Supporting Information

Completely Encapsulated Oligothiophenes up to 12-mer

Yutaka Ie, Han Aihong, Tetsuo Otsubo, and Yoshio Aso*

The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan, CREST, Japan Science and Technology Agency (JST), and Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

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General Information

Column chromatography was performed on silica gel, KANTO Chemical silica gel 60N (40–50 μm). TLC plates were visualized with UV, or in an iodine chamber. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration. Preparative gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908 equipped with a JAI-GEL 2.5H/3H. Analytical gel permeation liquid chromatography (GPLC) was performed on a Hitachi High-Technologies Corporation L-2420/L-2130 equipped with a shodex K-803L. Mass spectra were obtained on a Voyager Linear DE-H MALDI-TOF-MS, a PerSeptive Biosystems. Elemental analyses were performed on a Perkin Elmer LS-50B by the Elemental Analysis Section of Materials Analysis Center of ISIR, Osaka University. UV-visible spectra were recorded on a Shimadzu UV-3100PC spectrophotometer equipped with nonfocused optics in an environmental chamber Oxford Optistat-DN cryostat. All spectra were obtained in spectrograde solvents. The concentrations of solutions were adjusted to yield an absorptivity of A<0.1 in the absorption spectrum for any fluorescence experiments. Cyclic voltammetry was carried out on a BAS CV-50W Voltammetric Analyzer.

Materials: All reactions were carried out under a nitrogen or argon atmosphere. Solvents of the highest purity grade were used as received. Unless stated otherwise, all reagents were purchased from commercial sources and used without purification. 5,5-Bis(hydroxymethyl)cyclopenta[*c*]thiophene (**2**) was prepared by reported procedure.[1]

Experimental Procedure

5,5-Bis(*tert*-butyldiphenylsiloxy)cyclopenta[*c*]thiophene (**1T**). A mixture of 5,5-bis(hydroxymethyl)cyclopenta[*c*]thiophene (**2**) (1.35 g, 7.3 mmol), imidazole (2.01 g, 29.6 mmol) in DMF(25 mL) was added dropwise *tert*-butylchlorodiphenylsilane (TBDPSCl) (5.0 mL, 19.5 mmol) within 10 min. by syringe at room temperature in argon atmosphere, and the mixture was stirred for 4 h. After water was added, the reaction mixture was extracted with ethyl acetate, and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/chloroform=3/1) to give a colorless solid of 5,5-bis(*tert*-butyldiphenylsiloxy)cyclopenta[*c*]thiophene (**1T**) (4.69g, 97%), followed by recrystallization from hexane/acetone to give colorless plates of **1T**. Mp: 125-127 °C; ^1H NMR ($CDCl_3$): δ 1.03 (s, 18H), 2.60 (s, 4H), 3.74 (s, 4H), 6.69 (s, 2H), 7.26-7.42 (m, 12H), 7.60-7.64 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 19.48, 26.94, 32.74, 57.95, 66.25, 114.67, 127.53, 129.44, 133.45, 135.50, 146.58; MS (DI): *m/z* = 660 (M^+); Anal. Calcd. for $C_{41}H_{48}O_2SSi_2$ C, 74.49; H, 7.32. Found: C, 74.27; H, 7.24.

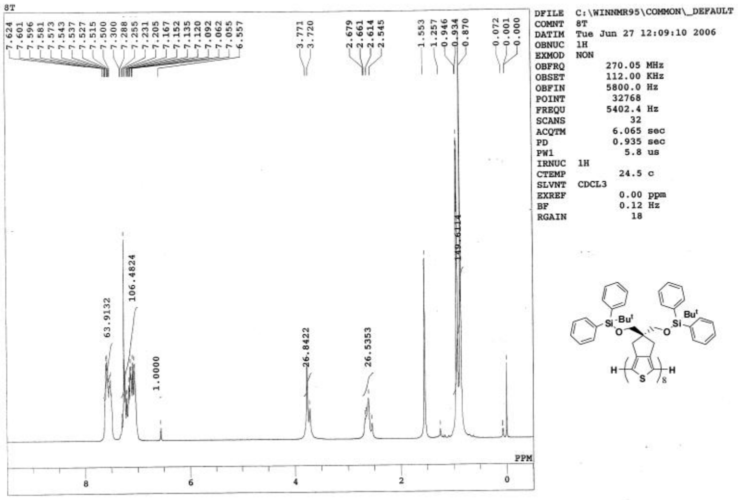
2T. Into an ice-cooled solution of **1T** (823 mg, 1.24 mmol) in dry THF (14 mL) was added dropwise *n*-butyllithium (1.9 mL, 3.0 mmol, 1.6 M solution in hexane) by syringe in argon atmosphere. The mixture was stirred for 1 h at 0 °C, and then iron(III) acetylacetonate ($Fe(acac)_3$) (888 mg, 2.51 mmol) was added at 0 °C. After reflux overnight, insoluble solid was filtered off, then washed with chloroform, and the filtrate was concentrated. The residue was firstly isolated by column chromatography on silica gel with hexane/chloroform (2/1) as eluent, and then the fraction containing **2T** was further purification by preparative gel permeation chromatography (JAIGEL 2.5H/3H) with chloroform as eluent to give a pale yellow powder of **2T** (700 mg, 86%). Mp: 76-77 °C; ^1H NMR ($CDCl_3$): δ 1.03 (s, 36H), 2.60 (s, 4H), 2.73 (s, 4H), 3.76 (s, 8H), 6.59 (s, 2H), 7.21-7.36 (m, 24H), 7.60-7.65 (m, 16H); ^{13}C NMR ($CDCl_3$): δ 19.48, 26.99, 33.06, 34.05, 57.98, 66.35, 113.13, 127.53, 127.56, 133.30, 133.43, 135.49, 135.51, 141.88, 146.85; MS (MALDI-TOF, trihydroxyanthracene, matrix) *m/z* 1324.2 (M^+, Calcd 1319.6); Anal. Calcd. for $C_{82}H_{94}O_4S_2Si_4$ C, 74.61; H, 7.18. Found: C, 74.62; H, 6.91.

4T and 6T. To a solution of **2T** (1.22 g, 0.93 mmol) in dry THF (20 mL) at –78 °C, *n*-butyllithium (0.93 mL, 1.49 mmol, 1.6 M solution in hexane) was added, and the temperature was kept for 1 h with stirring. After adding iron(III) acetylacetonate ($Fe(acac)_3$) (660 mg, 1.87 mmol) at –78 °C, the reaction mixture was heated to reflux overnight. The resulting mixture was cooled to room temperature, filtered, washed with THF, then the filtrate was concentrated. The residue was isolated by column chromatography on silica gel with hexane/chloroform (3/2) as eluent, followed by further purification by preparative gel-permeation liquid chromatography (JAIGEL 2.5H/3H) with chloroform as eluent to give a yellow solid of **4T** (737 mg, 60%) with a brown solid of **6T** (148 mg, 12%) and **8T** (22 mg, 2%). **4T**: Mp: 202-203 °C; ^1H NMR ($CDCl_3$): δ 0.97 (s, 36H), 0.99 (s, 36H), 2.56 (s, 4H), 2.68 (s, 4H), 2.72 (s, 8H), 3.75 (s, 8H), 3.81 (s, 8H), 6.57 (s, 2H), 7.12-7.34 (m, 48H), 7.55-7.66 (m, 32H); ^{13}C NMR ($CDCl_3$): δ 19.41, 26.93, 26.97, 33.64, 34.09, 34.78, 57.88, 57.97, 66.16, 113.23, 125.99, 126.07, 127.49, 127.53, 127.56, 129.42, 133.04, 133.07, 133.38, 133.49, 135.46, 135.50, 141.36, 141.36, 141.83, 142.56, 147.21; MS (MALDI-TOF, trihydroxyanthracene, matrix) *m/z* 2642.9 (M^+, Calcd 2637.1); Anal. Calcd. for $C_{164}H_{186}O_8S_4Si_8$ C, 74.66; H, 7.11. Found: C, 74.37; H, 6.99. **6T**: Mp: 208-210 °C; ^1H NMR ($CDCl_3$): δ 0.89 (s, 36H), 0.93 (s, 36H), 1.00 (s, 36H), 2.53 (s, 4H), 2.63 (s, 12H), 2.66 (s, 4H), 2.68 (s, 4H), 3.72 (s, 8H), 3.78 (s, 16H), 6.55 (s, 2H), 7.04-7.32 (m, 72H), 7.49-7.62 (m, 48H); ^{13}C NMR ($CDCl_3$): δ 19.24, 19.36, 26.87, 26.92, 32.00, 33.45, 33.46, 33.76, 34.31, 34.67, 35.07, 57.79, 57.89, 65.81, 66.17, 66.18, 113.22, 126.01, 126.05, 127.43, 127.44, 127.50, 127.53, 129.39, 132.94, 132.96, 132.99, 133.09, 133.42, 133.49, 135.43, 135.48, 141.28, 141.74, 141.95, 142.06, 142.65, 147.32; MS (MALDI-TOF, trihydroxyanthracene, matrix) *m/z* 3959.3 (M^+, Calcd 3955.7).

8T and 12T. To a solution of **4T** (737 mg, 0.28 mmol) in dry THF (10 mL) at –78 °C, *n*-butyllithium (0.67 mL, 1.07 mmol, 1.6 M solution in hexane) was added, and the temperature was kept for 1 h with stirring. After adding iron(III) acetylacetonate ($Fe(acac)_3$) (204 mg, 0.58 mmol) at –78 °C, the reaction mixture was heated to reflux overnight. The resulting mixture was cooled to room temperature, filtered, washed with THF, then the filtrate was concentrated. The residue was isolated by column chromatography on silica gel with chloroform as eluent, followed by further purification by preparative gel permeation chromatography (JAIGEL 2.5H/3H) with chloroform as eluent to give a yellow solid of **8T** (203 mg, 27%) with a red solid of **12T** (100 mg, 14%). **8T** was further purified by a reprecipitation method with $CHCl_3$/hexane. **8T**: Mp: 216-218 °C; ^1H NMR ($CDCl_3$): δ 0.87 (s, 72H), 0.93 (s, 36H), 0.95 (s, 36H), 2.55-2.68 (m, 32H), 3.72-3.77 (m, 32H), 6.56 (s, 2H), 7.06-7.30 (m, 96H), 7.50-7.63 (m, 64H); ^{13}C NMR ($CDCl_3$): δ 19.07, 19.21, 26.67, 26.69, 26.72, 26.75, 33.23, 33.48, 33.78(x2), 34.12, 34.54, 34.86, 35.09, 57.63, 57.66, 57.77, 57.84, 65.60, 66.06, 66.08, 113.09, 125.88, 125.91, 125.95, 127.28, 127.31, 127.36, 127.39, 129.25, 129.26, 132.73, 132.81, 132.91, 133.00, 133.30, 133.35, 135.25, 135.30, 131.14, 141.60, 141.77, 141.81, 141.93, 142.05, 142.58, 147.23; MS (MALDI-TOF, trihydroxyanthracene, matrix) *m/z* 5273.6 (M^+, Ca1cd 5272.2). **12T**; Mp: 228-231 °C; ^{1}H NMR ($CDCl_3$): δ 0.76-0.87 (m, 216H), 2.52-2.61 (m, 48H), 3.57-3.69 (m, 48H), 6.56 (s, 2H), 6.97-7.22 (m, 144H), 7.44-7.55 (m, 96H), MS (MALDI-TOF, trihydroxyanthracene, matrix) *m/z* 7913.3 (M^+, Ca1cd 7908.3).

Representative ^{1}H NMR Spectra and GPLC Charts

8T



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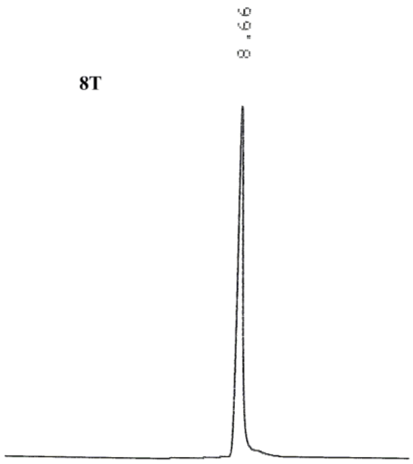

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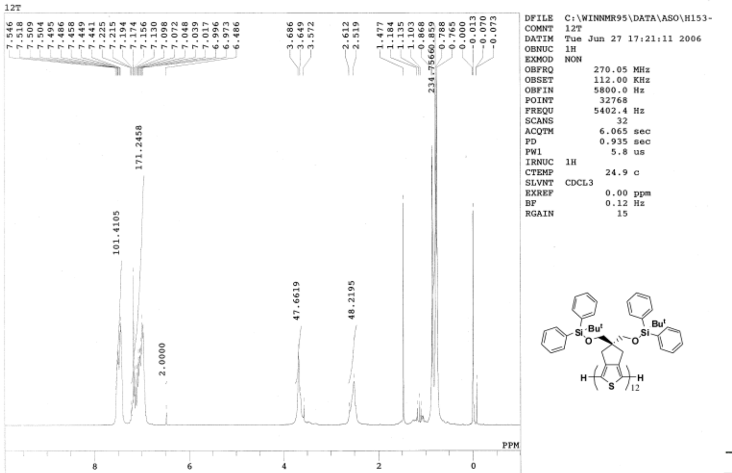

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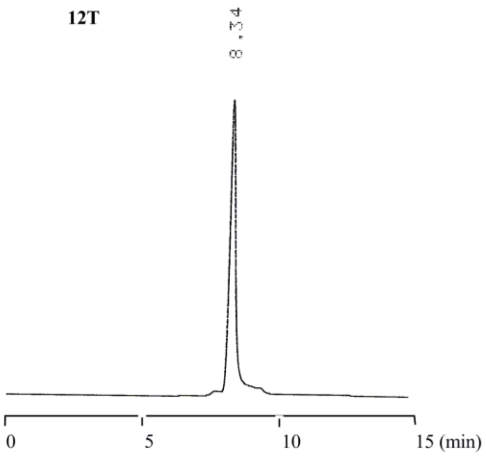
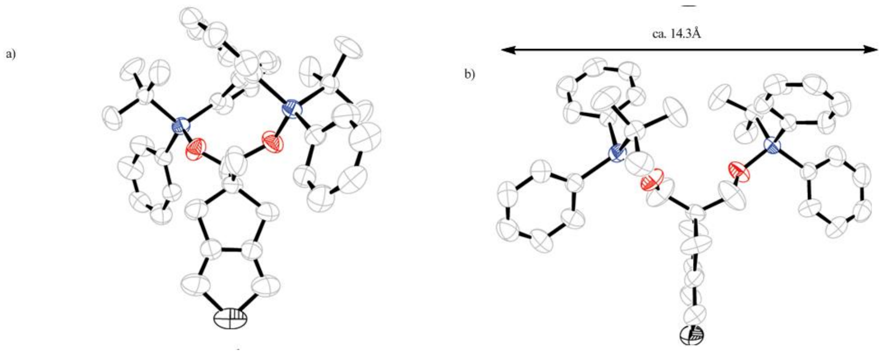


X-ray Structural Analysis

The diffraction data of **1T** and **4T** were collected on Rigaku AFC7R with monochromated Mo Kα (λ = 0.71069 Å) radiation. The structures were determined by a direct method (SIR 92). The non-hydrogen atoms were refined anisotropically. Structure refinement is not converged for **4T**, because the additional refinement cycles caused the diffusion of structure due to the presence of weak density of solvent. However, other crystal parameters have ensured the structural determination of **4T**. CCDC-664092 (**1T**) and CCDC-664093 (**4T**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif/. Single crystals of **1T** suitable for X-ray crystallography were obtained by recrystallization from hexane/acetone. Single crystal of composition **4T**•hexane•2(chloroform) suitable for X-ray crystallography was obtained by recrystallization from hexane/chloroform.

Crystal data for 1T: $C_{41}H_{48}SSi_2O_2$, M = 661.06, monoclinic, space group $C2/c$ (No. 15), a = 18.965(5), b = 11.822(2), c = 17.550(3) Å, β = 111.178(2)°, V = 3669.1(1) $Å^3$, Z = 4, D_{calc} = 1.197 g cm^{-3}, $F_{(000)}$ = 1416.00, μ = 1.872 cm^{-1} (MoK_α; λ = 0.71069 Å), 6182 reflections measured, 5358 unique (R_{int} = 0.029), R = 0.085, wR = 0.081 for $I>3\sigma(I)$, S = 2.50, $\Delta\rho_{max}$ = 2.17 e $Å^{-3}$, $\Delta\rho_{min}$ = –0.64 e $Å^{-3}$.

Fig. S1 Ortep drawing of **1T** at the 50% probability level. (a) top view (b) side view.



Reference

1) T. Izumi, S. Kobashi, K. Takimiya, Y. Aso and T. Otsubo, *J. Am. Chem. Soc.*, 2003, **125**, 5286–5287.