracted with hexane. Combined

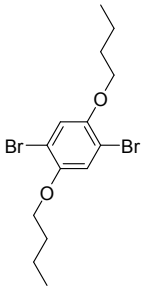
organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by recrystallization from MeOH to afford 1,4-dibutoxybenzene as a colorless crystal (26.70 g, 37%).



^{1}H NMR (600 MHz, $CDCl_3$) δ 6.81 (s, 4 H), 3.91 (t, *J* = 6.5 Hz, 4 H), 1.76-1.71 (m, 4 H), 1.51-1.45 (m, 4 H), 0.97 (t, *J* = 7.6 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.2, 115.3, 68.2, 31.4, 19.2, 13.9.

1,4-dibromo-2,5-dibutoxybenzene

Bromine (11.7 mL, 251.7 mmol) was added to a solution of 1,4-dibutoxbenzene (26.74 g, 120.3 mmol) in CCl_4 (61 mL), and the reaction mixture was stirred at 70 °C for 12 h. The mixture was cooled to room temperature, quenched with saturated aqueous Na_2SO_3, and extracted with $CHCl_3$. Combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by recrystallization from MeOH to afford 1,4-dibromo-2,5-dibutoxybenzene as a colorless crystal (42.87 g, 94%).

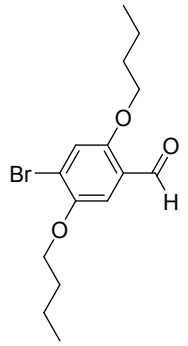


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (s, 2 H), 3.96 (t, *J* = 6.3 Hz, 4 H), 1.81-1.76 (m, 4 H), 1.56-1.48 (m, 4 H), 0.98 (t, *J* = 7.4 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.0, 118.3, 110.1, 31.2, 19.2, 13.8.

4-bromo-2,5-dibutoxybenzaldehyde

A flask was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. A solution of 1,4-dibromo-2,5-dibutoxybenzene (23.72 g, 62.40 mmol) in dry THF (400 mL) was added to the reaction flask via a syringe under a stream of nitrogen and then cooled to -78

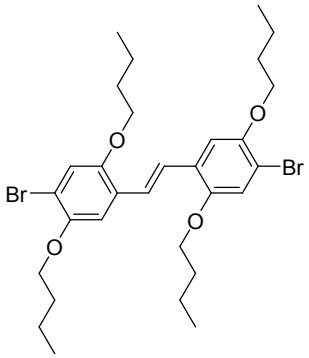
°C. 1.66 M *n*-Butyllithium in hexane (40 mL, 66.4 mmol) was slowly added under a stream of nitrogen, and the mixture was stirred at -78 °C for 30 min. The mixture was warmed up to -30 °C, and dry DMF (8.0 mL, 103.86 mmol) was added to the reaction mixture under a stream of nitrogen. The mixture was stirred at -30 °C for1.5 h and then warmed up to room temperature, followed by stirring overnight. The reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with Et_2O. Combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by recrystallization from MeOH to afford 4-bromo-2,5-dibutoxybenzaldehyde as a red crystal (6.98 g, 34%).



^{1}H NMR (600 MHz, $CDCl_3$) δ 10.41 (s, 1 H), 7.31 (s, 1 H), 7.23 (s, 1 H), 4.04-1.01 (m, 4 H), 1.84-1.78 (m, 4 H), 1.54-1.48 (m, 4 H), 1.00-0.97 (m, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.9, 155.7, 149.8, 124.24,120.9, 118.42, 110.6, 69.5, 69.1, 31.1, 19.19, 19.18, 13.80, 13.76.

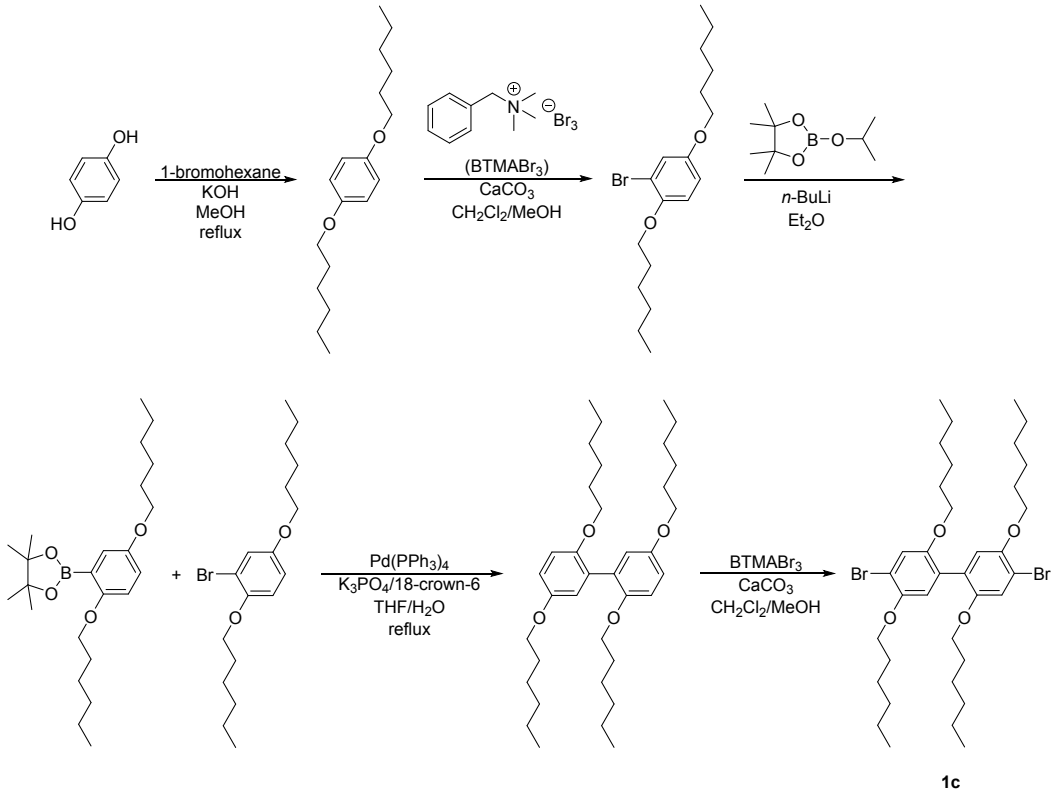
(*E*)-1,2-bis(4-bromo-2,5-dibutoxyphenyl)ethene (**1b**)[S2)]

Zinc powder (7.17 g, 109.67 mmol) was placed in a flask, and the flask was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. Dry THF (280 mL) was added to the flask under a stream of nitrogen, and then cooled to -10 °C. $TiCl_4$ (6.0 mL, 55.04 mmol) was slowly added, and a solution of 4-bromo-2,5-dibutoxybenzaldehyde (6.47 g, 19.65 mmol) in dry THF (90 mL) was added to the mixture. The mixture was refluxed for 5 h. The reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with Et_2O. Combined organic layers were washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by recrystallization from $CHCl_3$/MeOH to afford (*E*)-1,2-bis(4-bromo-2,5-dibutoxyphenyl)ethene (**1b**) as a yellow crystal (3.67 g, 59%).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (s, 2 H), 7.13 (s, 2 H), 7.08 (s, 2 H), 4.03 (t, J = 6.4 Hz, 4 H), 3.97 (t, J = 6.4 Hz, 4 H), 1.85-1.79 (m, 8 H), 1.58-1.51 (m, 8 H), 1.01-0.98 (m, 12 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.0, 149.8, 126.9, 123.6, 117.8, 111.8, 111.6, 69.9, 69.2, 31.4, 19.4, 19.3, 13.89, 13.86.

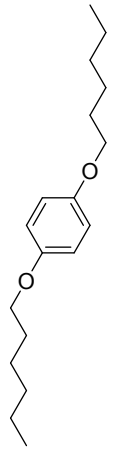
4,4'-dibromo-2,2',5,5'-tetrakis(hexyoxy)-1,1'-biphenyl (**1c**)



1,4-dihexyloxybenzene

Hydroquinone (13.03 g, 118.39 mmol) and KOH (16.91 g, 301.37 mmol) were placed in a flask, and the atmosphere in the flask was replaced with argon. MeOH (200 mL) was added, and the mixture was refluxed for 40 min. After cooling to room temperature, 1-bromohexane (68 mL, 481.98 mmol) was added to the flask, and the mixture was refluxed for 21 h. Solid byproducts was filtrated, and the

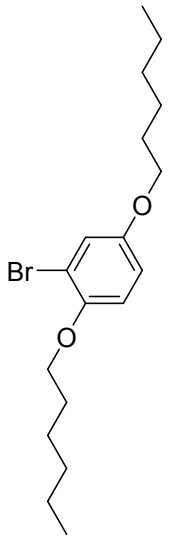
filtrate was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2. Organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by recrystallization from MeOH to afford 1,4-dihexyloxybenzene as a colorless crystal (18.54 g, 56%).



^{1}H NMR (600 MHz, $CDCl_3$) δ 6.81 (s, 4 H), 3.90 (t, *J* = 6.9 Hz, 4 H), 1.75 (quint, *J* = 7.1 Hz, 4 H), 1.44 (quint, *J* = 7.3 Hz, 4 H), 1.35-1.32 (m, 8 H), 0.90 (t, *J* = 6.9 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.2, 115.4, 68.7, 31.6, 29.4, 25.7, 22.6, 14.0.

2-bromo-1,4-bis(hexyloxy)benzene

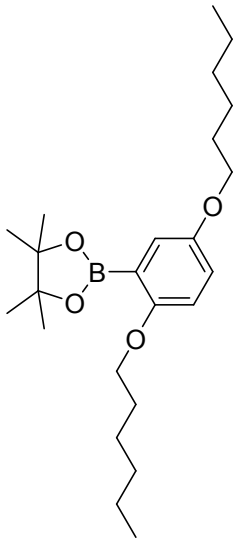
1,4-dihexyloxybenzene (18.50 g, 66.44 mmol), $CaCO_3$ (7.14 g, 71.33 mmol), and benzyltrimethylammonium tribromide ($BTMABr_3$) (27.24 g, 96.85 mmol) were placed in a flask. Mixed solvent of dry CH_2Cl_2/dry MeOH = 5/2 (200 mL) was added, and the mixture was stirred at room temperature for 24 h. The reaction mixture was filtrated and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 4/1) to afford 2-bromo-1,4-bis(hexyloxy)benzene as a pale yellow oil (10.21 g, 43%).



^{1}H NMR (500 MHz, $CDCl_3$) 7.10 (t, J = 2.9 Hz, 1 H), 6.83-6.77 (m, 2 H), 3.95 (t, J = 6.6 Hz, 2 H), 3.88 (t, J = 6.6 Hz, 2 H), 1.82-1.71 (m, 4 H), 1.52-1.41 (m, 4 H), 1.38-1.31 (m, 8 H), 0.91 (t, J = 6.6 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.6, 149.8, 119.5, 114.7, 114.4, 112.8, 70.2, 68.8, 31.5, 29.2, 25.7, 22.6, 14.0.

2-(2,5-bis(hexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

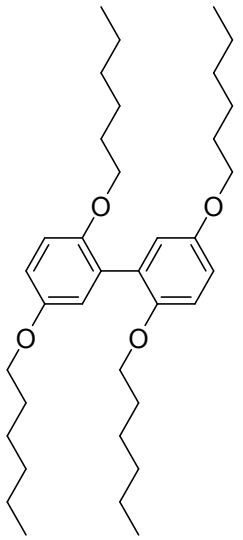
A flask was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. 2-Bromo-1,4-bis(hexyloxy)benzene (5.08 g, 14.21 mmol) was placed in the flask, and the atmosphere in the flask was replaced with argon. Dry Et_2O (300 mL) was added to the flask under a stream of nitrogen, and the solution was cooled at 0 ^{o}C. 1.6 M *n*-Butyllithium in hexane (9.8 mL, 15.68 mmol) was added to the flask slowly under a stream of nitrogen, and the mixture was stirred at 0 ^{o}C. After 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.3 mL, 21.24 mmol) was added at 0 ^{o}C under a stream of nitrogen, and the mixture was stirred at 0 ^{o}C for 1 h and at room temperature for 14 h. The reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with Et_2O. The combined organic layers were washed with brine and saturated aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to afford yellow oil (4.30 g, 105%). The crude product was used in the next reaction without further purification.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 3.4 Hz, 1 H), 6.91-6.88 (dd, *J* = 8.9 and 3.2 Hz, 1 H), 6.77 (d, *J* = 8.9 Hz, 1 H), 3.92-3.89 (m, 4 H), 1.77-1.71 (m, 4 H), 1.52-1.21 (m, 24 H), 0.92-0.89 (m, 6 H)

2,2',5,5'-tetrakis(hexyloxy)-1,1'-biphenyl

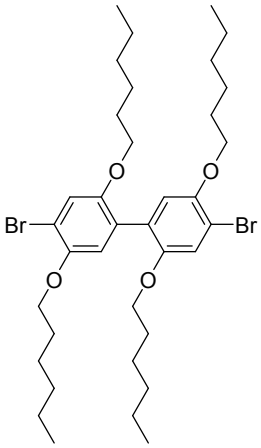
2-Bromo-1,4-bis(hexyloxy)benzene (3.73 g, 10.44 mmol), 2-(2,5-bis(hexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.05 g, 10.01 mmol), K_3PO_4 (11.10 g, 52.29 mmol), 18-crown-6 (13.58 g, 51.38 mmol), $(PPh_3)_4Pd$ (0.62 g, 0.54 mmol) were placed in a flask, and the atmosphere in the flask was replaced with argon. Dry THF (80 mL) and distilled water (20 mL) were added under a stream of nitorogen. The mixture was degassed with argon and refluxed for 3 days. The reaction was quenched with 1 mol/L HCl, and the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$ and concentration under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 9/1 and hexane/CH_2Cl_2 = 5/2) to afford 2,2',5,5'-tetrakis(hexyloxy)-1,1'-biphenyl as a pale yellow oil (4.46 g, 80%).



^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87-6.79 (m, 6 H), 3.90 (t, *J* = 6.4 Hz, 4 H), 3.81 (t, *J* = 6.6 Hz, 4 H), 1.75 (quint, *J* = 7.2 Hz, 4 H), 1.60-1.54 (m, 4 H), 1.47-1.41 (m, 4 H), 1.35-1.17 (m, 20 H), 0.90 (t, *J* = 7.0 Hz, 6 H), 0.83 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.8, 150.7, 129.3, 117.7, 114.2, 69.64, 68.57, 31.63, 31.56, 29.41, 29.39, 25.8, 25.7, 22.62, 22.58.

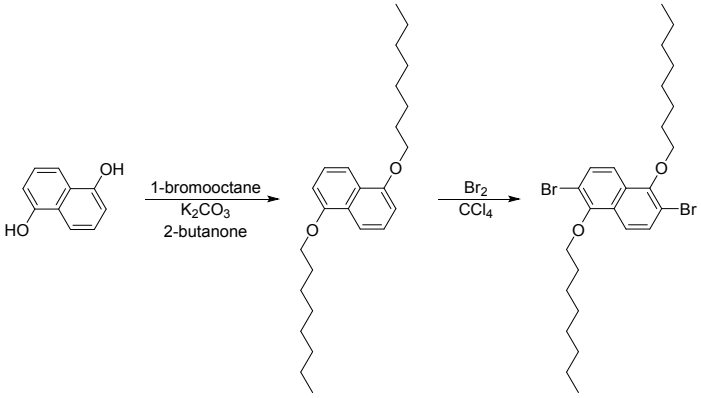
4,4'-dibromo-2,2',5,5'-tetrakis(hexyloxy)-1,1'-biphenyl (**1c**) [S3)]

2,2’,5,5’-Tetrakis(hexyloxy)-1,1’-biphenyl (3.32 g, 5.98 mmol) and $CaCO_3$ (1.27 g, 12.69 mmol) were placed in a flask. Mixed solvent of dry CH_2Cl_2/dry MeOH = 5/2 (100 mL) was added to the flask, and the mixture was stirred. When the solution became homogeneous, $BTMABr_3$ (4.68 g, 12.00 mmol) was added, and the reaction mixture was stirred at room temperature for 24 h. After filtration, the filtrate was diluted with CH_2Cl_2. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 4/1) to afford 4,4'-dibromo-2,2',5,5'-tetrakis(hexyloxy)-1,1'-biphenyl (**1c**) as a pale yellow white solid (3.60 g, 85%).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (s, 2 H), 6.86 (s, 2 H), 3.95 (t, *J* = 6.6 Hz, 4 H), 3.83 (t, *J* = 6.6 Hz, 4 H), 1.80 (quint, *J* = 7.1 Hz, 4 H), 1.59 (t, *J* = 6.9 Hz, 4 H), 1.51-1.45 (m, 4 H), 1.37-1.18 (m, 20 H), 0.90 (t, *J* = 7.0 Hz, 6 H), 0.85 (t, *J* = 6.9 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.7, 149.2, 127.1, 118.1, 117.3, 111.3, 70.1, 69.6, 29.3, 29.2, 25.7, 25.6, 22.6, 22.5, 14.01, 13.95.

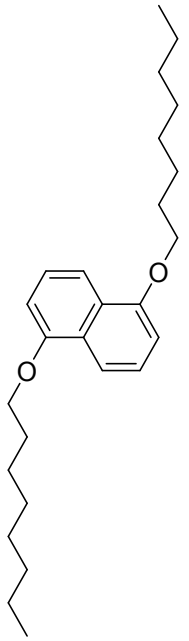
2,6-dibromo-1,5-bis(octyloxy)naphthalene (**1d**)



1d

1,5-bis(octyloxy)naphthalene

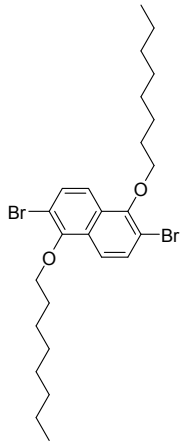
1,5-Dihydroxynaphthalene (5.05 g, 31.53 mmol) and K_2CO_3 (17.55 g, 126.99 mmol) were placed in a flask, and the atmosphere in the flask was replaced with argon. 2-Butanone (50.0 mL) and 1-bromooctane (22.0 mL, 126.79 mmol) were added to the flask under a stream of nitrogen, and the mixture was refluxed for 11 h. The reaction was quenched with water, and the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$ and concentration under reduced pressure to afford a yellow solid (13.10 g, 108%). The crude product was used in the next reaction without purification.



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.6 Hz, 2 H), 7.34 (t, *J* = 8.0 Hz, 2 H), 6.82 (d, *J* = 7.4 Hz, 2 H), 4.12 (t, *J* = 6.6 Hz, 4 H), 1.91 (quint, *J* = 7.0 Hz, 4 H), 1.59-1.53 (m, 4 H), 1.43-1.28 (m, 16 H), 0.89 (t, *J* = 6.9 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.7, 126.8, 125.0, 114.0, 105.2, 68.2, 31.8, 29.4, 29.33, 29.28, 26.3, 22.7, 14.1.

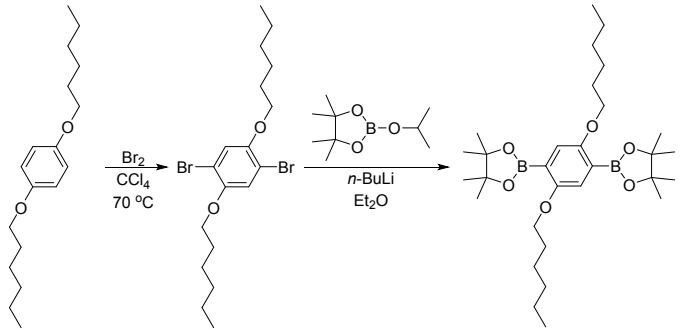
2,6-dibromo-1,5-bis(octyloxy)naphthalene (**1d**) [S4)]

Suspension of 1,5-bis(octyloxy)naphthalene (5.01 g, 13.03 mmol) in CCl_4 (60 mL) and acetic acid (10 mL) was cooled to 0 ^{o}C, and Br_2 (1.6 mL, 31.04 mmol) was added to the flask., followed by stirring at room temperature overnight. The reaction was quenched with 20 wt% aqueous NaOH, and the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water, saturated aqueous $NaHCO_3$, and 30 wt% aqueous $Na_2S_2O_3$, and dried over anhydrous $MgSO_4$. The organic layer was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 5/1), HPLC (elution: $CHCl_3$), and recrystallization from MeOH to afford 2,6-dibromo-1,5-bis(octyloxy)naphthalene (**1d**) as a colorless crystal (82.70 mg, 1%).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 2 H), 7.60 (d, *J* = 8.9 Hz, 2 H), 4.07 (t, *J* = 6.8 Hz, 2 H), 1.94 (quint, *J* = 7.2 Hz, 4 H), 1.59-1.65 (m, 4 H), 1.42-1.41 (m, 16 H), 0.90 (t, *J* = 6.9 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.8, 131.0, 130.1, 119.3, 113.7, 74.6, 31.8, 30.3, 29.5, 29.3, 26.0, 22.7, 14.1.

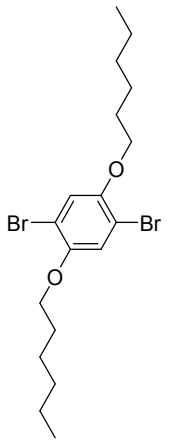
4. Synthesis of 2,2'-(2,5-bis(hexyloxy)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4)



4

1,4-dibromo-2,5-bis(hexyloxy)benzene

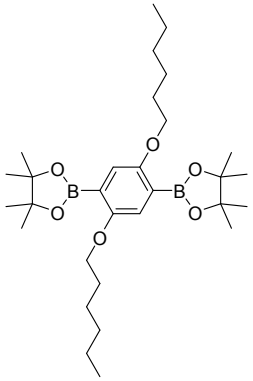
1,4-Dihexyloxybenzene (14.08 g, 50.57 mmol) was placed in a flask. CCl_4 (30 mL) was added to the flask, and the solution was cooled to 0 °C. Br_2 (7.8 mL, 152.23 mmol) was slowly added, and the mixture was stirred at 70 °C for 6 days. The reaction was quenched with 20 wt% aqueous $Na_2S_2O_3$, and the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$ and concentration under reduced pressure. The crude product was purified by silica gel column chromatography (hexane to CH_2Cl_2) and recrystallization from MeOH to afford colorless crystal (18.29 g, 83%).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (s, 2 H), 3.95 (t, *J* = 6.5 Hz, 4 H), 1.80 (quint, *J* = 7.0 Hz, 4 H), 1.48 (quint, *J* = 7.4 Hz, 4 H), 1,36-1.33 (m, 8 H), 0.91 (t, *J* = 7.0 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.1, 118.4, 111.1, 70.3, 31.5, 29.1, 25.6, 22.5, 14.0.

2,2'-(2,5-bis(hexyloxy)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4**)

A flask was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. 1,4-Dibromo-2,5-bis(hexyloxy)benzene (1.98 g, 4.54 mmol) was placed in the flask. Dry Et_2O (50 mL) was added to the flask under a stream of nitrogen, and the solution was cooled to 0 °C. 1.60 M *n*-Butyllithium in hexane (7.2 mL, 11.52 mmol) was slowly added to the reaction flask under a stream of nitrogen, and the mixture was stirred at 0 °C. After 10 min, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.5 mL, 17.29 mmol) was added at 0 °C under a stream of nitrogen, and the mixture was stirred at 0 °C. After 5 min, the mixture was warmed to room temperature, followed by stirring for 14 h. The reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by recrystallization from hexane to afford a colorless crystal (0.92 g, 38%).



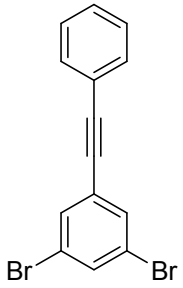
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (s, 2 H), 3.94 (t, *J* = 6.4 Hz, 4 H), 1.77-1.72 (m, 4 H), 1.53-1.48 (m, 4 H), 1.35-1.31 (m, 32 H), 0.90 (t, *J* = 6.9 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.6, 119.9,

83.4, 69.7, 31.7, 29.6, 25.7, 24.8, 22.7, 14.1.

5. Synthesis of dibromo monomers 3

1,3-dibromo-5-(phenylethynyl)benzene (**3a**)

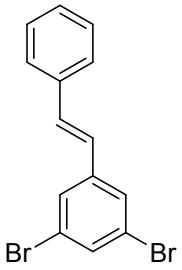
1,3,5-Tribromobenzene (3.00 g, 9.53 mmol), CuI (0.04 g, 0.21 mmol), and $(PPh_3)_4Pd$ (0.22 g, 0.19 mmol) were placed in a flask, and the atmosphere in the flask was replaced with argon. Dry THF (20 mL), Et_3N (3.00 mL, 21.52 mmol), and ethynylbenzene (0.95 mL, 8.64 mmol) were added under a stream of nitorogen. The mixture was degassed with argon and refluxed for 43 h. The reaction was quenched with saturated aqueous NH_4Cl, 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 crude product was purified by silica gel column chromatography (hexane) to afford a white solid (1.70 g, 59%).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (t, *J* = 1.7 Hz, 1 H), 7.61 (d, *J* = 8.6 Hz, 2 H), 7.53-7.49 (m, 2 H), 7.38-7.35 (m, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 133.9, 133.0, 131.7, 129.0, 128.5, 126.7, 122.6, 122.2, 91.9, 86.4.

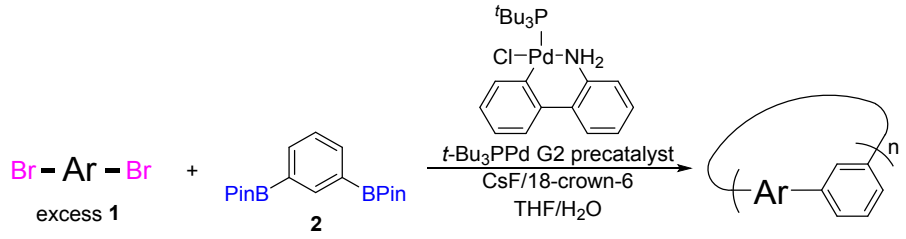
(*E*)-1,3-dibromo-3-styrylbenzene (**3b**)[S5)]

The atmosphere in a flask was replaced with argon. Triethyl phosphite (0.80 mL, 4.60 mmol) and benzylbromide (0.45 mL, 3.78 mmol) was added to the flask under a stream of nitrogen, and the mixture was heated at 150 °C for 18 h, followed by concentration under reduced pressure at 100 °C. The residue was cooled to room temperature, and then dry DMF (2.0 mL) was added under a stream of nitrogen. The solution was kept at 0 °C. In another flask, NaH (40% in oil, 176.3 mg, 2.98 mmol) was placed and washed with dry hexane. The solution of phosphonic acid ester in DMF in the previous flask was added to the flask containing NaH with a cannula at 0 °C, and the mixture was stirred at 0 °C. After 1 h, a solution of 3,5-dibromobenzaldehyde (0.98 g, 3.71 mmol) in dry DMF (5 mL) was added under a stream of nitrogen, and the mixture was stirred at room temperature for 24 h. Reaction was quenched with water, and the mixture was extracted with CH_2Cl_2. Combined organic layers were washed with water twice and brine, and dried over anhydrous $MgSO_4$. Organic layers were concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane) twice to afford a white solid (47.40 mg, 5%).

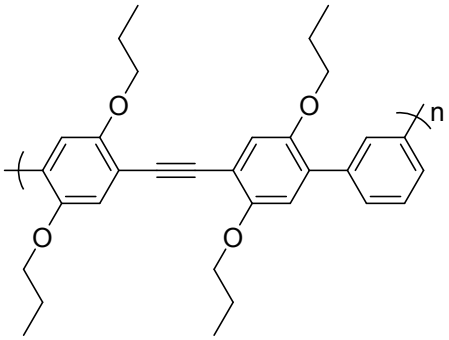


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, J = 1.7 Hz, 1 H), 7.50 (d, J = 7.4 Hz, 2 H), 7.38 (t, J = 7.4 Hz, 2 H), 7.30 (t, J = 7.2 Hz, 1 H), 7.10 (d, J = 16.0 Hz, 1 H), 6.96 (d, J = 16.0 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.0, 136.3, 132.6, 131.5, 128.7, 128.4, 128.1, 126.8, 125.6, 123.2.

6. General procedure for cyclic polymerization of 1 and 2



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** (36.2 mg, 0.064 mmol), **2** (16.3 mg, 0.049 mmol), CsF (36.1 mg, 0.24 mmol), 18-crown-6 (113.4 mg, 0.43 mmol), and *t*-Bu_3PPd G2 precatalyst **5** (1.2 mg, 0.0023 mmol) were placed in a 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 (eluent: $CHCl_3$) to afford 22.2 mg (94%) of poly(tolan-*alt*-*m*-phenylene).

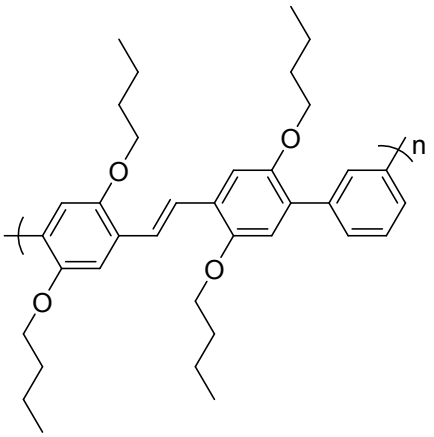


^{1}HNMR (600 MHz, $CDCl_3$) δ 7.74 (s, 1 H), 7.59-7.57 (m, 2 H), 7.44 (t, J = 7.7 Hz, 1 H), 7.15 (s, 2

H), 6.98 (s, 2 H), 4.06 (t, J = 6.6 Hz, 4 H), 3.91 (t, J = 6.6 Hz, 4 H), 1.91-1.81 (m, 4 H), 1.79-1.71 (m, 4 H), 1.11 (t, J = 7.5 Hz, 6 H), 0.95 (t, J = 7.3 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.0, 149.9, 137.9, 132.2, 130.3, 128.5, 127.3, 117.8, 116.2, 113.1, 90.3, 71.5, 71.0, 29.7, 22.8, 22.7, 10.64, 10.61; IR (KBr) 2961, 2921, 2874, 2850, 1655, 1655, 1509, 1467, 1379, 863, 800 cm^{-1}.

Cyclic polymerization of 1b and 2

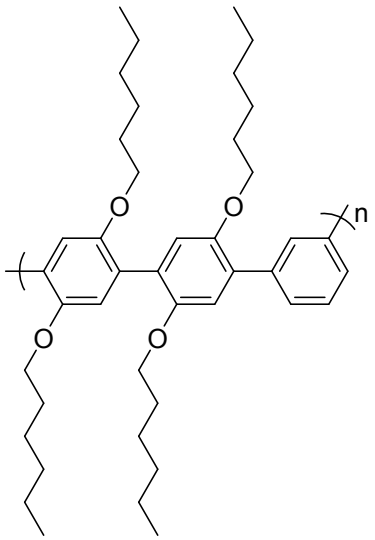
Polymerization was carried out according to the general procedure. Concentration of **2** was 8.3 mM in THF, and THF/H_2O ratio was 6.0/0.2, v/v. The polymerization time was 2 days. After purification with HPLC (eluent: $CHCl_3$), poly(stilbene-*alt*-*m*-phenylene) was obtained (21.8 mg, 82%).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (s, 1 H), 7.59 (d, J = 7.6 Hz, 2 H), 7.56 (s, 1 H), 7.44 (t, J = 7.9 Hz, 1 H), 7.29 (s, 2 H), 6.99 (s, 2 H), 4.05 (t, J = 6.2 Hz, 4 H), 3.99 (t, J = 5.8 Hz, 4 H), 1.87-1.84 (m, 4 H), 1.75-1.71 (m, 4 H), 1.61-1.56 (m, 4 H), 1.45-1.40 (m, 4 H), 1.01 (t, J = 7.6 Hz, 6 H, 0.90 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.1, 150.4, 138.2, 131.3, 130.3, 128.2, 127.2, 127.0, 123.5, 115.8, 111.5, 69.4, 69.3, 31.6, 31.5, 19.5, 19.3, 14.0, 13.8, 1.00; IR (KBr) 3055, 2959, 2930, 2871, 1508, 1467, 1259, 1202, 866, 799 cm^{-1}.

Cyclic polymerization of 1c and 2

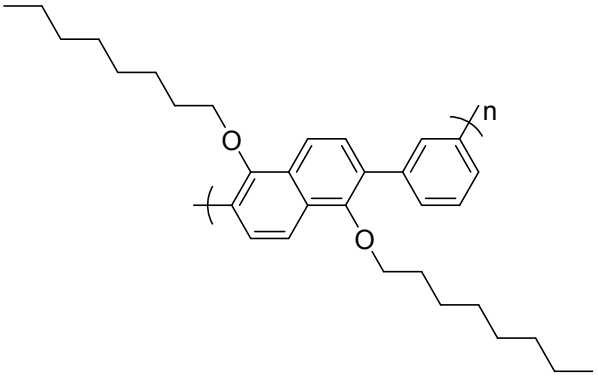
Polymerization was carried out according to the general procedure. After purification with HPLC (eluent: $CHCl_3$), poly(biphenylene-*alt*-*m*-phenylene) was obtained (23.4 mg, 74%).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1 H), 7.64 (d, *J* = 7.7 Hz, 2 H), 7.45 (t, *J* = 7.6 Hz, 1 H), 7.10 (s, 2 H), 7.07 (s, 2 H), 3.94 (t, *J* = 6.6 Hz, 8 H), 1.75-1.65 (m, 8 H), 1.75-1.65 (m, 8 H), 1.37-1.1.24 (m, 24 H), 0.86-0.81 (m, 12 H); ^{13}C NMR (140 MHz, $CDCl_3$) δ 150.4, 141.6, 140.3, 138.6, 130.8, 129.4, 128.7, 127.3, 127.1, 116.3, 69.7, 31.6, 29.5, 25.9, 22.5, 14.0; IR (KBr) 2957, 2929, 2858, 1467, 1376, 1261, 1207, 1087, 1060, 1023, 866, 799, 703 cm^{-1}.

Cyclic polymerization of 1d and 2

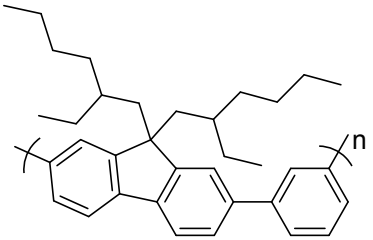
Polymerization was carried out according to the general procedure. After purification with HPLC (eluent: $CHCl_3$), poly(naphthalene-*alt*-*m*-phenylene) was obtained (22.0 mg, 98%).



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11-8.08 (m, 2 H), 8.06-8.04 (m, 1 H), 7.79-7.75 (m, 2 H), 7.65-7.61 (m, 2 H), 7.57 (t, *J* = 7.3 Hz, 1 H), 3.74-3.65 (m, 4 H), 1.70-1.66 (m, 4 H), 1.34-1.22 (m, 20 H), 0.90-0.82 (m, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.6, 138.9, 130.1, 129.9, 128.8, 128.4, 128.2, 118.6, 105.0, 74.1, 31.8, 30.4, 29.4, 29.2, 26.2, 22.6, 14.1; IR (KBr) 2957, 2925, 2850, 1597, 1459, 1261, 1090, 800, 705 cm^{-1}.

Cyclic polymerization of 1e and 2

Polymerization was carried out according to the general procedure. After purification with HPLC (eluent: $CHCl_3$), poly(fluorene-*alt*-*m*-phenylene) was obtained (20.0 mg, 88%).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97-7.88 (m, 1 H), 7.83 (d, *J* = 7.7 Hz, 2 H), 7.70-7.65 (m, 6 H), 7.59-7.57 (m, 1 H), 2.15-2.10 (m, 4 H), 0.91-0.51 (m, 30 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.3, 142.5, 142.42, 142.41, 142.3, 140.4, 139.7, 139.63, 139.57, 139.54, 139.50, 139.4, 129.20, 129.15, 129.11, 126.2, 126.02, 125.99, 125.91, 125.89, 125.84, 125.79, 123.07, 122.97, 122.94, 122.88, 122.77, 120.0, 55.2, 44.7, 34.7, 33.91, 33.88, 28.25, 28.21, 27.1, 22.8, 14.0, 10.45, 10.43; IR (KBr) 2959, 2920, 2854, 2600, 1459, 1094, 1028, 887, 822, 792, 757, 702 cm^{-1}.

7. MALDI-TOF mass spectra of the products, obtained by polymerization of 1.3 equivalent of 1b and 2, in the high molecular weight region.

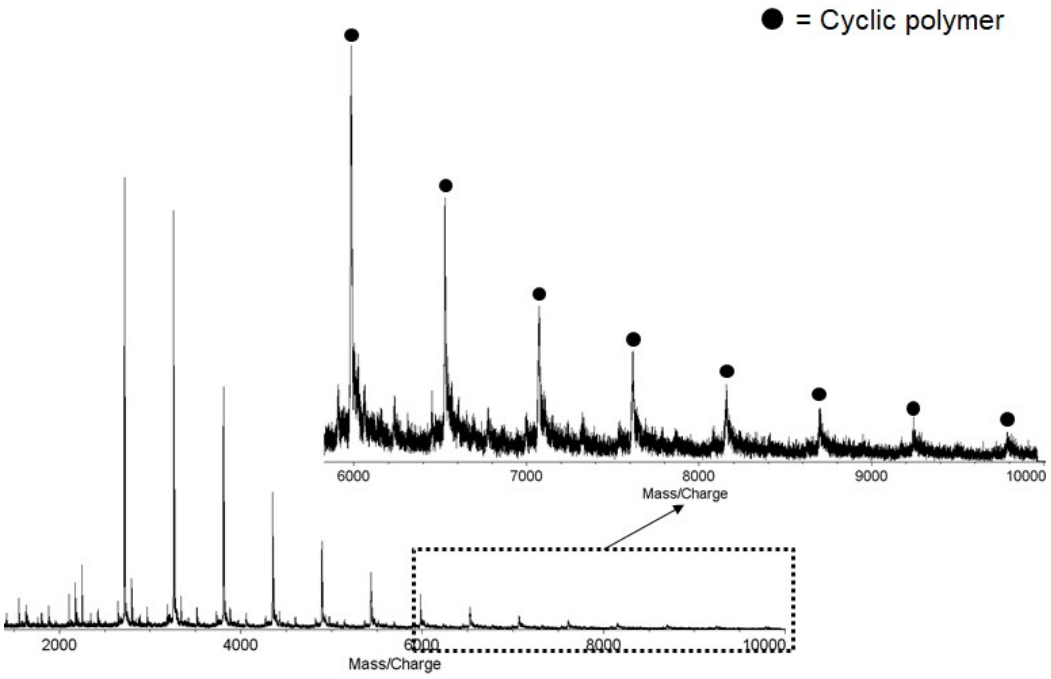


Figure S1. MALDI-TOF mass spectra of the products obtained by polymerization of 1.3 equivalent of **1b** and 1.0 equivalent of **2** in the presence of *t*-Bu_3PPd G2 precatalyst **5**, CsF, and 18-crown-6 in THF/H_2O at room temperature for two days.

8. MALDI-TOF mass spectrum of the products in polymerization of 1.2 equivalent of 1c and 2.

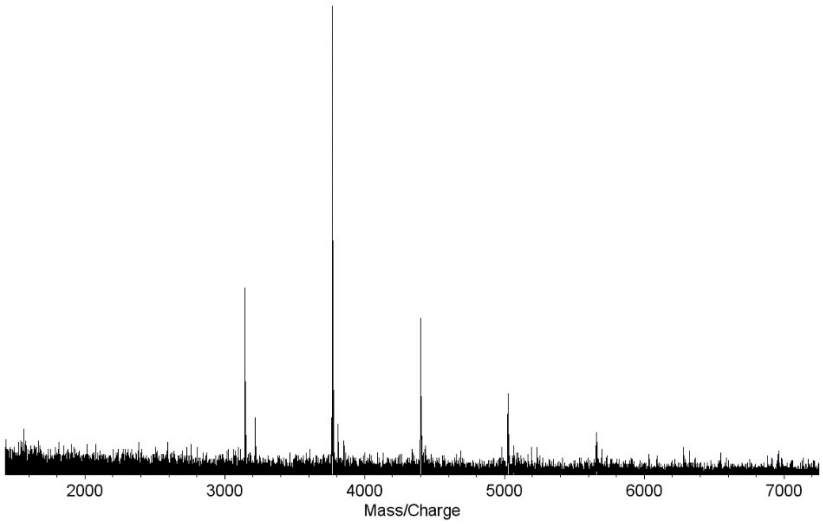
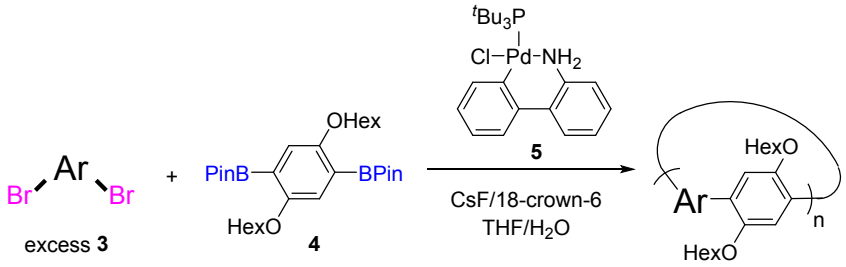
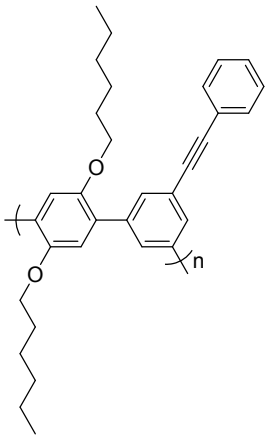


Figure S2. MALDI-TOF mass spectrum of the products obtained by polymerization of 1.2 equivalent of **1c** and 1.0 equivalent of **2** in the presence of *t*-Bu_3PPd G2 precatalyst **5**, CsF, and 18-crown-6 in THF/H_2O at room temperature for a day.

9. General procedure for cyclic polymerization of 3 and 4.



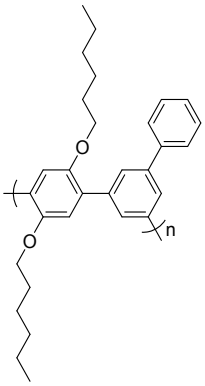
All glass apparatus was dried prior to use. Addition of reagents into a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. **3a** (21.8 mg, 0.065 mmol), **4** (26.3 mg, 0.050 mmol), CsF (30.1 mg, 0.20 mmol), 18-crown-6 (107.6 mg, 0.41 mmol), and *t*-Bu_3PPd G2 precatalyst **5** (1.4 mg, 0.0027 mmol) were placed in a 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 (eluent: $CHCl_3$) to afford poly(*p*-phenylene-*alt*-tolan) (22.4 mg, 98%).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83-7.80 (m, 3 H), 7.56-7.55 (m, 2 H), 7.36-7.35 (m, 3 H), 7.09 (s, 2 H), 3.98 (t, *J* = 6.3 Hz, 4 H), 1.74-1.71 (m, 4 H), 1.41-1.18 (m, 12 H), 0.81-0.78 (m, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.4, 138.3, 131.6, 131.4, 130.6, 130.3, 128.3, 128.1, 123.6, 122.5, 116.2, 89.9, 88.9, 69.7, 31.6, 29.5, 26.0, 22.6, 14.0; IR (KBr) 2957, 2929, 2858, 1587, 1508, 1467, 1441, 1377, 1261, 1207, 864, 802, 755, 690 cm^{-1}.

Cyclic polymerization of 3c and 4

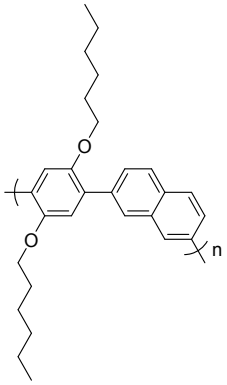
Polymerization was carried out according to the general procedure. After purification with HPLC (eluent: $CHCl_3$), poly(*p*-phenylene-*alt*-biphenylene) was obtained (17.3 mg, 80%).



^{1}H NMR (150 MHz, $CDCl_3$) δ 7.92-7.87 (m, 2 H), 7.85-7.84 (m, 1 H), 7.75-7.71 (m, 2 H), 7.50-7.45 (m, 2 H), 7.39-7.35 (m, 1 H), 7.17-7.13 (m, 2 H), 4.01-3.95 (m, 4 H), 1.76-1.71 (m, 4 H), 1.39-1.31 (m, 4 H), 1.26-1.11 (m, 8 H), 0.83-0.74 (m, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.4, 141.6, 140.3, 138.6, 130.8, 129.4, 128.7, 127.4, 127.3, 127.1, 116.3, 69.7, 31.6, 29.5, 25.9, 22.5, 14.0; IR (KBr) 2957, 2928, 2854, 1593, 1508, 1456, 1377, 1263, 1206, 1027, 866, 761 cm^{-1}.

Cyclic polymerization of 3d and 4

Polymerization was carried out according to the general procedure. After purification by HPLC (eluent: $CHCl_3$), poly(*p*-phenylene-*alt*-naphthalene) was obtained (17.0 mg, 86%).



^{1}H NMR (150 MHz, $CDCl_3$) δ 8.20 (s, 2 H), 7.93 (d, *J* = 11.7 Hz, 2 H), 7.84-7.80 (m, 2 H), 7.20-7.14 (m, 2 H), 4.00 (t, *J* = 6.4 Hz, 4 H), 1.75-1.69 (m, 4 H), 1.41-1.39 (m, 4 H), 1.27-1.25 (m, 8 H), 0.86-0.80 (m, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.7, 136.3, 133.4, 131.5, 131.1, 128.3, 128.1, 126.9, 116.8, 69.8, 31.5, 29.4, 25.8, 22.6; IR (KBr) 2957, 2928, 2858, 1493, 1459, 1379, 1261, 1205, 1093, 1023, 842, 803 cm^{-1}.

10. Supporting references

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