Dendrimer-Encapsulated Oligothiophenes

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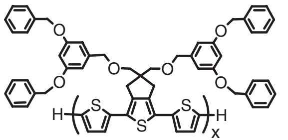
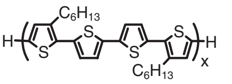
A series of novel oligothiophenes, trimer, hexamer, nonamer, and dodecamer, attached with benzyl ether dendrons at the molecular sides has been developed. Since the dendron pendants prevent the formation of π-dimers, the electronic absorption spectra of the dodecamer under doping reveal the involvement of chain dimers and bipolarons as other possible charge carrier species for conductive polythiophenes.

Insulating oligothiophenes are of current interest among conjugated nanomolecules.[1] Dendrimers are of good choice among bulky functional groups useful for the insulation of molecular cores from the outside. Fréchet reported a variety of dendrimer-incorporated oligothiophenes, although most of them are attached with dendrons at the end sites.[2] We are interested in the insulating system encapsulated with many dendrons at the molecular sides of oligothiophenes. We report herein the development of novel multidendron-encapsulated oligothiophenes **1** (abbreviated as **D-nT**) and their spectral properties as compared to those of the hexyl-substituted system **2** (**H-nT**)[3] and the octyl-substituted system **3** (**O-nT**).[4]



1 (**D-nT**)



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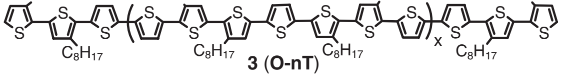


3 (**O-nT**)

The oligothiophenes **1** were synthesized as shown in Scheme 1. 2,5-Dibromo-3,4-bis(bromomethyl)thiophene (**4**)[5] was treated with diethyl malonate in the presence of sodium hydride to give 1,3-dibromo-5,5-bis(ethoxycarbonyl)-cyclopenta[c]thiophene (**5**) in 67% yield. The Stille coupling between **5** and two equivalents of 2-tributylstannylthiophene gave the terthiophene **6** in 56% yield. After the ester groups were reduced with lithium aluminium hydride (77% yield), the resulting alcohol **7** was subjected to the Williamson ether synthesis with 3,5-bis(benzyloxy)benzyl bromide to afford the terthiophene (**D-3T**) in 82% yield. The oxidative homo-coupling of **D-3T** with iron(III) perchlorate produced the higher homologous series, **D-6T** (25% yield), **D-9T** (10% yield), and **D-12T** (7% yield), which were separated by preparative gel-permeation liquid chromatography.[6]

As shown in Figure 1 and Table 1, the electronic absorption and emission spectra of the dendron-encapsulated oligothiophenes **1** show π–π^* transitions in the UV–vis region, which are characterized by progressive red-shifts with chain extension. Such red-shifts are generally observed for extended oligothiophenes **2** and **3**. However, the fluorescence quantum yields of **D-nT** except that of the trimer **D-3T** are beyond 0.5, much higher than those (0.3–0.4) of unhindered oligothiophenes **3**.[4] This suggests the prevention of intermolecular interactions due to the many dendrons of **1**.

There have been many documents on charge carriers for conducting polymers, which are generally doped to about 20%

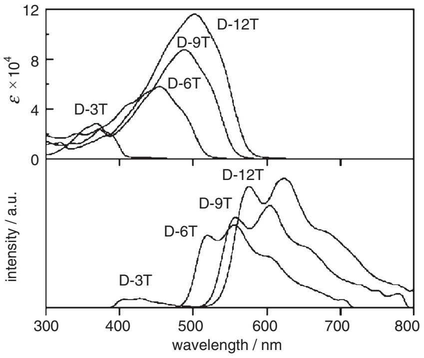
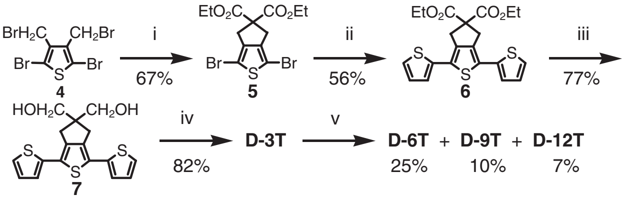


Figure 1. Electronic absorption spectra (upper) and emission spectra (lower) of oligothiophenes **1** in dichloromethane.

Table 1. Spectroscopic data and oxidation potentials of oligothiophenes **1**

Comp.	λ_{abs}/nm[a]	ε	λ_{flu}/nm[a,b]	ϕ_f[c]	$E_{1/2}(1)/V$[d]	$E_{1/2}(2)/V$[d]
D-3T	369	28200	407, 430	0.073	1.1 (irreversible)	
D-6T	455	57700	516, 551	0.51	0.72	0.97
D-9T	488	87400	557, 605	0.52	0.58	0.79
D-12T	502	116000	576, 616	0.57	0.52	unresolved

[a] UV–vis and EL spectra were measured in dichloromethane. [b] On excitation at 436 nm (366 nm for **D-3T**). [c] Quantum yields were determined relative to fluorescein standard (ϕ_f 0.90 in 0.1 M aq NaOH). [d] Cyclic voltammograms were measured in dichloromethane containing tetrabutylammonium perchlorate as supporting electrolyte and using an Ag/AgCl standard electrode and a Pt working electrode.



Scheme 1. Reagents and conditions: i) 1 equiv. diethyl malonate, 2 equiv. NaH, 10:1 toluene–DMF, 60 °C, 1.5 h; ii) 4 equiv. 2-tributylstannylthiophene, cat. $(Ph_3P)_4Pd$, xylene, reflux, 8 h; iii) 4 equiv. LAH, THF, reflux, 12 h; iv) 3,5-bis(benzyloxy)benzyl bromide, NaH, THF, reflux, 1.5 h; v) 1 equiv. $Fe(ClO_4)_3 \cdot xH_2O$, 2:1 $CHCl_3$–CH_3CN, rt, 7 h.

oxidation states. The 20% doping level of polythiophene corresponds to the presence of a radical cation (so-called polaron) per five-thiophene sequence.[7a] However, ESR silence under doped states indicates the involvement of spinless dimeric species, such as bipolaron,[7] π-dimer,[8] polaron couple on a single chain (chain dimer),[9] and σ-dimer.[10] Among these, π-dimers are accepted as the most possible charge carrier species, being evidenced by spectroscopic studies using short oligomers as model compounds. However, we recently speculated from the study of long oligothiophenes **3** that charge carrier species are a mixture of dimeric species involving π-dimers.[11] The insulating oligothiophenes **1** are expected to prevent the formation of π-dimers, and accordingly, to serve to identify the involved species other than π-dimers.

We here discuss charge carrier species based on the electronic absorption spectra of the longest dodecithiophene **D-12T** in the doped states, because the bipolarons and chain dimers of the short ones are hard to generate. Figure 2 demonstrates the spectral change of **D-12T** upon consecutive oxidation by addition of two-equimolar $FeCl_3$ per one-electron oxidation in dichloromethane. For comparison, the spectral change of the hexyl-substituted **H-12T** is also added. In both spectra, the oxidation causes the disappearance of neutral π–π^* bands and the concomitant appearance of two absorption bands in the near-infrared region (around 0.5 and 1.5 eV). The two bands observed in the initial oxidation are certainly due to polarons. The progressive oxidation of **H-12T** results in the large blue shifts of the two polaronic bands until two-electron oxidation. This is explained in terms of Davidov shifts due to the formation of π-dimers. On the other hand, the oxidation of **D-12T** causes a small blue shift for the low-energy band and little shift for the high-energy band. Evidently the bulky pendant dendrons prevent the formation of π-dimers. The two polaronic bands of **D-12T** are enhanced with progressive oxidation until one-electron oxidation. However, under one-electron oxidation, an ESR signal due to the polarons of **D-12T** is only 20% in intensity as compared to that observed for **D-6T**. This suggests that most of polarons dimerize to spinless species. Considering the small spectral change, one may speculate the involvement of chain dimers, as proposed by Janssen.[9] In the further oxidation, one absorption band at 0.7 eV becomes eminent. Based on the selection rule,[12] this is assignable to bipolarons. Note that even beyond two-electron oxidation, however, the band at around 1.5 eV due to the chain dimer still remains. These results evidently indicate that spinless species generated by high doping of insulating **D-12T** are a mixture of both chain dimers and bipolarons.

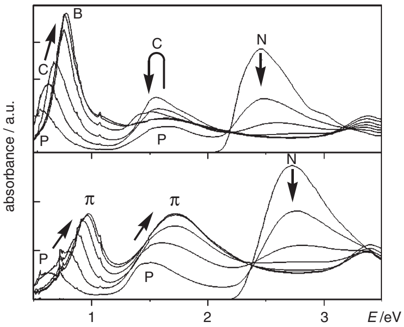


Figure 2. Spectral changes of **D-12T** (upper) and **H-12T** (lower) in dichloromethane under consecutive oxidation with $FeCl_3$. The spectra are recorded every 0.5-electron oxidation. N, P, B, C, and π denote neutral, polaronic, bipolaronic, chain-dimeric, and π-dimeric bands, respectively.

In conclusion, the present study has revealed that chain dimers and bipolarons, besides π-dimers, are involved as the spinless charge carrier species of conductive polymers. Presumably, these dimers are in equilibrium with active polarons, which undertake electric conduction under application of a bias voltage.

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6 All new compounds were satisfactorily characterized by spectroscopic measurements. Selective data of **D-3T**: light yellow crystals from hexane–chloroform; mp 59–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (s, 4H, CH_2), 3.53 (s, 4H, CH_2), 4.48 (s, 4H, CH_2), 4.96 (s, 8H, CH_2), 6.50 (t, $J = 2.2$ Hz, 2H, ArH), 6.56 (d, $J = 2.2$ Hz, 4H, ArH), 6.96 (dd, $J = 5.1$, 3.6 Hz, 2H, ArH), 7.07 (dd, $J = 3.6$, 1.0 Hz, 2H, ArH), 7.12 (dd, $J = 5.1$, 1.0 Hz, 2H, ArH); MS (FAB) m/z 953.9 (M^+, Calcd. 952.3); Anal. Found: C, 74.40; H, 5.58%. Calcd. for $C_{59}H_{52}O_6S_3$: C, 74.34; H, 5.50%. **D-6T**: orange solid; mp 67–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (s, 4H, CH_2), 2.81 (s, 4H, CH_2), 3.55 (s, 8H, CH_2), 4.49 (s, 8H, CH_2), 4.95 (s, 16H, CH_2), 6.50 (t, $J = 2.4$ Hz, 4H, ArH), 6.57 (d, $J = 2.4$ Hz, 8H, ArH), 6.90 (d, $J = 3.9$ Hz, 2H, ArH), 6.94 (d, $J = 3.9$ Hz, 2H, ArH), 6.97 (dd, $J = 5.1$, 3.7 Hz, 2H, ArH), 7.07 (dd, $J = 3.7$, 1.1 Hz, 2H, ArH), 7.13 (dd, $J = 5.1$, 1.1 Hz, 2H, ArH), 7.07 (dd, $J = 3.7$, 1.1 Hz, 2H, ArH), 7.13 (dd, $J = 5.1$, 1.1 Hz, 2H, ArH), 7.27–7.37 (m, 40H, ArH); MS (MALDI-TOF) m/z 1905.0 (M^+, Calcd. 1903.6); Anal. Found: C, 74.21; H, 5.37%. Calcd. for $C_{118}H_{102}O_{12}S_6$: C, 74.42; H, 5.40%. **D-9T**: red solid; mp 66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (s, 4H, CH_2), 2.82 (s, 8H, CH_2), 3.55 (s, 8H, CH_2), 3.56 (s, 4H, CH_2), 4.49 (s, 8H, CH_2), 4.50 (s, 4H, CH_2), 4.94 (s, 8H, CH_2), 4.95 (s, 16H, CH_2), 6.50 (t, $J = 2.2$ Hz, 6H, ArH), 6.57 (d, $J = 2.2$ Hz, 12H, ArH), 6.91 (d, $J = 3.8$ Hz, 4H, ArH), 6.95 (d, $J = 3.8$ Hz, 4H, ArH), 6.97 (dd, $J = 5.1$, 3.7 Hz, 2H, ArH), 7.08 (dd, $J = 3.7$, 1.0 Hz, 2H, ArH), 7.13 (dd, $J = 5.1$, 1.0 Hz, 2H, ArH), 7.26–7.37 (m, 60H, ArH); MS (MALDI-TOF) m/z 2854.9 (M^+, Calcd. 2854.8); Anal. Found: C, 74.21; H, 5.36%. Calcd. for $C_{177}H_{152}O_{18}S_9$: C, 74.45; H, 5.37%. **D-12T**: dark red solid; mp 68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (br s, 16H, CH_2), 3.55 (s, 8H, CH_2), 3.56 (s, 8H, CH_2), 4.49 (s, 8H, CH_2), 4.50 (s, 8H, CH_2), 4.93 (s, 16H, CH_2), 4.95 (s, 16H, CH_2), 6.50 (m, 8H, CH_2), 6.57 (m, 16H, ArH), 6.89 (d, $J = 3.7$, 1.1 Hz, 2H, ArH), 6.93 (d, $J = 3.9$ Hz, 6H, ArH), 6.96 (dd, $J = 5.1$, 3.7 Hz, 2H, ArH), 7.07 (dd, $J = 3.7$, 1.1 Hz, 2H, ArH), 7.12 (dd, $J = 5.1$, 1.1 Hz, 2H, ArH), 7.23–7.37 (m, 80H, ArH); MS (MALDI-TOF) m/z 3806.7 (M^+, Calcd. 3806.3); Anal. Found: C, 74.45; H, 5.39%. Calcd. for $C_{236}H_{202}O_{24}S_{12}$: C, 74.46; H, 5.35%.

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