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Cyclopentadithiophene (CPDT) Dimer Dication: Bipolaron Model for Quaterthiophenes

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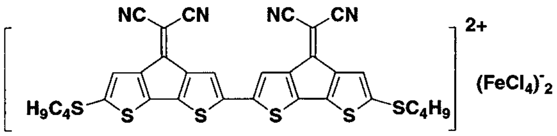
ABSTRACT



Cyclopentadithiophene (CPDT) dimers in which both 3,3′ and 4″,3‴ positions were bridged with 1,3-dioxalane, carbonyl, or dicyanovinylidene were prepared. These compounds have small HOMO–LUMO gaps (1.03–2.25 eV). The electrochemical oxidation of a dicyanovinylidene-bridged CPDT dimer gave a dication that had a quinoid-like structure.

Thiophene-based linear π-conjugated systems have attracted a great deal of attention due to their stability, structural versatility, and potential application to next-generation electronic and optical materials.[1] High conductivity (up to 370 S cm^{-1})[2] and even superconductivity[3] have been reported for doped polythiophenes. The mechanism for conduction, however, is controversial, and electron transportation via polarons, bipolarons, multipolarons along a polymer chain, and the intermolecular π-dimer of polarons has been theoretically proposed.[4,5] Because of the experimental difficulties involved in differentiating between mechanisms, there have recently been extensive oligomer-based approaches, resulting in the accumulation of a considerable amount of data on structure and conductivity. More importantly, insight into the structures of some oligothiophenes radical cations (chemical term for polarons) has been experimentally obtained.[5,6] However, no isolation of oligothiophene dications (chemical term for bipolarons) has been reported. Strong distortions, quinoid-like structures, are theoretically expected for oligothiophene dications.[7]

Of the thiophene-based polymers, cyclopentadithiophene (CPDT) polymers are interesting because of their high conductivities and narrow band gaps.[8] Here, CPDT dimers (**1**−**3**) were selected as model compounds of the polymers.[9] We report on synthesis and a large substituent effect on redox potentials and electronic spectra. Furthermore, we isolated the dicationic species for the electrochemical oxidation of

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[1] For recent reviews, see: (a) Roncali, J. *Chem. Rev.* **1992**, *92*, 711−738. (b) Roncali, J. *Chem. Rev.* **1997**, *97*, 173−204. (c) Mullen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCM: Weinheim, Germany, 1998. (d) Fichou, D. *J. Mater. Chem.* **2000**, *10*, 571−588. (e) Aso, Y.; Takimiya, K.; Otsubo, T. *J. Synth. Org. Chem., Jpn. (Yuki Gousei Kagaku Kyokaishi)* **2002**, *60*, 52−61.

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[3] Schön, J. H.; Dodabalapur, A.; Bao, Z.; Kloc, Ch.; Schenker, O.; Batlogg, B. *Nature* **2001**, *410*, 189−192.

[4] (a) Chung, T.-C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phy. Rev. B* **1984**, *30*, 702−710. (b) Miller, L. L.; Mann, K. R. *Acc. Chem. Res.* **1996**, *29*, 417−423. (c) van Haare, J. A. E. H.; Havinga, E. E.; van Dongen, J. L. J.; Janssen, R. A. J.; Cornil, J.; Brédas, J.-L. *Chem. Eur. J.* **1998**, *4*, 1509−1522.

[5] 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] Syntheses and properties of CPDT dimers with *n*-hexyl end groups were previously reported; see: Yonezawa, Y.; Kozaki, M.; Okada, K. *Synth. Met.* **2001**, *119*, 99−100.

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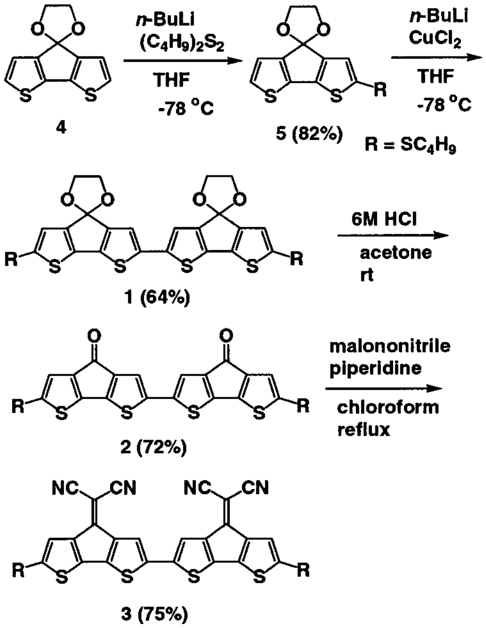
the dicyanovinylene-bridged **3** and clarified the crystal structure.

CPDT dimers (**1**−**3**) were synthesized from spiro[4*H*-cyclopenta[2,1-*b*;3,4-*b*′]dithiophene-4,2′-[1,3]dioxalan] (**4**)[10] as shown in Scheme 1. First, a butylthio group was introduced into **4** in 82% yield through lithiation followed by treatment with dibutyl disulfide. Oxidative dimerization of **5** with *n*-butyllithium-copper(II) chloride afforded CPDT dimer **1** in 64% yield. Acidic deprotection of carbonyl groups gave **2** in 72% yield. A piperidine-catalyzed Knoevenagel condensation of **2** with malononitrile gave **3** in 75% yield.[11]

Scheme 1. Synthesis of CPDT Dimers



The X-ray structure analysis of the spiro compound **1** revealed that the molecule had a crystallographic inversion center with high planarity (Figure 1).[12] Maximum deviation from the least-squares CPDT plane was only 0.079 Å. Two CPDT rings adopted an anti conformation. Planar anti conformations have also been observed for neutral quater- and other oligothiophenes[1d,13] The *n*-butyl side chains stood almost perpendicular to the CPDT ring. Both bond length and bond angle data are consistent with the quaterthiophene previously reported.[13]

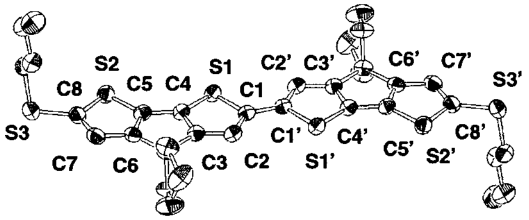


Figure 1. Molecular structure (ORTEP) and labeling of **1**; C1′, C2′, etc. are given by the inversion of the corresponding C1, C2, etc. relative to the molecular center (symmetry center of the molecule). Selected bond lengths (Å): S1−C1, 1.745(3); S1−C4, 1.712(3); S2−C5, 1.704(3), S2−C8, 1.742(3); S3−C8, 1.751(3); C1−C1′, 1.446(5); C1−C2, 1.384(3); C2−C3, 1.396(4); C3−C4, 1.378(3); C4−C5, 1.450(4); C5−C6, 1.383(3); C6−C7, 1.404(4); C7−C8, 1.366(4).

UV−vis−NIR spectra of CPDT dimers (**1**−**3**) were measured in chloroform or nitrobenzene (Table 1). A red shift of absorption maximum ($\Delta\lambda_{max} = 69$ nm) was observed for dimer **1** in comparison to unsubstituted quaterthiophene (λ_{max} = 390 nm).[14] The stronger electron-withdrawing bridging groups resulted in the larger shift for absorption maxima (λ_{max} = 582 for **2**, 740 nm for **3**). These λ_{max} values and the extent of red shift are larger than those reported for CPDT monomers (472 nm for the carbonyl-bridged and 576 nm for the dicyanovinylene-bridged compounds).[8] These

Table 1. Absorption,[a] Absorption Edge,[a] and Redox Potentials[b] of CPDT Dimers (**1**−**3**)

compd	λ_{max} (nm)	λ_{edge} (E_{gap}) (nm (eV))	$E^{1/2}_{ox}$	$E^{1/2}_{red1}$ V vs Fc/Fc$^+$	$E^{1/2}_{red2}$
1	459	550 (2.25)	0.23	−2.28	−2.56
2[c]	582	800 (1.55)	0.45[d]	−1.51	−1.67
3	740	1200 (1.03)	0.52	−0.92	−1.00

[a] In chloroform for **1** and **2**; in nitrobenzene for **3**. [b] In THF for **1** and **2** and in nitrobenzene for **3** containing 0.1 M TBAP, using Pt as a working electrodes. [c] An additional two reduction waves were also observed (Figure 2). [d] An additional irreversible overlapping peak with E^p_{ox} = +0.63 V was observed, and the CV sweep up to +0.65 V prevented the reversibility of the +0.45 V peak; the presented peculiar shape for the +0.45 V wave in Figure 2 is due to the contribution of the +0.63 V peak.

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(11) Spectral data. **1**, $C_{30}H_{30}O_4S_6$: MW 646.95; red needles; mp = 168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 6H, *J* = 7.32 Hz), 1.37−1.46 (m, 4H), 1.57−1.67 (m, 4H), 2.78 (t, 4H, *J* = 7.14 Hz), 4.28 (S, 4H), 6.99 (s, 2H), 7.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.60, 21.57, 31.49, 39.48, 65.34, 107.62, 117.59, 128.57, 136.75, 137.68, 139.29, 141.67, 149.28, 150.39; IR (KBr) 2951, 2920, 2882, 2665, 1431, 1300, 1196, 1150, 1030 cm^{-1}; MS (FAB) *m/z* 646.3. Anal. Calcd for $C_{30}H_{30}O_4S_6$: C, 55.70; H, 4.67. Found: C, 55.60; H, 4.72. **2**, $C_{26}H_{22}O_2S_6$: MW 558.85; dark-purple solid; mp = 280 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 6H, *J* = 7.32 Hz), 1.37−1.49 (m, 4H), 1.55−1.65 (m, 4H), 2.80 (t, 4H, *J* = 7.32 Hz), 7.04 (s, 2H), 7.04 (s, 2H); IR (KBr) 2956, 2925, 2860, 1703, 1439, 1331, 1279, 1223, 1151 cm^{-1}; MS (EI) *m/z* 558. Anal. Calcd for $C_{26}H_{22}O_2S_6$: C, 55.88; H, 3.97. Found: C, 55.92; H, 3.83. **3**, $C_{32}H_{22}N_4S_6$: MW 654.94; green solid; mp > 300 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.90 (t, 6H, *J* = 7.32 Hz), 1.37−1.49 (m, 4H), 1.59−1.69 (m, 4H), 2.91 (t, 4H), 7.30 (s, 2H), 7.38 (s, 2H); IR (KBr) 2955, 2932, 2870, 2226, 1589, 1358, 1173 cm^{-1}; MS(EI) *m/z* 654. Anal. Calcd for $C_{32}H_{22}N_4S_6$: C, 58.68; H, 3.39; N, 8.55. Found: C, 58.88; H, 3.26; N, 8.51.

(12) Crystallographic data for **1**: $C_{30}H_{30}O_4S_6$, monoclinic, space group $C2/c$, a = 23.493(2) Å, b = 5.3111(5) Å, c = 26.185(2) Å, β = 115.918(2)°, V = 2938.6(4) Å^3, Z = 4, ρ_{calcd} = 1.462 g/cm^3, T = 296 K, R_1 = 0.039, R_w = 0.101.

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results are explicable if we assume a decrease in the LUMO energy level caused by electron-withdrawing bridging groups as proposed by Ferraris and Lambert for the CPDT structure[8] and a high HOMO level for the dimerized CPDT. As a result, the HOMO−LUMO gaps (E_{gap}) estimated from the absorption edges (λ_{edge}) are considerably small (Table 1); the smallest E_{gap} of the dicyanovinylene-bridged derivative **3** (E_{gap} = 1.03 eV) is almost half that of the unsubstituted neutral polythiophene (2.1 eV).[4a]

We measured redox potentials of CPDT dimers (**1**−**3**) by cyclic voltammetry in THF or nitrobenzene containing 0.1 mol/dm^3 tetrabutylammonium perchlorate (TBAP) (Table 1). All CPDT dimers (**1**−**3**) exhibited an amphoteric redox nature. A highly reversible oxidation wave and multiple reduction waves were observed for **1**−**3**. Although the oxidation potentials were rather insensitive to bridging substituents, the reduction potentials were highly dependent on these and lined up in the order of **3** > **2** > **1**. These results clearly support the frontier orbital consideration described by the absorption spectra. Notably, the peak height for the first oxidation potential was almost twice the intensity, indicating that two-electron oxidation processes led to the dicationic species.

The reversible two-electron oxidation wave of **1**−**3** motivated us to isolate their dications. Constant current electrolyses (1.0−2.0 μA) of **1**−**3** were undertaken in chlorobenzene containing a suitable supporting electrolyte. After several unsuccessful attempts, we found that good black crystals were deposited on the Pt anode for compound **3** using TEAFeCl$_4$ as an electrolyte. [Elemental analysis data was in accordance with the formula. Calcd for $\mathbf{3}\cdot(FeCl_4)_2(C_6H_5Cl)_2(H_2O)$: C, 40.86; H, 2.65; N, 4.33. Found: C, 40.66; H, 2.36; N, 4.09].

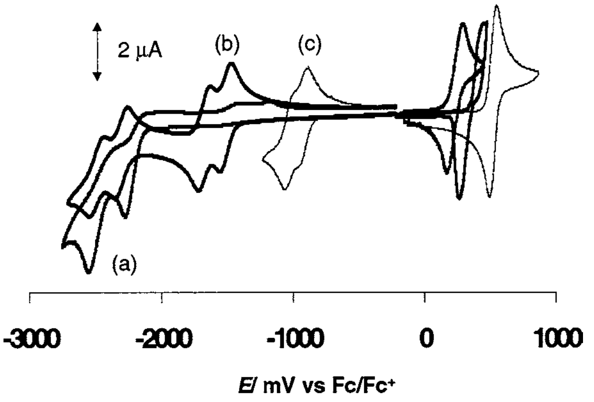


Figure 2. Cyclic voltammograms of (a) **1** (shadow line), (b) **2** (bold line), (c) **3** (solid line) measured in THF (for **1** and **2**) or nitrobenzene (for **3**).

Dication $\mathbf{3}^{2+}$ was extreme moisture-sensitive in solution, although the stability was much higher in the solid state.[15] To measure the electronic spectrum, dication $\mathbf{3}^{2+}$ was diluted with dry dichloromethane in a glovebox using a 1 mm cell.

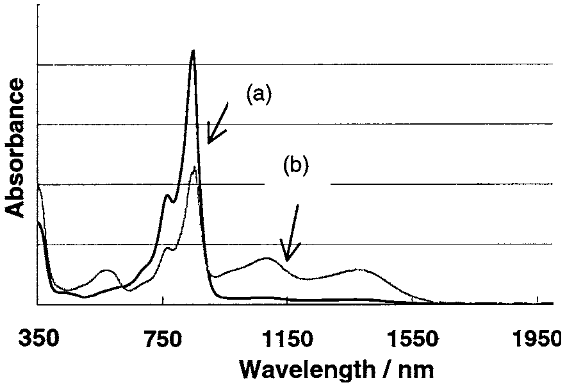
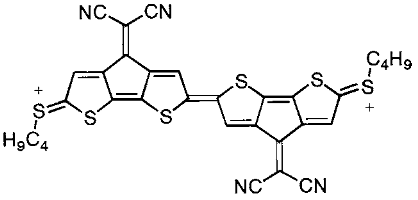


Figure 3. UV−vis−NIR spectra of (a) dication $\mathbf{3}^{2+}$ under a nitrogen atmosphere (solid line) and (b) dication $\mathbf{3}^{2+}$ after exposure to nondried air for 10 min (dotted line) measured in dichloromethane.

The UV−vis−NIR spectrum of $\mathbf{3}^{2+}$ is in Figure 3a. The deep blue $\mathbf{3}^{2+}$ solution had strong absorptions at 745 nm (log ϵ = 4.81) and 848 nm (log ϵ = 5.18) and slightly contaminated absorptions over 1000 nm. The intensity of the contaminated absorptions at 1086 and 1379 nm became pronounced when the solution was exposed to nondried air for about 30 min.

Although there have been many reports describing the bipolarons of oligothiphenes, there has not been much comparable data because of the wide range of absorption shapes that mainly depend on the oligomer length.[4c,5,13a,16] The observed absorption pattern is similar to the NOPF$_6$-doped dimethyl quaterthiophene (λ_{max} = 666 and 725 nm)[13a] and the electrochemically oxidized bis(trimethylsilyl)pentathiophene derivative (λ_{max} = 811 and 897 nm).[16a]

Contaminous absorptions at 1086 and 1379 nm are tentatively assigned as being due to mono(radical cation) $\mathbf{3}^{+}$, since two strong subgap absorptions in visible and/or NIR regions are characteristic of radical cation species.[7a]



Fortunately, we obtained a good single crystal of dicaton salt $\mathbf{3}\cdot(FeCl_4)_2(C_6H_5Cl)_2(H_2O)$ for X-ray structural analysis.[17] Two crystallograpically independent molecules (A and B)

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(15) Dication $\mathbf{3}^{2+}$ is perfectly stable toward molecular oxygen; the elementary analysis and the X-ray structure analysis were achieved under usual aerated conditions. This indicates that the dication has a closed shelled singlet electronic configuration in the ground state.

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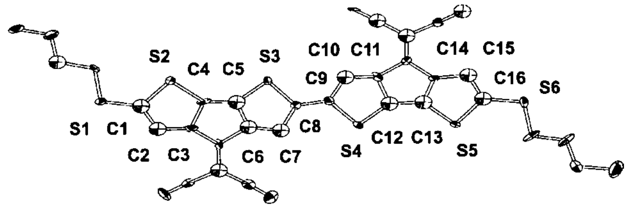

Figure 4. Molecular structure (ORTEP) and labeling of dication **3**$^{2+}$. Hydrogen atoms, counterions, and solvents were omitted for clarity. Selected bond lengths (Å) for molecule **A**: S1−C1, 1.69(3); S2−C1, 1.76(3); S2−C4, 1.72(3); S3−C5, 1.71(2); S3−C8, 1.72(3); S4−C9, 1.78(3), S4−C12, 1.69(3); S5−C13, 1.76(3); S5−C16, 1.71(3); S6−C16, 1.69(3); C1−C2, 1.40(4); C2−C3, 1.36(4); C3−C4, 1.39(4); C4−C5, 1.33(4); C5−C6, 1.47(4); C6−C7, 1.32(5); C7−C8, 1.46(4), C8−C9, 1.41(3); C9−C10, 1.43(4); C10−C11, 1.30(3); C11−C12, 1.46(3); C12−C13, 1.36(4); C13−C14, 1.49(4);C14−C15, 1.33(4); C15−C16, 1.40(4). Selected bond lengths (Å) for molecule **B**: S1−C1, 1.66(3); S2−C1, 1.80(3); S2−C4, 1.75(3); S3−C5, 1.70(3); S3−C8, 1.76(3); S4−C9, 1.76(3), S4−C12, 1.69(3); S5−C13, 1.75(3); S5−C16, 1.75(3); S6−C16, 1.69(3); C1−C2, 1.38(4); C2−C3, 1.34(4); C3−C4, 1.51(4); C4−C5, 1.34(4); C5−C6, 1.40(4); C6−C7, 1.34(4); C7−C8, 1.45(4); C8−C9, 1.38(3); C9−C10, 1.42(4); C10−C11, 1.30(4); C11−C12, 1.51(4); C12−C13, 1.40(4); C13−C14, 1.35(4); C14−C15, 1.41(4); C15−C16, 1.39(4).

were in a unit cell. These two molecules had similar structures, and one of their ORTEP structures is shown in Figure 4 as a representative example. Dication **3**$^{2+}$ had a highly planar structure. The dihedral angles between two mean-square planes formed by the two CPDT rings were 3.7(9) and 3.5(9)°. Two CPDT rings adopted an anti conformation, similar to the neutral **3**. The comparison of neutral and dication species structures is interesting. However, because of the small ratio of observed unique reflection (5357)/parameters in the X-ray structure analysis, the bond length could not be precisely determined. However, a bond length argument with ±0.05 Å is still possible. Figure 4 also lists the bond lengths for two independent molecules (**A** and **B**). While the thiophene rings in neutral **1** have a clear bond alternation, dication **3**$^{2+}$ has a reverse bond alternation. Namely, **3**$^{2+}$ has a quinoid-like structure. Quinoid-like alternation was more pronounced in the inner thiophene rings rather than in the terminal rings. This trend is in good agreement with theoretical calculations.[7] Furthermore, dication **3**$^{2+}$ has a shorter average C−S bond length between α-carbon atoms in terminal thiophenes and sulfur atoms in the *n*-butylthio chain than neutral **3**, suggesting a partial double-bond character for C−S bonds. In fact, *n*-butylthio chains lie in the plane of CPDT rings, which is explicable if we assume that the canonical VB structure (**I**) made a contribution.

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Supporting Information Available: Synthetic procedures and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Crystallographic data for **3**$^{2+}$: $C_{32}H_{22}N_4S_6(FeCl_4)_2(C_6H_5Cl)_2H_2O$, triclinic, $P1$, $a = 13.844(1)$ Å, $b = 13.846(1)$ Å, $c = 18.700(2)$ Å, $\alpha = 71.71(1)°$, $\beta = 71.68(1)°$, $\gamma = 60.87(1)°$, $V = 2915.9(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.475$ g/cm^3, $T = 173$K, $R_1 = 0.088$, $R_w = 0.124$.