Apolar *ortho* Phenylene Ethynylene Oligomers: Conformational Ordering Without Intermolecular Aggregation

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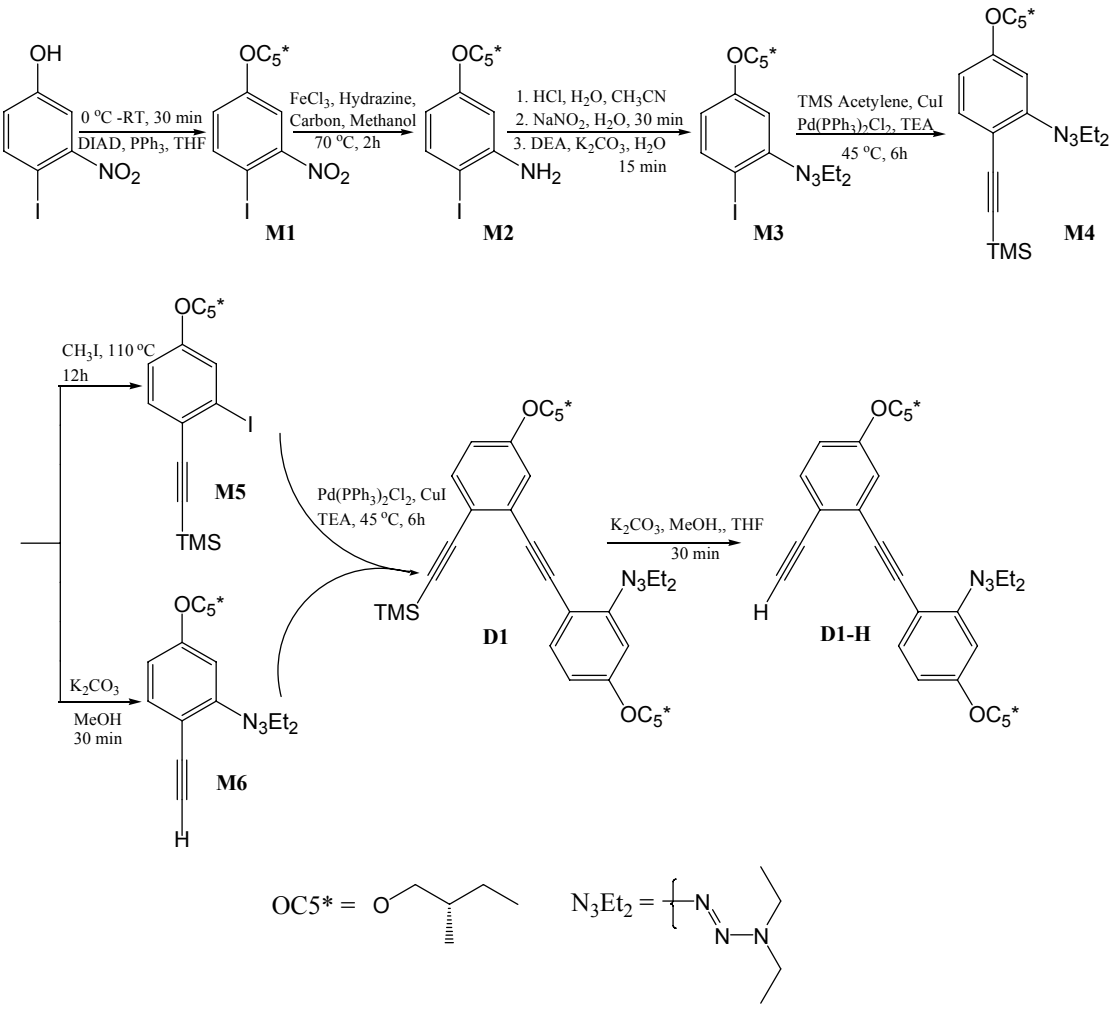
Supporting Information

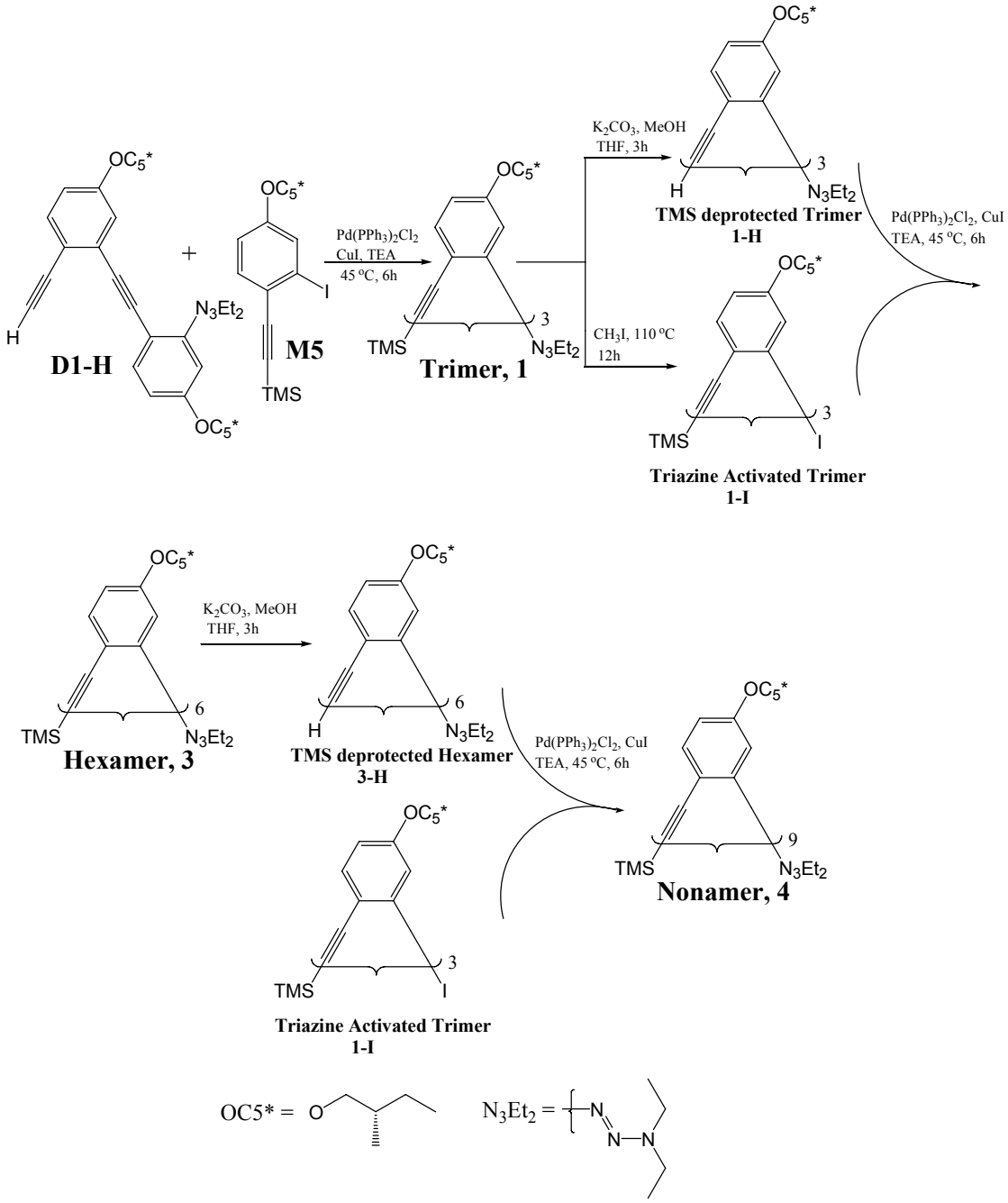
Materials and Instruments

Trans dichlorobis (triphenylphosphine) palladium ($Pd(PPh_3)_2Cl_2$) and tris(dibenzylidene acetone) dipalladium ($Pd_2(dba)_2$) was purchased from Strem Chemical. Trimethylsilyl acetylene was purchased from GFS chemicals. Copper (I) Iodide (CuI, 99.999%) was purchased from Alfa Aesar. All other reagents were purchased from Alfa Aesar or Aldrich Chemical Co. and all were used as received. All column chromatography was performed with 80-230 mesh silica from VWR.

^1H and ^{13}C NMR spectra were obtained from Bruker DPX 400 MHz spectrometer or 600 MHz spectrometer by means of a TXI probe with Z-gradient capabilities. The temperature was maintained at 305 K for all acquisitions. Mass spectral data were obtained at the University of Massachusetts Amherst mass spec facility, which is supported in part by the National Science Foundation. UV-visible spectra were recorded on a Hewlett-Packard 8453. CD Spectra were taken on a JASCO J720 spectrometer in rectangular cuvettes.



Scheme S1 Procedure of Monomers and Dimer



Scheme S1 Procedure of oligomers

1-Iodo-4-((S)-2-methyl-butoxy)-2-nitro-benzene (M1).

A flame-dried and N_2 filled 100 mL sidearm flask with magnetic stirbar was charged with 3-nitro-4-iodo phenol (2.0 g, 7.5 mmol, 1 mol eq.), S-2-methyl butanol (0.97 mL, 1.2 mol eq) and triphenylphosphine (2.9 g, 11mmol, 1.5 mol eq.) in 50 mL dry THF. The solution was cooled to 0 ^oC in an ice bath and diisopropylazodicarboxylate (DIAD) (2.2 mL, 1.5 mol eq.) was slowly added to the stirring solution. The reaction was then removed from the ice bath and allowed to warm to room temperature. The reaction was complete after a half hour at room temperature as determined by TLC. The solvent was removed under reduced pressure yielding an orange oil that was purified by flash chromatography to afford **M1** as a yellow oil (2.4 g) in 94% yield. ^1H NMR ($CDCl_3$, ppm) δ: 7.85 (d, 1H, phenyl H, J = 8.65 Hz), 7.40 (d, 1H, phenyl H, J = 2.85 Hz), 6.85 (dd, 1H, phenyl H, J_1 = 2.91 Hz, J_2 = 8.83 Hz), 3.73-3.86 (m, 2H, CH_2), 1.82-1.93 (m, 1H, CH) 1.48-1.62 (m, 1H, CH_2), 1.20-1.35 (m, 1H, CH_2), 1.01 (d, 3H, CH_3, J = 6.83 Hz), 0.95 (t, 3H, CH_3, J = 7.41 Hz). ^{13}C NMR ($CDCl_3$, ppm) δ: 159.9, 153.48, 142.07, 120.98, 111.82, 74.04, 73.75, 34.75, 26.06, 16.50, 11.35. MS: *m/z* 335.

2-Iodo-5-((S)-2-methyl-butoxy)-aniline (M2)

2.37 g (7.1 mmol, 1 mol eq) of **M1**, $FeCl_3$•$6H_2O$ (0.11 g, 0.06 mol eq.), and Carbon Black (0.28 g, 3.3 mol eq.) were dissolved/suspended in 120 mL of Methanol in a 250 mL flask with magnetic stir bar. The solution was heated to 70 ^oC. After 15 minutes, hydrazine (1.37 mL, 4 mol eq.) was slowly added to the stirring solution. The reaction was complete after a 2 hours at 70 ^oC as determined by TLC. The reaction solution was filtered through a pad of Celite to remove the carbon black and the solvent was removed under reduced pressure yielding a clear oil and a small amount of a second phase. This residue was diluted with water and ethyl acetate, extracted 3 times with ethyl acetate, dried over $MgSO_4$ and filtered through a pad of silica gel to afford 2.01 g of product (94%) which was used without further purification. ^1H NMR ($CDCl_3$, ppm) δ: 7.46 (d, 1H, phenyl H, J = 8.65 Hz), 6.33 (d, 1H, phenyl H, J = 2.57 Hz), 6.13 (dd, 1H, phenyl H, J_1 = 2.59, J_2 = 8.66 Hz), 4.04 (s, 2H, NH_2) 3.63-3.77(m, 2H, CH_2), 1.77-1.88 (m, 1H, CH) 1.47-1.61 (m, 1H, CH_2), 1.19-1.31 (m, 1H, CH_2), 0.98 (d, 3H, CH_3, J = 6.70 Hz), 0.93 (t, 3H, CH_3, J = 7.42 Hz). ^{13}C NMR ($CDCl_3$, ppm) δ: 160.9, 147.63, 139.15, 107.35, 101.23, 73.2, 72.99, 34.72, 26.20, 16.6, 11.39. MS: *m/z* 305.

***N,N*-Diethyl-*N'*-(2-Iodo-5-((S)-2-methyl-butoxy) phenyl)triazene (M3)**

A solution of **M2** (1.77 g, 5.9 mmol, 1mol eq.) in 120 mL acetonitrile, 20 mL of water, and 2.73 mL (5.6 mol eq) hydrochloric acid in a 250 mL flask was cooled in an ice-acetone bath to -5 ^oC. A cold solution of $NaNO_2$ (0.908 g, 13mmol, 2.25 mol eq) in 15 mL water was added dropwise over 10 minutes. This was allowed to react for 30 minutes taking care to maintain vigorous stirring and low temperature (below 0 ^oC). This mixture was transferred into a cold (-5 ^oC) solution of K_2CO_3 (4.85 g, 35 mmol, 6 mol eq.), diethylamine (1.82 mL, 17mmol, 3 mol eq.) and 20 mL water using a cannula. The reaction was allowed to warm to room temperature and stirred vigorously for an additional 15 minutes. The solution was extracted 3 times with ether, the organic phase was washed twice with brine, dried over $MgSO_4$ and evaporated to give a red oil. The residue was purified using flash chromatography to afford 1.50 g of the product (65%) as an orange oil. ^1H NMR ($CDCl_3$, ppm) δ: 7.66 (d, 1H, phenyl H, J = 8.68 Hz), 6.95 (d, 1H, phenyl H, J = 2.94 Hz), 6.49 (dd, 1H, phenyl H, J_1 = 2.95 Hz, J_2 = 8.66 Hz), 3.69-3.84 (m, 6H, CH_2), 1.81-1.88 (m, 1H,

CH), 1.51-1.60 (m, 1H, CH_2), 1.18-1.34 (m, 7H, CH_2, CH_3), 1.00 (d, 3H, CH_3, J = 6.84 Hz), 0.94 (t, 3H, CH_3, J = 7.42 Hz). ^{13}C NMR ($CDCl_3$, ppm) δ: 160.36, 151.14, 139.02, 103.59, 85.53, 77.38, 73.05, 49.02 34.72, 26.20, 16.6, 11.39. MS: *m/z* 389.

***N,N*-Diethyl-*N'*-[2-trimethylsilylethynyl-5-((S)-2-methylbutoxy) phenyl]triazene (M4)**

0.38 g of **M3** (0.97 mmol, 1 eq), 68 mg of $Pd(PPh_3)_2Cl_2$ (97.4 μmol, 0.1 mol eq.), and 37 mg of CuI (0.19 mmol, 0.2 eq) were combined in a schlenk flask with 10 mL TEA. TMS acetylene (0.17 mL, 0.11 mmol, 1.2 mol eq.) was added to the solution. The solution was stirred for 6h at 45 ^{o}C. Once done, the reaction solution was diluted with ether, filtered through a pad of Celite and concentrated. The oil was then purified using flash chromatography in DCM: Hexanes to afford the product (0.31 g, 90%) as an orange oil. ^{1}H NMR ($CDCl_3$, ppm) δ: 7.37 (d, 1H, phenyl H, J = 8.53 Hz), 6.91 (d, 1H, phenyl H, J = 2.68 Hz), 6.60 (dd, 1H, phenyl H, J_1 = 2.62 Hz, J_2 = 8.63 Hz), 3.71-3.85(m, 6H, CH_2), 1.79-1.90 (m, 1H, CH) 1.49-1.63 (m, 1H, CH_2), 1.18-1.34 (m, 8H, CH_2, CH_3), 1.00 (d, 3H, CH_3, J = 6.80 Hz), 0.94 (t, 3H, CH_3, J = 7.60 Hz), 0.22 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$, ppm) δ: 160.21, 154.22, 134.24, 111.93, 110.65, 103. 96, 101.98, 95.96, 76.87, 72.84, 49.11, 41.92, 34.82, 29.80, 26.22, 16.64, 11.43, 0.30. MS: *m/z* 359.

[2-Iodo-4-((S)-2-methyl-butoxy)-phenylethynyl]-trimethyl-silane (M5)

98 mg of **M4** (0.27 mmol) was dissolving in 3 mL CH_3I and heated to 110 ^{o}C in a sealed tube. After 12 hours, the reaction mixture was diluted with hexanes, filtered over Celite, concentrated and purified by column chromatography (hexanes) to afford the product as a beige oil (75 mg, 72%). ^{1}H NMR ($CDCl_3$, ppm) δ: 7.36 (d, 1H, phenyl H, J = 4.55 Hz), 7.34 (d, 1H, phenyl H, J = 1.47 Hz), 6.80 (dd, 1H, phenyl H, J_1 = 2.71 Hz, J_2 = 8.67 Hz), 3.67-3.80 (m, 2H, CH_2), 1.78-1.89 (m, 1H, CH) 1.47-1.61 (m, 1H, CH_2), 1.18-1.32 (m, 1H, CH_2, CH_3), 1.01 (d, 3H, CH_3, J = 6.77 Hz), 0.95 (t, 3H, CH_3, J = 7.62 Hz), 0.27 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$, ppm) δ: 159.38, 133.32, 124.63, 121.80, 114.58, 106.77, 101.89, 96.65, 77.42, 76.79, 73.21, 34.70, 26.12, 16.54, 11.38, 0.03. MS: *m/z* 386.

***N,N*-Diethyl-*N'*-(2-ethynyl 5-((S)-2-methyl-butoxy phenyl)triazene (M6)** 0.10 g (0.28 mmol, 1 mol eq) of **M4** and 0.10 g K_2CO_3 (0.70 mmol, 2.5 eq.) in 10 mL methanol were stirred in a nitrogen-flushed vial for 3 hours. Reaction was monitored by TLC. Upon completion the solution was diluted with ethyl acetate and water and washed twice with water. After drying the ethyl acetate layer over $MgSO_4$ and evaporation of solvent, the residue was purified by flash chromatography to give an orange oil (0.06 g, 80%). ^{1}H NMR ($CDCl_3$, ppm) δ: 7.39 (d, 1H, phenyl H, J = 8.17 Hz), 6.92 (d, 1H, phenyl H, J = 2.57 Hz), 6.63 (dd, 1H, phenyl H, J_1 = 2.44 Hz, J_2 = 8.36 Hz), 3.72- 3.86 (m, 6H, CH_2), 3.165 (s, 1H, CH), 1.80-1.91 (m, 1H, CH) 1.46-1.63 (m, 1H, CH_2), 1.19-1.33 (m, 7H, CH_2, CH_3), 1.01 (d, 3H, CH_3, J = 6.82 Hz), 0.94 (t, 3H, CH_3, J = 7.33 Hz).

TMS-Dimer-Triazene (D1)

97 mg of **M5** (0.25 mmol, 1 mol eq), and 80 mg of **M6** (0.28 mmol, 1.1 mol eq.), 8.8 mg $Pd(PPh_3)Cl_2$ (13 μmol, 0.05 mol eq.) and 4.8 mg CuI (25 μmol, 0.1 mol eq.) were combined in a schlenk flask with 10 mL TEA. The solution was stirred for 6h at 45 ^{o}C. Once done, the reaction solution was diluted with ether, filtered through a pad of Celite and concentrated. The oil was then

purified using flash chromatography in DCM: Hexanes to afford a beige solid (89 mg, 65%). ^{1}H NMR ($CDCl_3$, ppm) δ: 7.47 (d, 1H, phenyl H, J = 8.40 Hz), 7.37 (d, 1H phenyl H, J = 8.69 Hz), 6.96 (d, 1H, phenyl H, J = 0.90 Hz), 6.95 (d, 1H, phenyl H, J = 0.90 Hz), 6.75 (dd, 1H, phenyl H, J_1 = 2.64 Hz, J_2 = 8.69 Hz), 6.75 (dd, 1H, phenyl H, J_1 = 2.59 Hz, J_2 = 8.66 Hz), 3.67-3.88 (m, 8H, CH_2), 1.82-1.90 (m, 2H, CH) 1.46-1.64 (m, 2H, CH_2), 1.23-1.38 (m, 8H, CH_2, CH_3), 0.88-1.03 (m, 6H, CH_3), 0.24 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$, ppm) δ: 160.38, 159.14, 159.04, 153.95, 153.78, 134.26, 133.65, 133.89, 128.80, 128. 29, 117.91, 117.55, 117.28, 116.70, 115.93, 114.77, 112.17, 110.88, 104.26, 104.15, 102.22, 96.76, 96.34, 96.20, 95.64, 92.93, 92.70, 90.86, 77.65, 76.80, 72.95, 34.92, 34.74, 29.88, 26.32, 26.26, 16.76, 16.63, 11.53, 11.45, 0.34.

H-Dimer-Triazene (D1-H)

37 mg (67 μmol) of **D1** and 23 mg K_2CO_3 (0.17 mmol, 2.5 eq.) in 3 mL methanol were stirred in a nitrogen-flushed vial for 3 hours. Reaction was monitored by TLC. Upon completion the solution was diluted with ethyl acetate and water and washed twice with water. After drying the ethyl acetate layer over $MgSO_4$ and evaporation of solvent, the residue was purified by flash chromatography to give a beige oil (26 mg, 82%). ^{1}H NMR ($CDCl_3$, ppm) δ: 7.48 (d, 1H, phenyl H, J = 8.67 Hz), 7.4 (d, 1H phenyl H, J = 8.49 Hz), 7.00 (d, 1H, phenyl H, J = 2.49 Hz), 6.96 (d, 1H, phenyl H, J = 2.47 Hz), 6.77 (dd, 1H, phenyl H, J_1 = 2.64 Hz, J_2 = 8.72 Hz), 6.67 (dd, 1H, phenyl H, J_1 = 2.54 Hz, J_2 = 8.65 Hz), 3.69-3.88 (m, 8H, CH_2), 3.21 (s, 1H, CH), 1.81- 1.98 (m, 2H, CH) 1.48-1.62 (m, 2H, CH_2), 1.20-1.34 (m, 8H, CH_2, CH_3), 0.84-1.03 (m, 6H, CH_3).