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Synthesis and Spectroscopic Properties of [2.2]Quinquethiophenophane as an Ideal π-Dimer Model

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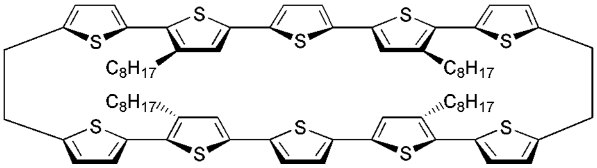
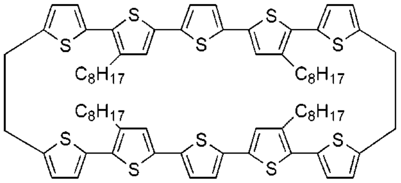
ABSTRACT



The title compound has been synthesized as the first oligothiophenophane that has the typical stacking structure of a layered cyclophane and can behave as an ideal π-dimer model.

Considerable controversy still exists concerning principal charge carriers for conductive polythiophenes and related polymers.[1] The removal of electrons from the conjugation systems gives rise to a local distortion corresponding to radical cationic species (polaron) extending over approximately 5 linked thiophene units. However, early studies of very weak ESR activity for the doped polymers excluded the involvement of polarons as charge carriers.[2] Instead, some spinless species formed by a combination of two polarons have been proposed, such as dicationic bipolaron,[2] intermolecular π-dimer,[3] and more recently two individual polarons on a single chain.[4] Of them, the bipolaron model is less supported by the spectral pattern of doped oligothiophenes, incompatible with the selection rule of $\pi-\pi^*$ transitions.[5] Although many studies have claimed the π-dimer model, the existence of the π-dimer has been principally studied only by low-temperature electronic spectra of oligothiophenes in the oxidation state.[3] It is, however, usually difficult to separate the intrinsic spectrum of the associated π-dimeric species from that of the monomeric one. Cyclophanes that are constructed by intramolecularly stacking two aromatic molecules have so far been studied exclusively as an excimer model[6] but might also be useful as a π-dimer model. Here we would like to report the synthesis and properties of tetraoctyl[2.2]quinquethiophenophane **1**, which can behave as an ideal π-dimer of dimethyldioctylquinquethiophene **2**.



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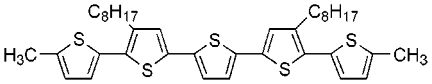

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[2.2]Quinquethiophenophane **1** was synthesized according to Scheme 1. First, 1,2-bis(3′-octyl-2,2′-bithiophen-5-yl)ethane **5** was obtained in 95% yield by a conventional Ni(II)-catalyzed aryl Grignard cross-coupling (Kumada coupling) of 1,2-bis(5-bromo-2-thienyl)ethane **3**[7] and the Grignard reagent **4**, freshly prepared from 2-bromo-3-octylthiophene,[8]

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(1) For comprehensive reviews on polythiophenes, see: (a) Roncali, J. *Chem. Rev.* **1992**, *92*, 711−738. (b) Schopf, G.; Kossmehl, G. *Polythiophenes-Electrically Conductive Polymers*; Springer: Berlin, 1997. (b) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93−116. (c) Fichou, D. *Handbook of Oligo- and Polythiophenes*; Wiley-VCH: Weinheim, 1999.

(2) Brédas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309−315.

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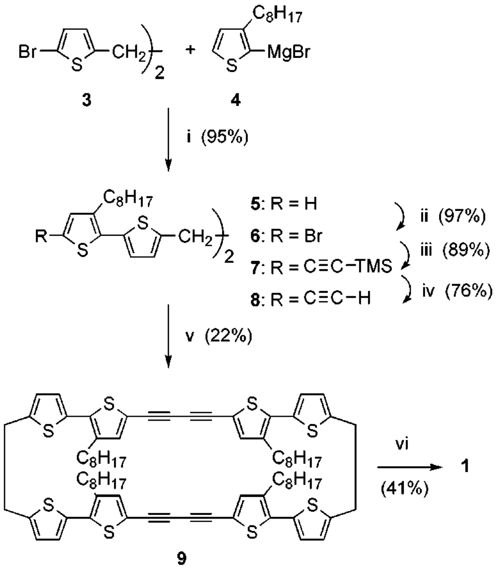
Scheme 1. Synthesis of **1**[a]



[a] Reagents and conditions: (i) Ni(dppp)Cl_2, ether, reflux, overnight; (ii) NBS, chloroform−acetic acid, room temperature, overnight; (iii) TMS-C≡CH, $(Ph_3P)_4Pd$, CuI, Et_3N, 80 °C, 12 h; (iv) KOH, benzene−methanol, room temperature, 4 h; (v) $Cu(OAc)_2$, pyridine, 45 °C, 20 h; (vi) $Na_2S{\cdot}9H_2O$, KOH, dioxane, reflux, overnight.

and then, on treatment with NBS, converted into the dibromo derivative **6** in 97% yield. A Sonogashira coupling reaction of **6** with trimethylsilylacetylene in the presence of $Pd(PPh_3)_4$ catalyst gave the bis(trimethylsilylethynyl) derivative **7** (89% yield), which was then deprotected with potassium hydroxide to give the ethynyl one **8** (76% yield). An Eglinton coupling reaction of **8** under dilution conditions gave a mixture of coupling products, which were separated by column chromatography followed by gel-permeation liquid chromatography to isolate the cyclic dimer **9** (22%). Subsequent treatment of **9** with sodium sulfide afforded the desired quinquethiophenophane **1** in 41% yield. The quinquethiophene **2** was similarly prepared from 2-bromo-5-methylthiophene.[9]

The ^1H NMR spectrum of **1** in deuteriochloroform is characterized by two singlets (δ 6.88 and 6.94) and two doublets (δ 6.76 and 6.92) for thiophene protons together with octyl signals and a bridged methylene singlet signal, as shown in Figure 1. The chemical shifts of the two singlets corresponding to the central thiophene protons and the next thiophene protons show upfield shifts of 0.15 and 0.04 ppm, respectively, relative to **2**, consistent with those usually seen for typical layered cyclophanes,[10] indicating a stacked structure for the central part of **1**. However, the two doublet signals for the outermost thiophene protons show small downfield shifts (0.05 and 0.01 ppm), suggesting that the opposite outer rings adopt an anti stacking conformation, as already found for [2.2](2,5)thiophenophane.[11]

The electronic absorption spectrum of **1** in dichloromethane exhibits a $\pi-\pi^*$ absorption band at λ_{max} 400 nm, which is blue-shifted by 15 nm as compared to that of **2**. In contrast, the former fluoresces at 6−8 nm longer wavelengths (λ_{max} 508 and 540 nm) than the latter (λ_{max} 502 and 532 nm). The blue shift of the absorption band as well as the red shift of the emission band is explained by exciton−exciton coupling termed Davidov shifts, which are fully coherent with the stack structure of **1**. The controlled oxidation of **1** with $FeCl_3$ in dichloromethane caused drastic spectral change, as shown in Figure 2. In one-electron oxidation, the spectrum shows three absorption peaks in the VIS/NIR region. The band at 410 nm is due to the nonoxidized quinquethiophene chromophore, which is almost equal to the neutral absorption of **2**. The remaining two bands (λ_{max} 754 and 1420 nm) are due to the oxidized quinquethiophene, and the absorption maxima are very similar to those of the radical cationic

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(3) (a) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J.-F. *J. Am. Chem. Soc.* **1992**, *114*, 2728−2730. (b) Hill, M. G.; Penneau, J.-F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1106−1113. (c) Bäuerle, P.; Segelbacher, U.; Gaudl, K.-U.; Huttenlocher, D.; Mehring, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 76−78. (d) Bäuerle, P.; Segelbacher, U.; Maier, A.; Mehring, M. *J. Am. Chem. Soc.* **1993**, *115*, 10217−10223. (e) Gunic, Y. Y. E.; Zinger, B.; Miller, L. L. *J. Am. Chem. Soc.* **1996**, *118*, 1013−1018. (f) Miller, L. L.; Mann, K. R. *Acc. Chem. Res.* **1996**, *29*, 417−423. (g) Graf, D. D.; Duan, R. G.; Campbell, J. P.; Miller, L. L.; Mann, K. R. *J. Am. Chem. Soc.* **1997**, *119*, 5888−5899.

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(9) All new compounds were fully characterized by spectroscopic and elemental analyses. (a) Selected data for **5**: yellow oil: ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 6H), 1.26 (m, 20H), 1.61 (quint, J = 7.8 Hz, 4H), 2.72 (t, J = 7.8 Hz, 4H), 3.20 (s, 4H), 6.76 (d, J = 3.5 Hz, 2H), 6.910 (d, J = 5.1 Hz, 2H), 6.912 (d, J = 3.5 Hz, 2H), 7.13 (d, J = 5.1 Hz, 2H); MS (EI) m/z 582 (M^+). Anal. Calcd for $C_{34}H_{46}S_4$: C, 70.05; H, 7.95. Found: C, 70.01; H, 8.05. (b) Selected data for **6**: yellow fine crystals, mp 39.0−40.0 °C; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 6.9 Hz, 6H), 1.25 (m, 20H), 1.56 (quint, J = 7.8 Hz, 4H), 2.64 (t, J = 7.8 Hz, 4H), 3.18 (s, 4H), 6.74 (d, J = 3.6 Hz, 2H), 6.85 (d, J = 3.6 Hz, 2H), 6.86 (s, 2H); MS (EI) m/z 738 (M^+), 740, 742. Anal. Calcd for $C_{34}H_{44}Br_2S_4$: C, 55.13; H, 5.99. Found: C, 55.28; H, 5.89. (c) Selected data for **7**: yellow oil; ^1H NMR ($CDCl_3$) δ 0.24 (s, 18H), 0.87 (t, J = 7.0 Hz, 6H), 1.25 (m, 20H), 1.56 (quint, J = 7.8 Hz, 4H), 2.65 (t, J = 7.8 Hz, 4H), 3.19 (s, 4H), 6.75 (d, J = 3.5 Hz, 2H), 6.92 (d, J = 3.5 Hz, 2H), 7.04 (s, 2H); MS (EI) m/z 774 (M^+). Anal. Calcd for $C_{44}H_{62}S_4Si_2$: C, 68.15; H, 8.06. Found: C, 68.40; H, 8.25. (d) Selected data for **8**: yellow fine crystals, mp 56.5−57.5 °C; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 6H), 1.25 (m, 20H), 1.56 (quint, J = 7.8 Hz, 4H), 2.66 (t, J = 7.8 Hz, 4H), 3.18 (s, 4H), 3.34 (s, 2H), 6.74 (d, J = 3.7 Hz, 2H), 6.92 (d, J = 3.7 Hz, 2H), 7.07 (s, 2H); MS (EI) m/z 630 (M^+). Anal. Calcd for $C_{38}H_{46}S_4$: C, 72.33; H, 7.35. Found: C, 72.35; H, 7.37. (e) Selected data for **9**: yellow semisolid; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 12H), 1.25 (m, 40H), 1.57 (m, 8H), 2.63 (t, J = 7.8 Hz, 8H), 3.17 (s, 8H), 6.73 (d, J = 3.6 Hz, 4H), 6.92 (d, J = 3.6 Hz, 4H), 7.11 (s, 4H); MS (FAB) m/z 1256 (M^+). Anal. Calcd for $C_{76}H_{88}S_8$: C, 72.56; H, 7.05. Found: C, 72.45; H, 7.15. (f) Selected data for **1**: yellow fine crystals, mp 175.0−177.0 °C; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 12H), 1.25 (m, 40H), 1.60 (quint, J = 7.8 Hz, 8H), 2.64 (t, J = 7.8 Hz, 8H), 3.13 (s, 8H), 6.76 (d, J = 3.5 Hz, 4H), 6.88 (s, 4H), 6.92 (d, J = 3.5 Hz, 4H), 6.94 (s, 4H); MS (FAB) m/z 1324 (M^+). Anal. Calcd for $C_{76}H_{92}S_{10}$: C, 68.83; H, 6.99. Found: C, 68.92; H, 7.16. (g) Selected data for **2**: yellow fine crystals, mp 86−87 °C; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 6H), 1.28 (m, 20H), 1.66 (quint, J = 7.8 Hz, 4H), 2.51 (d, J = 1.0 Hz, 6H), 2.70 (t, J = 7.8 Hz, 4H), 6.71 (m, 2H), 6.91 (d, J = 3.6 Hz, 2H), 6.98 (s, 2H), 7.03 (s, 2H); MS (EI) m/z 664 (M^+). Anal. Calcd for $C_{38}H_{48}S_5$: C, 68.62; H, 7.27. Found: C, 68.91; H, 7.16.

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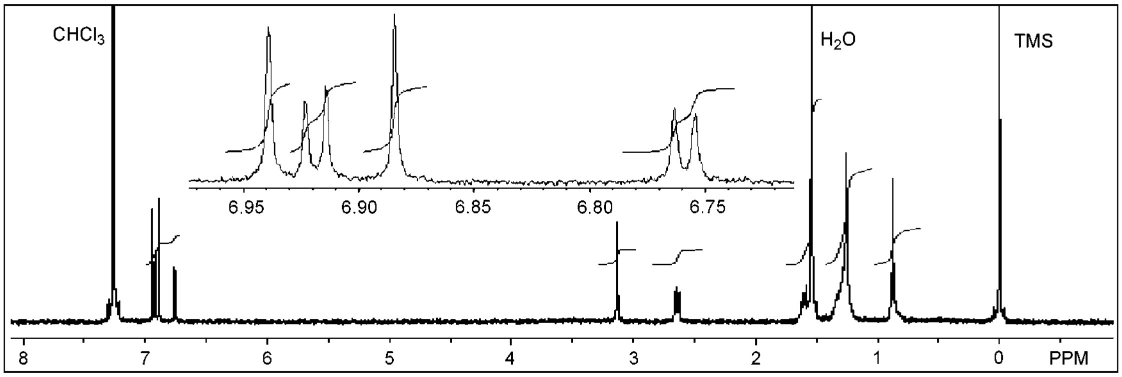

Figure 1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

species (polaron) prepared by mono-oxidation of **2** (λ_{max} 750 and 1410 nm). Clearly there is no through-space interaction between the two quinquethiophenes of **1** in the one-electron oxidation state. In two-electron oxidation, the spectrum completely changes to give three new bands at λ_{max} 704, 920, and 1390 nm. These three bands strongly indicate the formation of a π-dimer from the two monocationic species.[3] This was also supported by the disappearance of ESR signal in the two-electron oxidation state, althogh a strong ESR signal due to the radical cationic species was observed in the one-electron oxidation state. It is thus obvious that intramolecular π-dimerization of both quinquethiophenes of **1** readily occurs at ambient temperature. Further three- and four-electron oxidation reactions cause the appearance of a new single peak at λ_{max} 780 nm, which is characteristic of the dication species (bipolaron). A large blue shift of the bipolaronic band of **1** compared to the corresponding band (904 nm) of **2** can be explained by strong exciton−exciton interaction.

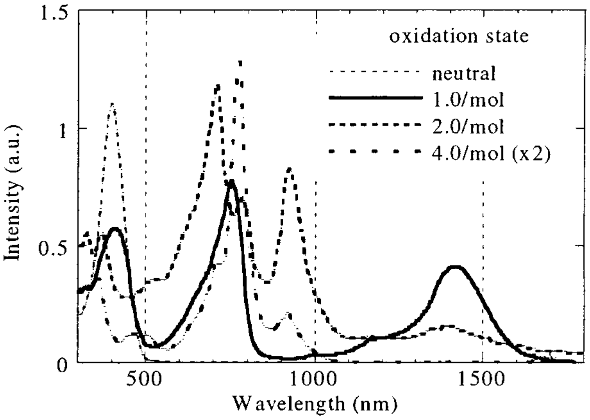

Figure 2. Electronic absorption spectra of **1** under oxidation with $FeCl_3$.

The cyclic voltammogram of **1**, similar to that of **2**, exhibits two reversible redox waves with $E_{1/2}$ 0.74 and 1.13 V vs Ag/AgCl in dichloromethane, which each involve two-electron oxidation processes. The first half-wave oxidation potential is somewhat lower than that (0.80 V) of **2**. The π-dimerization of **1** probably contributes to the lowering of the first oxidation potential. On the other hand, the second half-wave oxidation potential is higher than that (1.02 V) of **2**, suggesting Coulombic repulsion between two highly oxidized quinquethiophenes of **1**.

In summary, we have succeeded in synthesizing **1** as the first oligothiophenophane that is very useful as a model of the π-dimer. Its spectroscopic studies have shown that π-dimerization of **1** readily occurs at ambient temperature.

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