Supporting Information

Helical Twist Sense Bias in Oligo(Phenylene Ethynylene)s Induced by an Optically Active Flexible Tether

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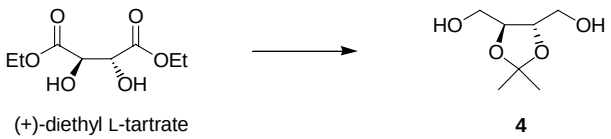
Experimental Procedures

General. Unless otherwise noted, all starting materials were obtained from commercial suppliers and were used without further purification. All air- or moisture-sensitive reactions were done under an atmosphere of dry nitrogen. Analytical thin layer chromatography (TLC) was performed on Kieselgel F-254 precoated silica gel plates. Eluting solvents are reported as volume ratios or volume percents. Visualization was accomplished with UV light or basic $KMnO_4$ or ceric ammonium molybdate (CAM) stains. Flash column chromatography was carried out with silica gel 60 (230-400 mesh) from EM Science. Dry triethylamine was obtained using a solvent-purification system from Anhydrous Engineering, and dry dichloromethane and acetonitrile were obtained by vacuum transfer from calcium hydride.

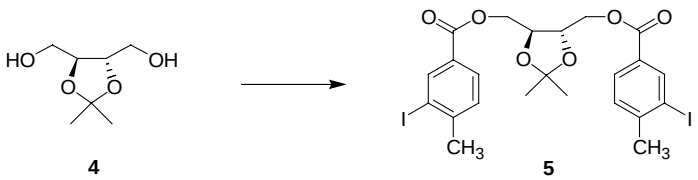
Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 400 or Varian Unity 500 spectrometer. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standard (δ 7.26 ppm for $CHCl_3$). Coupling constants, *J*, are reported in Hertz (Hz), and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), and app (apparent). Mass spectra were obtained through the Mass Spectrometry Facility, School of Chemical Sciences, Universtiy of Illinois. Low resolution fast atom bombardment (FAB) mass spectra were obtained on a Micromass ZAB-SE spectrometer, and low resolution matrix assisted laser desorption mass spectra were obtained using a PerSeptive Biosystems Voyager-DE STR spectrometer. High pressure liquid chromatography (HPLC) analysis was performed with a Rainin Dynamax solvent delivery system, model SD-200, using a Microsorb Si-80-125-C5 silica column and a UV detector operating at 290 nm.

The UV absorption spectra and CD spectra were recorded on an Olis DSM 17 UV/Vis CD spectrophotometer using 1 cm rectangular quartz cells (UV) or 1 cm cylindrical quartz cells (CD). Molar absorptivity, ε, in $M^{-1}cm^{-1}$ was determined for each compound by averaging the absorption spectra divided by concentration over a four-fold concentration range. CD spectra, recorded as θ in millidegrees, were converted to $\Delta\varepsilon$ using the equation $\Delta\varepsilon = \theta/(32982cl)$, where $\Delta\varepsilon$ is the difference in molar absorptivity for oppositely polarized light in $M^{-1}cm^{-1}$, *c* is the concentration of the sample in moles of oligomer per L, and *l* is the path length through the cell in cm.



(+)-diethyl L-tartrate **4**

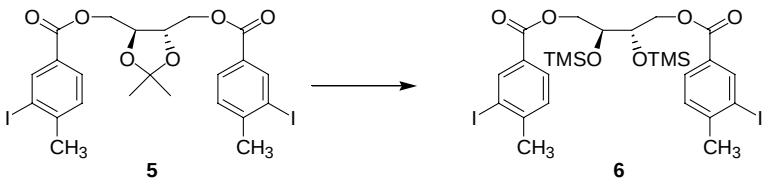
(4*S*,5*S*)-2,2-Dimethyl-1,3-dioxolane-4,5-dimethanol 4. To (+)-diethyl L-tartrate (3.4 mL, 20 mmol, 1 equiv) in 36 mL of acetone at 0 °C was added BF_3OEt_2 (3.0 mL, 24 mmol, 1.2 equiv) dropwise. The flask was removed from the ice bath, and the reaction was stirred at 23 °C for 5.5 h. The reaction was quenched with 160 mL of saturated aqueous $NaHCO_3$, and the aqueous layer was extracted with EtOAc (4 × 40 mL). The combined organic fractions were washed with 40 mL 1:1 saturated aqueous NaCl/ H_2O, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resultant crude material was purified by silica gel column chromatography (15% EtOAc/hexanes) to afford 3.9 g (80%) of isopropylidene-protected diethyl tartrate, R_f = 0.25 (6:1 hexanes/EtOAc, $KMnO_4$ stain). To a portion of this material (1 g, 4 mmol, 1 equiv) in 32 mL of THF was added a slurry of $LiAlH_4$ (300 mg, 8 mmol, 2 equiv) in 8 mL of THF. The resultant mixture was stirred at 23 °C for 1 h, then quenched by sequential treatment with H_2O (300 μL), 15% NaOH (300 μL), and more H_2O (900 μL). After stirring for 1.5 h, the mixture was filtered through a pad of Celite, rinsing with 150 mL of EtOAc. The filtrate was concentrated in vacuo, and the crude material was purified by silica gel column chromatography (5% MeOH, 45% EtOAc in hexanes, then 5% MeOH, 33% hexanes in EtOAc) to afford 0.61 g (94%) of product **4**:[1] R_f = 0.16 (5% MeOH in 1:1 hexanes/EtOAc, $KMnO_4$ stain); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 (m, 2H), 3.82 (br d, *J* = 11.8 Hz, 2H), 3.71 (m, 2H), 2.02 (br m, 2H), 1.44 (s, 6H).



4 **5**

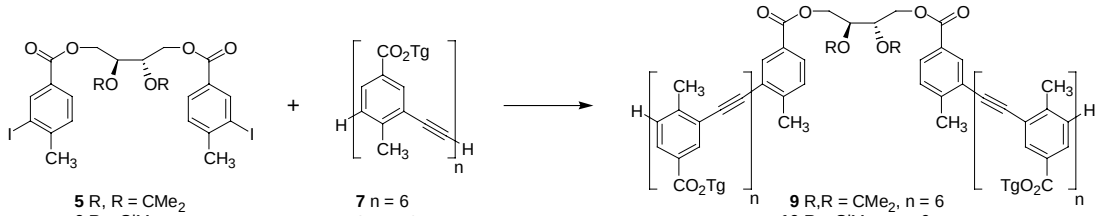
Tethered aryl iodide 5. To diol **4** (160 mg, 1.0 mmol, 1 equiv) in 10 mL of CH_2Cl_2 was added 3-iodo-4-methylbenzoic acid (660 mg, 2.5 mmol, 2.5 equiv) and 4-DMAP (24 mg, 0.20 mmol, 0.2 equiv). The mixture was cooled to 0 °C, and DCC (520 mg, 2.5 mmol, 2.5 equiv) was added. After stirring at 0 °C for 5 min, the reaction was stirred at 23 °C for 6 h, cooled back to 0 °C, and filtered through a pad of Celite, rinsing with 200 mL of cold CH_2Cl_2. The filtrate was concentrated in vacuo and the crude material was purified by silica gel column chromatography (10% EtOAc/hexanes; then 15% EtOAc/hexanes) to give 540 mg (84%) of **5**: TLC R_f = 0.27 (15% EtOAc/hexanes, UV and CAM stain); IR (thin film) ν 3044 (w), 2983, 2942, 2887, 1722 (s), 1596, 1555, 1446, 1378, 1287, 1248 (s), 1171, 1105, 1035, 991, 906, 838, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 1.8 Hz, 2H), 7.91 (dd, *J* = 7.9, 1.9 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 4.55 (dd, *J* = 11.9, 3.8 Hz, 2H), 4.47 (dd, *J* = 12.0, 4.8 Hz, 2H), 4.28 (m, 2H), 2.48 (s, 6H),

1.47 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165, 147, 140, 129.6, 129.4, 128.7, 111, 101, 76, 64, 28, 27; HRMS (FAB) calcd for $C_{23}H_{25}I_2O_6$ (M + 1) 650.9741, found 650.9733.



5 **6**

Bis-trimethylsilyl ether 6. To 114 mg of **5** (0.175 mmol, 1 equiv) was added 1.5 mL of CH_2Cl_2, 0.5 mL of CF_3CO_2H, and 10 μL of H_2O. The mixture was stirred at 23 °C for 45 min, then poured into 10 mL of CH_2Cl_2 and quenched with 10 mL of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (3 × 7 mL) and the combined organic layers were washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resultant crude oil was purified by silica gel column chromatography (3:2 hexanes/EtOAc) to afford 94 mg (88%) of the diol, R_f = 0.22 (3:2 hexanes/EtOAc). To a portion of the diol (34 mg, 56 μmol, 1 equiv) in 1.0 mL of CH_2Cl_2 was added a catalytic amount of 4-DMAP, Et_3N (43 μL, 0.31 mmol, 5.5 equiv), and chlorotrimethylsilane (24 μL, 0.19 mmol, 3.4 equiv). After 5 min the reaction mixture was loaded onto a silica gel chromatography column and eluted with 10% EtOAc in hexanes to give 41 mg (98%) of **6**: TLC R_f = 0.40 (10% EtOAc/hexanes); IR (thin film) ν 3067 (w), 2957, 2894, 1723 (s), 1598, 1558, 1446, 1377, 1288, 1252 (s), 1207, 1112 (s), 1034, 998, 962, 842 (s), 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 1.8 Hz, 2H), 7.91 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 4.50 (dd, *J* = 11.1, 4.0 Hz, 2H), 4.34 (dd, *J* = 11.2, 6.5 Hz, 2H), 4.09 (m, 2H), 2.48 (s, 6H), 0.17 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165, 147, 140, 129.6, 129.2, 129.1, 100, 71, 66, 28, 0.2; HRMS (FAB) calcd for $C_{26}H_{37}I_2O_6Si_2$ (M + 1) 755.0218, found 755.0220.



5 R, R = CMe_2
6 R = $SiMe_3$

7 n = 6
8 n = 12
Tg = $(CH_2CH_2O)_3CH_3$

9 R,R = CMe_2, n = 6
10 R = $SiMe_3$, n = 6
12 R = $SiMe_3$, n = 12

General procedure for Pd-catalyzed coupling of oligomers to tethered aryl iodides: Bis-trimethylsilyl ether 10.

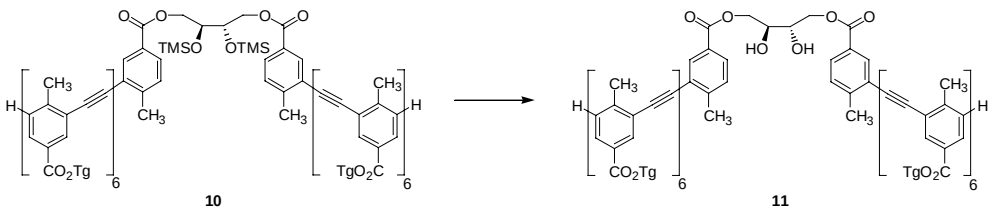
The catalyst solution was prepared by weighing $Pd(dba)_2$[2] (44 mg, 76 μmol, 1 equiv), CuI (15 mg, 76 μmol, 1 equiv), and Ph_3P (100 mg, 380 μmol, 5 equiv) into a 15 mL sealed tube flask. The atmosphere was evacuated and the flask was back-filled with N_2 three times. To the flask was added 2 mL of Et_3N and

8 mL of CH_3CN, and the solution was degassed 3 times. The flask was sealed and heated to 75 °C until a homogeneous orange solution was achieved (ca. 5 min), then cooled to room temperature.

To a solution of **6** (3.6 mg, 4.8 μmol, 1 equiv) and **7** (20 mg, 11 μmol, 2.2 equiv) in 0.45 mL of 20% Et_3N/CH_3CN was added the catalyst solution (70 μL, 0.5 μmol Pd, 0.1 equiv Pd). The resultant mixture was degassed twice and the flask was sealed and heated to 75 °C for 37 h. The solvents were removed in vacuo, and the resulting crude material was purified by silica gel column chromatography (gradient elution, 0, 2.5, 5, then 7.5% MeOH in 1:1:1 benzene/CH_2Cl_2/acetone) to give 14.5 mg (72%) of **10**: TLC R_f = 0.39 (plate run up twice: 0, then 5% MeOH in 1:1:1 benzene/CH_2Cl_2/acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24-8.17 (m, 24H), 7.54 (app dt, *J* = 8, 2 Hz, 4H), 7.33 (d, *J* = 7.4 Hz, 4H), 4.58-4.48 (m, 26 H), 4.37 (dd, *J* = 11, 6.6 Hz, 2H), 4.15-4.13 (m, 2H), 3.89-3.84 (m, 24H), 3.75-3.63 (m, 72H), 3.53-3.51 (m, 24H), 3.35-3.33 (m, 36H), 2.83-2.81 (m, 30H), 2.60 (s, 12H), 0.18 (s, 18H); MS (MALDI) calcd for $C_{230}H_{278}O_{66}Si_2Na$ (M + Na) 4177.8, found 4178.3; HPLC (1.0 mL/min, 6% ^{i}PrOH/$CHCl_3$ 5 min, ramp to 9% ^{i}PrOH/$CHCl_3$ over 10 min, hold at 9% ^{i}PrOH/$CHCl_3$ 10 min, retention time 13 min) indicated >95% purity.

Isopropylidene 9. In an analogous procedure 4.4 mg of **5** (6.8 μmol, 1 equiv) was reacted with 27 mg of **7** (15 μmol, 2.2 equiv) for 13 h. The crude material was subjected to silica gel chromatography (gradient elution, 0, 2, then 5% MeOH in 2:1 CH_2Cl_2/acetone) to give 26 mg of **9**. HPLC analysis (1.0 mL/min, 6% ^{i}PrOH/$CHCl_3$ 5 min, ramp to 9% ^{i}PrOH/$CHCl_3$ over 10 min, hold at 9% ^{i}PrOH/$CHCl_3$ 10 min, retention time 15 min) indicated the product was ca. 90% pure. The material was resubjected to silica gel column chromatography (gradient elution, 0, 1, 2, 3, 4, 5, 6, then 10% ^{i}PrOH in $CHCl_3$) to give 13 mg (46%) of pure **9**: TLC R_f = 0.41-0.59 (plate run up multiple times: 0, 2, 3, 4, 5, then 6% ^{i}PrOH/$CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23-8.18 (m, 24H), 7.94 (br d, *J* = 8 Hz, 4H), 7.33 (dd, *J* = 8.2, 3.2 Hz, 4H), 4.62 (br d, *J* = 11Hz, 2H), 4.54-4.48 (m, 26 H), 4.34 (br s, 2H), 3.89-3.85 (m, 24H), 3.75-3.64 (m, 72H), 3.54-3.51 (m, 24H), 3.35-3.33 (m, 36H), 2.83-2.81 (m, 30H), 2.61-2.60 (m, 12H), 1.50 (s, 6H); MS (MALDI) calcd for $C_{227}H_{266}O_{66}Na$ (M + Na) 4073.5, found 4072.3.

Bis-trimethylsilyl ether 12. A solution of **6** (3.5 mg, 4.7 μmol, 1 equiv) and **8** (36 mg, 9.9 μmol, 2.1 equiv) was reacted analogously for 62 h. The crude material was purified by silica gel column chromatography (gradient elution, 0, 6, 7, then 9% MeOH in 1:1:1 benzene/CH_2Cl_2/acetone) to give 12 mg of the monosubstituted product (TLC R_f = 0.38, plate run up multiple times, 0, 5, 6, then 7% MeOH in 1:1:1 benzene/CH_2Cl_2/acetone) and 14 mg (38%) of **12**: TLC R_f = 0.22 (plate run up multiple times, 0, 5, 6, then 7% MeOH in 1:1:1 benzene/CH_2Cl_2/acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22-8.14 (m, 48H), 7.94-7.91 (m, 4H), 7.34-7.30 (m, 4H), 4.56-4.46 (m, 50H), 4.39-4.32 (m, 2H), 4.13 (br s, 2H), 3.91-3.79 (m, 48H), 3.75-3.64 (m, 144H), 3.53-3.51 (m, 48H), 3.35-3.33 (m, 72H), 2.83-2.79 (m, 66H), 2.59 (s, 12H), 0.18 (s, 18H); MS (MALDI) calcd for $C_{434}H_{518}O_{126}Si_2Na$ (M + Na) 7829.9, found 7837.9; HPLC (1.0 mL/min, 10% ^{i}PrOH/$CHCl_3$ 10 min, ramp to 25% ^{i}PrOH/$CHCl_3$ over 10 min, hold at 25% ^{i}PrOH/$CHCl_3$ 15 min, retention time 23 min) indicated >95% purity.



Diol 11. Buffered Bu_4NF solution was prepared by adding glacial acetic acid (ca. 150-160 μL) to 2 mL of Bu_4NF (1 M in THF) until pH paper indicated the solution was neutral. This solution (10 μL, 10 μmol, 10 equiv) was added to a solution of **10** (4.2 mg, 1.0 μmol, 1 equiv) in 0.5 mL of THF. The reaction mixture was stirred at 23 °C for 8.5 h, then subjected to silica gel column chromatography (gradient elution, 0, 5, then 10% MeOH in 1:1:1 benzene/CH_2Cl_2/acetone) to give 3.4 mg (85%) of **11**: TLC R_f = 0-0.19 (plate run up twice: 0, then 5% MeOH in 1:1:1 benzene/CH_2Cl_2/acetone), R_f = 0.49 (same plate run up a third time, 10% MeOH in 1:1:1 benzene/CH_2Cl_2/acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21-8.17 (m, 24H), 7.93 (app tm, *J* = 7 Hz, 4H), 7.33 (d, *J* = 8 Hz, 4H), 4.57-4.48 (m, 28 H), 4.12 (br s, 2H), 3.90-3.84 (m, 24H), 3.75-3.64 (m, 72H), 3.54-3.52 (m, 24H), 3.35-3.33 (m, 36H), 2.83-2.81 (m, 30H), 2.60-2.59 (m, 12H); MS (MALDI) calcd for $C_{224}H_{262}O_{66}Na$ (M + Na) 4033.5, found 4032.2; HPLC (1.0 mL/min, 6% ^{i}PrOH/$CHCl_3$ 5 min, ramp to 9% ^{i}PrOH/$CHCl_3$ over 10 min, hold at 9% ^{i}PrOH/$CHCl_3$ 10 min, retention time 21 min) indicated >99% purity.

[1] Batsanov, A. S.; Begley, M. J.; Fletcher, R. J.; Murphy, J. A.; Sherburn, M. S. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1281.
[2] Rettig, M. F.; Maitlis, P. M. *Inorg. Synth* **1977**, *17*, 134.