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Conductive, Magnetic, and Optical Properties of Sterically Hindered Dodecithiophenes. Evidence for the Coexistence of Bipolaron and π-Dimer

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Conductive, magnetic, and optical properties of sterically hindered dodecithiophenes bearing bulky 2,2-bis(butoxymethyl)-1,3-propanediyl groups were examined. At high doping with $FeCl_3$, a completely hindered dodecithiophene had only a poor conductivity of $5 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$, but two partially hindered dodecithiophenes had relatively high conductivities of 1.9 and $0.6\,\mathrm{S\,cm^{-1}}$, which are one or two orders lower than the conductivity ($38\,\mathrm{S\,cm^{-1}}$) of the unhindered dodecithiophene. Despite having different structures and conductivities, all of the doped solids of these dodecithiophenes were magnetically inactive and demonstrated similar optical absorption spectra in the near infrared region, as generally observed for polythiophenes. On the other hand, their optical spectra in dichloromethane were quite different from one another. A solution spectrum of the unhindered dodecithiophene under high doping was characterized by two absorption transitions assignable to a π-dimer. On the other hand, a solution spectrum of the completely hindered dodecithiophene was characterized by an absorption transition due to a bipolaron. Furthermore, the solution spectra of two partially hindered dodecithiophenes could be explained as an overlap of both π-dimeric and bipolaronic bands. From these results, both π-dimer and bipolaron species appear to serve as active charge carriers in conductive poly(oligo)thiophenes.

The conduction mechanisms of doped polythiophenes and related polyaromatics have been a subject of intense investigation.[1] Despite considerable efforts, active charge-carrier species are still controversial. Generally, such conductive polymers are oxidized up to full doping levels of about 20–30%, which means the statistical presence of a delocalized radical cation (so-called polaron) per four- or five-aromatic sequence. Spin-carrying polarons were initially believed to be the principal charge-carrier species of conductive polymers,[2–5] but it has been shown that they can exist only at low doping levels. Many of the early optical, electrical, and magnetic studies support the involvement of spinless bipolarons at high doping levels.[6–15] For a long time, the electronic states and charge-transport mechanisms of conductive polymers have been clarified using a framework involving polaron/bipolaron models,[16–26] but the role of bipolaron in the charge-transport process has remained ambiguous. However, other spinless dimeric species, such as π-dimers,[27–40] σ-dimers,[41] and polaron pairs on a single chain,[42–46] have been proposed as alternatives to polaron and bipolaron. Among these, π-dimers are most often referred to in the literature. Most evidence for the existence of π-dimers has been obtained by spectroscopic, magnetic, and electrochemical experiments of appropriate model compounds, mostly oligothiophenes. In particular, our recent study on a cyclophane type of oligothiophenes **1** (Chart 1) has provided definite evidence for the formation of a π-dimer.[47] However, due to synthetic reasons, such model compounds have been restricted to short oligothiophenes consisting of several thiophene units, which do not have enough spaces to accommodate other long dimeric species, such as bipolaron and polaron pair. In order to fill up the size blank between short oligothiophenes and polythiophenes, we have synthesized a homologous series of long oligothiophenes **2** up to the 48-mer,[48] and based on conduction, magnetism, and optical spectrometry experiments, have concluded that π-dimers are involved together with other dimeric species.[49]

It is expected that sterically hindered oligothiophenes incapable of forming π-dimers will give information on dimeric charge-carrier species other than π-dimer. In fact, our previous study of dendrimer-encapsulated oligothiophenes **3** (Chart 2) suggests that bipolarons and polaron pairs are generated under doping.[50] However, some questions remain as to whether or not such sterically insulated oligothiophenes can be regarded as a model for conductive polymers. A systematical investigation of the steric influence on the conductivities and charge-carrier species of oligothiophenes is thus required. This has led us to study four different types of dodecithiophenes **4**–**7** bearing hexyl groups and/or 2,2-bis(butoxymethyl)-1,3-propanediyl groups at the β-sites of the skeletal thiophene rings. The attached hexyl groups do not sterically influence the intermolecular π-stacking of the dodecithiophene at all; thus, **4** represents an unhindered-type dodecithiophene. On the other hand, the bulky 2,2-bis(butoxymethyl)-1,3-propanediyl groups sterically interfere the intermolecular π-stacking; thus, **5** with the bulky groups on all thiophene rings represents a hindered-type dodecithiophene. The remaining two **6** and **7** with 2,2-bis(butoxymethyl)-1,3-propanediyl groups on half of the thiophene rings are considered to be partially hindered-type dodecithiophenes. Although complete overlapping is impossible for these partially hindered dodecithiophenes, **6** can stack at

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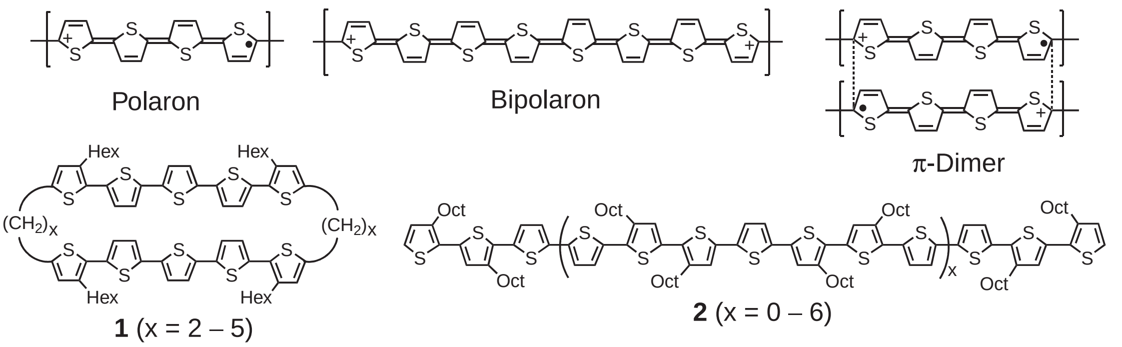


Chart 1.

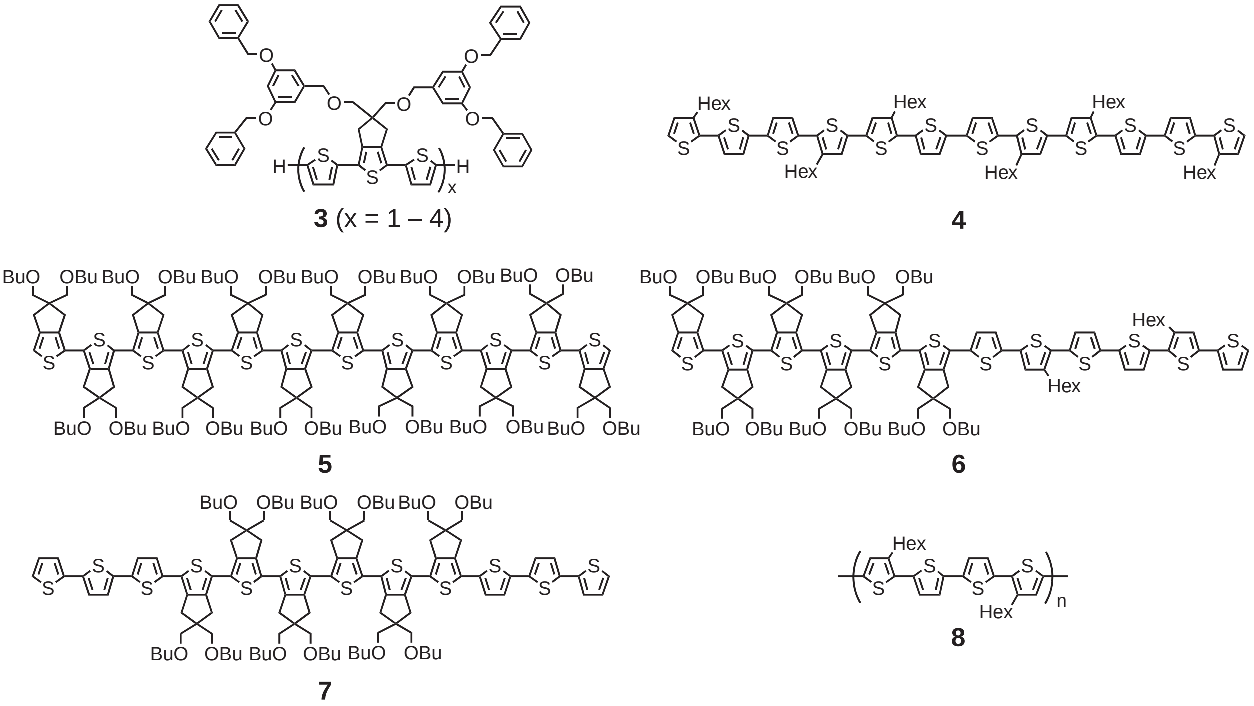


Chart 2.

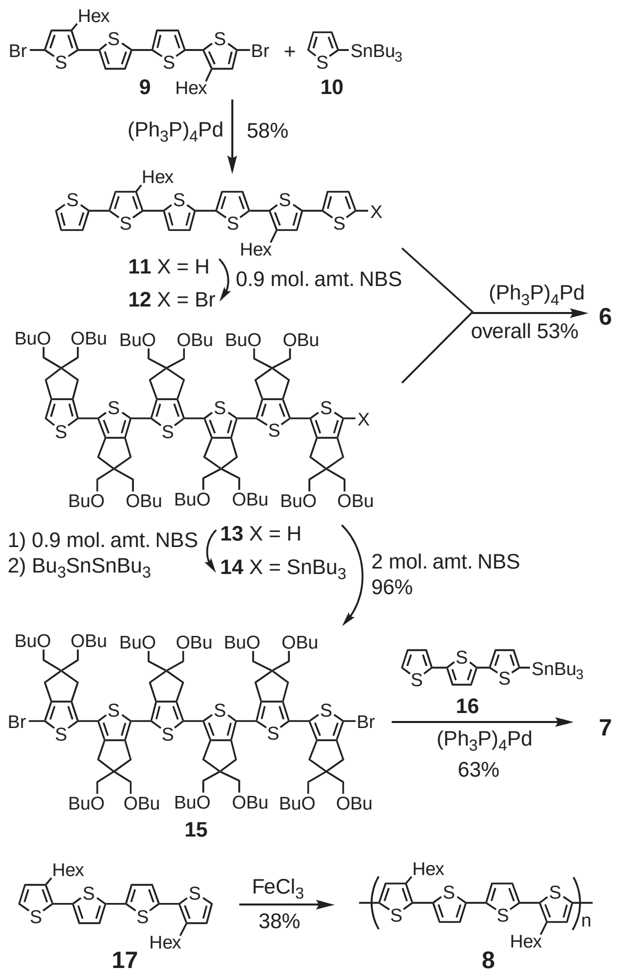
the half hexyl-substituted sexithiophene segment, and **7** can stack at both of its terminal nonsubstituted terthiophene segments. We now report the details of the conductive, magnetic, and optical properties of dodecithiophenes **4**–**7** together with those of poly(quaterthiophene) **8**, which provide very helpful information on active charge-carrier species involved in conductive oligo- and polythiophenes.

Results and Discussion

Synthesis. The preparations of hexyl-substituted dodecithiophene **4**[51] and 2,2-bis(butoxymethyl)-1,3-propanediyl-substituted dodecithiophene **5**[52] have been reported in our previous papers. Partially hindered dodecithiophenes **6** and **7** were unknown and synthesized from the previously obtained small oligothiophenes, as shown in Scheme 1. A Stille coupling between 5,5‴-dibromo-4,4‴-dihexylquaterthiophene (**9**)[51] and 2-tributylstannylthiophene (**10**)[53] gave 4′,3⁗-dihexylsexithiophene (**11**), which on subsequent treatment with a 0.9 molar amount of *N*-bromosuccinimide (NBS) was converted to the monobromo derivative **12**. Next, 2,2-bis(butoxymethyl)-1,3-propanediyl-substituted sexithiophene **13**[52] was converted to the tributylstannyl derivative **14** by bromination with a 0.9 molar amount of NBS followed by treatment with hexabutylditin and tetrakis(triphenylphosphine)palladium. Finally, Stille coupling between **12** and **14** gave partially hindered dodecithiophenes **6**. An alternative treatment of 2,2-bis(butoxymethyl)-1,3-propanediyl-substituted sexithiophene **13** with 2 molar amounts of NBS afforded the dibromo derivative **15**, which was then coupled with 5-tributylstannylterthiophene (**16**)[54] to give partially hindered dodecithiophenes **7**. Polymer **8** was prepared by chemical polymerization of 3,3‴-dihexylquaterthiophene (**17**) with $FeCl_3$ in chloroform at 50 °C for 5 d.[55]

Cyclic Voltammetry. Figure 1 shows the cyclic voltammograms of dodecithiophenes **4**–**7** measured in the anodic sweep range from 0 to +1.2 V (vs. Ag/AgCl) in dichloromethane. Table 1 summarizes the first oxidation potentials, together with the electronic absorption maxima and electrical conductivities. Hexyl-substituted dodecithiophene **4** shows an oxidation wave at E_{pa} +0.71 V tailed by a broad wave due to a subsequent multi-oxidation. On the other hand, **5**–**7** show a large oxidation wave covering from +0.3 to +1.2 V, with discernible multi-peaks, and the first oxidation peaks of **5** (E_{pa} 0.42 V), **6** (E_{pa} 0.46 V), and **7** (E_{pa} 0.51 V) are much lower than that of **4**. Evidently, the 2,2-bis(butoxymethyl)-1,3-propanediyl groups attached to the thiophene rings serve to stabilize markedly the resulting cationic states. The same groups also exercise a large substitution effect on the electronic absorption spectra of dodecithiophenes **4**–**7**; the π–π^* transition absorption bands of **5** (λ_{max} 2.44 eV), **6** (λ_{max} 2.49 eV), and **7** (λ_{max} 2.45 eV) in the visible region appear at much lower energies than that of **4** (λ_{max} 2.73 eV).

Electrical Conductivities. The cast films of dodecithiophenes **4**–**7** were oxidized (doped) by treatment with $FeCl_3$ in nitromethane at room temperature for 12 h. The oxidation reactions were controlled by adjusting the amount of $FeCl_3$, and the doping levels per thiophene unit were calculated by elemental analyses. The doped dodecithiophene films were stable under the atmospheric conditions, and their conductivities were measured on compressed pellets by the Van der Pauw method or by a two-probe method. Table 1 compares the electrical conductivities of **4**–**7** measured at different doping levels. All of these compounds are insulating ($<10^{-7}$ S cm^{-1}) in the neutral states and conductive in the doped states. The conductivities largely depend not only on the doping levels but also on the steric hindrance of the attached substituent groups. The conductivity of unhindered **4** markedly increased



Scheme 1.

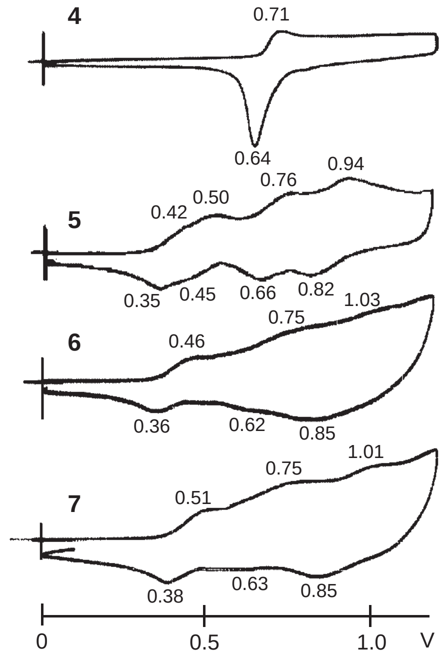


Fig. 1. Cyclic voltammograms of dodecithiophenes **4**–**7** in dichloromethane; measurement conditions: 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, platinium plates as working and counter electrodes, Ag/AgCl standard electrode, and 100 mV s^{-1} scan rate.

Table 1. First Oxidation Potentials, Electronic Absorption Maxima, and Electrical Conductivities of Dodecithiophenes **4**–**7**

Compd	E_{pa}/V[a]	λ_{max}/eV[b]	σ/S cm^{-1} [c] (doping level %)[d]
4	0.65	2.73	$<10^{-7}$ (0), 5×10^{-5} (1), 7×10^{-2} (7), 4×10^{-1} (14), 38 (24)
5	0.42	2.44	$<10^{-7}$ (0), $<10^{-7}$ (3), 10^{-6} (16), 1×10^{-4} (23), 5×10^{-4} (34)
6	0.46	2.49	$<10^{-7}$ (0), 1×10^{-4} (6), 6×10^{-2} (11), 1×10^{-1} (14), 1.9 (21)
7	0.51	2.45	$<10^{-7}$ (0), 1×10^{-2} (3), 2×10^{-2} (9), 5×10^{-2} (18), 6×10^{-1} (24)

a) Measured by cyclic voltammetry. Conditions: solvent, dichloromethane; supporting electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate; working and counter electrodes, platinum plates; reference electrode, Ag/AgCl; scan rate, 100 mV s^{-1}. b) Measured in dichloromethane. c) Conductivities were measured on compressed pellets of dodecithiophenes **4**–**7** doped with $FeCl_3$ by the Van der Pauw method or by a two-probe method for low-conductive samples with $<10^{-5}$ S cm^{-1}. d) Doping levels per thiophene unit were decided by elemental analyses.

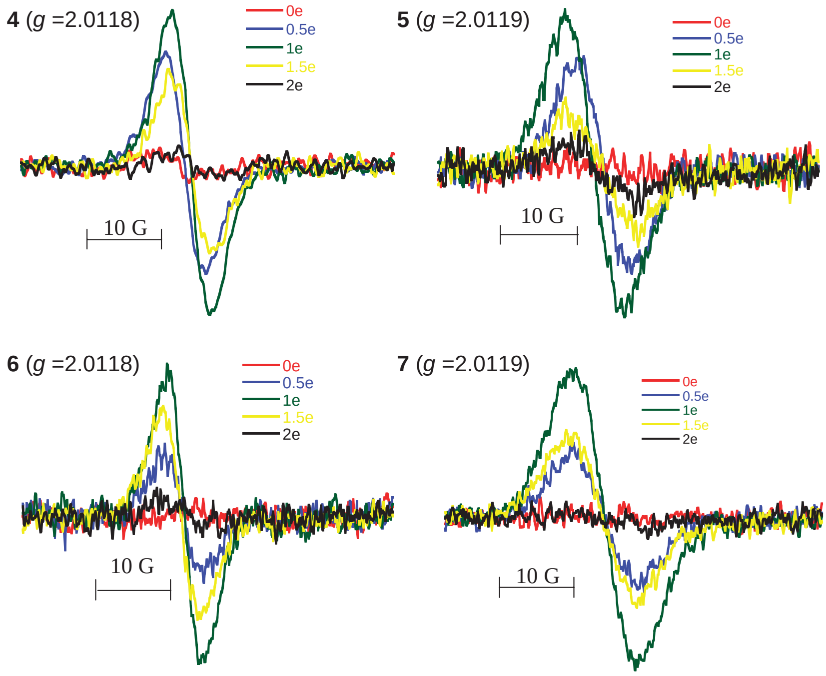


Fig. 2. ESR spectra of dodecithiophenes **4**–**7** in 10^{-6} M dichloromethane under controlled oxidation with $FeCl_3$.

upon doping and reached a high value of 38 S cm^{-1} at a full doping level of 24%, which is nearly the same as that (28 S cm^{-1}) of conductive poly(quaterthiophene) **8**. This result clearly indicates that dodecithiophene **4** can serve as a good model compound for conductive polythiophene. On the other hand, hindered **5** was easily doped up to a full doping level of 34% owing to the large substituent effect of the 2,2-bis(butoxymethyl)-1,3-propanediyl groups, but the conductivity barely increased with doping to reach only 5×10^{-4} S cm^{-1} even at full doping. Evidently, the attached 2,2-bis(butoxymethyl)-1,3-propanediyl groups prevent intermolecular π–π contacts required for charge transport. It is noteworthy that partially hindered dodecithiophenes **6** (1.9 S cm^{-1}) and **7** (0.6 S cm^{-1}) have fairly high conductivities at full doping (ca. 20–25%). Recent studies of self-organized conjugated polymer films have shown that strong π–π interactions over adjacent polymer chains are the origin for high mobilities along the stack.[56] Inconsistent with this description, the fairly high conductivities observed for **6** and **7** suggest that small π-intermolecular contacts are enough for charge transport.

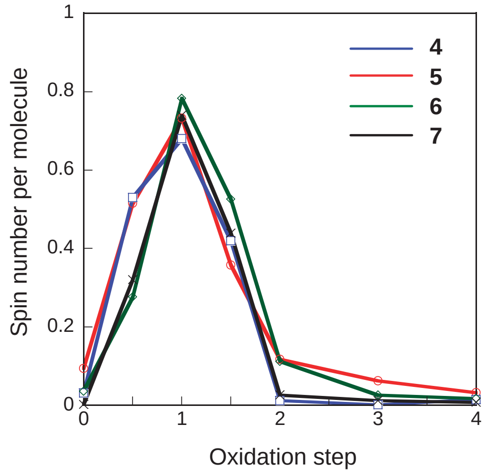


Fig. 3. Changes of spin numbers of dodecithiophenes **4**–**7** with consecutive oxidation; spin numbers were evaluated on the basis of ESR signal intensities using the DPPH standard.

Electron Spin Resonances. ESR spectroscopy is very useful for identifying actual charge-carrier species for conductive polymers. Nearly no ESR signals were detected for the doped film samples of dodecithiophenes **4**–**7** and poly(quaterthiophene) **8** used for measuring the conductivities. ESR inactivity is generally accepted for conductive polymers, indicating that spinless dimeric polaron species is involved. In order to obtain more detailed information, we systematically examined the ESR spectra of dodecithiophenes **4**–**7** in ca. 10^{-6} M dichloromethane solution under controlled oxidation by addition of two equimolar amounts of $FeCl_3$ per one-electron oxidation. Figure 2 shows ESR spectra of dodecithiophenes **4**–**7**, and Figure 3 depicts the changes of spin numbers per molecule evaluated on the basis of the intensities of these observed ESR signals using a DPPH standard. The changes in the spin numbers of **4**–**7** with each consecutive oxidation were very similar to one another. Even **5**, which has a poor conductivity, behaves similarly to **4**, **6**, and **7**, which have good conductivities. Initial strong ESR signals at a half- and one-electron-oxidation stages obviously indicate the generation of a polaron. Then, after two-electron oxidation and above, the ESR signals nearly disappeared. Since the two- and three-electron-oxidation stages of dodecithiophene formally correspond to 17 and 25% doping levels, respectively, this result agrees with the ESR inactivity observed for the doped solid films. Evidently, the spinless dimeric polaron species also prevails in solution at high doping.

Solid Optical Absorption Spectra. In order to obtain information on active charge-carrier species, we measured

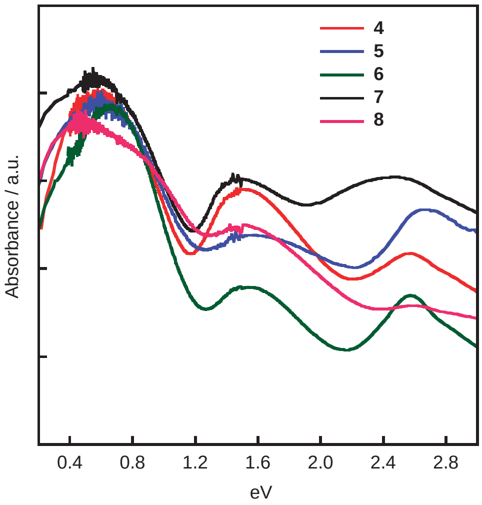


Fig. 4. Electronic absorption spectra of dodecithiophenes **4**–**7** and poly(quaterthiophene) **8** in solid films (doping level 20–25%).

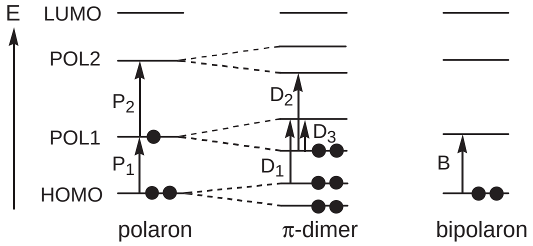


Fig. 5. Allowed electronic transitions of three oxidized species.

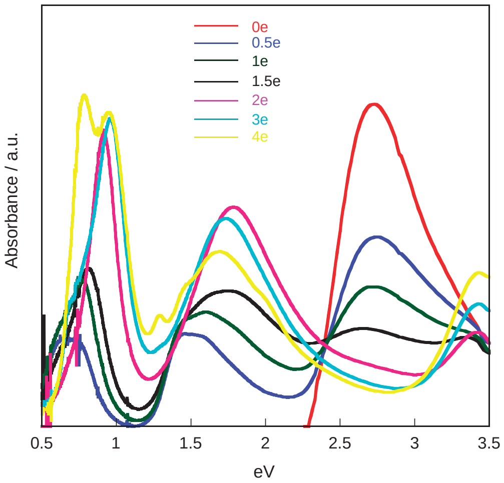


Fig. 6. Electronic absorption spectra of dodecithiophene **4** in 10^{-6} M dichloromethane under controlled oxidation with $FeCl_3$.

the electronic absorption spectra of dodecithiophenes **4**–**7** and poly(quaterthiophene) **8** in 20–25%-doped solid film states. As demonstrated in Fig. 4, the spectral shapes of **4**–**7** were, as a whole, similar to one another; two absorption bands appeared at around 0.5 and 1.5 eV in the near-infrared region and one absorption band at 2.4–2.6 eV in the visible region. In all spectra, the low-energy band at around 0.5 eV was very intense as compared to the two high-energy bands. These spectra also resembled those of poly(quaterthiophene) **8** and polythiophenes,[11a,12a] except that the visible band for the polymer was smaller. From the similar spectral features, it is reasonable to imagine that similar charge-carrier species may exist in the solid films of **4**–**8**. According to the selection rule, two electronic transitions for polaron, one for bipolaron, and three for π-dimer are allowed, as illustrated in Fig. 5.[57] As already stated, ESR inactivity for all samples **4**–**8** excludes the involvement of a polaron. It is possible that the two near-infrared bands in Fig. 4 are due to either π-dimer or polaron pair. However, the observed relative intensities of the two bands were quite different, and thus, it is difficult to explain in terms of the involvement of a π-dimer or a polaron pair alone. In addition, the formation of a π-dimer is not possible for **5**, which is completely hindered.

Solution Optical Absorption Spectra. In order to identify charge-carrier species involved in the above solid absorption spectra, we examined the electronic absorption spectra of dodecithiophenes **4**–**7** in 10^{-6} M dichloromethane solution under controlled oxidation with $FeCl_3$, allowing the successive formation of mono- di-, tri-, and tetra-cations. As demonstrated in Fig. 6, the initial 0.5-electron oxidation of **4** caused a decrease in the intensity of the neutral π–π^* transition absorption band (λ_{max} 2.73 eV) by ca. 50% and concomitantly gave rise to two new absorption bands (λ_{max} 0.72 and 1.50 eV) in the near-infrared region. These two near-infrared bands were assigned to the allowed transitions P_1 and P_2 of polaronic species. The existence of polarons agrees with the observation of a strong ESR signal at the 0.5 electron oxidation stage. Further oxidation of **4** caused a progressive increase and high-energy shifts in the two near-infrared absorption bands. In the spectrum, after the two-electron oxidation, the two near-infrared bands were located at λ_{max} 0.91 and 1.78 eV. In addition, the original neutral band nearly disappeared, and a small visible band appeared at λ_{max} 3.42 eV. These spectral changes as well as the above-stated ESR inactivity indicate the formation of a spinless π-dimeric species from polarons. The concentration-dependent high-energy shifts of the near-infrared bands can be rationalized by the Davidov blue shifts due to π-stacking.[29b,37,58] Although the selection rule for π-dimers allows three bands D_1, D_2, and D_3, the interchain transition D_3 is usually so weak that it can scarcely be detected[27e,27h,47a] or it is concealed by other transitions.[47b] Three-electron oxidation essentially gave rise to the same spectrum as at the two-electron oxidation stage, and four-electron oxidation gave rise to a new band at 0.78 eV. This single band is possibly due to bipolaronic species formed by confining many charges in a limited conjugated area, which is essentially similar to that observed in the two-electron oxidation of short oligothiophenes consisting of several thiophene units.[29,47,49]

The spectral change of the hindered dodecithiophene **5** with consecutive oxidation was quite different from that observed for **4** and similar to that previously observed for dendrimer-encapsulated oligothiophenes **3**.[50] As depicted in Fig. 7, the initial 0.5-electron oxidation gave two polaronic bands at 0.55 and 1.37 eV. Subsequent one-electron oxidation caused an increase in these two polaronic bands, but no transition energy shifts, which is quite different from the spectral change of **4**. This means that the polaronic species simply increases during

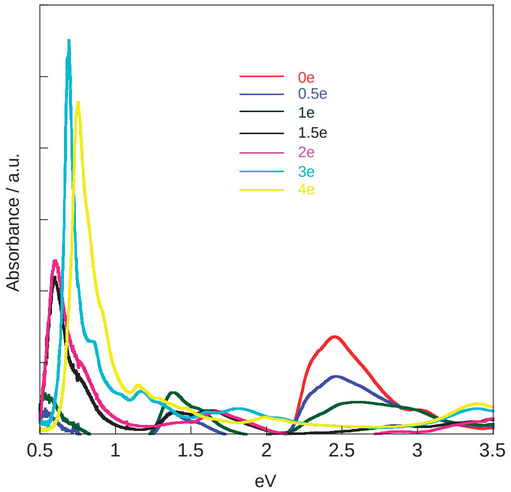


Fig. 7. Electronic absorption spectra of dodecithiophene **5** in 10^{-6} M dichloromethane under controlled oxidation with $FeCl_3$.

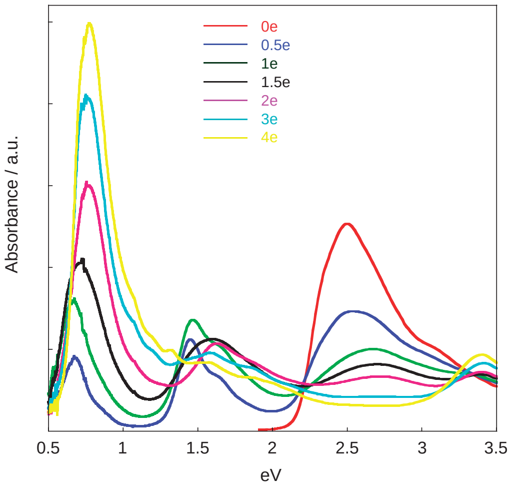


Fig. 8. Electronic absorption spectra of dodecithiophene **6** in 10^{-6} M dichloromethane under controlled oxidation with $FeCl_3$.

the early electron oxidation. Evidently, the bulky 2,2-bis(butoxymethyl)-1,3-propanediyl groups in **5** prevent the formation of π-dimers. However, two-electron oxidation gave rise to a new strong absorption band at 0.60 eV, instead of the two polaronic bands. Evidently, the sterically hindered dodecithiophene **5** prefers the formation of bipolarons. Three- and four-electron oxidations resulted in the enhancement and high-energy shift of the bipolaronic band, presumably because of an increase in the bipolaronic species.

The spectral changes of partially hindered dodecithiophenes **6** and **7** were different from both of those of **4** and **5**. As depicted in Fig. 8, the initial 0.5-electron oxidation of **6** gave two polaronic bands at 0.67 and 1.46 eV. Further oxidation leads to an increase and high-energy shifts in these bands, resulting in the appearance of two bands at 0.77 and 1.63 eV after two-electron oxidation. It is noteworthy that the high-energy shifts of these two bands were smaller than those induced by π-dimerization observed for **4**, and in addition, at two-electron oxidation stage, the low-energy band were much larger than the high-energy one. We think that the two bands are comprised of a superposition of π-dimeric and bipolaronic bands; that is, the low energy band is enhanced by overlapping of a bipolaronic band with one of the two π-dimeric bands. The dodecithiophene **6** can stack face-to-face with another molecule at the unhindered half segment. Presumably, a partially stacked π-dimer is not so stable as a fully stacked π-dimer, and thus, it can coexist with a bipolaron. Actually, a weak electronic interaction for the π-dimer of **6** is corroborated by the small Davidov blue shifts in the two bands. Further three- and four-electron oxidation markedly enhanced the low-energy band, owing to an increase of bipolaronic species.

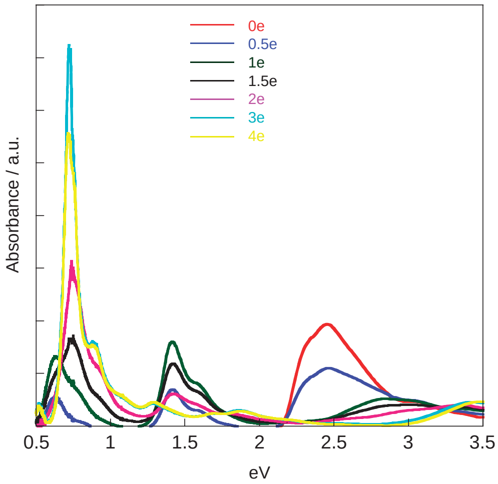


Fig. 9. Electronic absorption spectra of dodecithiophene **7** in 10^{-6} M dichloromethane under controlled oxidation with $FeCl_3$.

Figure 9 shows the spectral change in partially hindered **7**, which is, as a whole, similar to that of **6**. Thus, 0.5-electron oxidation gave two polaronic bands at 0.63 and 1.42 eV, two-electron oxidation gave a strong band at 0.74 eV and a weak band at 1.42 eV, and finally, further oxidation enhanced the bipolaronic low-energy band. A π-dimer of **7** can be formed only by partial stacking at the unhindered terminal terthiophene segments; accordingly, it is not so stable as that of **6**. This is supported by the observation that the high-energy band undergoes no Davidov blue shift with consecutive oxidation, and the relative intensity of the high-energy band to the low-energy band at the two-electron oxidation stage is smaller, when compared to that of **6**.

Concluding Remarks

Four doped dodecithiophenes of **4**–**7** showed similar electronic absorption spectra in the solid phase, but quite different absorption spectra in dichloromethane solution. The solution spectrum of unhindered dodecithiophene **4** under high doping was characterized by two absorption transitions, which were assigned to a π-dimer. On the other hand, the solution spectrum of completely hindered dodecithiophene **5** was characterized by an absorption transition due to bipolaron. It is noteworthy that the solution spectra of partially hindered **6** and **7** could be explained as a superposition of π-dimeric and bipolaronic bands. This spectral feature was similar to that observed for the solid films of **6** and **7**, meaning that both π-dimer and bipolaron species exist in the solid films. In addition, a close resemblance of the solid spectra of **4** and **5** to those of **6** and **7** suggests that both species may also exist in the solid films. It is thus speculated that the face-to-face stacked π-dimer of **4** does not form so readily in the solid film as it does in solution, presumably allowing the involvement of a bipolaron species. This means that π-dimers prevail in the ordered microcrystalline domains of the solid films, whereas bipolarons prevail in disordered amorphous domains. The π-dimer and bipolaron species exist in the solid film of poly(quaterthiophene) **8**, which showed with an analogous solid spectrum (see Fig. 4). Presumably, in conductive polyaromatic films, π-dimers and bipolarons coexist and cooperatively make a conductive network along conjugated chains, across stacked chains, or via interchain contacts.

Experimental

4′,3′′′′′-Dihexylsexithiophene (11). A mixture of 5,5‴-dibromo-3,3‴-dihexylquaterthiophene (**9**)[51] (214 mg, 0.326 mmol), 2-tributylstannylthiophene (**10**)[53] (243 mg, 0.651 mmol), tetrakis(triphenylphosphine)palladium (18 mg) in toluene (10 mL) was refluxed in the dark for 12 h under a nitrogen atmosphere. After the solvent was evaporated, the residual solid was purified by column chromatography (silica gel, 1:1 hexane–dichloromethane), then gel-permeation liquid chromatography (JAIGEL 1H/2H column assembly, chloroform), and finally recrystallization from chloroform to give orange needles of **11** (125 mg, 58% yield): mp 126–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, $J = 5.1$ Hz, $J' = 0.9$ Hz, 2H), 7.17 (dd, $J = 3.6$ Hz, $J' = 0.9$ Hz, 2H), 7.14 (d, $J = 3.9$ Hz, 2H), 7.05 (d, $J = 3.9$ Hz, 2H), 7.02 (dd, $J = 5.1$ Hz, $J' = 3.6$ Hz, 2H), 7.02 (s, 2H), 2.77 (t, $J = 7.8$ Hz, 4H), 1.68 (quin, $J = 7.8$ Hz, 4H), 1.60 (m, 4H), 1.45–1.30 (m, 8H), 0.93 (t, $J = 7.8$ Hz, 6H); MALDI-TOF-MS (1,8,9-trihydroxyanthracene matrix) m/z 660.8 (M^+, Calcd 662.1); Anal. Calcd for $C_{36}H_{38}S_6$: C, 65.21; H, 5.78%. Found: C, 65.23; H, 5.67%.

5-Bromo-4′,3′′′′′-dihexylsexithiophene (12). Into an ice-cooled solution of the dihexylsexithiophene (**11**) (100 mg, 0.151 mmol) in carbon disulfide (30 mL) was slowly added a solution of NBS (21.4 mg, 0.121 mmol) in DMF (10 mL), and then the mixture was stirred at rt for 12 h. After aqueous sat. sodium hydrogencarbonate (20 mL) was added with ice-cooling, the resulting insoluble white solid was removed by filtration through celite, and the filtrate was extracted with chloroform. The extract was dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by column chromatography (silica gel, chloroform) to give an orange oil of **12** (95 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, $J = 5.1$ Hz, $J' = 0.9$ Hz, 1H), 7.17 (dd, $J = 3.6$ Hz, $J' = 0.9$ Hz, 1H), 7.14 (d, $J = 3.9$ Hz, 2H), 7.05–7.01 (m, 3H), 7.02 (s, 1H), 6.98 (d, $J = 3.9$ Hz, 1H), 6.95 (s, 1H), 6.91 (d, $J = 3.9$ Hz, 1H), 2.76 (m, 4H), 1.67 (m, 4H), 1.55 (m, 4H), 1.45–1.30 (m, 8H), 0.90 (t, $J = 7.0$ Hz, 6H); MALDI-TOF-MS (1,8,9-anthracenetriol matrix) m/z 741.3 (M^+, Calcd 741.0 based on 1:1 ^{79}Br and ^{80}Br). This product was contaminated with a small amount of the unreacted material **11** (<15% based on ^{1}H NMR analysis), which was impossible to remove by conventional purification methods and used in the following step without further purification.

3,4:3′,4′:3″,4″:3‴,4‴:3′′′′,4′′′′:3′′′′′,4′′′′′-Hexakis[2,2-bis(butoxymethyl)-1,3-propanediyl]-5-tributylstannylsexithiophene (14). As described for the conversion of **11** to **12**, sexithiophene **13**[52] (237 mg, 0.134 mmol) was reacted with 0.9 molar amount of NBS (21.4 mg) to give the monobromo derivative (95 mg). The crude product was contaminated with a small amount of the unreacted **13** and directly refluxed with hexabutylditin (77 mg, 0.132 mmol) and tetrakis(triphenylphosphine)palladium (5.8 mg) in toluene (40 mL) under nitrogen for 12 h. The solvent was evaporated, and the residue was purified by column chromatography (alumina, chloroform) followed by gel-permeation liquid chromatography (JAIGEL 3H/4H column assembly, chloroform) to give a red oil of **14** (188 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (s, 1H), 3.44 (m, 48H), 2.77 (m, 22H), 2.62 (s, 2H), 1.56 (m, 24H), 1.38 (m, 24H), 0.92 (t, $J = 7.3$ Hz, 36H). This product was still contaminated with a small amount of sexithiophene **13** (<15% yield based on ^{1}H NMR analysis), which was impossible to remove by conventional purification methods and used in the next reaction without further purification.

Hexakis[2,2-bis(butoxymethyl)-1,3-propanediyl]dihexyldodecithiophene (6). A mixture of **12** (34 mg), **14** (95 mg), and tetrakis(triphenylphosphine)palladium (2.6 mg) in toluene (10 mL) was refluxed in the dark for 12 h under a nitrogen atmosphere. After evaporation of the solvent, the residue was purified by gel-permeation liquid chromatography (JAIGEL 3H/4H column assembly, chloroform) to allow removal of **11** and **13** contaminated in the preceding reactions, giving a red soft solid of **6** (53.4 mg, overall 53% yield from **12**): mp 110–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, $J = 5.1$ Hz, 1H), 7.17 (d, $J = 3.4$ Hz, 1H), 7.15 (d, $J = 3.7$ Hz, 2H), 7.08 (d, $J = 3.9$ Hz, 1H), 7.05 (d, $J = 3.4$ Hz, 2H), 7.03–7.00 (m, 4H), 3.45 (m, 48H), 2.78 (m, 26H), 2.62 (s, 2H), 1.72 (quin, $J = 7.81$ Hz, 4H), 1.57 (m, 28H), 1.42 (m, 32H), 0.93 (m, 42H); MALDI-TOF-MS (1,8,9-anthracenetriol matrix) m/z 2425.1 (M^+, Calcd 2429.2); Anal. Calcd for $C_{138}H_{194}O_{12}S_{12}$: C, 68.21; H, 8.05%. Found: C, 67.98; H, 8.01%.

5,5′′′′′-Dibromo-3,4:3′,4′:3″,4″:3‴,4‴:3′′′′,4′′′′:3′′′′′,4′′′′′-hexakis[2,2-bis(butoxymethyl)-1,3-propanediyl]sexithiophene (15). Into a solution of **13** (468 mg, 0.27 mmol) in a mixed solvent of chloroform (15 mL) and DMF (20 mL) was added NBS (101 mg, 0.57 mmol), and the mixture was stirred at rt for 13 h. After aq. sat. sodium hydrogensulfite (20 mL) was added, the mixture was extracted with chloroform (40 mL × 3). The extracts were combined, washed with brine, and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, chloroform) to give a pale orange oil of **15** (489 mg, 96% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.47–3.42 (m, 48H), 2.81–2.73 (m, 20H), 2.53 (s, 4H), 1.58–1.51 (m, 24H), 1.42–1.32 (m, CH_2), 0.93–0.89 (m, CH_3); MALDI-TOF-MS (1,8,9-anthracenetriol matrix) m/z 1928.7 (M^+, calcd 1926.4); Anal. Calcd for $C_{102}H_{156}Br_2O_{12}S_6$: C, 63.59; H, 8.16%. Found: C, 63.55; H, 8.80%.

Hexakis[2,2-bis(butoxymethyl)-1,3-propanediyl]dodecithiophene (7). A mixture of **15** (463 mg, 0.24 mmol), 5-tributylstannylterthiophene (**16**)[54] (290 mg, 0.54 mmol), and tetrakis(triphenylphosphine)palladium (28 mg) in toluene (45 mL) was refluxed for 14 h in the dark under a nitrogen atmosphere. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, dichloromethane) followed by gel-permeation liquid chromatography (JAIGEL 3H/4H column assembly, chloroform) to give a purple solid of **7** (293 mg, 51% yield): mp 194–196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, $J = 5.2$ Hz, 2H), 7.18 (d, $J = 3.2$ Hz, 2H), 7.11–7.07 (m, 8H), 7.03 (dd, $J = 3.6$ Hz, 5.2 Hz, 2H), 3.50–3.45 (m, 48H), 2.80–2.78 (m, 24H), 1.59 (m, 24H), 1.39 (sex, $J = 7.5$ Hz, 24H), 0.93 (t, $J = 7.5$ Hz, 36H); MALDI-TOF-MS (1,8,9-anthracenetriol matrix) m/z 2259.8

(M^+, Calcd 2260.9); Anal. Calcd for $C_{126}H_{170}O_{12}S_{12}$: C, 66.92; H, 7.58%. Found: C, 66.92; H, 7.59%.

Poly(quaterthiophene) (8). 3,3‴-Dihexylquaterthiophene (**17**)[51] (47 mg, 0.094 mmol) was treated with excess $FeCl_3$ (1.53 g) in 20 mL of chloroform at 50 °C for 5 d in a nitrogen atmosphere. Into the reaction mixture, aq. sat. sodium hydrogensulfite in water (40 mL) was added, and the mixture was stirred at rt for additional 3 h. The solid was removed by filtration, and the filtrate was extracted with chloroform (50 mL × 2). The extracts were combined, washed with brine, and dried ($MgSO_4$). Evaporation of the solvent gave a red semisolid of **8** (18 mg, 38%); Anal. Calcd for $(C_{28}H_{32}S_4)_n$: C, 67.72; H, 6.50%. Found: C, 66.59%; H, 6.73%.

Chemical Doping of 4–8. Chemical doping was carried out by treating samples of **4**–**8** with a controlled amount of $FeCl_3$ (0.0005–0.05 M) in nitromethane at rt for 12 h. The resulting insoluble material was collected by filtration, washed with acetone, and then air-died. The doping levels per thiophene unit were decided assuming $FeCl_4$ as the counter ion by elemental analyses. Analytical data for 1% doping sample of **4**: C, 66.35; H, 6.21%; 7% doping: C, 60.55; H, 5.93%; 14% doping: C, 55.16; H, 5.75%; 24% doping: C, 48.92; H; 4.69%. Analytical data for 3% doping sample of **5**: C, 67.84; H, 8.90%; 16% doping: C, 62.44; H, 8.56%; 23% doping: C, 60.16; H, 7.64%; 34% doping: C, 56.53; H, 7.46%. Analytical data for 6% doping sample of **6**: C, 64.39; H, 7.91%; 11% doping: C, 61.62; H, 7.23%; 14% doping: C, 59.74; H, 6.89%; 21% doping: C, 56.44; H, 6.56%. Analytic data for 3% doping sample of **7**: C, 64.86; H, 7.54%; 9% doping: C, 61.39; H, 7.04%; 14% doping: C, 55.98; H, 6.24%; 24% doping: C, 53.20; H, 5.85%. Analytic data for 23% doping sample of **8**: C, 49.80; H, 4.67%.

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