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Supplementary Material Available: Detailed synthetic procedures and characterization data for the synthesis of monomers 1-4 and polymers listed in Table 1 (8 pages). Ordering information is given on any current masthead page.

General Information. Chemical reagents and solvents were purchased from Aldrich Chemical and were used as supplied without further purification unless otherwise stated. House nitrogen filtered through a Labclear gas filter / dryer was used for all synthetic operations. ^1H NMR 400 MHz, proton decoupled ^{13}C NMR 100 MHz, and ^{19}F NMR 376 MHz spectra were obtained with a Varian Unity Plus NMR Superconducting Spectrometer system. Chloroform-*d* is used as solvent and chemical shifts reported are internally referenced to tetramethylsilane (0 ppm), CDCl_3 (77 ppm) and CFCl_3 (0 ppm) for ^1H , ^{13}C , and ^{19}F nuclei, respectively. Infrared (IR) analyses were performed on neat KBr disks using an ATI Mattson Genesis Series FTIR spectrophotometer or a Nicolet Magna 550 FTIR equipped with a deuterio triglycinesulfate (DTGS) detector at 4 cm^{-1} resolution. Gas chromatography / mass spectrometry (GC/MS) data were obtained from a Varian Saturn GC/MS using a 30m x 0.25mm DB-1 capillary column. Liquid chromatography / electron ionization mass spectral data were obtained on a Finnigan 4500 mass spectrometer. High-resolution electron impact mass spectroscopic (EI/HRMS) data were obtained on a Fisons Autospec mass spectrometer and the sample was introduced by direct exposure probe (DEP).

Thermal Characterization. Thermodynamic data and evaluations were obtained from a Mettler DSC 30S module in the TA 4000 System using Graph Ware 72 AT.2/.5 software for analyses. Typically a 1-3 mg sample was weighed into an aluminum crucible, the lid crimped, and the sample placed in the measuring cell under a nitrogen purge of 50 mL/min. Each sample underwent two heating cycles, each from 0°C to 450°C at a heating rate of $10^\circ\text{C}/\text{min}$ and had a background subtraction from the blank crucible run under exactly the same conditions. Thermomechanical analysis (TMA) data were obtained on DuPont 2940 TMA from 10°C to 450°C at a heating rate of $10^\circ\text{C}/\text{min}$ and a constant force of 0.05 N. Isothermal Dynamic mechanical spectroscopy (DMS) data were collected on a Rheometrics RMS 800 Mechanical Spectrometer with parallel plate fixtures at $\omega = 1\text{ Hz}$ and $\gamma = 50\%$ at 210°C .

Characterization by GPC. Gel Permeation Chromatography (GPC) data were collected using a Waters model 150C gel permeation chromatograph at 30°C equipped with two consecutive Polymer Labs PLGel 5 micron Mixed-C columns. Data acquisition and manipulation were performed using GPC-PRO software from Viscotek. The eluting solvent was HPLC grade THF at a flow rate of 1.0 mL/min. Retention times were calibrated against the following Polymer Labs Easical PS-2 polystyrene standards with M_w (M_w/M_n): 21600 (1.03), 11200 (1.03), 5110 (1.05), 3180 (1.05), 1440 (1.07), 640 (1.14).

Thermal Stability by TGA. Isothermal thermogravimetric analysis (TGA) of polymer prepared by curing monomer directly during the TGA experiment and for solution oligomerized samples were performed on a DuPont Instruments 951 Thermogravimetric Analyzer in nitrogen with a flow rate of 25-30 mL/min. A typical experiment included program heating at $20^\circ\text{C}/\text{min}$ to 300°C , isothermal cure for three hours, heating at $20^\circ\text{C}/\text{min}$ to 450°C , and isothermal heating for 10 hours. The slope of the equilibrium weight loss was determined by programmed calculation. Thermogravimetric analysis (TGA) of cured polymer films on silicon wafers were

performed on ca. 3/4x3/4 inch pieces on a modified Cahn 131 TGA controlled with a Camile 2000 system under ultra-high purity helium with a flow rate of ca. 400 mL/min.

Spin Coating and Cure on Silicon Wafer. Thin films were applied to oxidized silicon wafers using standard spincoating techniques at a spin rate of 2000 rpm. The majority of solvent carrier was removed by baking on a hot plate in air at 90°C. The films were cured under nitrogen with less than 20 ppm oxygen using the following cure schedule: Isothermal at 50°C for 20 min, ramping to 200°C in 30 min, isothermal at 200°C for 1 h, ramping to 300°C in 30 min, isothermal at 300°C for 1 h, ramping to 400°C in 1 h, isothermal at 400°C for 1 h, slow cooled to 25°C. Film thicknesses of the resulting films were measured with a Tencor Alpha Step 200 profilometer.

Dielectric Measurement. Dielectric constants were obtained by measuring the capacitance of parallel plate capacitors. The capacitance is related to the dielectric constant by: $C = \epsilon_r \epsilon_0 A/d$ where ϵ_r is the relative dielectric constant, ϵ_0 is the permittivity of free space (8.85×10^{-12} F/m), A is the plate area, and d is the dielectric thickness. The capacitors were constructed by solution casting polymer solutions onto salt substrates using typical spin coating methods and curing at 400°C in the normal way. The cured film was removed from the substrate in a water bath. The freely standing films were sputter coated on both sides with 50 nm of gold. Capacitors were punched out of the film with a 0.375 " diameter punch. Capacitance measurements were performed on a HP 4284A LCR meter operating at 100 kHz connected to a two point test fixture.

Synthesis of 1:

2,2-Bis(3-bromo-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane. To a 3 L reactor, equipped with a gas vent attached to an acid gas scrubber, containing 1.75 L of carbon tetrachloride and 250 mL glacial acetic acid (HOAc) maintained at room temperature was added, 150 g (0.446 moles) of 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane and 5.0 g iron powder (0.090 mol). 144.0 g of bromine (0.901 mole) was then added dropwise to the mixture over 6 hours. The solution was maintained <28°C for 48 hours then the reaction mixture was washed once with saturated aqueous sodium bicarbonate and twice with deionized water. The CCl_4 fraction was dried over anhydrous MgSO_4 , filtered and evaporated providing 214.1 g (0.433 mol) of a yellow powder (97%), mp 95-96°C. IR (cm^{-1}): 3506.7 (-OH), 1605.3, 1578.2, 1499.7 (Ar), 1256, 1208.9, 1175.3, 1136.7 (C-F), 1046 (C-O). GC/MS, m/z (%): 423 (45.4), 424 (57.2), 425 (88.9), 426 (65.5), 427 (52.0), 428 (33.2), 492 (45.1), 494 (100.0), 496 (37.5). HRMS for $\text{C}_{15}\text{H}_8\text{Br}_2\text{O}_2\text{F}_6$ calcd (found): 491.8795 (491.8774).

2,2-Bis(3-bromo-4-trifluoromethanesulfonylphenyl)-1,1,1,3,3,3-hexafluoropropane. The dibrominated bisphenol (210.0 g, 0.427 mole) was dissolved in 1.0 L of dichloromethane and 150 mL (1.08 mole) of dry triethylamine in a 2 L reactor. To this mixture, maintained at 8-12°C, was added 150 g trifluoromethanesulfonyl chloride (1.08 mole) dissolved in 30 mL of CH_2Cl_2 over 30 minutes. The reaction mixture was stirred at 16°C for three hours, then transferred to a separatory funnel and washed with two portions of aqueous 5% HCl (200 mL each), two portions of saturated sodium bicarbonate solution (200 mL each), then once with water. The CH_2Cl_2 solution was dried over anhydrous MgSO_4 , filtered, and evaporated to provide 314.2 g (0.415 mole, 97.1%) colorless crystals, mp 86.5-88°C. IR (cm^{-1}): 1479.0, 882.5, 737.3 (Ar), 1429.3, (SO₂), 1137.2, 1213.5 (C-F). ¹H NMR (400 MHz, CDCl_3): δ 7.4 (4H, br, m), 7.74 (2H, s). ¹³C NMR (100 MHz, CDCl_3): δ 63.64 (hept, $\text{C}(\text{CF}_3)_2$, $J = 30$ Hz), 116.57, 116.98, 122.97, 130.94, 133.71, 135.81, 147.83. ¹⁹F NMR (376 MHz, CDCl_3): δ -64.27 (6F, s), -73.86 (6F, s). DEP/MS,

m/z (%): 758(5), 624(4), 207(5), 69(100). HRMS for C₁₇H₆Br₂O₆F₁₂S₂ calcd (found): 755.7779 (755.7780).

2,2-Bis(3,4-di(phenylethynyl)phenyl)-1,1,1,3,3,3-hexafluoropropane (1) To a 2-L 5-neck flask fitted with a mechanical stirrer, thermocouple, and dropping funnel was added aryl dibromide ditriflate (102.4 g, 0.135 mole), DMF (400 mL), and triethylamine (400 mL). The solution was de-oxygenated and [P(Ph)₃]₂PdCl₂ (7.0 g, 0.01 mole) was added at 65°C. De-oxygenated phenylacetylene (68.0 g, 0.667 mole) was then added drop-wise in 3-10 min and the mixture was heated at 90°C for 2.5 hours, diluted with CH₂Cl₂ (500 mL), washed with 10% HCl, evaporated, and crystallized from acetone/water giving 82.6 g (87%), mp 189°-191°C. IR (cm⁻¹): 3058.5, 3020.03 (ArH), 2213.9 (-CCPh), 1598.7 (Ar), 1500.4, 1442.5, 1413.6 (w), 1321.0 (w), 1251.6 (st, CF), 1207.2 (st, CF), 1182.2 (st, CF), 1135.9 (sh), 1097.3, 1068.7, 991.3, 966.2, 912.1 (w), 877.5 (ArH lone and adj.), 825.4 (ArH lone and adj.), 752.1 (st, mono-subst. Ph wag), 686.6 (st, mono-subst. Ph bend). ¹H NMR (400 MHz, CDCl₃): δ 7.30-7.40 (13H, br, m), 7.52-7.62 (13H, br, m). ¹³C NMR (100 MHz, CDCl₃): δ 64.0 (hept, C(CF₃)₂, *J* = 30 Hz), 87.23, 87.48, 94.54, 95.38 (-CCPh) 122.77, 126.16, 126.93, 128.36, 128.40, 128.71, 128.78, 129.4, 131.63, 131.72, 132.51, 133.11. ¹⁹F NMR (376 MHz, CDCl₃): δ -63.84 (s). HRMS for C₄₇H₂₆F₆ calcd (found): 704.1939 (704.1926).

Synthesis of 2:

3,3'-Dibromo-4,4'-dihydroxyphenyl ether. To a 2-L 5-neck flask fitted with a mechanical stirrer, a thermocouple, and a dropping funnel was added 1 L of CH₂Cl₂, 20 mL of HOAc, 100 g (0.495 mol) of 4,4'-dihydroxyphenyl ether (Dow Chemical), and 0.74 grams (0.013 mol) of iron powder. The mixture was stirred and cooled to 10°C under nitrogen and 170 g (1.06 mol) of bromine was slowly added to the reaction mixture over a period of 2 hours and 15 minutes with vigorous stirring. The temperature of the reaction was maintained <10°C during addition. When completed, the temperature was raised to 18°C and held with stirring for 18 hours. The resulting mixture was washed with 2 L of water and 500 mL of saturated aqueous sodium bicarbonate. The organic fraction was filtered to remove suspended solids, and evaporated. The solid was washed with water and dried under vacuum, then washed with hexane, and dried providing 155 g (86.3%) as a white crystalline solid, mp 101-102.5°C. IR (cm⁻¹): 799 (0.29), 859 (0.30), 880 (0.09), 922 (0.37), 1031 (0.13), 1184 (0.81), 1259 (0.40), 1331 (0.35), 1475 (1.00), 1577 (0.10), 1600 (0.13), 3395 (0.35), 3421 (0.38). GC/MS, *m/z* (%): 51 (16.0), 53 (27.0), 63 (30.0), 79 (16.5), 144 (7.4), 199 (7.3), 200 (13.0), 359 (42.2), 360 (100), 362 (46.9). HRMS for C₁₂H₈Br₂O₃ calcd (found): 357.8838 (357.8839).

3,3'-Dibromo-4,4'-di(trifluoromethanesulfonato)phenyl ether. To a 2 L, 5-necked flask equipped with a mechanical stirrer, a thermocouple, and a dropping funnel under nitrogen, was added 1 L of CH₂Cl₂ and 155 g (0.432 mol) of 3,3'-dibromo-4,4'-dihydroxyphenyl ether. The solution was cooled to 10°C and triethylamine (97.75 g, 0.968 mol) was added dropwise over a period of 30 minutes, while maintaining the reaction temperature at 10°C. Trifluoromethanesulfonic acid anhydride (250.8 g, 0.889 mol) was added at a rate that maintained a reaction temperature between 10-20°C. Upon complete addition, the reaction mixture was stirred at 15°C for 3 hours and then washed with two 500 mL portions of water, followed by one 250 mL portion of saturated aqueous sodium bicarbonate. The CH₂Cl₂ was evaporated and the residue was dissolved in acetonitrile giving a 50% (w/w) solution which was extracted five times with 250 mL portions of hexane. The extracts were combined, the solvent

reduced and the product was isolated by filtration giving 165 g (65%) of a white crystalline powder, mp 46-47°C. IR (cm⁻¹): 823 (0.12), 878 (0.75), 1036 (0.12), 1137 (0.68), 1162 (0.72), 1212 (1.00), 1296 (0.17), 1426 (0.81), 1474 (0.82), 583 (0.21). GC/MS, m/e (%): 63 (41.0), 69 (59.1), 142 (6.8), 144 (5.5), 198 (6.3), 356 (10.4), 357 (7.6), 490 (11.0), 491 (35.5), 492 (100), 493 (46.6), 494 (7.1), 621 (1.5), 623 (2.7), 625 (1.5). HRMS for C₁₄H₆Br₂O₇F₆S₂ calcd (found): 621.7886 (621.7856).

3,3',4,4'-Tetra(phenylethynyl)phenyl ether (2). To a 1 L 5-neck flask, equipped as before, was added 50 g 3,3'-dibromo-4,4'-bis(trifluoromethanesulfonato)diphenyl ether (0.080 mole), triethylamine (180 mL), and DMF (180). The mixture was de-oxygenated with nitrogen for 30 minutes and 3.0 g (4.3 mmol) of [P(Ph)₃]₂PdCl₂ was added and the temperature was raised to 75°C. De-oxygenated phenylacetylene (49 g, 0.4803 mol) was added at a rate to maintain a reaction temperature of 80-95°C and the temperature was held at 90-91°C for two hours. An additional 2.5 g (0.025 mol) of phenylacetylene was then added to the reaction mixture and the mixture heated at 90-91°C for an additional 45 minutes. After cooling to room temperature, 350 mL of CH₂Cl₂ was added and the mixture washed with three 500 mL portions of 10% HCl solution, followed by one 500 mL wash with deionized water. The organic solution was evaporated and the residue was purified by flash chromatography on silica gel using CCl₄ as eluent giving 45 g (0.0789 mole, 98%) as a light yellow crystalline powder, mp 107-108°C. IR (cm⁻¹): 689 (0.77), 784 (0.59), 824 (0.39), 878 (0.34), 913 (0.27), 970 (0.42), 1025 (0.25), 1071 (0.28), 1084 (0.28), 1139 (0.33), 1214 (1.00), 1252 (0.52), 1323 (0.47), 1378 (0.17), 1415 (0.41), 1443 (0.38), 1471 (0.64), 1495 (0.82), 1553 (0.40), 1588 (0.65), 2210 (0.16), 3058 (0.27). ¹H NMR (400 MHz, CDCl₃): δ 6.96-6.98 (2H, dd), 7.17 (2H, d), 7.30 (12H, m), 7.51-7.53 (8H, m). ¹³C NMR (100 MHz, CDCl₃): δ 87.63 (1C, -CC-), 87.74 (1C, -CC-), 93.23 (1C, -CC-), 94.41 (1C, -CC-) 119.23 (1C), 121.44 (1C), 121.77 (1C), 122.90 (1C), 123.28 (1C), 127.59 (1C), 128.37 (4C), 128.64 (1C), 131.57 (2C), 131.72 (2C), 133.50, (1C), 156.11 (1C). MS m/z (%): 263 (10.1), 265 (10.7), 274 (6.9), 275 (5.65), 276 (2.33), 463 (5.71), 464 (4.33), 539 (4.17), 570 (100), 571 (36.3), 572 (9.51). HRMS for C₄₄H₂₆O₆ calcd (found): 570.2038 (570.2011).

Synthesis of 3:

3,3'-Dibromo-4,4'-dihydroxybiphenyl. Into a 3-L, 5-necked flask equipped with a mechanical stirrer, a thermocouple, and a dropping funnel was placed 200.83 g 4,4'-biphenol (1.07 mole), 2.5 liters of CH₂Cl₂, 40 mL of HOAc, and 1.37 g of iron powder (0.0245 mole). The reaction mixture was cooled to 10°C, and 370.86 g of bromine (2.32 moles) was added over two days while maintaining the temperature from 10-18°C. The reaction mixture was filtered and the filtrate was evaporated, washed with saturated aqueous sodium bicarbonate and deionized water then dissolved in 1 L of CCl₄ at 60°C. The solution was cooled and the product was collected and washed with two portions of 250 mL of hot hexane yielding 230 g as a white crystalline solid (61.5%), m.p. of 118-121°C. IR (cm⁻¹): 676.6 (0.19), 733.8 (0.20), 809.4 (.054), 823.0 (0.61), 865.7 (0.27), 964.9 (0.12), 1040.4 (0.50), 1061.0 (0.16), 1137.0 (0.50), 1206.5 (0.91), 1245.3 (0.53), 1275.3 (0.87), 1341.1 (0.65), 1370.4 (0.47), 1427.7 (1.00), 1490.2 (0.82), 1571.4 (0.18), 1603.5 (0.27), 3315.6 (.056). GC/MS, m/z (%): 53 (20.4), 62 (15.6), 63 (18.4), 74 (20.5), 75 (16.6), 77 (12.8), 124 (12.4), 125 (16.5), 126 (24.7), 152 (12.2), 153 (18.0), 154 (17.3), 155 (46.9), 156 (14.1), 342 (9.14), 343 (14.9), 344 (100), 345 (15.6), 346 (47.7), 347 (6.1). HRMS for C₁₂H₈O₂Br₂ calcd (found): 341.8891 (341.8890).

3,3'-Dibromo-4,4'-di(trifluoromethanesulfonato)biphenyl (Method 1). To a 2 L reactor was added 229 g (0.670 mole) of 3,3'-dibromo-4,4'-dihydroxybiphenyl and 1 L of CH₂Cl₂. The solution was cooled to 10°C and 138 g (1.37 mole) of triethylamine was slowly added to the mixture so as to maintain the temperature from 10-15°C. Trifluoromethanesulfonic acid anhydride (378.0 g, 1.34 mole) was then added dropwise over 2 h and 10 min while maintaining the temperature <14°C. After the addition, the mixture was heated to 22°C for 16 h, washed with 500 mL of water followed by 500 mL of saturated sodium bicarbonate and then again by 500 mL of deionized water. The CH₂Cl₂ was evaporated and the residue was dissolved in hot hexane saturated with acetonitrile. The solution was cooled and the hexane phase was isolated, heated to 60°C and cooled giving 110 g (33%) as a white crystalline solid. Characterization follows Method 2.

3,3'-Dibromo-4,4'-di(trifluoromethanesulfonato)biphenyl (Method 2). In an alternate procedure, 28.56 g of 3,3'-dibromo-4,4'-biphenol (0.083 mole) was dissolved/suspended in 160 mL of CH₂Cl₂ in a 1 L, 5-necked flask. Triethylamine (25 mL) was added and the solution was cooled to 10°C then 28 g of trifluoromethanesulfonylchloride (0.166 mole) dissolved in 40 mL of CH₂Cl₂ was added dropwise over 30 minutes. After complete addition, the solution was warmed to 22°C and stirred overnight. The crude reaction mixture was washed twice with 5% HCl (100 mL each), saturated aqueous NaHCO₃ (75 mL), and deionized water (100 mL). The CH₂Cl₂ solution was separated and dried over anhydrous MgSO₄, filtered and evaporated to provide 42 g (83.2%) of the trifluoromethanesulfonate ester (0.069 mole) as a light brown powder, m.p. 69-70.5°C. IR (cm⁻¹): 723.4 (0.12), 747.0 (0.17), 839 (0.23) 886.0 (0.50), 1036.4 (0.23), 1135.4 (0.58), 1180.0, 0.38), 1206.4 (1.00), 1248.8 (0.37), 1433.1 (0.88), 1469.0 (0.38). LC/MS, m/z (%): 69 (22.3), 126 (44.6), 127 (10.4), 381 (8.0), 383 (17.3), 385 (7.8), 473 (39.3), 473 (39.3), 474 (23.0), 475 (100), 476 (22.7), 477 (47.3), 478 (10.0), 606 (5.6), 608 (10.6), 610 (5.5). HRMS for C₁₄H₆O₆F₆S₂Br₂ calcd (found): 605.7877 (605.7877).

3,3',4,4'-Tetra(phenylethynyl)biphenyl (3). To a 1 L 5-necked flask equipped as before, was added, 60.85 g 3,3'-dibromo-4,4'-di(trifluoromethanesulfonato)biphenyl (0.10 mole), DMF (270 mL), and triethylamine (270 mL). The mixture was de-oxygenated by sparging with nitrogen for 20 minutes and 4.9 g (7 mmol) [P(Ph)₃]₂PdCl₂ was added and the mixture was heated to 60°C. De-oxygenated phenylacetylene 16.5 g (1.62 mol) was then added drop-wise, resulting in an exotherm that increased the temperature to 80°C. The mixture was cooled to 70°C and the temperature was maintained at 70-80°C, while an additional 33.5 g (0.166 mol) of phenylacetylene was added dropwise. The temperature was held at 75°C for 3 hours after which analysis of the reaction mixture by LC indicated a significant amount of unreacted starting material and products of intermediate conversion. An additional 10 g (0.050 mol) of phenylacetylene and 1 g (1.4 mmol) of [P(Ph)₃]₂PdCl₂ were added and the mixture was heated at 85°C for one additional hour after which time, LC analysis indicated conversion was complete. The cooled reaction mixture was diluted with 500 mL of CH₂Cl₂ and washed with three 1 L portions of 10% HCl. The CH₂Cl₂ solution was evaporated and the crude solid was suspended in hexane, filtered, and purified by washing excessively with hot CCl₄. The monomer was further purified by chromatography over neutral alumina using tetrahydrofuran as an eluent giving 32.0 g (58%) as a light yellow solid, m.p. of 172-174°C. IR (cm⁻¹): 485.9 (0.17), 503.8 (0.15), 527.9 (0.23), 623.7 (0.05), 687.7 (0.70), 752.8 (1.00), 822.7 (0.38), 886.1 (0.11), 911.5 (0.12), 1022.6 (0.08), 1067.0 (0.12), 1273.9 (0.04), 1384.9 (0.10), 1439.9 (0.18), 1492.44 (0.49), 1534.2 (0.06), 1592.0 (0.19), 2214 (0.05), 2967.2 (0.04), 3028.9 (0.07), 3050.2 (0.08). ¹H NMR (400 MHz,

CDCl₃): δ 7.30-7.40 (12H, br, m), 7.52-7.62 (12H, br, m), 7.82 (2H). ¹³C NMR (100 MHz, CDCl₃): δ 88.23 (-CCPh, 4C), 93.94 (-CCPh, 2C) 94.66 (-CCPh, 2C), 123.5 (4C), 125.26 (2C), 126.49 (4C), 128.5 (m, 12C), 130.16 (2C), 131.76 (8C), 132.38 (2C), 139.19 (2C). LC/MS, m/z (%): 80 (4), 183 (3.5), 236 (6.2), 237 (9.1), 238 (3.4), 261 (6.8), 262 (8.0), 268 (6.2), 269 (6.0), 274 (22.1), 275 (21.2), 276 (20.0), 277 (21.0), 472 (3.6), 474 (8.8), 476 (4.7), 554 (100), 555 (46.5), 556 (10.6). HRMS for C₄₄H₂₆ calcd (found): 554.2077 (554.2056).

Synthesis of 4:

9,9-Bis(3-bromo-4-hydroxyphenyl)fluorene. To a 2-L 5-necked flask, equipped as before, was added 700 mL of CH₂Cl₂, 50 mL of HOAc, 104 g (0.297 mol) of 9,9-bis(4-hydroxyphenyl)fluorene, and 1.0 g (0.018 mol) of iron powder. The mixture was stirred and cooled to 10°C under nitrogen and 99 g (0.616 mol) bromine was added over 1 hour and 45 minutes while the temperature was maintained <10°C. Upon complete addition, the mixture was heated to 22°C and stirred for 18 hours then washed with 1.5 L of water followed by 500 mL of saturated aqueous sodium bicarbonate, evaporated, and dissolved in hot hexane which had been saturated with acetonitrile. Upon cooling, the acetonitrile phase (containing colored impurities) separated and the hexane layer was evaporated giving 115 g (77%) as a white crystalline solid, mp 119-120°C. IR (cm⁻¹): 743 (0.36), 782 (0.30), 844 (0.21), 932 (0.78), 1017 (0.20), 1096 (0.79), 1129 (0.76), 1167 (0.77), 1199 (1.00), 1272 (0.11), 1326 (0.52), 1447 (0.17), 1503 (0.49), 3065 (0.06). GC/MS, m/z (%): 63 (16.9), 226 (17.8), 335 (13.7), 427 (9.6), 428 (27.8), 429 (22.3), 430 (15.4), 507 (6.6), 508 (33.3), 509 (100), 510 (36.8), 511 (8.2). HRMS for C₂₅H₁₆O₂Br₂ calcd (found): 505.9517 (505.9535).

9,9-Bis(3-bromo-4-trifluoromethanesulfonatophenyl)fluorene. Into a 2-L 5-necked flask as used above was added, 500 mL CH₂Cl₂ and 111.75 g (0.221 mol) of 9,9-bis(3-bromo-4-hydroxyphenyl)fluorene. The solution was cooled to 10°C and 97.75 g triethylamine was added over 30 minutes while maintaining the reactor temperature at 10°C. Trifluoromethanesulfonic acid anhydride, 250.8 g (0.889 mol), was then added at a rate that maintained a reaction temperature from 10-20°C. The reaction mixture was stirred at 15°C for 3 hours then washed with two 500 mL portions of water followed by one 250 mL portion of saturated aqueous sodium bicarbonate. The CH₂Cl₂ was evaporated and the residue dissolved in acetonitrile to give a 50% (w/w) solution which was extracted with 250 mL portions of hexane. The extracts were combined reduced to crystallize the product providing 165 g (65%), m.p. 46-47°C. IR (cm⁻¹): 738 (0.39), 786 (0.16), 826 (0.15), 880 (0.50), 1037 (0.29), 1137 (0.68), 1214 (1.00), 1428 (0.74), 1479 (0.42), 1579 (0.10), 3039 (0.07), 3068 (0.09). LC/MS, m/z (%): 143 (13.2), 145 (9.8), 224 (12.5), 226 (64.4), 227 (21.0), 263 (23.5), 276 (12.0), 277 (7.9), 287 (25.6), 288 (11.1), 289 (86.5), 290 (39.0), 291 (7.9), 317 (16.5), 318 (41.1), 334 (11.4), 345 (14.3), 346 (27.0), 347 (7.07), 369 (11.2), 397 (45.1), 398 (10.5), 399 (37.1), 400 (10.3), 424 (11.20), 425 (46.2), 426 (21.1), 427 (50.1), 428 (10.6), 637 (43.8), 639 (100), 641 (40.4), 770 (25.8), 772 (52.8), 774 (26.0). HRMS for C₂₇H₁₄O₆F₆S₂Br₂ calcd (found): 769.8529 (769.8516).

9,9-Bis(3,4-di(phenylethynyl)phenyl)fluorene (4). To a 1 L 5 neck flask equipped with a mechanical stirrer, a dropping funnel, a gas dispersion tube and a thermocouple, was added 50 g (0.065 mol) of 9,9-Bis(3-bromo-4-trifluoromethanesulfonatophenyl)fluorene, 150 g triethylamine, and 180 mL N,N-dimethylformamide. The mixture was stirred and sparged with nitrogen at 45°C and 3.0 g (4.2 mmol) of [P(Ph)₃]₂PdCl₂ was added. The reaction mixture was heated to 70°C and 33.0 g (0.324 mol) of de-oxygenated phenylacetylene was added over 30

minutes so as to maintain the temperature <90°C. After complete addition, the temperature was maintained at 90°C for 2 hours and 45 minutes at which time an additional 4.7 g (0.046 mol) of phenylacetylene was added all at once and the reaction maintained at 90°C for additional 45 minutes. The mixture was cooled to room temperature and diluted with 400 mL of CH₂Cl₂ and washed with 2 L of 10% HCl, evaporated, and purified by column chromatography on silica gel using CCl₄ as an eluent to provide 32.5 g (69.6%), mp 104-106°C. IR (cm⁻¹): 662 (0.12), 688 (0.63), 737 (0.63), 754 (1.00), 823 (0.24), 913 (0.09), 1027 (0.11), 1067 (0.11), 1090 (0.09), 1140 (0.07), 1160 (0.08), 1213 (0.07), 1278 (0.07), 1401 (0.13), 1443 (0.35), 1495 (0.61), 1593 (0.22), 2210 (0.07), 3031 (0.14), 3055 (0.16). ¹H NMR (400 MHz, CDCl₃): δ 7.75-7.81 (4H, dd), 7.52-7.54 (12H, m), 7.38-7.44 (12H, m), 7.27-7.30 (12H, m), 7.13-7.16 (4H, dd). ¹³C NMR (100 MHz, CDCl₃): δ 64.90 (1C, *spiro*), 88.08 (1C, -CC-), 88.36 (1C, -CC-), 93.72 (1C, -CC-), 93.88 (1C, -CC-), 120.45, 123.07, 123.24, 124.57, 125.89, 126.04, 127.89, 128.04, 128.11, 128.28, 128.31, 128.37, 128.42, 131.01, 131.60, 131.65, 131.87, 140.16, 145.53, 149.52. LC/MS, m/z (%): 305 (8.2), 311 (8.3), 312 (9.7), 318 (8.3), 319 (12.1), 363 (16.3), 437 (13.4), 439 (11.1), 441 (20.7), 638 (8.2), 639 (14.8), 640 (12.9), 641 (13.6), 718 (100), 719 (22.4), 720 (12.5). HRMS for C₅₇H₃₄ calcd (found): 718.26605 (718.2667).

General Monomer Purification. Each of the bis(*o*-di(phenylethynyl)phenyl) monomers 1-4 were purified to 99% (LC) by flash chromatography (Biotage Flash 75™) on Biotage silica gel pre-packaged disposable columns using CCl₄/cyclohexane (70/30) as eluent. Monomers were dried overnight at 80-100°C under vacuum and stored under nitrogen at room temperature.

General Polymerization. A general procedure for solution polymerization is as follows: To a clean, dry, and nitrogen filled 25 mL schlenck flask equipped with stopcock top for sampling via syringe, nitrogen inlet side-arm, and magnetic stir bar was added 1.5 g of bis(*o*-di(phenylethynyl)phenyl) monomer and 1.5 g (50 wt%) tri-*i*-propylbenzene (or other solvent). The mixture was heated slowly below 100°C and mixed with constant nitrogen purge until completely dissolved and then sparged with nitrogen for several minutes via a syringe. The homogeneous solution was placed in a stirred oil bath which had been pre-heated to 210°C and the nitrogen purge was decreased to a slight positive pressure. Within 60 seconds, in all cases, the light yellow transparent solution turned darker yellow, then orange, and eventually dark red within 1 hour. Samples were analyzed by GPC over time and qualitatively examined for their ability to form a coating by diluting to 30% (w/w with solvents such as tri-*i*-propylbenzene, phenyl ether, cyclopentanone, or cyclohexanone) and spotting on silicon or glass. The desired molecular weight was obtained for spin coating (typically M_w=3,000-10,000) when a homogeneous film was obtained without crystallization of the monomer upon evaporation of the solvent at 90°C. The mixture was allowed to cool to room temperature under nitrogen and then diluted with tri-*i*-propylbenzene or mesitylene to 30-40% (w/w) solids. For bulk polymerization in the absence of solvent, an identical apparatus with mechanical stirring was used.

Polymer from 1. Monomer 1 (1.5 g, 2.1 mmol) and 1,3,5-tri-*i*-propylbenzene (1.5 g) were combined and heated for 46 h as described above giving M_w=24,400, M_n=2,259 (M_w/M_n=10.8) by GPC analysis. Alternatively, polymerization was carried out in diphenyl ether, dodecane, or di-*t*-butyl benzene. Bulk polymerization was carried out in the absence of solvent at 210°C for 4.4 h giving mesitylene soluble oligomers of M_w=10,600, M_n=1,413 (M_w/M_n=7.5) by GPC. Samples were diluted, spin coated on silicon, and cured to 450°C as described above or cured in a TGA experiment giving an insoluble network structure. IR (KBr, cm⁻¹): 3069.6, 3025 (ArH),

1596.5 (Ar), 1488.0, 1435.1, 1254.3 (st, CF), 1201.4 (st, CF), 1135.9 (w, sh), 1074.2 (w), 1029.8 (w), 966.2, 894.8 (ArH lone and adj.), 827.3 (ArH lone and adj.), 755.9 (st, mono-subst. Ph wag), 700.0 (st, mono-subst. Ph bend).

Polymer from 2. Monomer 2 (1.5 g, 2.6 mmol) was heated at 210°C with mechanical stirring for 6 h as described above giving $M_w=4,249$, $M_n=991$ ($M_w/M_n=4.3$) by GPC analysis. Samples were diluted, spin coated on silicon, and cured to 450°C as described above or cured in a TGA experiment giving an insoluble network structure. IR (KBr, cm^{-1}): 3054.7, 3023.9 (ArH), 1596.8 (Ar), 1490.7, 1442.5 (br), 1261.2, 1207.2 (st, br), 1178.3 (sh), 1157.1 (sh), 1072.2 (w), 1027.9 (w), 966.2, 881.3 (ArH lone and adj.), 819.6 (ArH lone and adj.), 754.0 (st, mono-subst. Ph wag), 698.1 (st, mono-subst. Ph bend).

Polymer from 3. Monomer 3 (1.5 g, 2.7 mmol) was heated at 200°C with mechanical stirring for 9.4 h as described above giving $M_w=7,492$ $M_n=1,041$ ($M_w/M_n=7.2$) by GPC analysis. Samples were diluted, spin coated on silicon, and cured to 450°C as described above or cured in a TGA experiment giving an insoluble network structure. IR (KBr, cm^{-1}): 3052.8, 3022.0 (ArH), 1596.8 (Ar), 1490.7, 1440.6, 1155.2, 1072.2, 1027.9, 885.2 (ArH lone and adj.), 817.7 (ArH lone and adj.), 754.0 (st, mono-subst. Ph wag), 698.1 (st, mono-subst. Ph bend).

Polymer from 4. Monomer 4 (1.5 g, 2.1 mmol) was heated at 210°C with mechanical stirring for 7.5 h as described above giving $M_w=3,083$ and $M_n=1,177$ ($M_w/M_n=2.6$) by GPC analysis. Samples were diluted, spin coated on silicon, and cured to 450°C as described above or cured in a TGA experiment giving an insoluble network structure. IR (KBr, cm^{-1}): 3054.7, 3022.0 (ArH), 1598.7 (Ar), 1492.7, 1475.3, 1446.4, 1155.2, 1072.2, 1029.8, 821.5 (ArH lone and adj.), 740.5 (st, mono-subst. Ph wag), 698.1 (st, mono-subst. Ph bend).