

Supplementary Material for:

Poly (Salphenyleneethynylene)s: Soluble, Conjugated Metallopolymers That Exhibit Unique Supramolecular Crosslinking Behavior

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Equipment. All reactions were carried out under N₂ atmosphere using standard high-vacuum or Schlenk line techniques unless otherwise noted. 300 MHz ¹H NMR spectra and 75.5 MHz ¹³C NMR spectra were recorded on a Bruker AV-300 spectrometer. UV-Vis spectra were obtained in THF (ca. 5x10⁻⁶ M) on a Varian Cary 5000 UV-vis/near-IR spectrometer using a 1 cm cuvette. Fluorescence spectra were obtained in distilled THF (ca. 5x10⁻⁶ M) on a Photon Technology International (PTI) Quantamaster fluorimeter using a 1 cm cuvette. Quantum yields were referenced to a solution of anthracene in EtOH (Φ = 0.30). IR spectra were obtained as KBr discs with a Bomens MB-series spectrometer. Absolute molecular weights were measured by gel permeation chromatography (GPC) using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel® columns (4.6 × 300mm) HR2 × 2, and HR4 and a Waters 2410 differential refractometer (refractive index detector, λ = 9401 nm), Wyatt Tristar miniDAWN (laser light scattering detector, λ = 690 nm) and a Wyatt Viscostar viscometer. A flow rate of 0.3 mL/min was used and samples were dissolved in THF (ca. 1 mg/mL) and filtered before injection. Matrix assisted laser desorption/ionization (MALDI) mass spectra were obtained at the UBC Microanalytical Services Laboratory on a Bruker Biflex IV time-of-flight (TOF) mass spectrometer equipped with a MALDI ion source. Samples were analyzed in a dithranol matrix. Electrospray ionization (ESI) mass spectra were obtained at the UBC Microanalytical Services Laboratory on a Micromass LCT time-of-flight (TOF) mass spectrometer equipped with an electrospray ion source. The sample was analyzed in MeOH/CHCl₃ at 1 μM. Electron impact (EI) mass spectra and elemental analyses were performed at the UBC Microanalytical Services Laboratory. Melting points were obtained on a Fisher-John's melting point apparatus and are corrected.

1,2-Bis(2-butyloctyloxy)benzene (7). Catechol (2.21 g, 20.1 mmol), NaH (1.0 g, 0.42 mmol), and a spatula tip of Bu₄NBr were combined in 500 mL of THF. The reaction was refluxed for 1 h until a thick white precipitate formed. 2-Butyloctylbromide (20.0 g, 80.2 mmol) was then added dropwise over a period of 2 h, followed by reflux for an additional 72 h. After cooling the reaction to room temperature, the precipitate was removed by filtration and the THF was removed from the filtrate via rotary evaporation. Excess 2-butyloctylbromide was removed by distillation under high vacuum. Flash chromatography in CH₂Cl₂ furnished **7** (8.60 g, 19.3 mmol, 96% yield) as a colorless oil (Found: C, 79.40; H, 11.81 Calc. for C₃₀H₅₄O₂ requires C, 80.65; H, 12.18%); δ_H (400 MHz; CDCl₃) 6.87 (s, 4H, aromatic CH), 3.84 (d, J=5.6 Hz, 4H, OCH₂), 1.80 (m, J=5.6, 23.2 Hz, 2H, CH₂), 1.25-1.55 (m, 32H, CH₂), 0.89 (m, 12H, CH₃); δ_C (100.6 MHz, CDCl₃) 149.9, 121.0, 114.1, 72.1, 38.4, 32.1, 31.6, 31.3, 30.0, 29.3, 27.1, 23.3,

22.9, 14.3; m/z (EI) 446.4 (M^+ $C_{30}H_{54}O_2$ requires 446.41), 278.2 (15%), 166.1 (11%), 108.6 (100%).

1,2-Bis(2-butyloctyloxy)-4,5-dinitrobenzene (8). Compound **7** (6.00 g, 13.4 mmol) was added to 100 mL of HNO_3 in a 1 L round bottom flask under air. The reaction was heated to 110 °C for ca. 5 mins until a brown gas evolved, then the temperature of the reaction was lowered to 80 °C and left stirring for 16 h. After cooling to room temperature, 100 mL of water was added. The product was then extracted into $CHCl_3$, washed with H_2O , followed by 5% $NaHCO_3$ solution. The resulting yellow $CHCl_3$ solution was dried over $MgSO_4$ and rotary evaporated to dryness. Flash chromatography in CH_2Cl_2 afforded **8** (6.05 g, 11.3 mmol, 84%) as a yellow oil (Found: C, 67.29; H, 9.80; N, 5.18. Calc. for $C_{30}H_{52}N_2O_6$ requires C, 67.13; H, 9.76; N, 5.22%); δ_H (300 MHz, $CDCl_3$) 7.24 (s, 2H, aromatic CH), 3.93 (d, $J=3.0$ Hz, 4H, OCH_2), 1.83 (m, 2H, CH_2), 1.20-1.50 (m, 32H, CH_2), 0.87 (m, 12H, CH_3); δ_C (100.6 MHz, $CDCl_3$) 152.3, 136.6, 107.7, 72.8, 38.0, 32.0, 31.4, 31.1, 29.9, 29.2, 27.0, 23.2, 22.9, 14.3, 14.2; m/z (EI) 536.2 (M^+ $C_{30}H_{52}N_2O_4$ requires 536.38), 506.3 (22%), 184.0 (25%), 168.1 (20%), 109.8 (45%).

1,2-bis(2-butyloctyloxy)-4,5-diaminobenzene (9). Compound **8** (5.00 g, 9.31 mmol) was dissolved in 50 mL of dry THF under N_2 . Approximately 0.1 g of Raney Nickel and 5 mL of hydrazine monohydrate was added to the reaction. The reaction was heated to reflux for 2 h until the evolution of H_2 gas ceased, and then an additional 5 mL of hydrazine monohydrate was added. The reaction was again heated to reflux for 3 h, cooled to room temperature, and filtered through celite with a Schlenk frit to remove the nickel catalyst. Removal of solvent in vacuo afforded **9** (3.61 g, 7.56 mmol, 81%) as a light brown oil (Found: C, 75.79; H, 11.98; N, 6.10. Calc. for $C_{30}H_{56}N_2O_2$ requires C, 75.57; H, 11.84; N, 5.88%); δ_H (400 MHz, $CDCl_3$) 6.35 (s, 2H, aromatic CH), 3.74 (d, $J=6.0$ Hz, 4H, OCH_2), 3.16 (s, 4H, NH_2), 1.73 (m, 2H, CH_2), 1.25-1.70 (m, 32H, CH_2), 0.87 (m, 12H, CH_3); δ_C (100.6 MHz, $CDCl_3$) 143.9, 123.4, 106.8, 13.7, 38.5, 32.1, 31.5, 31.2, 30.0, 29.3, 27.1, 23.3, 22.4, 14.31, 14.29; m/z (EI) 476 (M^+ $C_{30}H_{56}N_2O_2$ requires 476.43), 140 (50%).