

Functional oligothiophenes toward molecular wires in single-molecular electronics*

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Abstract: The synthesis of 3-hexylthiophene-based oligothiophenes with a length of approximately 10 nm bearing anchor units at both terminal positions has been accomplished. In addition, we have designed and synthesized completely encapsulated oligothiophenes to investigate single-molecule conductance. Their properties are evaluated by UV–vis absorption spectra and cyclic voltammetry (CV) measurements. The conductance of a single-molecule junction for thiol-introduced oligothiophenes was measured by 10-nm-scale nanogap gold electrodes or modified scanning tunneling microscope (STM) techniques.

Keywords: aromatic compounds; electronic structures; encapsulation; molecular electronics; molecular wires; oligomers; oligothiophenes; organic semiconductors; structure–function.

INTRODUCTION

Since the concept of single-molecular electronics has emerged as a complement to silicon-based electronics in terms of the bottom-up approach and ultimate miniaturization [1,2], molecules for building components such as anchor units [3,4], switching units [5], and wiring units [6,7] have been widely developed. Structurally well-defined oligothiophenes have become one of the most actively investigated molecules as molecular wires in the single-molecular devices for the following two reasons [7]: (1) oligothiophenes exhibit the longest effective conjugation length of known organic oligomers [8], leading to small energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which is favorable for carrier injection from metal electrodes; and (2) the high polarizability of the sulfur atom in thiophene effectively stabilizes the cationic species in various oxidation states, which is advantageous for intramolecular charge transport properties. However, the measurement of electrical conductance of oligothiophenes to reveal their potentials for molecular wires is still limited [9–11], owing to the difficulty of suitable molecular design and synthesis. Herein, we present our research on the development of oligothiophenes with a length of 10 nm bearing anchor units for metal electrodes, completely encapsulated oligothiophenes, and

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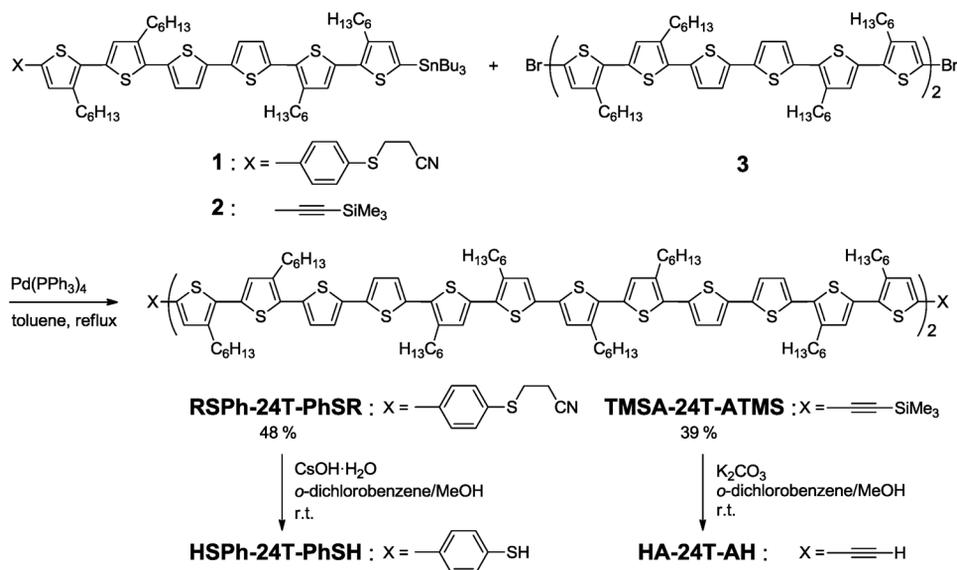
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completely encapsulated oligothiophenes with anchor units. We will also present the single-molecule conductivity of thiol-introduced oligothiophenes.

RESULTS

Oligothiophenes with a length of 10 nm bearing anchor units

Recent progress of organic synthesis has enabled us to access structurally well-defined long π -conjugated systems, and several groups have reported the syntheses of 10-nm-scale aryleneethynylene or arylenevinylene molecular wires terminated with anchor groups [12]. These molecular wires are suitable for the electrical measurement of a single wire using nanometer-spaced electrodes [13]. We have previously reported the synthesis of long oligothiophenes whose molecular lengths far exceed 10 nm [8,14]. However, the synthesis of long oligothiophenes with a length of 10-nm scale having anchor units has never been accomplished [9b,15]. This situation motivated us to synthesize fully conjugated thiophene 24-mers **RSPH-24T-PhSR** and **TMSA-24T-ATMS** bearing protected thiol and trimethylsilylethynyl anchor groups, respectively, at both terminal positions [16]. Our synthetic strategy is based on a block-coupling method of large building components, which is advantageous to the easy isolation and purification of the desired product from starting components on the basis of their molecular sizes. After experimental screening of appropriate building components, we have chosen tetrahexyl-substituted sexithiophene shown in Scheme 1 as a building block, because its alkyl groups and symmetrical structure contribute to maintaining the sufficient solubility of the target thiophene 24-mer and to preventing the formation of regioisomers, respectively. Thus, the key components **1–3** were easily synthesized from tetrahexyl-substituted sexithiophene derivatives, and then Stille coupling of **3** with an excess of **1** or **2** yielded **RSPH-24T-PhSR** (48 %) or **TMSA-24T-ATMS** (39 %), respectively (Scheme 1).



Scheme 1 Synthesis of thiophene 24-mers having anchor units at both terminal positions.

The electronic absorption spectra of both **RSPH-24T-PhSR** and **TMSA-24T-ATMS** in CHCl_3 exhibit a characteristic absorption band with a maximum at 458 nm attributed to the π - π^* transition (Table 1), which resemble those reported for similar thiophene 20- and 27-mers in tetrahydrofuran

(THF) (461 nm) [14a]. The cyclic voltammograms (CVs) of these oligothiophenes measured in CHCl_3 containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) showed a broad oxidation wave with first oxidation onset potentials at +0.05 V vs. ferrocene/ferrocenium (Fc/Fc^+) for **RSPH-24T-PhSR** and at +0.07 V for **TMSA-24T-ATMS** (Table 1). These results clearly indicate that the presence of terminal anchor groups has little influence on the electronic structure of the π -conjugated system.

Table 1 Electronic absorption and CV data of thiophene 24-mers bearing anchor units.

Comp.	Abs _{max} /nm ^a	$E_{\text{onset}}/\text{V}^{\text{b}}$
RSPH-24T-PhSR	458	+0.05
TMSA-24T-ATMS	458	+0.07

^aIn CHCl_3 .

^bIn CHCl_3 0.1 M TBAPF_6 , V vs. Fc/Fc^+ .

To measure the single-molecule conductivity, the 2-cyanoethyl protecting groups of **RSPH-24T-PhSR** was removed by treatment with an excess amount of cesium hydroxide monohydrate in *o*-dichlorobenzene/methanol at room temperature to give **HSPH-24T-PhSH**, which was characterized by mass spectroscopy. Note that the prolonged exposure of a solution of **HSPH-24T-PhSH** to air formed insoluble materials probably owing to polymeric disulfide formation. This thiol-terminated oligothiophene was modified to nanogap gold electrodes by self-assembly in a droplet of a dilute dichlorobenzene solution, and then current–voltage (I – V) characteristics were measured in vacuum conditions at room temperature [17]. As shown in Fig. 1, the electrical conductance of **HSPH-24T-PhSH** was observed. The deprotection of the trimethylsilyl groups for **TMSA-24T-ATMS** was performed by treatment with K_2CO_3 in *o*-dichlorobenzene/methanol at room temperature to give **HA-24T-AH**. The electrical measurement of **HA-24T-AH** by using nanogap silicon electrodes is underway in our group.

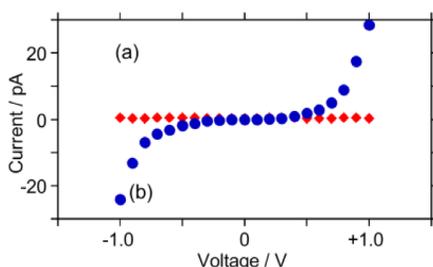


Fig. 1 I – V characteristics of the junction before (a) and after (b) modification with **HSPH-24T-PhSH** molecules.

Completely encapsulated oligothiophenes

As mentioned above, the synthesis of tetrahexylsexithiophene-based oligothiophenes is straightforward to both the elongation of the molecular length and the introduction of the anchor units. However, it is generally recognized that the elongation of π -conjugated systems induces strong intermolecular π – π interactions as well as π -dimer formation [18], which result in difficulties in elucidating single-molecule properties. In fact, as shown in Fig. 2a, the image of scanning tunneling microscope (STM) for **HSPH-24T-PhSH** on a gold substrate partly showed dense parallel arrangements, indicating spontaneous aggregation of long oligothiophenes. In order to circumvent π – π interactions caused by aggregation, we have planned to encapsulate the backbone. Although many encapsulated π -conjugated

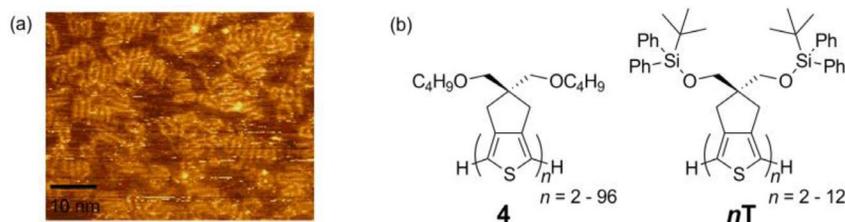
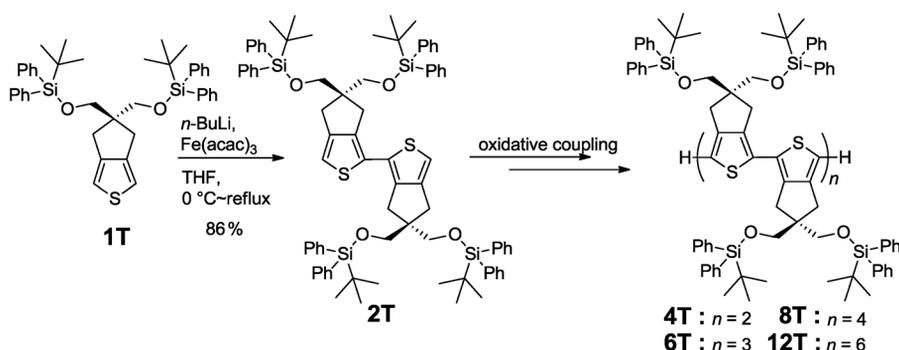


Fig. 2 (a) STM image of **HSPH-24T-PhSH** on gold and (b) chemical structures of **4** and ***nT***.

systems have been developed by the introduction of dendrons or by the self-assembly of supramolecular structure [19], there have been known only a few conjugated systems that have the covalently attached insulating groups at *all* repeating units [20–23]. This is due to a crucial difficulty in designing an appropriate repeating unit possessing the compatibility of insulation by bulky substituents with keeping effective conjugation of the backbone. In this context, we have focused on the skeletal structure of a series of oligothiophenes **4** (Fig. 2b), because their effective conjugation is maintained up to 96-mer in spite of the presence of annelated cyclopentanes at the β -positions of all the repeating units [8]. Thus, we have designed oligothiophenes ***nT***, whose structures are based on the combination of cyclopentane annelation and bulky *t*-butyldiphenylsilyl (TBDPS) groups (Fig. 2b) [24].

As shown in Scheme 2, the dimer (**2T**) was synthesized by iron(III)-mediated oxidative coupling of the lithiated monomer in a good yield. A similar oxidative coupling method was repeated to afford **4T**, **6T**, **8T**, and **12T**. It is important to note that these oligothiophenes were separated from reaction mixtures by preparative gel-permeation liquid chromatography.



Scheme 2 Synthesis of completely encapsulated oligothiophenes **2T–12T**.

The electronic absorption spectra of **2T–12T** in CH_2Cl_2 are shown in Fig. 3a, and their photophysical data are summarized in Table 2. The absorption maxima of ***nT*** are bathochromically shifted with chain extension. When their π – π^* transition energies (E) are plotted against inverse thiophene-ring numbers ($1/n$), a linear relation is revealed with a calculated equation of E (eV) = 2.03 + 3.86/ n , whose slope is very close to, or even steeper than, those for **4** (3.64) [8] and non-substituted oligothiophenes (3.76) [25]. This result indicates that the bulky TBDPS groups little disturb the effective conjugation. The CV of **2T** measured in CH_2Cl_2 showed an irreversible oxidation peak at a high potential, while the longer oligomers exhibited reversible oxidation waves (Table 2), indicating the formation of stable radical cationic species for **4T–12T**. Positively charged oligothiophenes tend to spontaneously form π -dimers, which we can exploit to evaluate the effect of encapsulation upon suppressing intermolecular interactions. Thus, we measured the UV–vis–NIR spectra of **6T** oxidized

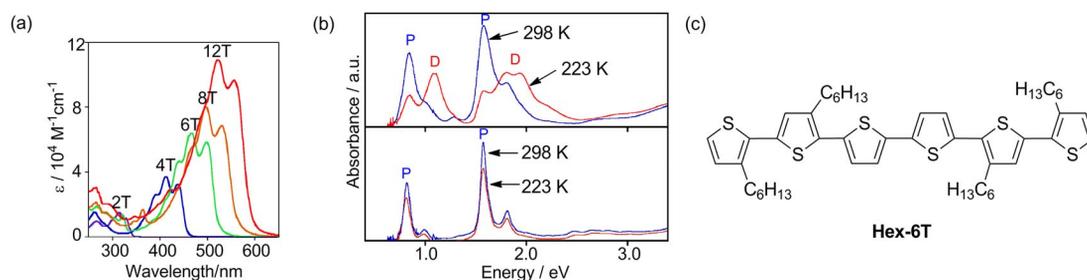


Fig. 3 (a) UV-vis spectra of **2T**–**12T** in CH_2Cl_2 , (b) UV-vis-NIR spectra of **Hex-6T**⁺ (top) and **6T**⁺ (bottom) in CH_2Cl_2 at 298 K and at 223 K, and (c) chemical structure of un-encapsulated **Hex-6T**. P and D denote polaronic and π -dimeric bands, respectively.

progressively with FeCl_3 at room temperature in CH_2Cl_2 and compared it with the behavior of the un-encapsulated **Hex-6T**. As shown in Fig 3b, the UV-vis-NIR spectra at room temperature showed little difference in shapes between **6T**⁺ and **Hex-6T**⁺. However, they exhibited significant differences at low temperature. When the solution of **Hex-6T**⁺ was cooled to 223 K, the polaronic bands at 0.8 and 1.6 eV became a decrease along with a concomitant increase in new bands at 1.2 and 1.9 eV. These high-energy shifts of polaronic bands are the typical characteristics of π -dimer formation [26]. On the other hand, **6T**⁺ exhibited no significant spectral change at 223 K. This different behavior can be explained by the encapsulation effect on suppressing the π -dimer formation of **6T**⁺ and thus insulating the π -conjugated backbone.

Table 2 Electronic absorption and CV data of $n\text{T}$.

Comp.	Abs _{max} /nm ^a	$E^{1/2}/\text{V}^b$
2T	314, 328	+0.80 ^c
4T	413, 439	+0.23, +0.75
6T	466, 497	+0.07, +0.41
8T	497, 529	+0.01, +0.26, +0.79
12T	521, 555	−0.04, +0.12, +0.37, +0.57

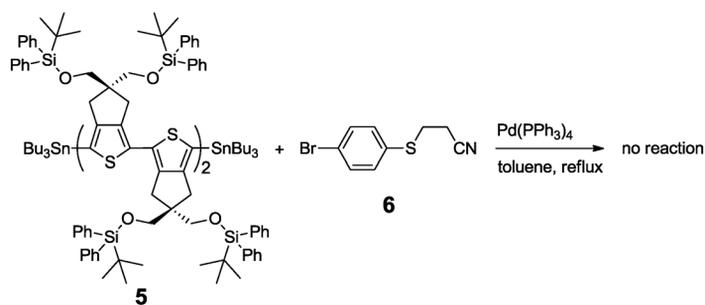
^aIn CH_2Cl_2 .

^bIn CH_2Cl_2 0.1 M TBAPF₆, V vs. Fc/Fc⁺.

^cIrreversible anodic peak.

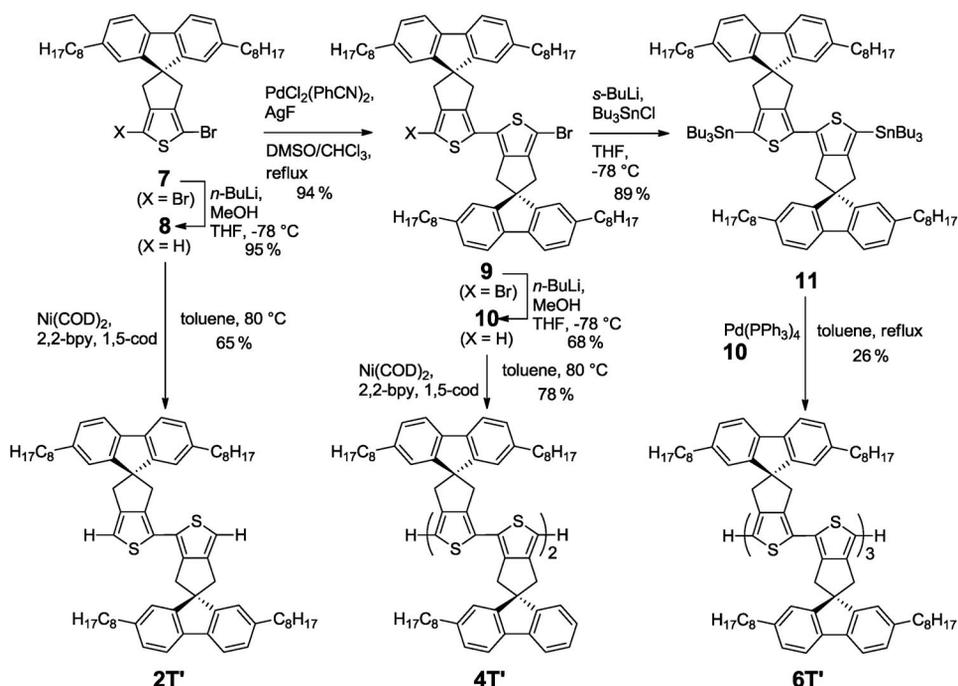
Completely encapsulated oligothiophenes bearing anchor units

To introduce anchoring groups for conductivity measurements, the Stille coupling reaction of bisstannylated quarterthiophene **5** with 4-(2-cyanoethylthio)bromobenzene (**6**) was attempted. However, no desired product was obtained (Scheme 3). This result indicates that the steric bulk of the TBDPS groups restricted the introduction of anchoring functional groups at the terminal α positions of $n\text{T}$.

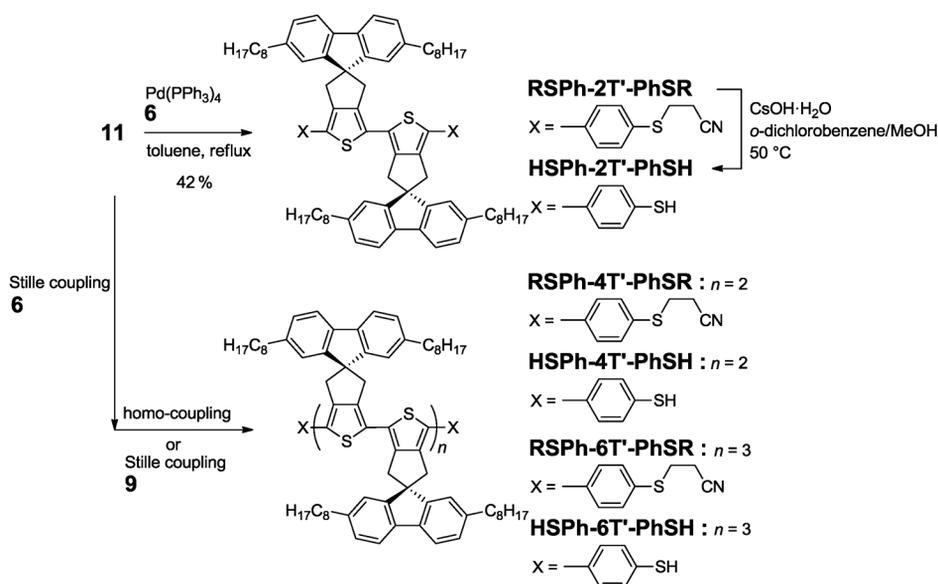


Scheme 3 Attempt to introduce anchor units.

On the basis of the low reactivity of **5** toward a Stille coupling reaction, we predicted that a alkylated planar fluorene group in place of the TBDPS groups as an encapsulation unit for cyclopentene-annulated thiophene would enhance the reactivity at the α positions. Thus, we have developed the appropriate oligothiophenes ***nT'*** as well as the anchoring-group-introduced oligothiophenes **HSPH-*nT'*-PhSH** for the measurement of single-molecule conductivity [27]. The synthetic routes to ***nT'*** ($n = 2, 4,$ and 6) are depicted in Scheme 4. Dibromothiophene **7** was readily converted to monobromothiophene **8**, which was then treated with Ni(COD)₂ in the presence of 2,2'-bipyridine and 1,5-cyclooctadiene to give **2T'** in 65 % yield. To obtain dibromothiophene **9**, **8** underwent palladium-catalyzed oxidative homo-coupling in the presence of AgF [28]. In a similar way to obtaining **2T'**, quaterthiophene **4T'** was synthesized from **9** in two steps. The addition of *s*-BuLi to a mixture of **9** and tributylstannylchloride afforded bisstannylated bithiophene **11** in 89 % yield. A subsequent Pd-catalyzed Stille coupling reaction between **11** and 2.5 equiv of **10** gave sexithiophene **6T'** in 26 % yield. The synthesis of **HSPH-*nT'*-PhSH** ($n = 2, 4,$ and 6) is outlined in Scheme 5. As we expected, the pro-



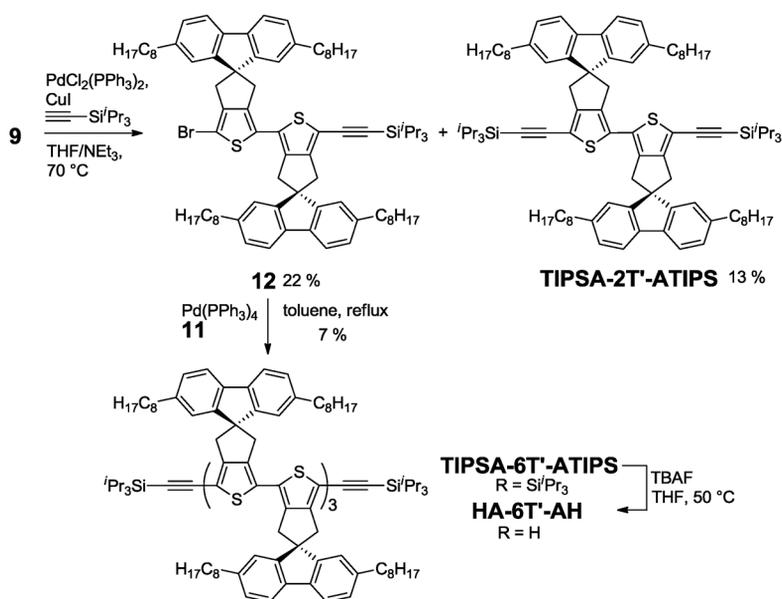
Scheme 4 Synthesis of **2T'**, **4T'**, and **6T'**.



Scheme 5 Synthesis of **RSPH-*n*T'-PhSR** and **HSPH-*n*T'-PhSH** ($n = 2, 4,$ and 6).

tected thiol functional group could be successfully introduced to stannylated bithiophene **11** by a Stille coupling reaction with **6** to give **RSPH-2T'-PhSR**. Likewise, after the mono-functionalization of **11** with **6**, Pd-catalyzed homo-coupling or Stille coupling with **9** gave **RSPH-4T'-PhSR** or **RSPH-6T'-PhSR**. The 2-cyanoethyl protecting groups in **RSPH-2T'-PhSR**, **RSPH-4T'-PhSR**, and **RSPH-6T'-PhSR** were easily removed by treatment with excess amounts of cesium hydroxide monohydrate in *o*-dichlorobenzene/EtOH at 50 °C to give **HSPH-2T'-PhSH**, **HSPH-4T'-PhSH**, and **HSPH-6T'-PhSH**, respectively.

To develop the oligothiophenes for single-molecule conductance measurement with the nanogap silicon electrodes, we have also synthesized encapsulated oligothiophenes bearing triisopropylsilylethynyl anchor groups (Scheme 6). Diethynyl derivative **TIPSA-2T'-ATIPS** and monoethynyl derivative **12** were obtained by the Sonogashira coupling reaction of **9** with triisopropylsilylacetylene. The Stille coupling reaction between **12** and **11** afforded **TIPSA-6T'-ATIPS**. The treatment of **TIPSA-6T'-ATIPS** with TBAF gave deprotected **HA-6T'-AH**.



Scheme 6 Synthesis of **TIPSA-2T'-ATIPS** and **TIPSA-6T'-ATIPS**.

To assess the photophysical properties of the oligomers, the electronic absorption spectra of $n\mathbf{T}'$ ($n = 2, 4,$ and 6) and $\mathbf{RSPh-}n\mathbf{T}'\text{-PhSR}$ ($n = 2, 4,$ and 6) were measured in dichloromethane solutions, and their absorption maxima are summarized in Table 3. As shown in Fig. 4, the spectra of both the series of compounds show an absorption band in the visible region corresponding to the $\pi\text{-}\pi^*$ transition of the oligothiophene backbones together with the $\pi\text{-}\pi^*$ transition of the fluorene unit centered at 280 nm. The absorption maxima derived from the $\pi\text{-}\pi^*$ transitions of the oligothiophene backbones shift to a longer wavelength when the number of thiophene rings increases from two to six, while the absorption maxima of $\mathbf{RSPh-}n\mathbf{T}'\text{-PhSR}$ ($n = 2, 4, 6$) are red-shifted compared with those of the corresponding terminal-unsubstituted $n\mathbf{T}'$ ($n = 2, 4, 6$) owing to the extension of the conjugation onto the phenyl rings. The linear relationship of the $\pi\text{-}\pi^*$ transition energy (E) against the inverse of the number of thiophene rings ($1/n$) for $n\mathbf{T}'$ is calculated to be E (eV) = $2.03 + 3.85/n$. Its slope (3.85) is almost identical to that of $n\mathbf{T}$ (3.86), indicating that the encapsulating dioctylfluorene units also little affect the effective conjugation of the oligothiophene backbone.

Table 3 Electronic absorption and CV data of $n\mathbf{T}'$ and $\mathbf{RSPh-}n\mathbf{T}'\text{-PhSR}$.

Comp.	Abs _{max} /nm ^a	$E^{1/2}/\text{V}^b$
2T'	314	+1.02 ^c
4T'	413	+0.37, +0.86
6T'	466	+0.21, +0.49
RSPh-2T'-PhSR	399	+0.53
RSPh-4T'-PhSR	457	+0.29, +0.55
RSPh-6T'-PhSR	488	+0.11, +0.37

^aIn CH₂Cl₂.

^bIn CH₂Cl₂ 0.1 M TBAPF₆, V vs. Fc/Fc⁺.

^cIrreversible anodic peak.

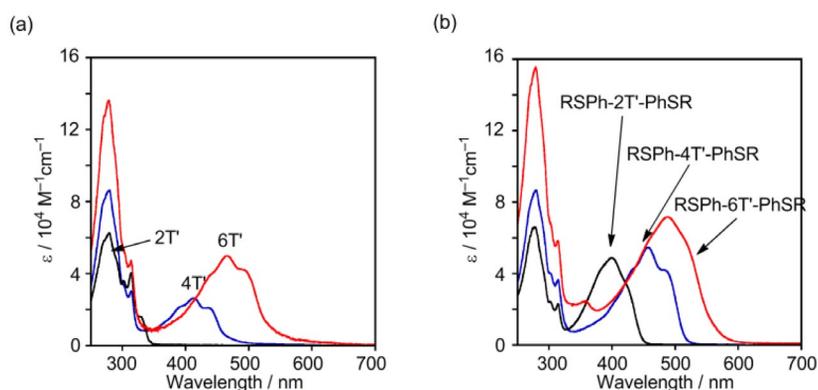


Fig. 4 UV-vis absorption spectra of (a) nT' and (b) $RSPH-nT'-PhSR$ in CH_2Cl_2 .

The electrochemical properties of nT' and $RSPH-nT'-PhSR$ were studied by CV measurement in a dichloromethane solution containing 0.1 M TBAPF₆, and their oxidation potentials are listed in Table 3. Except for $2T'$, reversible oxidation waves were observed in all the oligothiophenes. The first oxidation potentials decrease with an increase in the number of thiophene rings, which is in good agreement with the trend of nT . In order to investigate the encapsulating effect similarly to the case of nT , we measured the UV-vis-NIR spectrum of $6T'$ oxidized with $SbCl_5$ in dichloromethane. As we expected, the polaronic species of $6T'$ exhibited no spectral band transposition to a higher energy even upon cooling to 223 K (Fig. 5), which is also in good agreement with $6T$, indicating the insulation of the conjugated backbone.

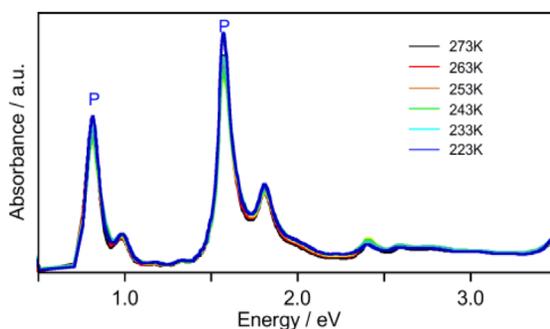


Fig. 5 UV-vis-NIR spectra of $6T'+$ in CH_2Cl_2 . P denotes polaronic bands.

The electronic absorption spectra and CVs of $TIPSA-nT'-ATIPS$ ($n = 2$ and 6) showed similar characteristics to those of $RSPH-nT'-PhSR$ as shown in Fig. 6. The red shifts of the oligothiophene $\pi-\pi^*$ transition bands and the low potential shifts of the oxidation waves compared with those of the corresponding terminal-unsubstituted nT' ($n = 2$ and 6) are attributable to the extension of the conjugation onto the ethynyl groups.

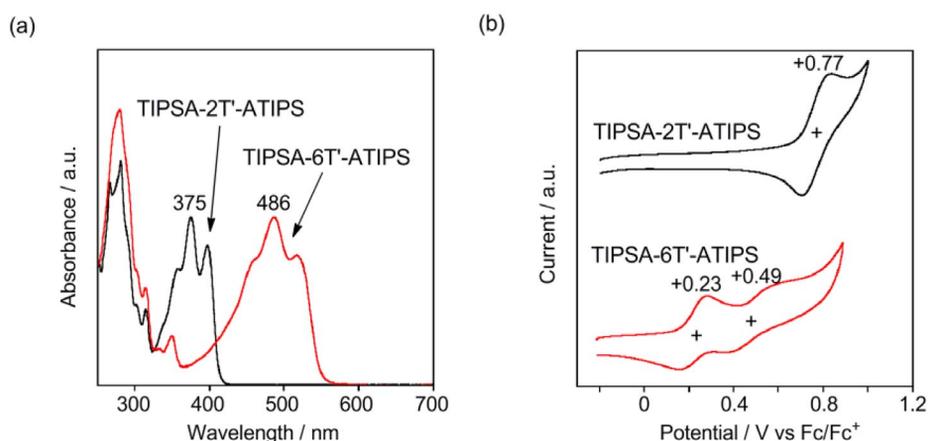


Fig. 6 (a) UV-vis spectra of **TIPSA-2T'-ATIPS** and **TIPSA-6T'-ATIPS** in CHCl_3 . (b) CVs of **TIPSA-2T'-ATIPS** and **TIPSA-6T'-ATIPS** in CHCl_3 containing 0.1 M TBAPF_6 .

Electrical conductance of **HSPH- n T'-PhSH** ($n = 2, 4$, and 6) was measured using the break junction (BJ) method by STM [3]. This measurement was carried out using mechanically cut gold tips in a $\sim 0.1 \mu\text{M}$ mesitylene solution of the molecules at room temperature. Figure 7 shows conductance histograms obtained from the 500–1000 transient conductance measurements of **HSPH- n T'-PhSH**. The solid arrows in Fig. 6 indicate the peak positions attributed to the single-molecule conductance. A semi-log plot of the conductance as a function of the calculated molecular length indicated an exponential decrease in the conductance with molecular length, thus the tunneling transport is evident, which is expressed as $G \times \exp(-\beta L)$, where β is a decay constant, and L is the length of the conduction channel. The decay constant of the present oligothiophenes was estimated to be $\beta = 1.9 \text{ nm}^{-1}$ from the plot. Since this value is in good agreement with that obtained from theoretical calculations for non-substituted oligothiophenes ($\beta = 2.11 \text{ nm}^{-1}$) [29], the present completely encapsulated oligothiophenes **HSPH- n T'-PhSH** possess the intrinsic electronic structures and transport properties of defect-free oligothiophenes with effective conjugation.

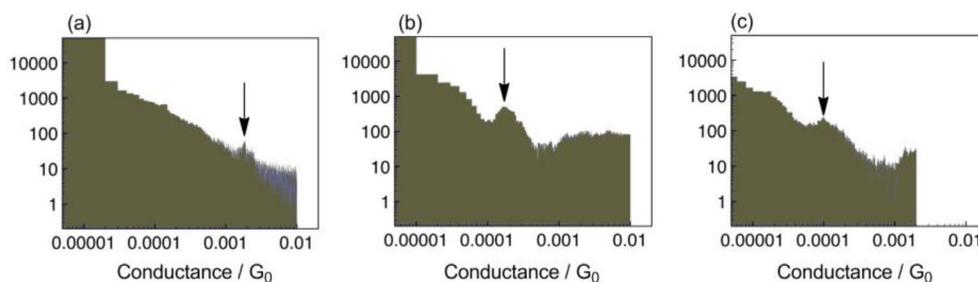


Fig. 7 Conductance histograms for **HSPH- n T'-PhSH** (a) $n = 2$, (b) $n = 4$, and (c) $n = 6$.

CONCLUSION

Starting from the synthesis of 3-hexylthiophene-based oligothiophenes with a length of 10-nm scale bearing anchor units at both terminal positions and the electrical measurement of the thiol-terminated thiophene 24-mer with nanogap gold electrodes, we have designed and successfully synthesized two series of ideal encapsulated oligothiophenes, whose structures are based on the combination of

cyclopentene-annulated thiophene and orthogonally oriented encapsulation units, TBDPS or octyl-substituted fluorene groups. All the spectroscopic and CV data exemplified that there is no interruption of conjugation along the oligothiophene backbone. The formation of π -dimers for the thiophene 6-mers is perfectly prohibited by the encapsulation effect, indicating the electrical insulation of the π -conjugated backbone. The fluorene units play an important role as sterically compact encapsulating units, which enabled us to introduce anchoring functional groups at the terminal positions of the oligothiophenes. The measurement of the single-molecule conductance was successfully carried out using modified STM techniques, and the decay constant β was estimated to be 1.9 nm^{-1} . To our knowledge, this is the first experimentally determined β value of oligothiophenes composed by an electronically equivalent repeating unit. Furthermore, since we have obtained this result by the use of highly planar oligothiophenes in the absence of intermolecular interactions, this value could become a standard for forthcoming π -conjugated systems.

EXPERIMENTAL

Synthesis of **12** and TIPSA-2T'-ATIPS

9 (500 mg, 0.43 mmol), triisopropylsilylacetylene (94 mg, 0.52 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (15 mg, 0.022 mmol), and CuI (4 mg, 0.02 mmol) were placed in a test tube with screw cap and dissolved in THF/ NEt_3 (6 mL). The reaction mixture was stirred at 70°C for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give TIPSA-2T'-ATIPS (75 mg, 0.055 mmol, 13 %) and a mixture of **9** and **12**, which was further separated by preparative GPC (JAIGEL 1H/2H, CHCl_3) to give **12** (119 mg, 0.095 mmol, 22 %).

12: Pale yellow solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 0.87 (t, $J = 7.2$ Hz, 12H), 1.01 (s, 18H), 1.20–1.36 (m, 27H), 1.56–1.64 (m, 8H), 2.60 (t, $J = 7.2$ Hz, 8H), 3.05 (s, 2H), 3.17 (s, 2H), 3.26 (s, 4H), 3.35 (s, 4H), 7.06 (s, 2H), 7.09 (s, 2H), 7.15 (m, 4H), 7.56 (d, $J = 7.8$ Hz, 2H), 7.57 (d, $J = 7.8$ Hz, 2H); MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z 1252.1 (M^+ , Calcd 1252.7).

TIPSA-2T'-ATIPS: Pale yellow solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 0.87 (t, $J = 7.2$ Hz, 12H), 1.01 (s, 36H), 1.20–1.36 (m, 30H), 1.56–1.64 (m, 8H), 2.60 (t, $J = 7.2$ Hz, 8H), 3.18 (s, 4H), 3.32 (s, 4H), 7.10 (s, 4H), 7.15 (d, $J = 7.8$ Hz, 4H), 7.57 (d, $J = 7.8$ Hz, 4H); MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z 1354.8 (M^+ , Calcd 1354.9).

Synthesis of TIPSA-6T'-ATIPS

12 (55 mg, 44 μmol), **11** (27 mg, 17 μmol), $\text{Pd}(\text{PPh}_3)_4$ (2 mg, 2 μmol), and toluene (1 mL) were placed in a microwave-proof-walled glass vial equipped with a snap cap. The glass vial was purged with argon, securely sealed, and heated in a microwave reactor with keeping a temperature at 180°C for 10 min. The reaction mixture was stirred at 120°C for 24 h. After removal of the solvent under reduced pressure, the residue was filtered over alumina with CHCl_3 as eluent, followed by purification with preparative GPC (JAIGEL 1H/2H, CHCl_3) to give TIPSA-6T'-ATIPS (4 mg, 7 %). Red solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 0.83 (t, $J = 7.2$ Hz, 36H), 0.96 (s, 36H), 1.12–1.28 (m, 126H), 1.42–1.64 (m, 24H), 2.44–2.56 (m, 24H), 3.08 (s, 4H), 3.15 (s, 12H), 3.20 (s, 4H), 3.26 (s, 4H), 6.96 (s, 4H), 6.99 (s, 4H), 7.00–7.09 (m, 16H), 7.43 (d, $J = 7.8$ Hz, 4H), 7.47 (d, $J = 7.8$ Hz, 4H), 7.49 (d, $J = 7.8$ Hz, 4H); MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) m/z 3340.4 (M^+ , Calcd 3340.2).

Synthesis of HA-6T'-AH

To a stirred solution of TIPSA-6T'-ATIPS (1.0 mg, 0.29 μmol) in THF (3 mL) was added 1.0 N tetrabutylammonium fluoride (TBAF) (0.3 mL, 0.3 mmol), and the mixture was degassed by a freeze-thaw technique. The mixture was stirred at 50°C for 5 h. The resulting solution was washed with water

and dried over Na₂SO₄. After filtration through a membrane filter, the solvent was removed under reduced pressure, and the resulting solid was dissolved in mesitylene to give a solution containing **HA-6T'-AH**. MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 3025.2 (M⁺, Calcd 3027.9).

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