

Supporting Information

Synthesis and Properties of an Acetal-bridged Ladder Poly(*p*-phenylene)

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Received May 6, 2011, Accepted June 11, 2011

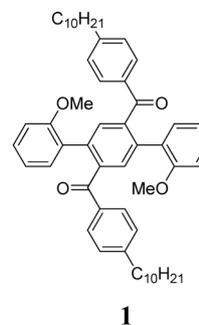
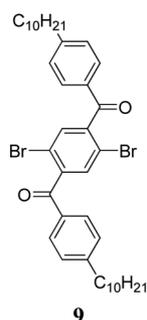
Key Words : Conjugated polymer, Ladder poly(*p*-phenylene), Chemical cyclization

Experimental

Melting points were determined using Büchi 510 melting point apparatus and uncorrected. IR spectra were recorded on a Nicolet MAGNA 560-FTIR spectrometer. ¹H NMR spectra were recorded on a Bruker Advance DPX-300 and Bruker Advance DPX-500 instruments using deuteriochloroform as reference or internal deuterium lock. The chemical shift data for each signal are given in units of δ (ppm) relative to tetramethylsilane (TMS) where δ (TMS) = 0, and referenced to the solvent residual. ¹³C NMR spectra were recorded on a Bruker Advance-300 (75.4 MHz) instrument using internal deuterium lock and proton decoupling. Mass spectra were obtained on a JEOL JMS-AX505WA instrument. UV-visible absorption spectra were measured with Hewlett Packard 8452A diode array spectrometer using spectral grade THF as a solvent. The measurements were carried out at 25 °C using a quartz cell with a path length of 1 cm. All electrochemical measurements were made with a COMPACTSTAT potentiostat (IVIUM Technologies) using an Pt wire reference electrode in 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) in anhydrous CH₃CN. Typical cyclic voltammograms were recorded using ITO electrodes as the working electrode and a platinum coil counter electrode. The ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as an external reference. The potential values were converted to versus Ag/AgCl. Molar masses were determined by Gel Permeation Chromatography (GPC) using two PL Gel 30 cm 5 μ m mixed C columns at 30 °C running in THF and calibrated against polystyrene (M_n = 600-10⁶ g/mol) standards using a Knauer refractive index

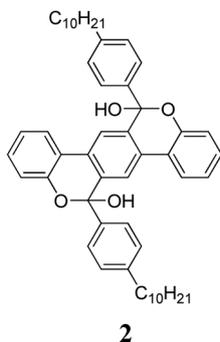
detector. Reagents were purified and dried by standard technique. All air and water-sensitive synthetic manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques.

Synthesis of 2',5'-dibromo-4-decyl-4'-(4-decylbenzoyl)-benzophenone 9. To a solution of 2,5-dibromoterephthaloyl dichloride (0.44 g, 1.22 mmol) **8** and aluminium trichloride (0.44 g, 3.26 mmol) in 5 mL of dichloromethane, a mixture of decylbenzene (1.33 mL, 6.09 mmol) in dichloromethane (2 mL) was added dropwise. After stirring at room temperature for 2 days, the reaction mixture was poured into an ice cold hydrochloric acid (2 M; 20 mL). The organic layer was separated and washed with water several times, dried and the solvent was evaporated. The residue was recrystallized from acetone to give the product **9** as a white crystal (0.76 g, 83%); mp 248-250 °C; R_f 0.38 (30:1 hexane:EtOAc); ν_{\max} (CHCl₃)/cm⁻¹ 3062, 2925, 1711, 1601, 1421, 1362, 1105, 669 and 614; ¹H NMR (300 MHz, CDCl₃, δ) 7.76 (4H, d, J = 8.0, 4 \times COArH), 7.58 (2H, s, 2 \times ArH), 7.32 (4H, d, J = 8.0, 4 \times COArH), 2.69 (4H, t, J = 7.6, 2 \times COArCH₂), 1.65 (4H, br signal, 2 \times COArCH₂CH₂), 1.32-1.29 (28H, m, 2 \times COAr(CH₂)₂-(CH₂)₇), 0.88 (6H, t, J = 6.6, 2 \times COAr(CH₂)₉CH₃); ¹³C NMR (75.4 MHz, CDCl₃, δ) 193.4, 150.6, 143.36, 132.9, 130.5, 129.0, 128.4, 128.2, 118.4, 36.2, 31.9, 31.0, 29.6, 29.5, 29.4, 29.3, 22.7 and 14.1; m/z (FAB) 725 [(M+H)⁺, 7%] and 105 (100%).



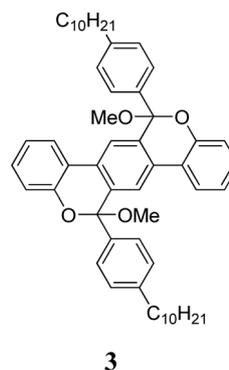
Synthesis of the Dimethoxy Diketone 1. Boronic ester **10** (0.07 g, 0.31 mmol), dibromo diketone **9** (0.11 g, 0.15 mmol), aliquat 336 (0.06 g, 0.023 mmol), aqueous Na₂CO₃ (2.0 M; 0.3 mL) and toluene (3 mL) were added in a Schlenk flask

and purged with nitrogen for 30 min. To this tetrakis(tri-phenylphosphine)palladium (16 mg, 0.01 mmol) was added and the reaction mixture was heated at 110 °C under nitrogen for 2 days to produce a black suspension. The reaction mixture was cooled to room temperature and water (2 mL) was added. The mixture was extracted with dichloromethane (3 × 5 mL) and the combined organic layers were washed with HCl (1 M; 5 mL), water (5 mL), brine (5 mL), dried over MgSO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography (1:10 EtOAc:hexane) to give the product **1** as a white crystal (0.11 g, 93%); mp 138-140 °C; *R*_f 0.29 (10:1 hexane:EtOAc); ν_{\max} (CHCl₃)/cm⁻¹ 3019, 2929, 1711, 1661, 1604, 1488, 1463, 1215, 973 and 668; ¹H NMR (300 MHz, CDCl₃, δ) 7.79 (4H, d, *J* = 7.5, 4×COAr*H*), 7.56 (2H, s, 2×Ar*H*), 7.32-7.25 (6H, m, 6×Ar*H*), 7.17 (4H, d, *J* = 7.5, 4×COAr*H*), 6.93 (2H, dd, *J* = 7.0, 2×Ar*H*), 6.68 (2H, d, *J* = 8.0, 2×Ar*H*), 3.36 (6H, s, 2×OCH₃), 2.62 (4H, t, *J* = 7.0, 2×COArCH₂), 1.63 (4H, br signal, 2×COArCH₂CH₂), 1.28 (28H, m, 2×CO(CH₂)₂(CH₂)₇), 0.88 (6H, t, *J* = 6.4, 2×COAr(CH₂)₉CH₃); ¹³C NMR (75.4 MHz, CDCl₃, δ) 195.8, 155.4, 148.3, 140.6, 136.2, 134.5, 131.0, 130.4, 129.2, 128.5, 128.1, 120.9, 110.2, 54.3, 36.0, 31.9, 31.1, 29.7, 29.6, 29.6, 29.5, 29.3, 22.7 and 14.1; *m/z* (FAB) 780 [(M+H)⁺, 100%], 781 (60%) and 782 (19%); [Found: (M+H)⁺ 779.5039. C₅₄H₆₇O₄ requires *M*, 779.5039].

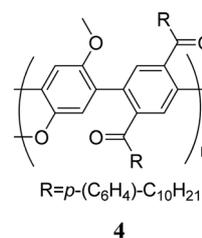


Cyclization of 1 to Produce the Hemiacetal-bridged Model Compound 2. To a solution of the non-cyclized precursor **1** (0.20 g, 0.26 mmol) in dry dichloromethane (4 mL), BBr₃ (1.03 mL of 1.0 M in dichloromethane, 1.03 mmol) was added at room temperature under nitrogen. TLC analysis showed immediate and complete conversion to the product. The reaction mixture was further left to stir for 5 min at room temperature, followed by the addition of water (5 mL). The solution was extracted with dichloromethane (3 × 15 mL) and the combined organic layers were washed with HCl (1 M; 15 mL), water (15 mL), brine (15 mL), dried over MgSO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography (1:10 EtOAc:hexane) to give the cyclized product **2** as a white crystal (0.19 g, 100%); mp 123-125 °C; *R*_f 0.45 (10:1 hexane:EtOAc); ν_{\max} (CHCl₃)/cm⁻¹ 3425, 3020, 1604, 1438 and 1215; ¹H NMR (400 MHz, CDCl₃, δ) 7.61 (2H, d, *J* = 7.5, 2×Ar*H*), 7.53 (4H, d, *J* = 8.0, 4×COAr*H*), 7.48 (2H, s,

2×COAr*H*), 7.28-7.24 (6H, m, 2×Ar*H* and 4×COAr*H*), 7.09-7.00 (4H, m, 2×Ar*H*), 3.36 (6H, s, 2×OCH₃), 2.62 (4H, t, *J* = 7.5, 2×COArCH₂), 1.65-1.56 (4H, m, 2×COArCH₂CH₂), 1.31-1.25 (28H, m, 2×CO(CH₂)₂(CH₂)₇), 0.88 (6H, t, *J* = 6.5, 2×CO-Ar(CH₂)₉CH₃); ¹³C NMR (75.4 MHz, CDCl₃, δ) 150.7, 143.9, 135.6, 129.4, 126.8, 123.0, 122.4, 120.5, 99.7, 35.7, 31.9, 31.3, 29.6, 29.5, 29.3, 22.7 and 14.1; *m/z* (FAB) 751 [(M+H)⁺, 15%] and 733 (100%).

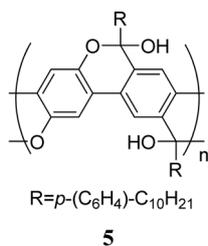


Methylation of 2 to Produce the Acetal-bridged Ladder-type Model Compound 3. To a solution of **2** (0.07 g, 0.21 mmol) in a mixture of dichloromethane (17 mL) and methanol (17 mL) was added CF₃COOH (1 mL) at room temperature and the mixture was stirred at this temperature for 24 h. The reaction mixture was washed with NaHCO₃ (5 mL × 3), and the organic layer was dried over Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography (30:1 hexane:EtOAc) to give the product **3** as a white crystal (0.069 g, 100%); mp 119-121 °C; *R*_f 0.33 (30:1 hexane:EtOAc); ν_{\max} (CHCl₃)/cm⁻¹ 3020, 2958, 2928, 2855, 1610, 1518, 1487, 1421, 1362 and 1205; ¹H NMR (300 MHz, CDCl₃, δ) 7.54 (4H, d, *J* = 8.0, 4×COAr*H*), 7.52 (2H, m, 2×Ar*H*), 7.46 (2H, s, 2×Ar*H*), 7.27 (4H, d, *J* = 8.0, 4×COAr*H*), 7.25 (2H, m, 2×Ar*H*), 7.12 (2H, d, *J* = 7.5, 2×Ar*H*), 7.03 (2H, d, *J* = 7.0, 2×Ar*H*), 3.30 (6H, s, 2×OCH₃), 2.67 (4H, t, *J* = 7.0, 2×COArCH₂), 1.65 (4H, br signal, 2×COArCH₂CH₂), 1.3 (28H, m, 2×CO(CH₂)₂(CH₂)₇), 0.88 (6H, t, *J* = 6.0, 2×COAr(CH₂)₉CH₃); ¹³C NMR (75.4 MHz, CDCl₃, δ) 151.17, 143.53, 136.43, 134.30, 129.65, 128.70, 127.55, 122.88, 122.21, 121.27, 120.79, 117.89, 102.81, 51.95, 35.70, 31.92, 31.36, 29.66, 29.56, 29.35, 22.70 and 14.12; *m/z* (FAB) 780 [(M+H)⁺, 100%], 781 (60%); [Found: (M+H)⁺ 779.5039. C₅₄H₆₇O₄ requires *M*, 779.5039].



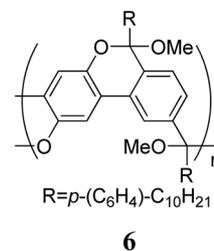
Synthesis of the Polymer 4. Diboronic acid **11** (0.04 g, 0.18 mmol), diketone **9** (0.13 g, 0.18 mmol), aqueous K₃PO₄

(2.0 M; 0.35 mL) and dimethylformamide 1.5 mL were added in a Schlenk flask and purged with nitrogen for 60 min. To this tetrakis(triphenyl-phosphine)palladium (0.02 g, 0.01 mmol) was added and the reaction mixture was heated at 110 °C under nitrogen for 2 days to produce a black suspension. The reaction mixture was cooled to room temperature and water (2 mL) was added. A black solid was collected by suction filtration. The filtrate was dissolved in dichloromethane then precipitated into methanol followed by stirring. This was repeated twice and the polymer **4** was obtained as a brown solid (0.079 g, 47%); (Found: C, 82.4; H, 8.5. $C_{48}H_{62}O_4$ requires C, 82.0; H, 8.9%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3060, 1710, 1521, 1421, 1362, 116, 929 and 619; $^1\text{H NMR}$ (300 MHz, CDCl_3 , δ) 7.91-7.75 (4H, m, $4\times\text{COArH}$), 7.60-7.56 (2H, m, $2\times\text{ArH}$), 7.33-7.19 (2H, m, $4\times\text{COArH}$), 6.91-6.89 (2H, m, $2\times\text{ArH}$), 6.62-6.57 (2H, m, $2\times\text{ArH}$), 3.67-3.61 (3H, m, OCH_3), 3.30-3.26 (3H, m, OCH_3), 2.66-2.64 (4H, m, $2\times\text{COArCH}_2$), 1.62-1.60 (4H, m, $2\times\text{COArCH}_2\text{CH}_2$), 1.26 (28H, m, $2\times\text{CO}(\text{CH}_2)_2(\text{CH}_2)_7$), 0.87-0.85 (6H, m, $2\times\text{COAr}(\text{CH}_2)_9\text{CH}_3$).



Cyclization of 4 to Produce the Hemiacetal-bridged Ladder Poly(*p*-phenylene) 5. To a solution of the non-cyclized precursor polymer **4** (0.06 g, 0.09 mmol) in dichloromethane (1.5 mL), BBr_3 (0.4 mL of 1.0 M in dichloromethane) was added at room temperature under nitrogen. The mixture was stirred for 10 min at room

temperature, followed by the addition of water (2 mL). A dark brown solid was collected by suction filtration. The filtrate was dissolved in dichloromethane then precipitated into methanol followed by stirring. This was repeated twice and the hemiacetal-bridged polymer **5** was obtained as a brown solid (0.059 g, 100%).



Methylation of 5 to Produce the Acetal-bridged Ladder Poly(*p*-phenylene) 6. To a solution of **5** (0.03 g, 0.04 mmol) in a mixture of dichloromethane (10 mL) and methanol (10 mL) was added CF_3COOH (1 mL) at room temperature, and the mixture was stirred at this temperature for 24 h. The reaction mixture was washed with 3% NaHCO_3 (5 mL \times 3). A brown solid was collected by suction filtration. The filtrate was dissolved in dichloromethane then precipitated into methanol followed by stirring. This was repeated twice and the acetal-bridged polymer **6** was obtained as a brown solid (0.03 g, 100%); (Found: C, 82.0; H, 8.5. $C_{48}H_{63}O_4$ requires C, 81.8; H, 9.0%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3030, 1605, 1423, 1217 and 670; $^1\text{H NMR}$ (300 MHz, CDCl_3 , δ) 7.71-7.54 (6H, m, $4\times\text{COArH}$ and $2\times\text{ArH}$), 7.40 (4H, m, $4\times\text{COArH}$), 7.02-6.99 (2H, m, $2\times\text{ArH}$), 2.40 (6H, s, $2\times\text{OCH}_3$), 2.04-2.02 (4H, m, $2\times\text{COArCH}_2$), 1.57 (4H, m, $2\times\text{COArCH}_2\text{CH}_2$), 1.25 (28H, m, $2\times\text{CO}(\text{CH}_2)_2(\text{CH}_2)_7$), 0.88-0.83 (6H, m, $2\times\text{COAr}(\text{CH}_2)_9\text{CH}_3$); GPC (THF, RI)Da M_n 4.4×10^3 M_w 1.2×10^4 and M_w/M_n 2.7.