ORGANIC
LETTERS

2004
Vol. 6, No. 6
997−1000

α,*ω*-Bis(quinquethienyl)alkanes as a *π*-Dimer Model of Polythiophene

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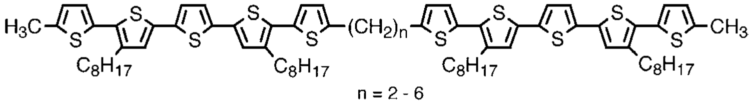
Received January 11, 2004

ABSTRACT



A series of the title dimeric quinquethiophenes linked with a di- to hexamethylene spacer was synthesized and examined as a *π*-dimer model of polythiophene. Upon two-electron oxidation with iron(III) chloride in dichloromethane, they readily form intramolecular *π*-dimer species, except for the dimethylene-linked dimer that cannot be bent into a *π*-stacked structure.

Although the removal of electrons from conjugated polymers formally gives rise to radical cation species termed polarons,[1] the principal charge carriers of conductive polymers are generally accepted to be spinless dimeric species, such as bipolarons,[1,2] *π*-dimers,[3] two polarons on a single chain,[4] and *σ*-dimers,[5] formed by a combination of two polarons. Many recent investigations using appropriate oligothiophenes as model compounds have substantiated the existence of *π*-dimers in solution at high concentrations or at low temperatures[6−11] or in the solid state.[12] Specifically, upon one-electron oxidation with iron(III) chloride, the electronic spectrum of dioctyldimethylquinquethiophene (**1**) in dichloromethane at 213 K demonstrates two characteristic absorption bands due to *π*-dimeric species (λ_{max} 610−670 and 1084 nm). In this measurement, however, it is hard to observe the genuine spectrum of the *π*-dimer because it is overlapped with that of the polaron species (λ_{max} 751 and 1412 nm)

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10.1021/ol0499396 CCC: $27.50

which exists in equilibrium with the π-dimer. As a more suitable model of π-dimer, we previously studied the dimeric oligothiophenophane (**2**), which completely produced a π-dimer in contrast to the case of **1**.[13] It is natural to imagine that the inherent stacking structure of **2** constructed by the two ethylene bridges is advantageous to its ready π-dimerization. However, we have found that even simple dimers linked with a single polymethylene spacer can also form π-dimers readily. Here, we report the synthesis and spectrochemical behaviors of α,ω-bis(quinquethienyl)alkanes (**3a**−**e**) as another π-dimer model of polythiophene (Figure 1).

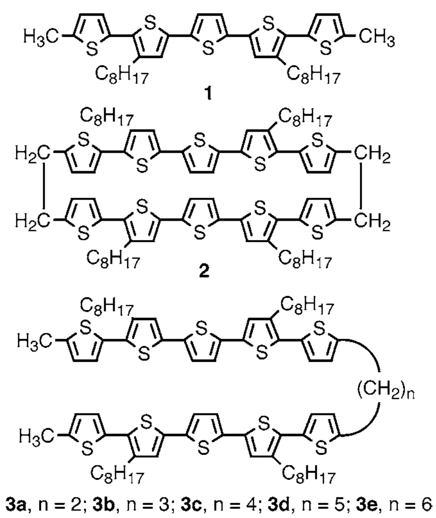
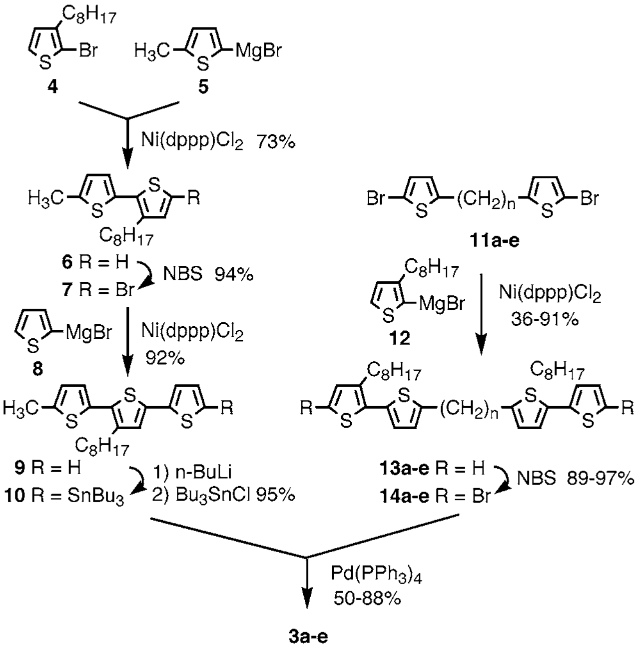


Figure 1.

α,ω-Bis(quinquethienyl)alkanes (**3a**−**e**) were prepared by Kumada coupling[14] or Stille coupling reactions,[15] as shown in Scheme 1. Thus, the Kumada coupling of 2-bromo-3-octylthiophene (**4**)[16] and 5-methyl-2-thienylmagnesium bromide (**5**) gave 5′-methyl-3-octyl-2,2′-bithiophene (**6**), which was then reacted with NBS to the bromo derivative **7**. The repeated Kumada coupling of **7** and 2-thienylmagnesium bromide (**8**) produced the terthiophene derivative **9**, which was subsequently converted to the tributylstannyl derivative **10**. The Kumada coupling of α,ω-bis(5-bromo-2-thienyl)alkanes (**11a**−**e**)[17] and 3-octyl-2-thienylmagnesium bromide (**12**) gave α,ω-bis(3′-octyl-2,2′-bithien-5-yl)alkanes (**13a**−**e**), which were converted to the dibromo derivatives **14a**−**e**. Finally, the Stille coupling of **10** and **14a**−**e** gave **3a**−**e**.

Scheme 1. Synthesis of α,ω-Bis(quinquethienyl)alkanes



All new compounds **3a**−**e** were definitely characterized by NMR and MS spectroscopy and elemental analyses. The chemical shifts of the thienyl proton signals of the single-linked dimers **3a**−**e** are roughly similar to the corresponding ones of the monomeric quinquethiophene **1**, suggesting that the single-linked dimers **3a**−**e** adopt nonstacked, possibly stretched conformations, in contrast to the cyclophane dimer **2**. The electronic spectra of **3a**−**e** in dichloromethane show a broad π−π* absorption band and a vibronic emission band in the visible region, as observed for **1**. Table 1 summarizes these spectral data of **3a**−**e** and the absorption data of their oxidized species, together with those of **1** and **2**. The absorption and emission peaks of **3a**−**e** are nearly the same in wavelength position and in unit intensity as those of **1**.

Table 1. Electronic Spectral Data of Quinquethiophenes **1**−**3**[a]

	neutral band		polaronic band	π-dimeric band
compd	$\lambda_{max}{}^{abs}$/nm[b]	$\lambda_{max}{}^{emis}$/nm	$\lambda_{max}{}^{abs}$/nm	$\lambda_{max}{}^{abs}$/nm
1	417 (44 000)	503, 533	751, 1412	610−670, 1084[c]
2	400 (73 000)	508, 540	754, 1420	704, 920, 1390[d]
3a	418 (88 000)	504, 534	752, 1419	nonobserved
3b	418 (89 000)	504, 534	753, 1422	676, 1193
3c	417 (89 000)	504, 534	756, 1415	683, 1112
3d	417 (89 000)	504, 534	756, 1412	623 sh, 678,[e] 1095
3e	417 (88 000)	504, 534	756, 1412	618, 670 sh,[e]1086

[a] Electronic absorption and emission spectra were measured in dichloromethane. [b] Molar absorption coefficients are given in parentheses. [c] The π-dimer bands are observed at a low temperature (213 K). [d] Three absorption bands characteristic of a π-dimer are observed. [e] The low energy band is broadening and deformed into a fine structure.

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This strongly supports no substantial electronic interaction between the two quinquethiophenes, being consistent with nonstacked molecular structures as deduced above on the basis of NMR spectroscopy.

The controlled oxidation of **3a**−**e** with $FeCl_3$ in dichloromethane at room temperature allows the formation of polaron species from each quinquethiophene, as monitored by vis/NIR spectroscopic measurements.[18] As shown in Figure 2, the one-electron oxidation of the dimer **3a** demonstrates two polaronic bands at 752 and 1419 nm together with one neutral band at 418 nm. Upon two-electron oxidation, the neutral band completely disappears and the polaronic bands increase to nearly double. This result indicates that the two quinquethiophenes independently generate their individual polarons, which do not interact with each other at all.

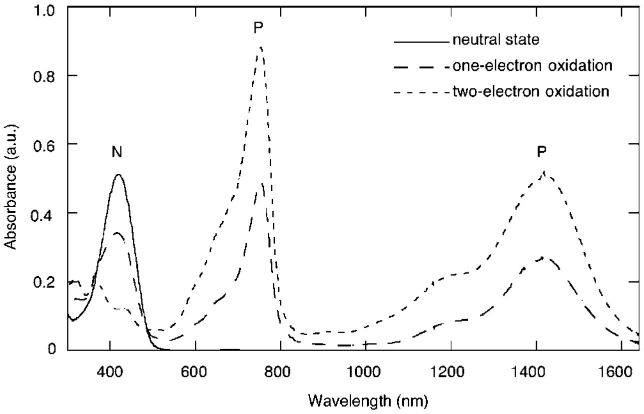

Figure 2. Electronic absorption spectra of **3a** in dichloromethane under controlled oxidation with $FeCl_3$. N and P denote neutral and polaronic bands, respectively.

The dimer **3b** with a longer trimethylene spacer demonstrates a quite different spectral change. As shown in Figure 3, its one-electron oxidation causes the appearance of not only two polaronic bands (753 and 1422 nm) but also two high-energy sidebands (676 and 1193 nm). Because of a striking similarity in wavelength to the π-dimeric bands of **1**, the sidebands can be considered to be due to a π-dimer. Under two-electron oxidation, the polaronic bands decrease, and instead, the π-dimeric bands are predominant, although a certain amount of the polaronic bands still remains.

The ready formation of the π-dimer is also corroborated by ESR measurements at room temperature. As shown in Figure 4, the one-electron oxidation of **3b** gives a broad ESR signal with $g = 2.0022$ due to the polaron species, and the signal intensity under two-electron oxidation drastically decreases. This strongly supports the formation of an ESR-inactive π-dimer species by the dimerization of polarons. Taking account of the nonstacked structure of **3b** in the neutral state as well as the appearance of the π-dimer even under one-electron oxidation, one can imagine a strong association force for the π-dimerization of **3b**. In addition, one may notice that the π-dimeric spectrum of **3b** is substantially different in shape and wavelength from that of **2**. This suggests different structures for these π-dimers; presumably the π-dimer of **2** constructed by two ethylene bridges must have a more interactive and strained structure.

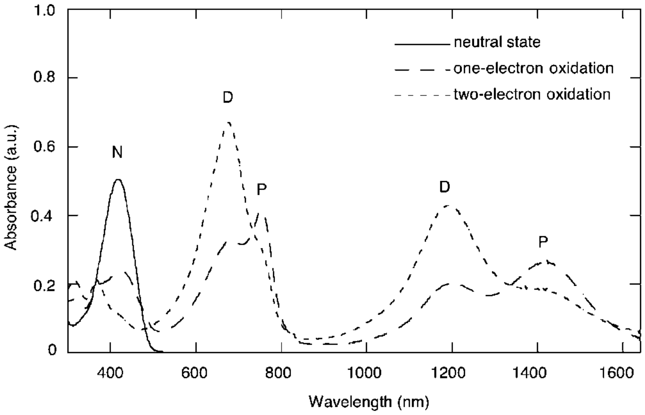

Figure 3. Electronic absorption spectra of **3b** in dichloromethane under controlled oxidation with $FeCl_3$. N, P, and D denote neutral, polaronic, and π-dimeric bands, respectively.

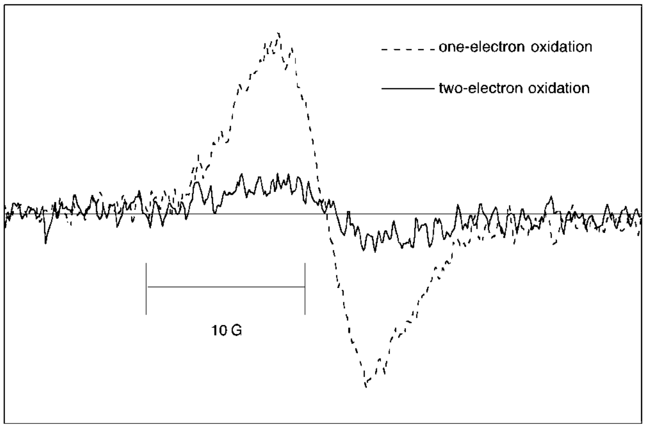

Figure 4. ESR spectra of **3b** in dichloromethane under controlled oxidation with $FeCl_3$.

The higher homologues **3c**−**e** also undergo similar spectral changes by forming π-dimers, but the π-dimerization in the one-electron oxidation state is hard to achieve. Thus, the one-electron oxidation of the tetramethylene-linked dimer **3c** shows an electronic spectrum essentially comprised of polaronic and neutral bands (Figure 5). The π-dimeric bands are obscure owing to overlapping with the high energy shoulders of the polaronic bands, as compared to those of

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[18] A typical controlled oxidation experiment was performed by adding an appropriate aliquot (10−25 μL) of $FeCl_3$ (2.0×10^{-3} M) in dichloromethane into the 2.0 mL dichloromethane solution of **3a**−**e** (5×10^{-6} M). Two-equimolar $FeCl_3$ is necessary for one-electron oxidation.

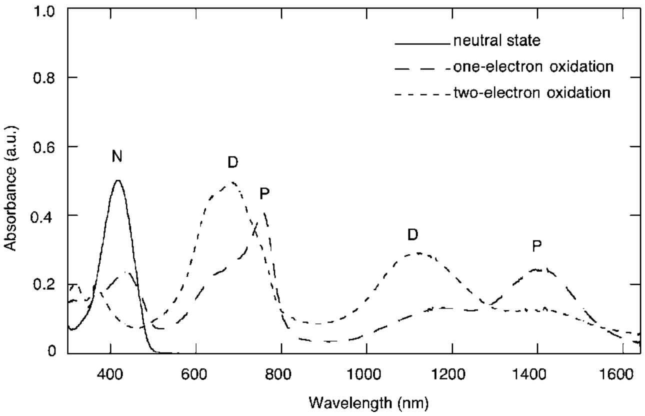

Figure 5. Electronic absorption spectra of **3c** in dichloromethane under controlled oxidation with $FeCl_3$. N, P, and D denote neutral, polaronic, and π-dimeric bands, respectively.

3b. However, the two-electron oxidation gives the distinct spectrum of the π-dimeric bands. Similarly, **3d** and **3e** give respective π-dimeric spectra in the two-electron oxidation state.

The present results evidently indicate that the linkage of two oligothiophenes with a single polymethylene spacer facilitates the formation of π-dimers. The different behaviors of **3a**−**e** for intramolecular π-dimerization can be explained in terms of the bending strain of the polymethylene chains. Brocks estimated on the basis of density functional calculations that the interplanar distance of π-dimeric quaterthiophene is around 3.1 Å.[19] Mann and co-workers reported on the basis of X-ray structural analysis that the interplanar distance of the stacked radical cation salts of 3′,4′-dibutyl-2,5″-diphenyl-2,2′:5′,2″-terthiophene is 3.47 Å.[20] A molecular model indicates that the dimer **3a** with a dimethylene chain cannot be bent into such a π-dimeric structure owing to severe strain. On the other hand, the dimer **3b** with a trimethylene chain can be smoothly deformed into an interactive π-stack structure. Furthermore, the bending of **3c**−**e** with a longer chain also gives stacking structures, but overlapping the two oligothiophenes to a π-interactive position causes some torsional strain within the polymethylene chain. In this regard, it is worth mentioning that the longer wavelength bands of the π-dimers are highly dependent on the chain lengths of the homologous series **3b**−**e**. The π-dimeric band of **3e** with the longest chain is at almost the same absorption position as that of the intermolecular π-dimer derived from **1**, but the absorption positions for **3b**−**d** are successively red-shifted with the chain shortening. This suggests that the present intramolecular π-dimers are more closely stacked and accordingly, more strongly interactive, as compared to the normal intermolecular π-dimer of **1**.[21]

In summary, we have developed simple oligothiophene dimers linked with a single polymethylene spacer, α,ω-bis(quinquethienyl)alkanes **3b**−**e**, which can readily form π-dimers. Because they are relatively accessible as compared to the preceding sophisticated quinquethiophenophane **2**, these compounds are very useful in studying the π-dimer of polythiophene in detail.

Acknowledgment. This research was partly supported by Grants-in-Aid of Scientific Research (Category A, No. 1330405, Exploratory Research, No. 13874091, and Priority Areas of Molecular Conductors, No. 15073218) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Synthetic experimental details and characterization data for compounds **3a**−**e**, **6**−**10**, **13a**−**e**, and **14a**−**e** and electronic absorption spectra of **3d** and **3e** under controlled oxidation. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0499396

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