

(Supporting Information)

Synthesis and Chiroptical Properties of Optically Active,

Regioregular Oligothiophenes

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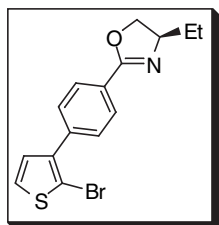
Measurements. ^1H (500 or 300 MHz) and ^{13}C (125 or 75 MHz) NMR spectra were measured on a Varian VXR-500S or Varian Mercury-300 spectrometer using tetramethylsilane (TMS) as an internal standard. IR spectra were recorded with a Jasco Fourier Transform IR-620 spectrophotometer. Optical rotation was measured in a 5-cm quartz cell equipped with a temperature controller (EYELA NCB-2100) on a Jasco P-1030 polarimeter in dry chloroform (CHCl_3). Absorption and CD spectra were taken on a Jasco V-570 spectrophotometer and a Jasco J-725 spectropolarimeter, respectively. The concentration of oligothiophenes was calculated based on monomer units. Recycling preparative HPLC was performed using a LC-918 liquid chromatograph equipped with a UV-visible detector (JAI UV 310). HPLC columns, JAIGEL-1H and JAIGEL-2H were connected in series, and CHCl_3 was used as the eluent. Low and high-resolution mass spectra were recorded on a JEOL JMS-AX505HA spectrometer in FAB mode.

Materials. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl, distilled onto lithium aluminum hydride (LiAlH_4) under nitrogen, and then distilled under high vacuum just before use. *N,N*-dimethylformamide (DMF) was dried over calcium hydride (CaH_2) and distilled under reduced pressure. Acetonitrile (CH_3CN), CHCl_3 and diisopropylamine were dried over CaH_2 and distilled under nitrogen. These solvents were stored under nitrogen over molecular sieves 4 Å (Nacalai Tesque, Kyoto, Japan). *n*-Butyllithium (*n*-BuLi) (1.54 M in *n*-hexane), *N*-

bromosuccinimide (NBS), and chlorotrimethylsilane were purchased from Kanto Chemical (Tokyo, Japan), Kishida Chemical (Osaka, Japan), and Aldrich, respectively. Tetra-*n*-butylammonium fluoride (TBAF) was obtained from Tokyo Kasei (Tokyo, Japan) and tris(dibenzylideneacetone)dipalladium was from Wako (Osaka, Japan). Triphenyl phosphite ($\text{P}(\text{PhO})_3$) and copper(II) oxide (CuO) were purchased from Nacalai Tesque.

General procedures for the bromination of oligothiophenes. The thiophene monomer (**1**) was prepared according to the previously reported method.¹ Regioselective bromination of oligothiophenes (**1**, **7a**, and **7b**) was carried out using NBS in a similar way reported previously.^{1,2}

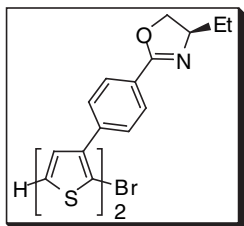
(*R*)-2-Bromo-3-(4-(4-ethyl-2-oxazolin-2-yl)phenyl)thiophene (2). Yield 89% (slightly yellow



oil). IR (neat, cm^{-1}): 3106, 2963, 2931, 1647, 1359, 1079, 1062, 1019, 988, 950, 872, 850, 719. ^1H NMR (500 MHz, CDCl_3): δ 1.01 (t, CH_3 , $J = 7.4$ Hz, 3H), 1.63 (m, CH_3CH_2 , 1H), 1.80 (m, CH_3CH_2 , 1H), 4.09 (t, OCH_2 , $J = 8.0$ Hz, 1H), 4.28 (m, OCH_2CH , 1H), 4.51 (dd, OCH_2 , $J = 9.4, 8.0$ Hz, 1H), 7.06 (d, Th- H_5 , $J = 5.6$ Hz, 1H), 7.42 (d, Th- H_4 , $J = 5.6$ Hz, 1H), 7.67 (d, Ph, $J =$

8.4 Hz, 2H), 7.76 (d, Ph, $J = 8.4$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 10.01, 28.63, 68.02, 72.16, 109.28, 126.17, 127.00, 128.27, 128.50, 128.91, 137.73, 140.34, 163.12. Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{BrNOS}$: C, 53.58; H, 4.20; N, 4.17. Found: C, 53.58; H, 4.26; N, 4.20.

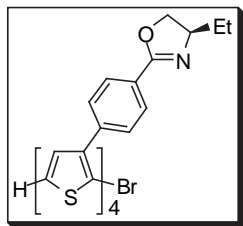
(*R*)-2-Bromo-3,3'-bis(4-(4-ethyl-2-oxazolin-2-yl)phenyl)-5,2'-bithiophene (8a). Yield 90%



(slightly yellow powder). mp 53.5–54.2 °C. IR (KBr, cm^{-1}): 3066, 2960, 2928, 1647, 1357, 1242, 1062, 948, 896, 853, 831, 725. ^1H NMR (CDCl_3 , 300 MHz): δ 1.01 (m, CH_3 , 6H), 1.62 (m, CH_3CH_2 , 2H), 1.78 (m, CH_3CH_2 , 2H), 4.06 (t, OCH_2 , $J = 8.1$ Hz, 2H), 4.26 (m, OCH_2CH , 2H), 4.49 (m, OCH_2 , 2H), 6.98 (s, Th- H_4 , 1H), 7.08 (d, Th- H_4' , $J = 5.1$ Hz, 1H), 7.31 (d, Th- H_5' , $J = 5.1$ Hz, 1H), 7.45 (d, Ph, $J = 8.4$ Hz, 2H), 7.55 (d, Ph, $J = 8.4$ Hz, 2H), 7.97 (m, Ph, 4H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 9.98, 10.10, 28.58, 28.63, 67.92, 67.99, 72.06, 72.12, 109.45,

124.81, 126.93, 126.99, 127.69, 128.07, 128.22, 128.26, 128.97, 130.19, 130.66, 135.85, 137.13, 138.33, 138.60, 140.24, 162.84, 162.91.

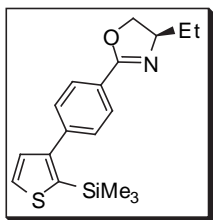
(*R*)-2-Bromo-3,3',3'',3'''-tetrakis(4-(4-ethyl-2-oxazolin-2-yl)phenyl)-5,2':5',2'':5'',2'''-quaterthiophene (8b). Yield 91% (yellow powder). mp 122.1–122.9 °C. IR (KBr, cm⁻¹): 2960,



1648, 1357, 1063, 1018, 949, 833, 750. ¹H NMR (CDCl₃, 300 MHz): δ 1.01 (m, CH₃, 12H), 1.62 (m, CH₃CH₂, 4H), 1.76 (m, CH₃CH₂, 4H), 4.07 (t, OCH₂, *J* = 8.1 Hz, 4H), 4.25 (m, OCH₂CH, 4H), 4.50 (m, OCH₂, 4H), 6.87 (s, Th-H₄, 1H), 6.90 (s, Th-H₄', 1H), 7.01 (s, Th-H₄'', 1H), 7.10 (d, Th-H₄'', *J* = 5.1 Hz, 1H), 7.33 (d, Th-H₅'', *J* = 5.1 Hz, 1H), 7.38 (d, Ph, *J* =

9.0 Hz, 2H), 7.45 (d, Ph, *J* = 9.0 Hz, 2H), 7.50 (d, Ph, *J* = 9.0 Hz, 2H), 7.52 (d, Ph, *J* = 9.0 Hz, 2H), 7.94 (m, Ph, 8H). ¹³C NMR (CDCl₃, 75 MHz): δ 9.99, 10.12, 28.60, 28.64, 67.93, 68.00, 72.05, 72.12, 109.70, 124.74, 126.92, 127.09, 127.15, 127.65, 128.04, 128.26, 128.99, 129.43, 129.65, 130.41, 130.97, 130.99, 131.12, 134.07, 134.59, 135.25, 137.05, 137.80, 138.08, 138.46, 138.55, 140.23, 162.84, 162.87, 162.88, 162.95.

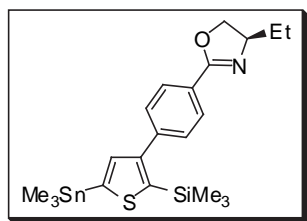
(*R*)-2-Trimethylsilyl-3-(4-(4-ethyl-2-oxazolin-2-yl)phenyl)thiophene (3). This compound was prepared from **2**. To a solution of **2** (5.00 g, 14.9 mmol) in THF (76 mL) was added dropwise 11 mL of *n*-BuLi in hexane (1.54 M, 16.4 mmol) under nitrogen at -98 °C. After the reaction mixture was stirred for 5 min, chlorotrimethylsilane (2.45 mL, 19.4 mmol) was added slowly to the mixture at -98 °C and the solution was stirred for 20 min. The reaction mixture was allowed to warm to room temperature slowly and the solvent was removed by evaporation. The residue was diluted with ether and the ethereal solution was washed with water, and dried over MgSO₄. After the solvent was removed by evaporation, the crude product was purified by silica gel chromatography with *n*-hexane-ethyl acetate (8/1, v/v) as the eluent to give **3** (4.42 g, 90%) as



a colorless oil. IR (KBr, cm⁻¹): 2958, 2894, 1649, 1408, 1352, 1249, 1061, 996, 838, 752. ¹H NMR (CDCl₃, 300 MHz): δ 0.168 (s, SiCH₃, 9H), 1.03 (t, CH₃, *J* = 7.2 Hz, 3H), 1.64 (m, CH₃CH₂, 1H), 1.79 (m, CH₃CH₂, 1H), 4.07 (t, OCH₂, *J* = 8.1 Hz, 1H), 4.26 (m, OCH₂CH, 1H), 4.50 (t, OCH₂, *J* = 9.3 Hz, 1H), 7.18 (d, Th-H₄, *J* = 4.8 Hz, 1H), 7.41 (d, Ph, *J* = 8.7 Hz, 2H), 7.58

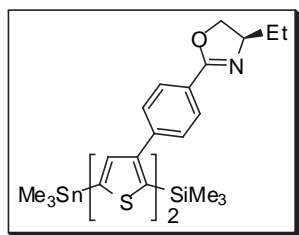
(d, Th-H₅, $J = 4.8$ Hz, 1H), 7.96 (d, Ph, $J = 8.7$ Hz, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ 0.81, 10.13, 28.66, 68.00, 72.11, 126.47, 127.68, 128.81, 129.58, 130.68, 135.59, 141.81, 149.44, 163.06.

General procedures for the stannylation at the 5-position of 2-trimethylsilyloliogothiophenes. Regioselective stannylation of 2-trimethylsilyloliogothiophenes was carried out according to the reported method¹ with a slight modification. Typical experimental procedure for the synthesis of (*R*)-2-trimethylsilyl-5-trimethylstannyl-3-(4-(4-ethyl-2-oxazolin-2-yl)phenyl)thiophene (**4**) was described below. Dry diisopropylamine (7.5 mL, 54 mmol) and dry THF (34 mL) were placed in a two-necked flask equipped with a magnetic stirrer bar and a three-way stopcock under dry nitrogen. The solution was cooled to -78 °C and to this solution was added *n*-BuLi (33 mL in hexane, 50 mmol). The solution was then warmed to room temperature, stirred for 5 min, and then cooled back to -78 °C. To a mixture of **3** (8.15 g, 24.7 mmol) and Me₃SnCl (9.9 g, 50 mmol) in THF (62 mL) at -78 °C was added the LDA solution prepared above via a cannula under stirring for 20 min, and the reaction mixture was allowed to warm to room temperature slowly. After the solvent was removed by evaporation, the residue was diluted with ether and the ethereal solution was washed with water, and then dried over MgSO₄. After evaporation of the solvent, the crude product was purified by silica gel chromatography with *n*-hexane-ethyl acetate (1/1, v/v) as the eluent to give **4** as a colorless oil



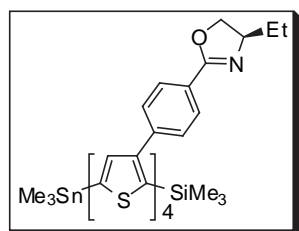
(11.9 g, 99%). IR (neat, cm⁻¹): 2960, 2897, 1650, 1356, 1250, 1065, 996, 949, 841, 755. ¹H NMR (CDCl₃, 300 MHz): δ 0.170 (s, SiCH₃, 9H), 0.392 (t, SnCH₃, $J = 27.3$ Hz, 9H), 1.03 (t, CH₃, $J = 7.5$ Hz, 3H), 1.63 (m, CH₃CH₂, 1H), 1.79 (m, CH₃CH₂, 1H), 4.07 (t, OCH₂, $J = 7.8$ Hz, 1H), 4.26 (m, OCH₂CH, 1H), 4.50 (t, OCH₂, $J = 8.1$ Hz, 1H), 7.24 (t, Th-H₄, $J = 12.0$ Hz, 1H), 7.43 (d, Ph, $J = 8.4$ Hz, 2H), 7.96 (d, Ph, $J = 8.4$ Hz, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ -8.10, 0.87, 10.15, 28.68, 68.02, 72.10, 126.30, 127.63, 128.82, 138.56, 141.97, 142.02, 142.61, 150.53, 163.14.

(*R*)-2-Trimethylsilyl-5'-trimethylstannyl-3,3'-bis(4-(4-ethyl-2-oxazolin-2-yl)phenyl)-5,2'-bithiophene (9a). Yield 99% (slightly yellow powder). mp 69.5–69.9 °C. IR (KBr, cm⁻¹): 2960,



2895, 1649, 1355, 1250, 1064, 1019, 1000, 949, 950, 839, 753. ^1H NMR (CDCl_3 , 300 MHz): δ 0.120 (s, SiCH_3 , 9H), 0.410 (s, SnCH_3 , $J = 28.8$ Hz, 9H), 1.01 (t, CH_3 , $J = 7.2$ Hz, 6H), 1.63 (m, CH_3CH_2 , 2H), 1.78 (m, CH_3CH_2 , 2H), 4.05 (m, OCH_2 , 2H), 4.25 (m, OCH_2CH , 2H), 4.49 (t, OCH_2 , $J = 7.8$ Hz, 2H), 6.97 (s, Th- H_4 , 1H), 7.14 (t, Th- H_4' , $J = 12.3$ Hz, 1H), 7.33 (d, Ph, $J = 8.4$ Hz, 2H), 7.47 (d, Ph, $J = 8.4$ Hz, 2H), 7.92 (d, Ph, $J = 7.8$ Hz, 4H). ^{13}C NMR (CDCl_3 , 75 MHz): δ -8.14, 0.80, 10.07, 10.11, 28.64, 67.94, 67.97, 72.02, 72.08, 126.38, 126.48, 127.66, 128.04, 128.67, 128.87, 129.55, 136.26, 137.41, 137.62, 138.20, 139.05, 139.19, 139.86, 141.47, 149.55, 163.04, 163.07.

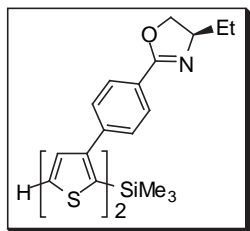
(*R*)-2-Trimethylsilyl-5'''-trimethylstannyl-3,3',3'',3'''-tetrakis(4-(4-ethyl-2-oxazolin-2-yl)phenyl)-5,2':5'',2'''-quaterthiophene (9b). Yield 98% (yellow powder). mp



128.5–129.6 °C. IR (KBr, cm^{-1}): 2960, 2930, 1648, 1357, 1250, 1064, 1019, 950, 838, 752. ^1H NMR (CDCl_3 , 500 MHz): δ 0.091 (s, SiCH_3 , 9H), 0.427 (t, SnCH_3 , $J = 28.8$ Hz, 9H), 1.01 (t, CH_3 , $J = 7.5$ Hz, 12H), 1.61 (m, CH_3CH_2 , 4H), 1.77 (m, CH_3CH_2 , 4H), 4.05 (t, OCH_2 , $J = 7.8$ Hz, 4H), 4.24 (m, OCH_2CH , 4H), 4.48 (m, OCH_2 , 4H), 6.90 (s, Th- H_4 , 1H), 6.91 (s, Th- H_4' , 1H), 6.99 (s, Th- H_4'' , 1H), 7.13 (t, Th- H_4''' , $J = 13.5$ Hz, 1H), 7.31 (d, Ph, $J = 8.7$ Hz, 2H), 7.38 (d, Ph, $J = 8.4$ Hz, 2H), 7.44 (d, Ph, $J = 8.4$ Hz, 2H), 7.51 (d, Ph, $J = 8.4$ Hz, 2H), 7.92 (m, Ph, 8H). ^{13}C NMR (CDCl_3 , 125 MHz): δ -8.12, 0.73, 10.02, 10.08, 28.62, 67.92, 67.97, 72.01, 72.07, 126.52, 126.68, 126.71, 126.89, 127.65, 128.06, 128.21, 128.68, 128.86, 128.95, 128.99, 129.16, 129.46, 130.16, 131.12, 131.98, 133.82, 134.72, 136.81, 136.93, 137.86, 138.02, 138.23, 138.33, 138.40, 138.91, 139.59, 141.29, 149.47, 162.97, 163.03.

General procedures for the Stille cross-coupling of 2-bromooligothiophenes and 2-trimethylsilyl-5-trimethylstannyloligothiophenes. Typical experimental procedures for the synthesis of (*R*)-2-trimethylsilyl-3,3'-bis(4-(4-ethyl-2-oxazolin-2-yl)phenyl)-5,2'-bithiophene (**5a**) was as follows. **2** (3.50 g, 10.4 mmol) was mixed with $\text{Pd}_2(\text{dba})_3$ (0.48 g, 0.52 mmol, 5 mol%), $\text{P}(\text{PhO})_3$ (2.7 mL, 10 mmol), CuO (0.83 g, 10 mmol) and DMF (70 mL) in a round bottomed flask under nitrogen and the mixture was stirred for 10 min at room temperature. To

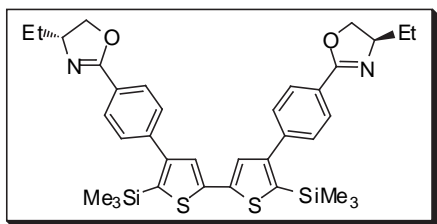
this was added **4** (6.15 g, 12.5 mmol) and the mixture was stirred at 100 °C for 15 h. The reaction mixture was then allowed to cool down to room temperature, filtered off, diluted with diethyl ether and washed with brine. After the organic layer was dried over MgSO₄, the solvent was removed by evaporation. The crude product was purified by silica gel chromatography with *n*-hexane-ethyl acetate-triethylamine (5/1/0.06, v/v/v) as the eluent to give **5a** as a slightly yellow powder (5.16 g, 85%) and **6** as a H-H byproduct (6%). **5a**: mp 44.3–45.1 °C. IR (KBr, cm⁻¹):



3068, 2959, 1648, 1357, 1250, 1062, 1018, 998, 947, 838, 752. ¹H NMR (CDCl₃, 300 MHz): δ 0.122 (s, SiCH₃, 9H), 1.01 (m, CH₃, 6H), 1.62 (m, CH₃CH₂, 2H), 1.77 (m, CH₃CH₂, 2H), 4.05 (t, OCH₂, *J* = 7.8 Hz, 2H), 4.25 (m, OCH₂CH, 2H), 4.49 (t, OCH₂, *J* = 8.1 Hz, 2H), 6.99 (s, Th-H₄, 1H), 7.10 (d, Th-H₄', *J* = 5.4 Hz, 1H), 7.29 (d, Th-H₅', *J* = 5.4 Hz, 1H), 7.33 (d, Ph, *J* = 8.4 Hz, 2H), 7.46 (d, Ph, *J* = 8.4 Hz, 2H), 7.92 (d, Ph, *J* = 7.8 Hz, 4H). ¹³C NMR (CDCl₃, 75 MHz): δ 0.78, 10.07, 10.12, 28.64, 67.94, 67.97, 72.04, 72.09, 124.47, 126.55, 127.69, 128.08, 128.67, 128.87, 130.13, 130.21, 131.64, 136.67, 137.83, 138.89, 139.51, 141.36, 149.54, 163.01.

(R)-2,2'-Bis(trimethylsilyl)-3,3'-bis(4-(4-ethyl-2-oxazolin-2-yl)phenyl)-5,5'-bithiophene

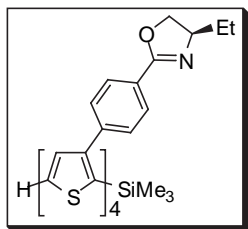
(6). Yield 6% (slightly yellow powder). mp 48.8–49.6 °C. IR (KBr, cm⁻¹): 2959, 1650, 1356,

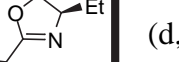


1250, 1065, 998, 839, 753, 691. ¹H NMR (CDCl₃, 300 MHz): δ 0.177 (s, SiCH₃, 18H), 1.03 (t, CH₃, *J* = 7.5 Hz, 6H), 1.64 (m, CH₃CH₂, 2H), 1.81 (m, CH₃CH₂, 2H), 4.08 (t, OCH₂, *J* = 8.0 Hz, 2H), 4.26 (m, OCH₂CH, 2H), 4.51 (t, OCH₂, *J* = 8.5 Hz, 2H), 7.28 (s, Th-H₄, 2H), 7.44 (d, Ph, *J* = 8.0 Hz, 4H), 7.97 (d, Ph, *J* = 8.0 Hz, 4H). ¹³C NMR (CDCl₃, 75 MHz): δ 0.77, 10.15, 28.66, 68.01, 72.12, 126.65, 127.50, 127.74, 128.67, 135.33, 140.66, 141.39, 150.04, 163.01.

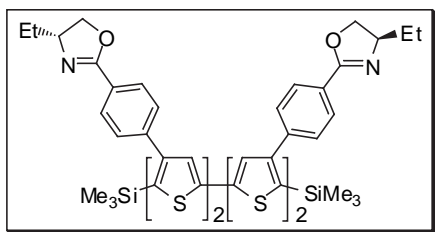
(R)-2-Trimethylsilyl-3,3',3'',3'''-tetrakis(4-(4-ethyl-2-oxazolin-2-yl)phenyl)-

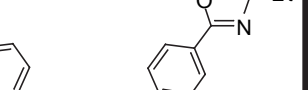
5,2':5',2'':5'',2'''-quaterthiophene (5b). Yield 84% (yellow powder). mp 126.5–127.2 °C. IR (KBr, cm⁻¹): 2959, 1647, 1356, 1249, 1063, 1018, 949, 837, 751, 681. ¹H NMR (CDCl₃, 300 MHz): δ 0.088 (s, SiCH₃, 9H), 1.00 (t, CH₃, *J* = 7.2 Hz, 12H), 1.61 (m, CH₃CH₂, 4H), 1.76 (m, CH₃CH₂, 4H), 4.05 (t, OCH₂, *J* = 7.8 Hz, 4H), 4.25 (m, OCH₂CH, 4H), 4.49 (t, OCH₂, *J* = 8.1 Hz,




4H), 6.90 (s, Th-H₄, 1H), 6.91 (s, Th-H₄', 1H), 7.00 (s, Th-H₄'', 1H), 7.10 (d, Th-H₄'', *J* = 5.1 Hz, 1H), 7.31 (d, Ph, *J* = 8.4 Hz, 2H), 7.32 (d, Th-H₅'', *J* = 5.1 Hz, 1H), 7.37 (d, Ph, *J* = 8.1 Hz, 2H), 7.45 (d, Ph, *J* = 8.4 Hz, 2H), 7.50 (d, Ph, *J* = 8.4 Hz, 2H), 7.95 (m, Ph, 8H). ¹³C NMR (CDCl₃, 75 MHz): δ 0.72, 10.01, 10.07, 28.60, 67.90, 67.95, 72.00, 72.07, 124.64, 126.50, 126.68, 126.86, 126.94, 127.64, 128.05, 128.24, 128.67, 128.84, 128.93, 128.97, 129.55, 129.59, 130.17, 130.37, 131.05, 131.45, 132.09, 133.64, 134.34, 136.97, 137.85, 138.20, 138.34, 138.37, 138.58, 138.85, 141.26, 149.47, 162.93, 162.96, 163.01.

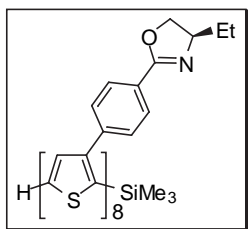
(R)-2,2'''-Bis(trimethylsilyl)-3,3',3'',3'''-tetrakis(4-(4-ethyl-2-oxazolin-2-yl)phenyl)-5,2':5',5'':2'',5'''-quaterthiophene (HH-5b). Yield 3% (yellow solid). mp 129.2–129.9 °C. IR





(KBr, cm^{-1}): 2959, 1648, 1357, 1250, 1064, 997, 950, 839, 752. ^1H NMR (CDCl_3 , 300 MHz): δ 0.125 (s, SiCH_3 , 18H), 1.02 (t, CH_3 , $J = 7.5$ Hz, 12H), 1.62 (m, CH_3CH_2 , 4H), 1.79 (m, CH_3CH_2 , 4H), 4.07 (m, OCH_2 , 4H), 4.26 (m, OCH_2CH , 4H), 4.51 (m, OCH_2 , 4H) 7.01 (s, Th- H_4 , H_4''' , 2H), 7.19 (s, Th- H_4' , H_4'' , 2H), 7.34 (d, Ph, $J = 8.7$ Hz, 4H), 7.50 (d, Ph, $J = 8.7$ Hz, 4H), 7.94 (m, Ph, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 0.75, 10.09, 10.10, 28.63, 67.97, 72.07, 72.09, 126.60, 126.85, 126.91, 127.71, 128.18, 128.65, 128.86, 130.00, 130.81, 134.90, 136.94, 138.44, 139.06, 141.20, 149.64, 162.93, 162.99.

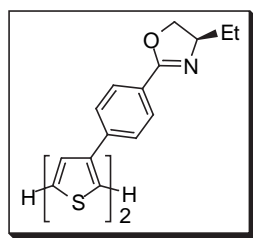
(R)-2-Trimethylsilyl-3,3',3'',3''',3''''',3''''',3''''''-octakis(4-(4-ethyl-2-oxazolin-2-yl)phenyl)-5,2':5'',2''':5''',2''''':5''''',2''''':5''''',2''''''-octithiophene



(5c). Yield 75% (orange powder). mp 172 °C (dec.). IR (KBr, cm⁻¹): 2960, 2929, 1648, 1358, 1250, 1064, 1018, 949, 837, 751, 688. ¹H NMR (CDCl₃, 500 MHz): δ 0.088 (s, SiCH₃, 9H), 1.00 (m, CH₃, 24H), 1.60 (m, CH₃CH₂, 8H), 1.77 (m, CH₃CH₂, 8H), 4.04 (m, OCH₂, 8H), 4.24 (m, OCH₂CH, 8H), 4.48 (m, OCH₂, 8H), 6.87 (s, Th-H₄'', H₄'', H₄'', 3H), 6.89 (s, Th-H₄', H₄', 2H), 6.91 (s, Th-H₄, 1H), 7.01 (s, Th-H₄'''', 1H), 7.09 (d, Th-H₄'''', *J* = 5.0 Hz, 1H), 7.30 (d, Ph, *J* = 8.5 Hz, 2H), 7.31 (d, Th-H₅'''', *J* = 5.0 Hz, 1H), 7.36 (d, Ph, *J* = 8.5 Hz, 2H),

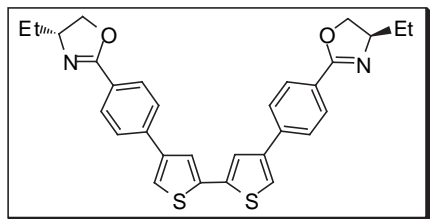
7.42 (m, Ph, 8H), 7.45 (d, Ph, $J = 8.5$ Hz, 2H), 7.50 (d, Ph, $J = 8.5$ Hz, 2H), 7.92 (m, Ph, 16H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 0.54, 9.86, 9.93, 28.47, 67.82, 67.88, 71.96, 72.03, 124.77, 126.53, 126.68, 126.91, 126.94, 127.03, 127.05, 127.07, 127.70, 128.11, 128.27, 128.32, 128.74, 128.92, 129.05, 129.61, 129.66, 129.71, 130.22, 130.46, 131.06, 131.32, 131.45, 131.49, 131.53, 131.66, 132.18, 133.65, 133.78, 133.87, 133.91, 133.98, 134.56, 137.04, 137.90, 138.13, 138.19, 138.21, 138.25, 138.38, 138.42, 138.44, 138.50, 138.65, 138.93, 141.36, 149.55, 163.07, 163.17.

General procedures for the deprotection of 2-trimethylsilyloliogothiophenes. Desilylation of 2-trimethylsilyloliogothiophenes was carried out in THF with Bu_4NF (1.0 M in THF). Typical experimental procedure for the synthesis of (*R*)-4,3'-bis(4-(4-ethyl-2-oxazolin-2-yl)phenyl)-2,2'-bithiophene (**7a**) was described below. To a solution **5a** (5.16 g, 8.82 mmol) in THF (60 mL), Bu_4NF (25 mL in THF, 25 mmol) was added dropwise and the mixture was stirred for 20 min at room temperature. After the solvent was removed by evaporation, the residue was diluted with ether and the ethereal solution was washed with brine. The organic layer was dried over MgSO_4 and the solvent was removed by evaporation. The crude product was purified by silica gel chromatography with *n*-hexane-ethyl acetate 2/1 (v/v) as the eluent to give **7a** as a slightly yellow powder (4.32 g, 96%). mp 45.4–46.3 °C. $[\alpha]_{\text{D}}^{25} + 59.0^\circ$ ($c = 1.00$, CHCl_3). IR (KBr, cm^{-1}): 2960,



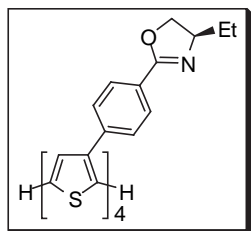
2874, 1645, 1358, 1288, 1063, 1017, 948, 831, 724. ^1H NMR (CDCl_3 , 500 MHz): δ 1.00 (t, CH_3 , $J = 7.5$ Hz, 6H), 1.62 (m, CH_3CH_2 , 2H), 1.78 (m, CH_3CH_2 , 2H), 4.05 (t, OCH_2 , $J = 8.0$ Hz, 2H), 4.24 (m, OCH_2CH , 2H), 4.48 (t, OCH_2 , $J = 8.5$ Hz, 2H), 7.11 (d, Th- H_4' , $J = 5.5$ Hz, 1H), 7.31 (d, Th- H_5' , $J = 5.5$ Hz, 1H), 7.32 (d, Th- H_3 , $J = 1.5$ Hz, 1H), 7.38 (d, Th- H_5 , $J = 1.5$ Hz, 1H), 7.44 (d, Ph, $J = 8.5$ Hz, 2H), 7.54 (d, Ph, $J = 8.5$ Hz, 2H), 7.94 (m, Ph, 4H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 9.89, 9.96, 28.51, 28.54, 67.89, 67.94, 72.00, 72.07, 121.85, 124.62, 125.64, 125.87, 126.48, 126.81, 128.23, 128.65, 129.10, 130.16, 131.66, 136.51, 137.85, 138.41, 138.81, 141.23, 163.07, 163.13. HRMS (FAB $^+$): Calcd for $\text{C}_{30}\text{H}_{29}\text{N}_2\text{O}_2\text{S}_2$ ($\text{M}+\text{H}$), 513.1673; Found, 513.1667. Anal. Calcd for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2\text{S}_2$: C, 70.28; H, 5.50; N, 5.46. Found: C, 70.19; H, 5.45; N, 5.51.

(R)-4,4'-Bis(4-(4-ethyl-2-oxazolin-2-yl)phenyl)-2,2'-bithiophene (HH-7a). Yield 88%



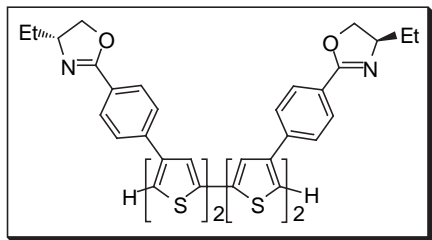
(slightly yellow solid). mp 252.3–253.3 °C. $[\alpha]_D^{25} + 54.3^\circ$ ($c = 0.50$, CHCl_3). IR (KBr, cm^{-1}): 3105, 2956, 2930, 2871, 1644, 1397, 1074, 977, 867, 850, 730. ^1H NMR (CDCl_3 , 300 MHz): δ 1.04 (t, CH_3 , $J = 7.5$ Hz, 6H), 1.65 (m, CH_3CH_2 , 2H), 1.81 (m, CH_3CH_2 , 2H), 4.07 (t, OCH_2 , $J = 7.8$ Hz, 2H), 4.26 (m, OCH_2CH , 2H), 4.50 (t, OCH_2 , $J = 7.8$ Hz, 2H), 7.44 (d, Th- H_3 , $J = 1.5$ Hz, 2H), 7.53 (d, Th- H_5 , $J = 1.5$ Hz, 4H), 7.66 (d, Ph, $J = 8.4$ Hz, 4H), 7.99 (d, Ph, $J = 8.4$ Hz, 4H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 10.05, 28.62, 67.94, 72.05, 120.26, 122.69, 125.84, 126.54, 128.60, 137.71, 137.81, 141.82, 162.90. HRMS (FAB+): Calcd for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2\text{S}_2$ (M^+), 512.1594; Found, 513.1588. Anal. Calcd for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2\text{S}_2$: C, 70.28; H, 5.50; N, 5.46. Found: C, 70.05; H, 5.43; N, 5.37.

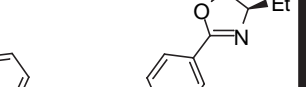
(R)-4,3',3'',3'''-Tetrakis(4-(4-ethyl-2-oxazolin-2-yl)phenyl)-2,2':5',2'':5'',2'''-quaterthiophene (7b). Yield 92% (yellow powder). mp 112.0–112.6 °C. $[\alpha]_D^{25} + 57.2^\circ$ ($c =$



1.00, CHCl_3). IR (KBr, cm^{-1}): 2959, 2928, 1646, 1358, 1064, 1018, 949, 833. ^1H NMR (CDCl_3 , 500 MHz): δ 1.00 (t, CH_3 , $J = 7.0$ Hz, 12H), 1.61 (m, CH_3CH_2 , 4H), 1.78 (m, CH_3CH_2 , 4H), 4.05 (m, OCH_2 , 4H), 4.25 (m, OCH_2CH , 4H), 4.48 (m, OCH_2 , 4H), 6.92 (s, Th- H_4' , 1H), 7.01 (s, Th- H_4'' , 1H), 7.10 (d, Th- H_4''' , $J = 5.5$ Hz, 1H), 7.22 (d, Th- H_3 , $J = 1.5$ Hz, 1H), 7.32 (d, Th- H_5''' , $J = 5.5$ Hz, 1H), 7.33 (d, Th- H_5 , $J = 1.5$ Hz, 1H), 7.36 (d, Ph, $J = 8.5$ Hz, 2H), 7.46 (d, Ph, $J = 8.5$ Hz, 2H), 7.50 (d, Ph, $J = 8.5$ Hz, 2H), 7.51 (d, Ph, $J = 8.5$ Hz, 2H), 7.93 (m, Ph, 8H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 9.88, 9.94, 9.97, 9.98, 28.52, 67.87, 67.92, 67.94, 71.99, 72.06, 72.10, 122.03, 124.78, 125.64, 125.89, 126.44, 126.95, 126.96, 127.08, 128.22, 128.36, 128.61, 129.05, 129.10, 129.11, 129.48, 129.73, 130.49, 131.13, 131.44, 132.09, 133.86, 134.57, 135.91, 137.75, 138.28, 138.29, 138.39, 138.42, 138.53, 138.70, 141.20, 163.087, 163.094, 163.14. MS (FAB+): Calcd for $\text{C}_{60}\text{H}_{55}\text{N}_4\text{O}_4\text{S}_4$ (M^+H), 1023; Found, 1023. Anal. Calcd for $\text{C}_{60}\text{H}_{54}\text{N}_4\text{O}_4\text{S}_4$: C, 70.42; H, 5.32; N, 5.47. Found: C, 70.42; H, 5.24; N, 5.53.

quaterthiophene (HH-7b). Yield 91% (yellow solid). mp 269.4–270.1 °C. $[\alpha]_{\text{D}}^{25} + 52.9^{\circ}$ ($c =$

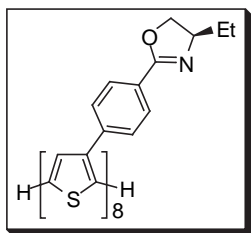


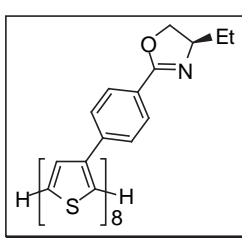


0.50, CHCl_3). IR (KBr, cm^{-1}): 2959, 1646, 1360, 1066, 1019, 957, 821, 733. ^1H NMR (CDCl_3 , 500 MHz): δ 1.01 (m, CH_3 , 12H), 1.60 (m, CH_3CH_2 , 4H), 1.78 (m, CH_3CH_2 , 4H), 4.06 (m, OCH_2 , 4H), 4.26 (m, OCH_2CH , 4H), 4.49 (m, OCH_2 , 4H), 7.22 (s, Th- H_4' , Th- H_4'' , 2H), 7.35 (d, Th- H_3 , Th- H_3''' , $J = 1.5$ Hz, 2H), 7.38 (d, Th- H_5 , Th- H_5''' , $J = 1.5$ Hz, 2H), 7.49 (d, Ph, $J = 8.4$ Hz, 4H), 7.55 (d, Ph, $J = 8.4$ Hz, 4H), 7.96 (m, Ph, 8H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 10.04, 10.13, 28.60, 28.63, 67.89, 67.98, 72.01, 72.12, 121.92, 125.44, 125.76, 126.44, 126.72, 127.08, 128.24, 128.56, 129.01, 130.81, 134.88, 135.92, 137.55, 138.19, 138.86, 141.19, 162.87, 162.88. MS (FAB $^+$): Calcd for $\text{C}_{60}\text{H}_{55}\text{N}_4\text{O}_4\text{S}_4$ ($\text{M}+\text{H}$), 1023; Found, 1023. Anal. Calcd for $\text{C}_{60}\text{H}_{54}\text{N}_4\text{O}_4\text{S}_4$: C, 70.42; H, 5.32; N, 5.47. Found: C, 70.29; H, 5.33; N, 5.33.

(R)-4,3',3'',3''',3''',3''',3''',3'''-Octakis(4-(4-ethyl-2-oxazolin-2-yl)phenyl)-

2,2':5',2'':5'',2''':5''',2''':5''',2''':5''',-2''':5''',2''':5'''-octithiophene (7c). Yield



 81% (red solid). mp 165 °C (dec.). $[\alpha]_{\text{D}}^{25} + 56.2^{\circ}$ ($c = 1.00$, CHCl_3). IR (KBr, cm^{-1}): 2959, 2928, 1646, 1358, 1064, 1018, 949, 834, 751, 680. ^1H NMR (CDCl_3 , 500 MHz): δ 1.01 (m, CH_3 , 24H), 1.61 (m, CH_3CH_2 , 8H), 1.77 (m, CH_3CH_2 , 8H), 4.04 (m, OCH_2 , 8H), 4.23 (m, OCH_2CH , 8H), 4.48 (m, OCH_2 , 8H), 6.88 (s, Th- H_4'' , H_4''' , H_4'''' , 3H), 6.89 (s, Th- H_4''''' , 1H), 6.91 (s, Th- H_4' , 1H), 7.01 (s, Th- H_4'''''' , 1H), 7.10 (d, Th- H_4''''''' , $J = 5.0$ Hz, 1H), 7.21 (d, Th- H_3 , $J = 1.5$ Hz, 1H), 7.31 (d, Th- H_5'''''' , $J = 5.0$ Hz, 1H), 7.32 (d, Th- H_5 , $J = 1.5$ Hz, 1H), 7.35 (d, Ph, $J = 8.5$ Hz, 2H), 7.43 (m, Ph, 10H), 7.50 (m, Ph, 4H), 7.88 (d, Ph, $J = 8.5$ Hz, 2H), 7.92 (m, Ph, 12H), 7.96 (d, Ph, $J = 8.5$, 2H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 9.89, 9.96, 28.52, 67.87, 67.94, 71.99, 72.08, 122.02, 124.80, 125.62, 125.89, 126.43, 126.92, 126.98, 127.06, 127.11, 127.14, 128.20, 128.36, 128.61, 129.10, 129.48, 129.76, 130.50, 131.11, 131.37, 131.49, 131.52, 131.53, 131.58, 132.10, 133.80, 133.94, 133.96, 134.03, 134.60, 135.92, 137.75, 138.18, 138.20, 138.25, 138.27, 138.37, 138.40, 138.46, 138.50, 138.55, 138.69, 141.18, 163.10, 163.14.

MS (FAB+): Calcd for $C_{120}H_{107}N_8O_8S_8$ (M+H), 2044; found, 2044. Anal. Calcd for $C_{120}H_{106}N_8O_8S_8$: C, 70.49; H, 5.23; N, 5.48. Found: C, 70.53; H, 5.24; N, 5.35.

References

- (1) Yashima, E.; Goto, H.; Okamoto, Y. *Macromolecules* **1999**, *32*, 7942-7945.
- (2) Barbarella, G.; Zambianchi, M.; Bongini, A.; Antolini, L. *Adv. Mater.* **1994**, *6*, 561-564.

Table S-1. Analytical Data of Oligothiophenes

oligothiophene	mp (°C)	[α] _D ^a	absorption ^b	emission ^c		elemental analysis		molecular weight	
			λ_{max} (nm)	λ_{ex} (nm)	λ_{em} (nm)	Calcd	Found	Calcd	Found ^d
1 (monomer)	104.5-105.0	62	287	331	393	C, 70.01; H, 5.87; N, 5.44	C, 70.02; H, 5.93; N, 5.44	257.0874	257.0909
7a (2-mer)	45.4-46.3	59	275	358	447	C, 70.28; H, 5.50; N, 5.46	C, 70.19; H, 5.45; N, 5.51	513.1673	513.1667
7b (4-mer)	112.0-112.6	57	282, 390	444	510	C, 70.42; H, 5.32; N, 5.47	C, 70.42; H, 5.24; N, 5.53	1023	1023
7c (8-mer)	165 (dec.)	56	281, 435	508	561	C, 70.49; H, 5.23; N, 5.48	C, 70.53; H, 5.24; N, 5.35	2044	2044
HH-dimer (6)	252.3-253.3	54 ^e	285 ^f	352	385	C, 70.28; H, 5.50; N, 5.46	C, 70.05; H, 5.43; N, 5.37	512.1594	512.1588
HH-tetramer	269.4-270.1	53 ^e	284, 393 ^f	449	476, 500	C, 70.42; H, 5.32; N, 5.47	C, 70.29; H, 5.33; N, 5.33	1023	1023

^a 1.0 g/dL in CHCl₃ at 25 °C. ^b 0.25 mg/mL in CHCl₃ at rt. ^c 0.15 mg/mL in CHCl₃ at rt. ^d Estimated by fast atom bombardment (FAB) mass spectra.

^e 0.50 g/dL in CHCl₃ at 25 °C. ^f 0.15 mg/mL in CHCl₃ at rt.

Metal-Induced Chirality Induction

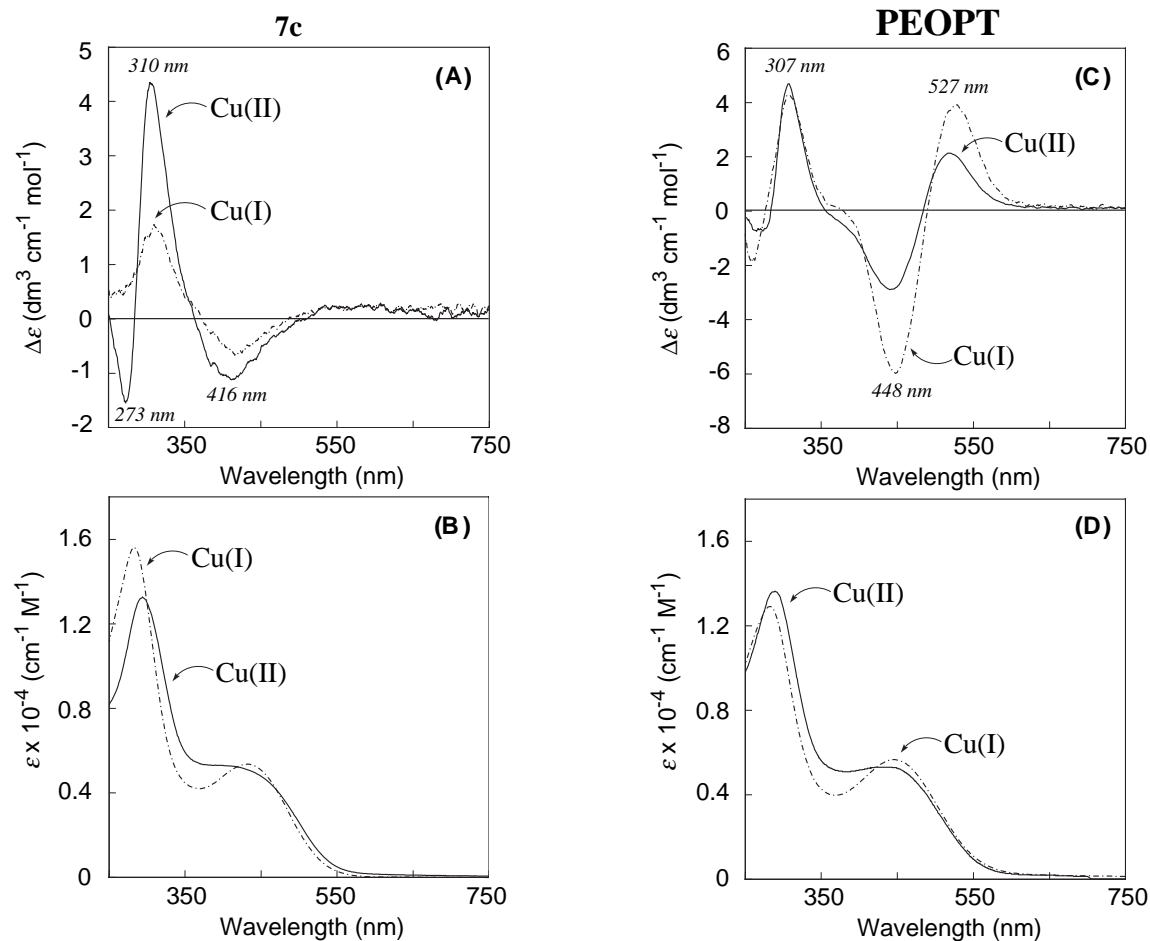


Figure S-1. CD (A, C) and UV-visible (B, D) spectra of **7c** and **PEOPT** in the presence of $\text{Cu}(\text{OTf})_2$ and $\text{Cu}(\text{OTf}) \cdot 0.5\text{C}_6\text{H}_6$ in chloroform at rt. $[\text{Cu}]/[\text{Monomer units of } \mathbf{7c} \text{ or } \mathbf{PEOPT}] = 0.5$.