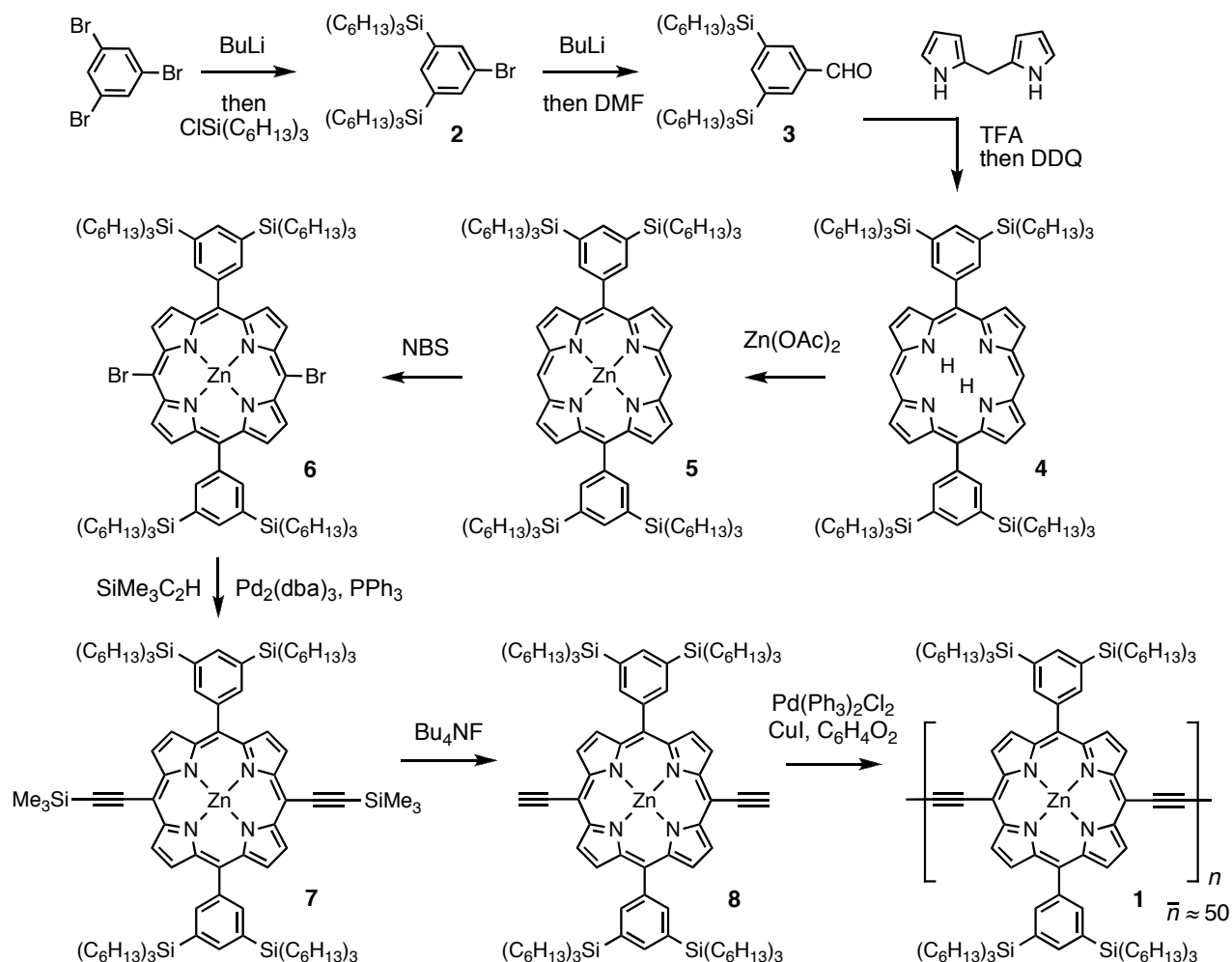


Supramolecular Control of Charge Transport in Molecular Wires

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Scheme S1: Synthesis of polymer **1**. This new trihexylsilyl-solubilized polymer was synthesized specially so as to achieve high solubility in nonpolar solvents for the time-resolved microwave conductivity study reported in this Communication. The other porphyrin polymers synthesized previously in Oxford had insufficient solubility in benzene, particularly as their double-strand Bipy complexes.

Synthetic Experimental Details

3,5-Bis(trihexylsilyl)bromobenzene **2**

To a stirring solution of 1,3,5-tribromobenzene (5.00 g, 15.8 mmol) in Et₂O (125 mL) at -78°C, was added *n*-butyl lithium (1.6 M in hexane, 20.8 mL, 33.3 mmol) dropwise, under inert atmosphere. The solution was stirred for 90 min before adding trihexylsilylchloride (13.5 mL, 34.9 mmol) dropwise via a syringe. The solution was allowed to warm to room temperature. After stirring for another 90 min, the reaction mixture was washed with water, dried over MgSO₄ and filtered. The solution was concentrated and passed through a silica plug with Petroleum Ether. The solvent was removed to give 10.6 g of a 3:1 mixture of 3,5-bis(trihexylsilyl)bromobenzene **2** and 1,3,5-tris(trihexylsilyl)benzene. This crude product was used without further purification.

3,5-Bis(trihexylsilyl)benzaldehyde **3**

n-Butyl lithium (1.6 M in hexane, 27.5 mL, 44 mmol) was added dropwise to a solution of 3,5-bis(trihexylsilyl)bromobenzene **2** (10.6 g, 14.7 mmol) in dry Et₂O (70 mL) under N₂ at 0°C. The solution was stirred at this temperature for 30 min and then at room temperature for 90 min. *N,N*-Dimethylformamide (5.3 mL, 70 mmol) was added and the mixture was stirred for 1 hr. Aqueous saturated ammonium chloride solution (100 mL) was added and the organic layer was separated. The aqueous layer was extracted with Et₂O. The combined organic layer was washed with an aqueous solution of NaHCO₃ and with water, dried over MgSO₄ and filtered. The crude product was purified by column chromatography on silica gel eluting with a gradients of CH₂Cl₂ and 40–60°C petroleum ether (starting from 0% to 10% CH₂Cl₂). The solvent was removed to give 3,5-bis(trihexylsilyl)benzaldehyde **3** (4.3 g, 41% over two steps) as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 10.04 (s, 1H), 7.93 (s, 2H), 7.85 (s, 1H), 0.81–1.31 (m, 78H); ¹³C NMR (100 MHz, CDCl₃): δ 193.5, 146.1 138.3, 135.9, 134.6, 33.4, 31.5, 23.8, 22.6, 14.1, 12.3; *m/z* (Tof MS ESI) 693.58 ([M+Na]⁺, C₄₃H₈₂NaOSi₂, requires 693.58).

2.1.3. 5,15-Bis[3,5(trihexylsilyl)phenyl]porphyrin **4**

3,5-Bis(trihexylsilyl)benzaldehyde **3** (2.55 g, 3.8 mmol) and dipyrromethane (0.56 g, 3.8 mmol) were dissolved in CH₂Cl₂ (700 mL). The solution was saturated with nitrogen, then TFA (0.5 mL, 7.6 mmol) was added and the mixture was stirring for 3 hrs in the dark. Then, DDQ (1.5 g, 6.6 mmol) was added and the mixture was stirred for a further 20 min. Finally, triethylamine (3.8 mL) was added to quench the acid. The solution was concentrated and pass through a short silica plug eluting with a mixture of 40–60°C petroleum ether and CH₂Cl₂ (80/20). The solvent was removed to give the free base porphyrin **4** (1.63 g, 29%) as red crystals. ¹H NMR (400 MHz, CDCl₃): δ 10.35 (s, 2H), 9.40 (d, *J* = 4.5, 4H), 9.09 (d, *J* = 4.5, 4H), 8.37 (s, 4H), 8.02 (s, 2H), 0.87–1.52 (m, 156H), -3.03 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 147.5, 145.1, 141.7, 139.15, 139.2, 135.4, 131.5, 131.2, 120.3, 105.2, 33.6, 31.7, 24.1, 22.7, 14.2, 12.7; UV (CH₂Cl₂): λ_{max} (log ε) = 410 (5.81), 505 (4.37), 541 (3.98), 577 (3.86), 632 (3.45); MS (MALDI-TOF) *m/z* 1598.36 (M⁺, C₁₀₄H₁₇₄N₄Si₄ requires 1591.28).

[5,15-Bis(3,5(trihexylsilyl)phenyl)porphyrinato]zinc(II) **5**

A solution of Zn(OAc)₂·2H₂O (0.92 g, 4.2 mmol) in MeOH (10 mL) and added to a solution of 5,15-bis[3,5(trihexylsilyl)phenyl]porphyrin **4** (1.33 g, 0.83 mmol) in CHCl₃ (70 mL). The mixture was stirred at room temperature for 3.5 hrs, then evaporated and passed through a short silica plug, eluting with a mixture of 40–60°C petroleum ether and CH₂Cl₂ (80/20). The solvent was removed to give the zinc porphyrin **5** (1.39 g, 99%) as pink crystals. ¹H NMR (400 MHz, CDCl₃): δ 10.39 (s, 2H), 9.47 (d, *J* = 4.5, 4H), 9.17 (d, *J* = 4.5, 4H), 8.37 (s, 4H), 8.03 (s, 2H), 0.82-1.52 (m, 156H); ¹³C NMR (100 MHz, CDCl₃): δ 150.5, 149.5, 140.9, 140.7, 139.1, 134.9, 132.7, 131.7, 121.4, 106.2, 33.6, 31.7, 24.1, 22.7, 14.2, 12.7; UV (CH₂Cl₂): λ_{max} (log ε) = 422 (5.74), 553 (4.46), 590 (3.90); MS (MALDI-TOF) *m/z* 1653.71 (M⁺, C₁₀₄H₁₇₂N₄Si₄Zn requires 1653.19).

[5,15-Bis(3,5(trihexylsilyl)phenyl)-10,20-dibromoporphyrinato]zinc(II) 6

A solution of *N*-bromosuccinimide (0.11 g, 0.6 mmol) in CHCl₃ (10 mL) was added to a solution of porphyrin **5** (0.5 g, 0.3 mmol) in pyridine (0.2 mL) and CHCl₃ (14 mL). The reaction mixture was stirred at room temperature for 15 min before adding acetone (0.3 mL) to quenched excess of NBS. The solution was concentrated and pass through a short silica plug eluting with a mixture of 40–60°C petroleum ether and CH₂Cl₂ (80/20). The solvent was removed to give the dibromoporphyrin **6** (0.54 g, 98%) as purple crystals. ¹H NMR (400 MHz, CDCl₃): δ 9.74 (d, *J* = 4.8, 4H), 8.95 (d, *J* = 4.8, 4H), 8.25 (s, 4H), 8.01 (s, 2H), 0.87–1.51 (m, 156H); ¹³C NMR (100 MHz, CDCl₃): δ 151.3, 150.2, 140.6, 140.2, 139.1, 135.1, 133.8, 133.2, 123.7, 105.3, 33.6, 32.0, 24.1, 22.7, 14.2, 12.7; UV (CH₂Cl₂): λ_{max} (log ε) = 428 (5.81), 558 (4.40), 597 (3.96); MS (MALDI-TOF) *m/z* 1818.07 (M⁺, C₁₀₄H₁₇₀Br₂N₄Si₄Zn requires 1809.02).

[5,15-Bis(3,5(trihexylsilyl)phenyl)-10,20-bis((trimethylsilyl)ethynyl)porphyrinato] zinc(II) 7

A solution of porphyrin **6** (0.54 g, 0.3 mmol) was dissolved in a mixture of toluene (25 mL) and triethylamine (22 mL). The solution was saturated with nitrogen before adding tris-(dibenzylideneacetone)-di-palladium(0) (0.036 g, 0.3 mmol), PPh₃ (0.08 g, 0.3 mmol), CuI (0.03 g, 0.15 mmol) and trimethylsilylacetylene (0.13 mL, 0.9 mmol). The solution was stirred at 50°C for 2 hrs. The product was purified by column chromatography on silica gel eluting with increasing gradients of CH₂Cl₂ in 40–60°C petroleum ether (starting from 2% to 5% of CH₂Cl₂) to yield porphyrin **7** as green crystals (0.465 g, 83%). ¹H NMR (400 MHz, CDCl₃): δ 9.70 (d, *J* = 4.5, 4H), 8.92 (d, *J* = 4.5, 4H), 8.26 (s, 4H), 8.00 (s, 2H), 0.88–1.50 (m, 156H), 0.60 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 152.2, 150.6, 140.5, 140.2, 139.2, 135.0, 133.0, 131.2, 123.9, 107.4, 101.8, 101.4, 33.6, 31.7, 24.1, 22.7, 14.2, 12.7, 0.30. UV (CH₂Cl₂): λ_{max} (log ε) = 436 (5.82), 445 (5.67), 577 (4.33), 624 (4.68). MS (MALDI-TOF) *m/z* 1848.86 (M⁺, C₁₁₄H₁₈₈N₄Si₆Zn requires 1845.27).

[5,15-Bis(3,5(trihexylsilyl)phenyl)-10,20-bis(ethynyl)porphyrinato]zinc(II) 8

TBAF (1.0 M in THF, 0.2 mL, 0.17 mmol) was added to a solution of porphyrin **7** (0.130 g, 0.07 mmol) in CH₂Cl₂ (15 mL). After 30 min, anhydrous CaCl₂ (100 mg) was added and the crude product was passed through a short silica plug eluting with a mixture of 40–60°C petroleum ether and CH₂Cl₂ (80/20). Further chromatography (40–60°C petroleum ether/CH₂Cl₂ 90/10) yielded pure porphyrin **8** as a green solid (0.11 g, 96%). ¹H NMR (400 MHz, CDCl₃): δ 9.75 (d, *J* = 4.8, 4H), 8.96 (d, *J* = 4.8, 4H), 8.27 (s, 4H), 8.01 (s, 2H), 4.19 (s, 2H), 0.86–1.50 (m, 156H); ¹³C NMR (100 MHz, CDCl₃): δ 152.3, 150.7, 140.6, 140.2, 139.2, 135.1, 131.2, 123.9, 100.1, 85.9, 83.9, 33.6, 31.7, 24.1, 22.7, 14.2, 12.7, 0.30; UV (CH₂Cl₂): λ_{max} (log ε) 430 (5.53), 438 (5.47), 568 (4.23), 612 (4.26); MS (MALDI-TOF) *m/z* 1703.02 (M⁺, C₁₀₈H₁₇₂N₄Si₄Zn requires 1701.19).

Porphyrin polymer 1

1,4-Benzoquinone (6.4 mg, 0.036 mmol), copper(I) iodide (2.7 mg, 0.014 mmol), and Pd(PPh₃)₂Cl₂ (1.0 mg, 0.0014 mmol) were loaded into a flask. The vessel was evacuated and refilled with argon. Toluene (4 mL) and diisopropylamine (2 mL) were added to the flask. Lastly, a solution of porphyrin **8** (80 mg, 0.047 mmol) in toluene (5 mL) was added, and the mixture was stirred at 50°C for 2.5 hrs. The mixture was treated with methanol (20 mL) and the precipitate was separated by centrifugation (1500 rpm, 10 min). The precipitate was resuspended and centrifuged twice with methanol. Then the polymer was dissolved in a mixture of toluene and THF (1:1), centrifuged (1700 rpm, 10 min), decanted and centrifuged again to remove all insoluble material. The polymer solution was concentrated to a minimum and then precipitated into EtOH, centrifuged and dried under the vacuum, to yield polymer **1** as a black solid (85 mg, 71%). ¹H NMR (400 MHz, CDCl₃): δ 9.90 (s, 4H), 8.96 (s, 4H), 8.33 (s, 4H), 8.03 (s, 2H), 0.86–1.55 (m, 156H); UV (CHCl₃): λ_{max} (log ε) 468 (5.01), 780 (4.83). Elemental analysis calcd (%) for C₁₀₈H₁₇₀N₄Si₄Zn: C 76.20, H 10.07, N 3.29; found C 76.19, H 10.03, N 2.89. GPC (THF; Polymer Laboratories Plgel 5 μm MIXED-D column): *M_n* = 83,700; *M_w* = 15,7000 (corresponding to a number-average degree of polymerization of 50 repeat units).

These polymerization conditions are derived from those of: Williams, V. E.; Swager, T. M. *J. Polym. Sci.: Part A: Polym. Chem.* **2000**, 38, 4669–4676.

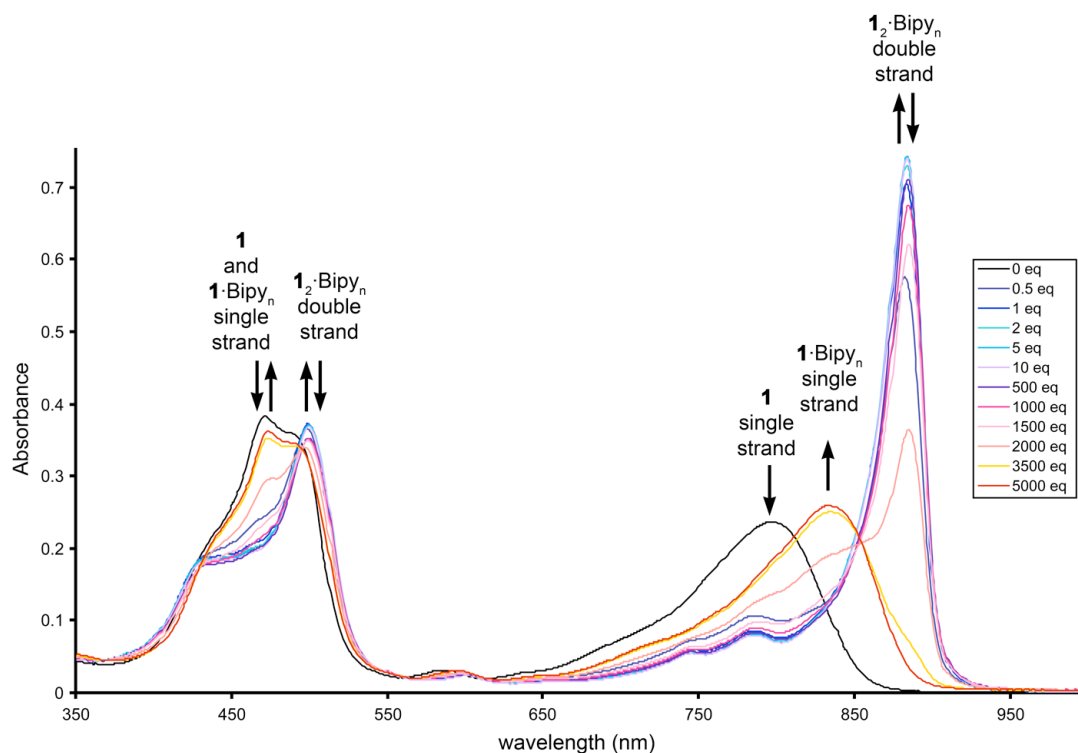


Figure S1: UV-vis-NIR Titration of Polymer 1 with Bipy in benzene; [1] = 4.8 μM per repeat unit; 1 cm cuvette; key indicates number of equivalents of Bipy per zinc porphyrin unit.

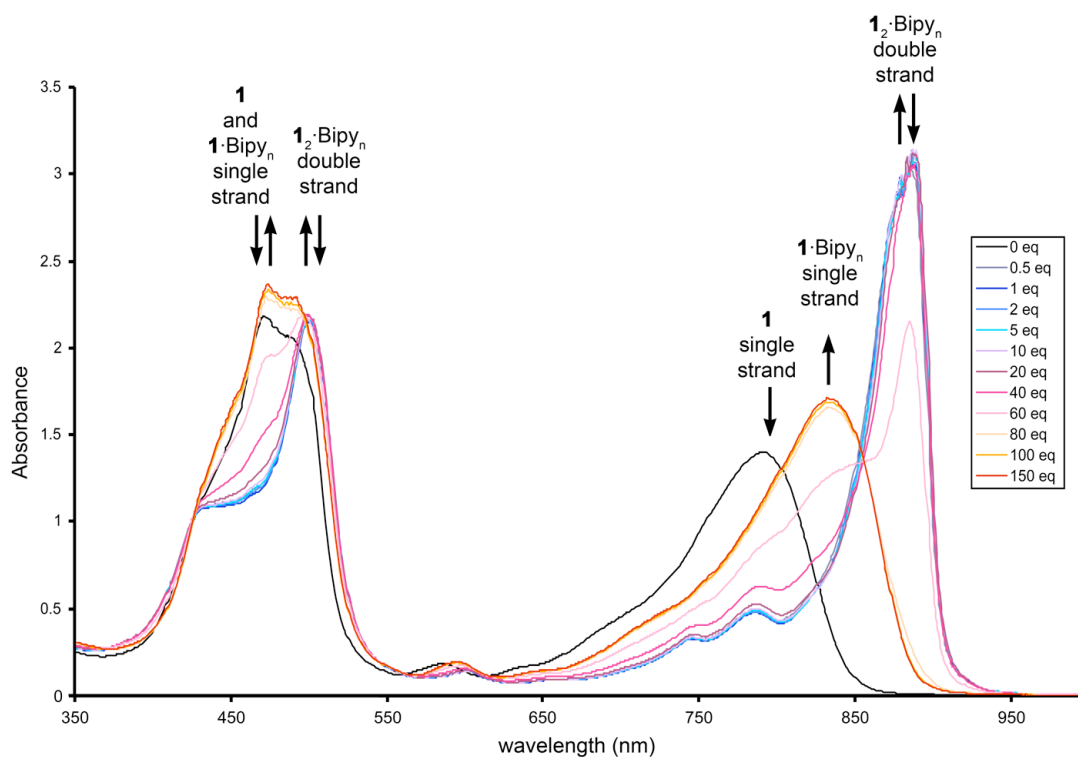


Figure S2: UV-vis-NIR Titration of Polymer 1 with Bipy in benzene; [1] = 0.25 mM per repeat unit; 1 mm cuvette; key indicates number of equivalents of Bipy per zinc porphyrin unit. Note that this titration was carried out at the same concentration as the TRMC experiment and it shows that under these conditions the double-strand complex is stable with up to 60 equivalents of Bipy, corresponding to a Bipy concentration of 15 mM.