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Synthesis of 10-nm Scale Oligothiophene Molecular Wires Bearing Anchor Units at Both Terminal Positions

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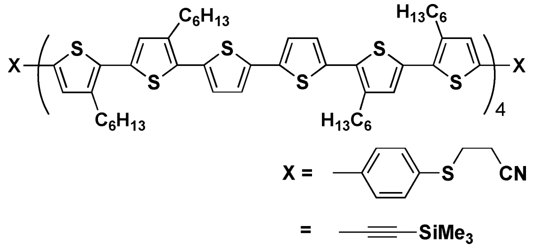

Oligothiophenes with the length of ca.10 nm bearing anchor units (a protected thiol group or trimethylsilylethynyl) at both terminal positions in the conjugated backbone have been synthesized by the block-coupling synthetic strategy. Their electronic properties were clarified by spectroscopic and electrochemical measurements.

Nanometer-scale π-conjugated molecules are recently attracting great attention due to their potential application as molecular wires in developing single-molecule electronics and related fields.[1] Electrical characterization of these molecular wires is thus a real issue for the fundamental science of molecular electronics and has been actively investigated by using few-nanometer conjugated molecules with scanning probe, break-junction, and electromigration methodologies.[2] For further practical progress, the electrical measurement requires a chemically synthesized nanostructure whose size is comparable to the 10-nm scale separations of metallic electrodes connected to macroscopic electric circuits, which has usually been accomplished by current nanofabrication technology based on electron beam lithography.[3] Recent outstanding progress in organic synthetic techniques has enabled us to access lengthened conjugated oligomers,[4] and several groups have reported the syntheses of the 10-nm scale aryleneethynylene or arylenevinylene molecular wires terminated with anchor groups that could be covalently connected to metal electrode surfaces.[5] We have previously reported the synthesis of long oligothiophenes whose molecular lengths far exceed 10 nm and have revealed that oligothiophenes are one of the most promising molecular wires due to their long effective conjugation lengths and high carrier transport properties.[6,7] We now report the synthesis of the fully conjugated thiophene 24-mers **RS−24T−SR** and **TMSA−24T−ATMS** bearing protected thiol and trimethylsilylethynyl anchor groups, respectively, at both terminal positions.[8,9] Their molecular sizes correspond to the length of ca. 10 nm.

The synthesis of **RS−24T−SR** and **TMSA−24T−ATMS** is outlined in Scheme 1. Our synthetic strategy relies on a block-coupling method of the three large building components for ease of isolation and purification of the desired products from the starting blocks based on their molecular sizes. The tetrahexyl-substituted sexithiophene **6T**[7a] was chosen as the block element because the number of the alkyl groups and their symmetrical arrangement guarantee not only to maintain sufficient solubility of the thiophene 24-mer but also to prevent the formation of regioisomers. Thus, one terminal building block **2** bearing the

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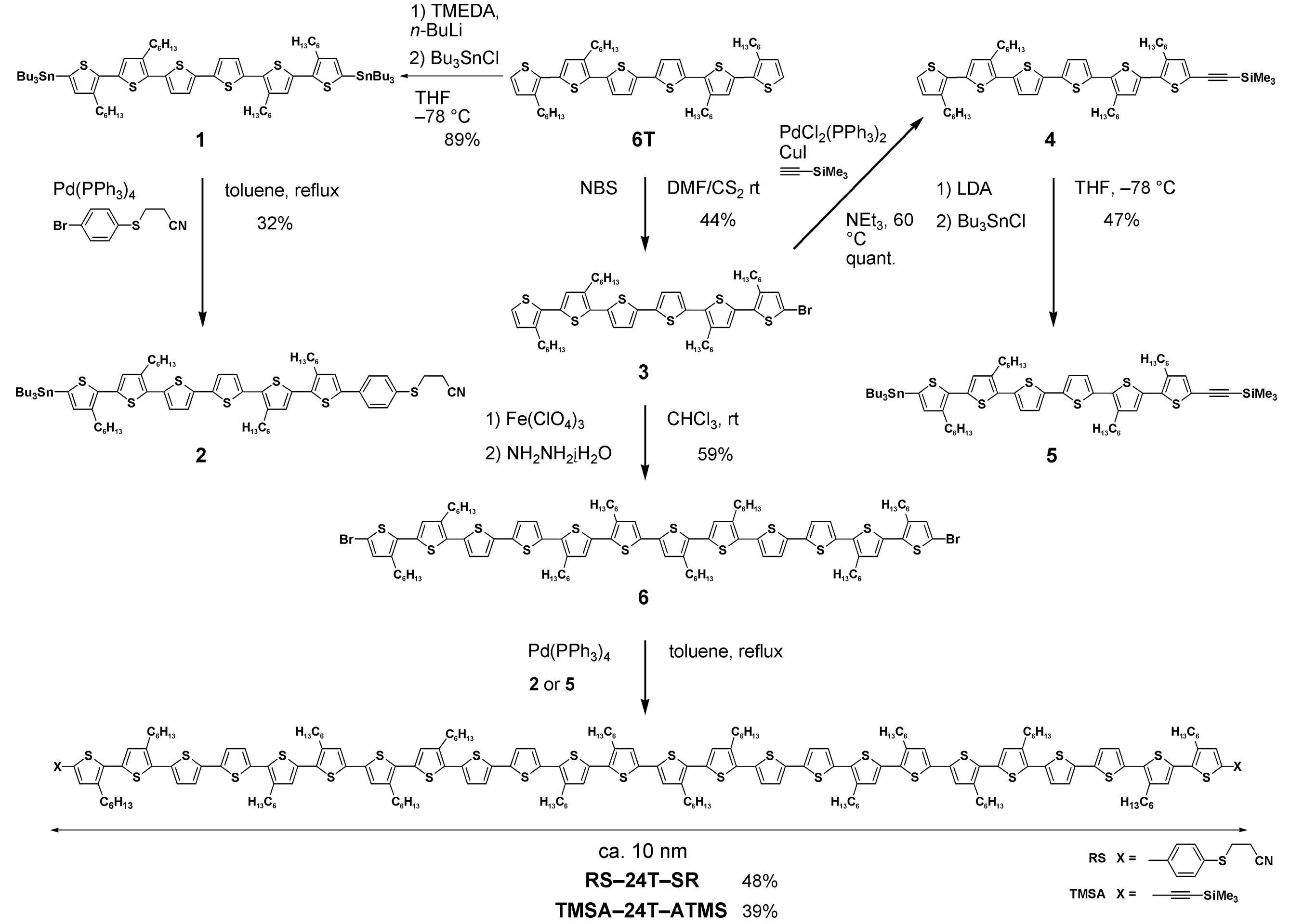
SCHEME 1. Synthetic Routes of RS−24T−SR and TMSA−24T−ATMS



protected thiol group was synthesized in 32% yield by palladium-catalyzed Stille coupling of 1.0 equiv of 4-(2-cyanoethylthio)bromobenzene[10] with bisstannylated sexithiophene **1**, which was prepared in 89% yield from the dianion of **6T** with tributyltin chloride. The other terminal building block **5** with a trimethylsilylethynyl group was synthesized by the three-step conversion. Monobromo derivative **3** was prepared in 44% yield by the reaction of **6T** with 1.0 equiv of NBS in DMF/CS$_2$. Subsequent Pd-catalyzed Sonogashira coupling of **3** with trimethylsilylacetylene in THF/NEt$_3$ gave the corresponding terminal ethynyl-functionalized derivative **4** in quantitative yield. Then, the treatment of **4** with LDA at −78 °C followed by stannylation with tributyltin chloride provided **5** in 47% yield. Because of the difficulty of selective dibromination of the terminal α-positions in long oligothiophenes, the central dibromododecithiphene building block **6** was prepared by the oxidative coupling of **3** with Fe(ClO$_4$)$_3$ in CHCl$_3$ at room temperature in 59% yield. In the final step, the Stille coupling of **6** with an excess of **2** or **5** yielded **RS−24T−SR** (48%) or **TMSA−24T−ATMS** (39%), respectively. As we expected, **RS−24T−SR** and **TMSA−24T−ATMS** are soluble in organic solvents such as chloroform, THF, and *o*-dichlorobenzene and are successfully purified by preparative GPC. These long oligothiophenes as well as all the building blocks were unambiguously characterized by ^{1}H NMR, ^{13}C NMR, and MALDI-TOF MS measurements and elemental analyses. It is important to note that, as shown in Figure 1, the mass spectra of **RS−24T−SR** and **TMSA−24T−ATMS** showed only a peak attributable to the molecular ion. This and analytical GPC (Figure S1 in the Supporting Information) confirmed the perfect homogeneity of these oligomers. The 2-cyanoethyl protecting groups were easily removed by the treatment of **RS−24T−SR** with excess amounts of cesium hydroxide monohydrate in *o*-dichlorobenzene at room temperature.[11] Although prolonged exposure of a solution of the deprotected product to air easily formed insoluble polymeric materials probably owing to disulfide formation, the appropriate treatment (see the Supporting Information) gives a solution containing pure **HS−24T−SH** (Figures S2 and S3 in the Supporting Information).

As shown in Figure 2, the electronic absorption and fluorescence spectra of both **RS−24T−SR** and **TMSA−24T−ATMS** in CHCl$_3$ exhibit a characteristic absorption band with a maximum at 458 nm attributed to the $\pi-\pi^*$ transition and an emission peak at 567 nm, respectively, which well resemble those of the known thiophene 20- and 27-mers in THF: absorption maximum at 461 nm and emission peak at 577 nm.[7a] The fluorescence quantum yield of **RS−24T−SR** ($\Phi_f = 0.15$) is slightly reduced as compared with that of **TMSA−24T−ATMS** ($\Phi_f = 0.21$). The cyclic voltammograms of these oligothiophenes measured in chloroform have a very broad and

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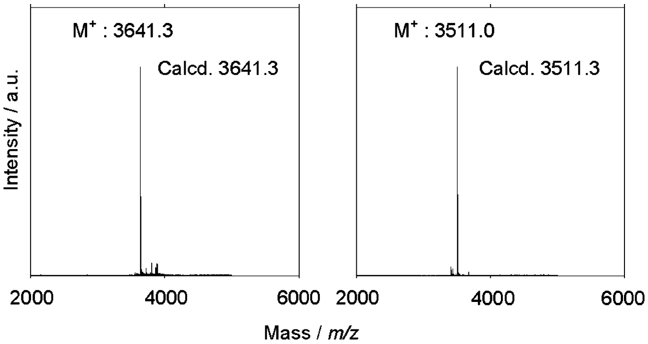

FIGURE 1. MALDI-TOF mass spectra of **RS−24T−SR** (left) and **TMSA−24T−ATMS** (right).

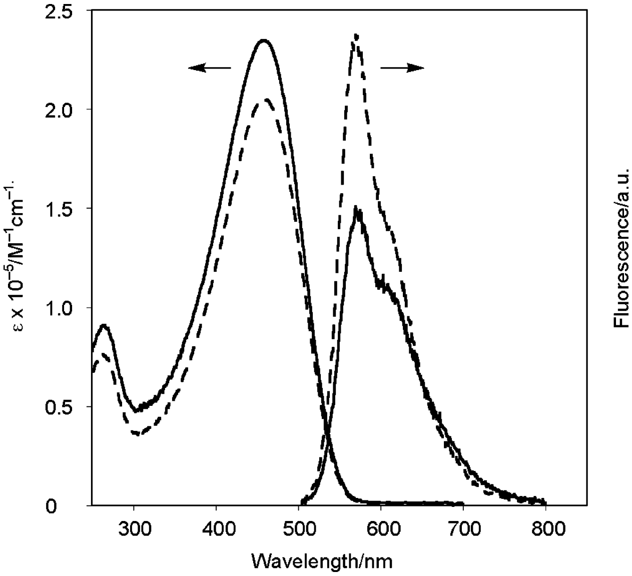

FIGURE 2. Electronic absorption and fluorescence spectra of **RS−24T−SR** (solid line) and **TMSA−24T−ATMS** (dashed line) in CHCl$_3$.

scarcely structured oxidation wave, which is the characteristic multistep oxidations for long oligothiophenes,[7a] and show the first oxidation onset potentials at +0.05 V versus Fc/Fc$^+$ for **RS−24T−SR** and at +0.07 V for **TMSA−24T−ATMS** (Figure S4 in the Supporting Information). These results indicate that the incorporated terminal anchor groups have little influence on the electronic structure of the π-conjugated system.

In conclusion, we have succeeded in synthesizing the terminal-functionalized 10 nm oligothiophenes. To the best of our knowledge, these are the longest oligothiophenes reported to date where the anchor groups are introduced at both terminal positions.[12] They are expected to contribute to the elucidation of electrical characterizations of molecular wires, and efforts toward achieving the goals are underway.

Experimental Section

RS−24T−SR. Dibromothiophene 12-mer **6** (58 mg, 31 μmol), **2** (100 mg, 78 μmol), and tetrakis(triphenylphosphine)palladium(0) (3 mg, 3 μmol) were placed in a test tube and dissolved with toluene (10 mL). The mixture was stirred at 115 °C for 12 h. After being cooled to room temperature, the mixture was first separated by column chromatography on silica gel with chloroform as eluent, and then the fraction containing **RS−24T−SR** was further purified by preparative gel permeation chromatography (JAIGEL 1H/2H) with chloroform as eluent to give pure **RS−24T−SR** (54 mg, 15 μmol, 48% yield). Analytically pure **RS−24T−SR** was obtained by recrystallization from toluene.

Dark red amorphous solid; TLC R_f = 0.50 (7/3 hexane/CHCl$_3$); ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.88−0.94 (m, 48H), 1.26−1.49 (m, 96H), 1.63−1.75 (m, 32H), 2.62 (t, J = 7.3 Hz, 4H), 2.74−2.84 (m, 32H), 3.15 (t, J = 7.3 Hz, 4H), 6.98 (s, 6H), 7.00 (s, 8H), 7.06 (d, J = 3.8 Hz, 8H), 7.15 (d, J = 3.8 Hz, 8H), 7.16 (s, 2H), 7.42 (d, J = 8.1 Hz, 4H), and 7.56 (d, J = 8.1 Hz, 4H); ^{13}C NMR(CDCl$_3$) δ 14.1, 18.3, 22.6, 29.3, 29.5, 29.6, 29.6, 30.4, 30.5, 30.5, 30.6, 31.7, 117.9, 124.0, 124.0, 126.3, 126.4, 126.5, 126.6, 126.7, 128.6, 128.8, 129.6, 129.6, 130.3, 130.3, 130.4, 130.7, 132.0, 132.1, 133.7, 134.1, 134.1, 134.8, 135.0, 135.0, 135.1, 136.8, 136.8, 136.9, 140.1, 140.2, 140.5, and 140.8; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z 3641.3 (M$^+$, calcd 3641.3). Anal. Calcd for $C_{210}H_{256}N_2S_{26}$: C, 69.25; H, 7.08; N, 0.77. Found: C, 69.15; H, 7.01; N, 0.76. UV−vis (CHCl$_3$) λ_{max}^{abs} 458 nm (log ϵ 5.37), λ_{max}^{ems} 567 nm (Φ_f 0.15).

TMSA−24T−ATMS. Dibromothiophene 12-mer **6** (67 mg, 37 μmol), **5** (112 mg, 92 μmol), and tetrakis(triphenylphosphine)palladium(0) (4 mg, 4 μmol) were placed in a test tube and dissolved with toluene (10 mL). The mixture was stirred at 115 °C for 12 h. After being cooled to room temperature, the mixture was first isolated by column chromatography on silica gel with chloroform as eluent, and then the fraction containing **TMSA−24T−ATMS** was further purified by preparative gel permeation chromatography (JAIGEL 1H/2H) with chloroform as eluent to give pure **TMSA−24T−ATMS** (49 mg, 14 μmol, 39% yield). Analytically pure **TMSA−24T−ATMS** was obtained by recrystallization from toluene.

Dark red amorphous solid; R_f = 0.30 (8/2 hexane/CHCl$_3$); ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.25 (s, 18H), 0.88−0.94 (m, 48H), 1.32−1.49 (m, 96H), 1.59−1.70 (m, 32H), 2.69−2.82 (m, 32H), 6.95 (s, 2H), 6.98 (s, 6H), 7.00 (s, 6H), 7.04−7.07 (m, 10H), and 7.13−7.16 (m, 8H); ^{13}C NMR(CDCl$_3$) δ −0.1, 14.1, 22.6, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 30.4, 30.5, 30.5, 31.7, 31.7, 97.6, 99.8, 120.7, 124.0, 124.0, 126.4, 126.6, 126.6, 128.6, 129.1, 129.6, 130.3, 130.3, 130.8, 132.4, 133.4, 134.1, 134.8, 134.8, 135.0, 135.1, 135.7, 136.7, 136.8, 137.0, 139.3, 140.1, and 140.5; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z 3511.0 (M$^+$, calcd 3511.3). Anal. Calcd for $C_{202}H_{258}S_{24}Si_2$: C, 69.08; H, 7.40. Found: C, 69.25; H, 7.23. UV−vis (CHCl$_3$) λ_{max}^{abs} 458 nm (log ϵ 5.31), λ_{max}^{ems} 567 nm (Φ_f 0.21).

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Supporting Information Available: Synthesis and characterization of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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