4424 *Chem. Mater.* **2003,** *15,* 4424−4430

Polarons, Bipolarons, and π-Dimers of Bis(3,4-ethylene-dioxythiophene)-(4,4′-dialkyl-2,2′-bithiazole)-*co*-Oligomers. Direct Measure of the Intermolecular Exciton Transfer Interaction

Jie Cao and M. David Curtis*

Department of Chemistry and the Macromolecular Science and Engineering Center,
University of Michigan, Ann Arbor, Michigan 48109-1055

Received June 13, 2003. Revised Manuscript Received September 1, 2003

The oxidative behavior of bithiazole-ethylenedioxythiophene co-oligomers is described. The acceptor−donor−acceptor (A−D−A) compounds, 5,5′-bis(4,4′-dialkyl-2,2′-bithiazol-5-yl)-(3,4,3′,4′-bis(ethylenedioxy)-2,2′-dithienyl) (**1**, **2**), are sequentially oxidized by $NOBF_4$ through the paramagnetic monocation to the diamagnetic dication. The monocations form diamagnetic π-dimers, the allowed $\pi-\pi$ electronic transitions of which are interpreted in terms of molecular exciton theory to give nearest-neighbor exciton coupling constants, $J \cong 0.2$ eV. The spectra of the dications show that they are bipolarons; that is, the two charges share a common lattice deformation. The D−A−D co-oligomers, 5,5′-bis(3,4-ethylenedioxythien-2-yl)-4,4′-dibutyl-2,2′-bithiazole (**3**) and 5,5′-bis(3,4,3′,4′-bis(ethylenedioxy)-2,2′-dithien-5-yl)-4,4′-dibutyl-2,2′-bithiazole (**4**), are oxidized in a single step to the corresponding bipolarons.

Introduction

Organic conjugated materials have been intensively studied as the active components in electronic applications, for example, thin-film transistors[1−5] and light-emitting diodes.[6,7] Most of these applications would benefit from a full understanding of transport properties. Although charge transport theory has been developed in the framework of a polaron/bipolaron model,[8,9] the role of bipolarons in the transport process remains controversial. Studies of cation radicals of various materials, such as oligothiophenes,[10−14] oligopyrroles,[15−17] and oligophenylene-vinylenes,[18] have led to the conclusion that π-dimers, as an alternative to bipolarons, may be the entities that are responsible for the decrease in spin concentration and other spectral changes that are seen as the dopant concentration increases. Miller et al. first reported the single-crystal structure of substituted terthiophene cation radicals.[19] The molecular packing clearly shows the formation of face-to-face π-dimers. Therefore, studies of π-dimers are very useful for understanding intermolecular interactions of charged species.

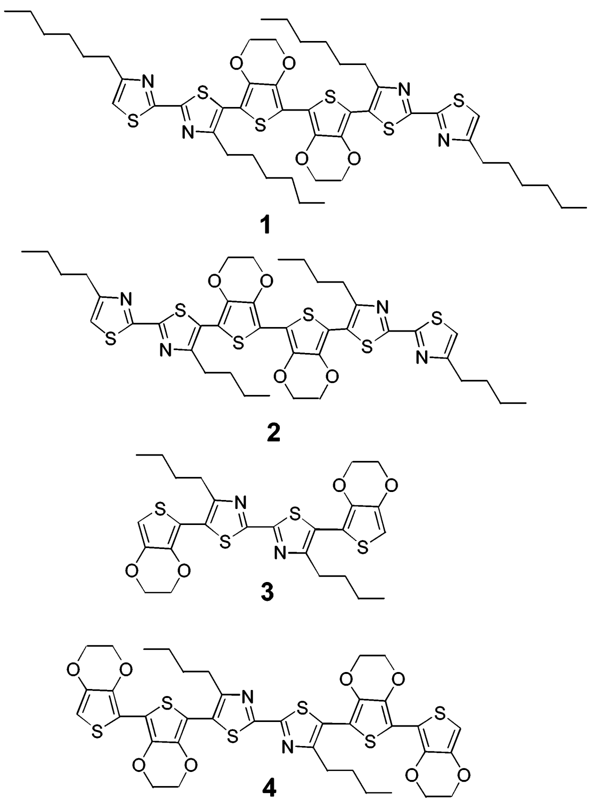
There is increasing evidence that π-stacked structures may provide higher carrier mobilities as a result of larger intermolecular overlap.[20−23] We have shown previously that polymers and oligomers of 4,4′-dialkyl-2,2′-bithiazoles adopt π-stacked structures that engender close intermolecular contacts (ca. 3.4 Å).[24−27] However, the presence of the nitrogen in the bithiazole ring increases the oxidation potential and renders the materials unstable with respect to p-doping. Although n-doping is possible, the reduction potentials are near −2 V vs ferrocene/ferrocenium and the n-doped materials react with water vapor or oxygen in the environment.[28,29] Hence, we sought to prepare “co-oligomers”

---

(1) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.
(2) Katz, H. E.; Bao, Z. *J. Phys. Chem. B* **2000**, *104*, 671.
(3) Horowitz, G. *J. Mater. Chem*. **1999**, *9*, 2021.
(4) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365.
(5) Lovinger, A. J.; Rothberg, L. J. *J. Mater. Res.* **1996**, *11*, 1581.
(6) Mitschke, U.; Bäuerle, P. *J. Mater. Chem*. **2000**, *10*, 1471.
(7) Hudson, A. J.; Weaver, M. S. *Organic Electroluminescence*; John Wiley & Sons: New York, 2000.
(8) Chung, T. C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1984**, *30*, 702.
(9) Brédas, J. L.; Themans, B.; Andre, J. M.; Chance, R. R.; Silbey, R. *Synth. Met.* **1984**, *9*, 265.
(10) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 2728.
(11) Bauerle, P.; Segelbacher, U.; Maier, A.; Mehring, M. *J. Am. Chem. Soc.* **1993**, *115*, 10217.
(12) Miller, L. L.; Yu, Y.; Gunic, E.; Duan, R. *Adv. Mater.* **1995**, *7*, 547.
(13) Yu, Y.; Gunic, E.; Zinger, B.; Miller, L. L. *J. Am. Chem. Soc.* **1996**, *118*, 1013.
(14) Levillain, E.; Roncali, J. *J. Am. Chem. Soc.* **1999**, *121*, 8760.
(15) vanHaare, J.; Groenendaal, L.; Havinga, E. E.; Janssen, R. A. J.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 638.
(16) vanHaare, J.; Groenendaal, L.; Havinga, E. E.; Meijer, E. W.; Janssen, R. A. J. *Synth. Met.* **1997**, *85*, 1091.
(17) Apperloo, J. J.; Janssen, R. A. J. *Synth. Met.* **1999**, *101*, 373.
(18) Sakamoto, A.; Furukawa, Y.; Tasumi, M. *J. Phys. Chem. B* **1997**, *101*, 1726.
(19) Graf, D. D.; Campbell, J. P.; Miller, L. L.; Mann, K. R. *J. Am. Chem. Soc.* **1996**, *118*, 5480.
(20) Graf, D. D.; Duan, R. G.; Campbell, J. P.; Miller, L. L.; Mann, K. R. *J. Am. Chem. Soc.* **1997**, *119*, 5888.
(21) Lee, K.; Heeger, A. J. *Synth. Met.* **2002**, *128*, 279.
(22) Brédas, J. L.; Beljonne, D.; Cornil, J.; Calbert, J. P.; Shuai, Z.; Silbey, R. *Synth. Met.* **2001**, *125*, 107.
(23) Cornil, J.; Beljonne, D.; Calbert, J.-P.; Brédas, J.-L. *Adv. Mater.* **2001**, *13*, 1053.
(24) Koren, A. B.; Curtis, M. D.; Francis, A. H.; Kampf, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 5040.
(25) Lee, J.-H.; Curtis, M. D.; Kampf, J. W. *Macromolecules* **2000**, *33*, 2136.
(26) Cao, J.; Kampf, J. W.; Curtis, M. D. *Chem. Mater.* **2003**, *15*, 404.
(27) Gonzalez-Ronda, L.; Martin, D. C.; Nanos, J.; Politis, J. K.; Curtis, M. D *Macromolecules* **1999**, *32*, 4558.

10.1021/cm034484k CCC: $25.00

Scheme 1



1

2

3

4

of bithiazoles and 3,4-ethylenedioxythiophene (EDOT), compounds **1**−**4** (Scheme 1), in the hope that the cooligomers would crystallize with the π-stacked morphology characteristic of the bithiazoles but possess the ease of oxidation characteristic of EDOT.[30a] Compounds **1** and **2** may be classified as acceptor−donor−acceptor (A−D−A) type molecules because the bithiazole rings have relatively low-energy LUMOs (electron acceptor), and the thiophene rings have high-energy HOMOs (electron donor).[30] Compounds **3** and **4** are of the type D−A−D and were studied as comparisons of compounds **1** and **2**.

Herein, we report the optical and electrochemical properties of cation radicals and dications of the bithiazole-EDOT oligomers, **1**−**4** (Scheme 1). All these compounds have a molecular structure that promotes the formation of π-stacks in the solid state.[26] This is the first report in which we provide evidence that these compounds form π-dimers in solution upon oxidation. The optical spectra are interpreted in terms of the electronic structures of these compounds.

Experimental Section

The syntheses of 5,5′-bis(4,4′-dialkyl-2,2′-bithiazol-5-yl)-(3,4,3′,4′-bis(ethylenedioxy)-2,2′-dithienyl) (**1**, **2**), 5,5′-bis(3,4-ethylenedioxythien-2-yl)-4,4′-dibutyl-2,2′-bithiazole (**3**), and 5,5′-bis(3,4,3′,4′-bis(ethylenedioxy)-2,2′-dithien-5-yl)-4,4′-dibutyl-2,2′-bithiazole (**4**) were based on Stille coupling reactions and have been published elsewhere.[26] Cyclic voltammetry (CV) was performed with a Princeton Applied Research Potentiostat Model 263A interfaced to a PC computer. The solvent was dry CH_2Cl_2 or THF and the supporting electrolyte was tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (0.10 M).[31] The reported potentials are versus the ferrocene/ferrocenium (Fc/Fc^+) couple, obtained by adding a crystal of ferrocene to the solution. All experiments were carried out in solutions deaerated by bubbling argon through them, and all solvent transfers were performed under a blanket of Ar or N_2 with a cannula or a disposable syringe with a stainless steel needle.

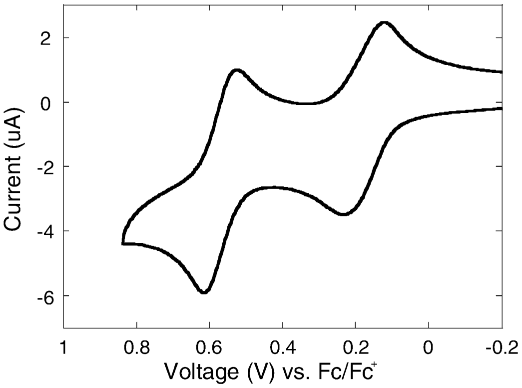


Figure 1. Cyclic voltammogram for compound **1** in CH_2Cl_2, 0.1 M $TBAPF_6$; reference electrode Ag/AgCl, scan rate 50 mV/s.

Chemical oxidation of the neutral oligomers was accomplished with nitrosonium tetrafluoroborate in CH_3CN solution. Solid $NOBF_4$ was weighed into a 20-mL vial inside a N_2-filled drybox. The vial was sealed by a rubber septum and transferred outside the drybox. Dry CH_3CN was added to the $NOBF_4$ to form a solution. Oligomer solutions in dry CH_2Cl_2 as solvent were prepared in 3.7-mL vials sealed with rubber septa. The concentration of the solution was calculated by measuring the weight of the added oligomer and solvent. For spectral measurements, oxidation of the solution was performed directly in a quartz cell that was sealed by a rubber septum. The oligomer solution was first injected using a syringe and needle; then, the $NOBF_4$ solution was added dropwise. For every step, the weight of the quartz cell was measured and the weight change was converted to the ratio, mol of $NOBF_4$/mol of oligomer.

The UV−vis−NIR spectra were recorded immediately using a Shimadzu 3101PC or a Perkin-Elmer Lambda 19 spectrometer. The temperature dependence of the optical spectra was recorded with the cell placed in a cryostat. ESR spectra were obtained on a Bruker EMX spectrometer using a 4102-ST cavity with a variable-temperature cryostat cooled by cold nitrogen gas. The sample tube was sealed by a rubber septum and charged with the solution via a cannula under Ar. Then, the tube was quenched in liquid N_2 for ESR measurement. The measurement temperature was typically at 175 K.

Results

The cyclic voltammograms of compounds **1** and **2** in CH_2Cl_2 exhibit two quasi-reversible oxidations corresponding to the generation of the cation radical and the dication, as shown in Figure 1. The results are listed in Table 1. Introduction of longer alkyl chains on the bithiazole rings increased the solubility of the compounds, but the oxidation potentials varied only slightly with the length of the side chain. For example, compound **1** shows two oxidation processes ($E^{1/2}{}_{ox}$) at 0.18 and 0.57 V vs Fc/Fc^+. The low oxidation potentials are

---

(28) Politis, J. K.; Curtis, M. D., He, Y.; Kanicki, J. *Macromolecules* **1999**, *32*, 2484.

(29) Politis, J. K.; Curtis, M. D.; Gonzales Ronda, L.; Martin, D. C.; He, Y.; Kanicki, J. *Chem. Mater.* **1998**, *10*, 1713.

(30) (a) Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Adv. Mater.* **1997**, *9*, 795. (b) Salzner, U.; Köse, M. E. *J. Phys. Chem. B* **2002**, *106*, 9221. (c) Raimundo, J, M.; Blanchard, P.; Gallego-Planas, N.; Mercier, N.; Ledoux-Rak, I.; Hierle, R.; Roncali, J. *J. Org. Chem.* **2002**, *67*, 205.

(31) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, 1997.

Table 1. Cyclic Voltammetry and UV−Vis−NIR Spectra of Compounds 1−4

	CV (oxid.)[a] (V vs Fc/Fc$^+$)		CV (red.)[b] (V vs Fc/Fc$^+$)		UV−vis−NIR peak maxima[c] (eV)			
name	E_{ox}^{p}	$E^{1/2}_{ox}$	E_{red}^{p}	$E^{1/2}_{red}$	neutral	cation	π-dimer	dication
1	0.232	0.179	−2.37	−2.32	2.66	1.74 (M_1)	1.96 (D_1)	1.96(DC)
	0.619	0.574				1.03 (M_2)	1.20 (D_2)	
2	0.250	0.209	−2.38	−2.31	2.66	1.75 (M_1)	1.97 (D_1)	1.97 (DC)
	0.623	0.582				1.03 (M_2)	1.20 (D_2)	
3	0.637[d]		−2.42	−2.31	3.02			2.11
4	0.130[e]		−2.35	−2.26	2.66			2.55
	0.220							

[a] Oxidative CVs of compounds **1**−**3** were performed in CH_2Cl_2/$TBAPF_6$ solution. [b] Reductive CVs of compounds **1**−**4** and oxidation of compound **4** were measured in THF/$TBAPF_6$ solution. Potentials are referenced to Fc/Fc$^+$ couple. [c] The UV−vis−NIR measurements were performed in CH_2Cl_2 solution after chemical oxidation using $NOBF_4$. M_1, M_2: cation radical bands. D_1, D_2: π-dimer bands. DC: dication bands. [d] An oxidation wave was observed at +0.347 V on the return sweep. [e] An oxidation wave was observed at −0.120 V on the return sweep.

mainly attributed to the presence of the $EDOT_2$ portion of the molecule because of its electron-rich nature.[30] The stability of the two oxidation states of **1** and **2** results from the bithiazole end caps, which not only block polymerization but also contribute to the stabilization of the cation by delocalization of the charge. As a result, the oxidation waves of compounds **1** and **2** were invariant after 10 oxidation−reduction cycles.

The observed oxidation processes for compound **3** are quite different from **1** and **2**: there is one oxidation wave for compound **3** at 0.637 V and a returning reduction wave at 0.347 V vs Fc/Fc$^+$. However, two oxidation waves were observed for compound **4** at 0.130 and 0.220 V with only one returning wave at −0.120 V vs Fc/Fc$^+$. The electrochemical irreversibility of the oxidation waves of these compounds is in stark contrast to the stability of the cations formed by chemical oxidation as described below. Possible reasons for the discrepancy include the fact that the CV data were obtained in a different solvent with different counterions. If the cationic material reacts with the counterions in the electrolyte or forms a film on the electrode, or if the electron transfer kinetics are slow, then the CV scan will not be reversible. We do not ascribe the irreversibilty of the oxidative CV scans to the polymerization of the oxidized material because the chemically produced dications are stable in solution (see below).

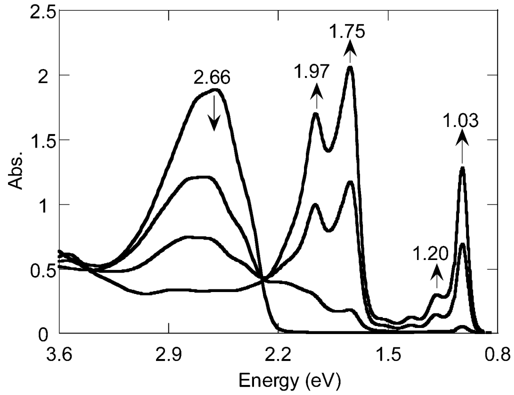


Figure 2. UV−vis−NIR spectra recorded during the chemical oxidation of **2** (2.7×10^{-4} M) by $NOBF_4$ (8.0×10^{-3} M). The mole ratios of $NOBF_4$/**2** are 0, 0.4, 0.8, and 1.0. During the addition of increasing amounts of $NOBF_4$, the absorption peak at 2.66 eV decreased while the peaks at 1.97, 1.75, 1.20, and 1.03 eV increased.

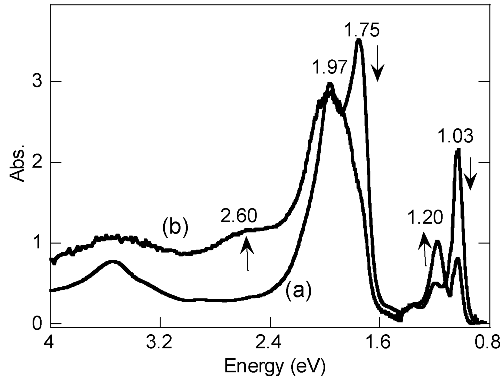


Figure 3. UV−vis−NIR spectra of **2**$^+$ as function of temperature during the chemical oxidation of **2** (6.3×10^{-5} M) by $NOBF_4$ (7.0×10^{-3} M). The mole ratio of $NOBF_4$/**2** is 1.3. (a) T = 20 °C; (b) T = −63 °C.

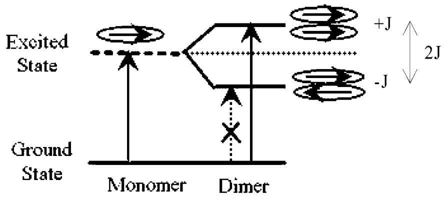
The controlled oxidation of compounds **1**−**4** was accomplished chemically with $NOBF_4$ in CH_3CN as the oxidant. The corresponding optical changes were monitored by UV−vis−NIR spectra, and the results are listed in Table 1. The UV−vis−NIR spectra of compounds **1** and **2** are similar to each other. Figure 2 illustrates the changes in the electronic absorption spectra of compound **2** that correspond to the generation of **2**$^+$ by the addition of increasing amounts of $NOBF_4$ until the mole ratio of $NOBF_4$/**2** = 1.0 is reached. The absorption maximum of the neutral species at 2.66 eV (466 nm) decreased while several low-energy bands emerged at 1.97, 1.75, 1.20, and 1.03 eV (629, 709, 1033, and 1169 nm, respectively). The number and relative ordering of the absorption bands closely resemble the spectral characteristics of oxidized thiophene oligomers.[10,11,13,20,32] The peak maxima at 1.75 and 1.03 eV may be assigned to cation radicals, **2**$^+$, and the maxima at 1.97 and 1.20 eV are attributed to a spin-paired, π-dimer of the cation radical, (**2**$^+$)$_2$. To corroborate these peaks assignments, low-temperature optical spectra were collected, as given in Figure 3. The intensities of the bands assigned to the cation radical decreased at low temperatures, while the intensity of the π-dimer bands increased. Since the temperature dependence of the optical spectra is totally reversible, the result suggested that the equilibrium, $2M^+ \leftrightarrow M_2^{2+}$, shifted in favor of forming π-dimers at low temperatures. This result is in accordance with the negative heats of formation observed for other π-dimers.[32,33]

---

(32) Hill, M. G.; Penneau, J. F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1106.

(33) van Haare, J. A. E. H.; Havinga, E. E.; van Dongen. J. L. J.; Janssen, R. A.; Cornil, J,; Brédas, J.-L. *Chem. Eur. J.* **1998**, *4*, 1509.

Scheme 2



The blue shift of π-dimer optical spectra as compared to that of the monomer may be interpreted in terms of molecular exciton theory and gives a direct measure of the nearest-neighbor exciton coupling, represented by the transfer integral, $J = \langle \phi_u \phi_v^* | V_{uv} | \phi_u^* \phi_v \rangle$, often approximated as a coupling between the transition dipole moments (TDM) of the individual monomers, $J \approx \beta M_u \cdot M_v / 4\pi\epsilon\epsilon_o r^3$, where r is the distance between the centers of the two interacting TDMs and β is a geometrical factor related to the relative orientation of the TDMs.[34-36] The interaction of the TDMs of two cation radicals in a co-facial π-dimer gives rise to two energy levels, as illustrated in Scheme 2. In the lower energy level, the net TDM is zero, and electric dipole transitions to this state are forbidden. However, transitions to the upper state are optically dipole-allowed, which result in a blue shift of the absorption spectrum compared to the monomer. The coupling constant, J, may be extracted directly from the observed shift (Scheme 2). The energy difference between the 1.97-eV transition of the dimer and the 1.75-eV transition of the monomer corresponds to $J_1 = (1.97 - 1.75) = 0.22$ eV. Similarly, the 1.20 and 1.03 eV transitions give a value for $J_2 = (1.20 - 1.03) = 0.17$ eV. It is noteworthy that the more intense absorption has the larger coupling constant. The intensity of the absorption is proportional to the oscillator strength, f, which is, in turn, proportional to the square of the TMD so that $J \sim (\beta/r^3)(f_1 f_2)^{1/2}$. In a comparison of the two coupling constants, the geometrical factors are the same for both transitions, but the more intense absorption has the greater oscillator strength and the larger exciton coupling constant.

Although the molecular exciton theory was first developed over 40 years ago and has been used to interpret the spectra of π-dimers of porphyrins, phthalocyanines, dyes, and so forth[36] and theoretical interpretations of the spectra of cations and π-dimers have appeared recently,[37] the role of exciton coupling in the spectra of π-dimers of conjugated oligomers and polymers has not been widely appreciated. We are aware of only one mention of “Davydov splitting” as the source of the blue shift associated with the dimer spectra.[38] From reported values of the $\lambda_{\max}$ of π-dimers of oligomers of thiophenes[13,32,33,38-40] and thienylene vinylenes,[41,42] we calculate values of the blue shift, corresponding to the coupling constant, J, in the range,0.25−0.50 eV for the former compounds and 0.16−0.18 eV for the latter. These coupling constants are slightly larger than those extracted from the solid-state absorption spectra of the π-stacked, neutral bithiazole oligomers: $J = 0.09 - 0.15$ eV.[24,26]

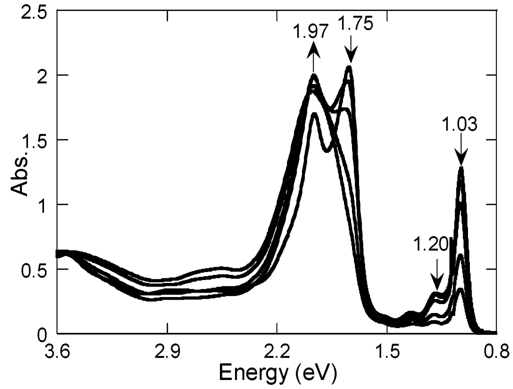


Figure 4. UV−vis−NIR spectra recorded during the chemical oxidation of **2** (2.7×10^{-4} M) by excess $NOBF_4$ (8.0×10^{-3} M). The mole ratios of $NOBF_4$/**2** are 1.0, 1.9, 2.9, 3.9, and 4.5. During the addition of excess $NOBF_4$, the absorption peaks at 1.75, 1.37, 1.20, and 1.03 eV decrease while the peak at 1.97 eV increases until the $NOBF_4$/**2** mole ratio is over 2.

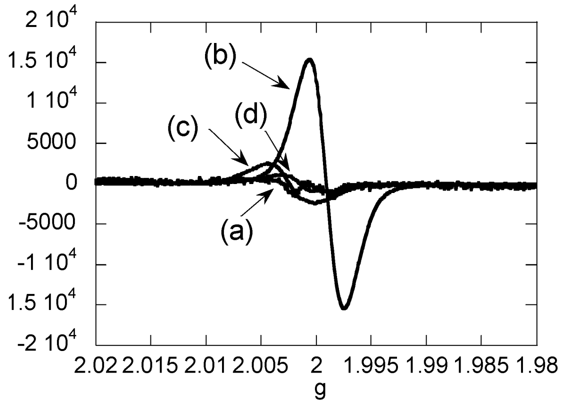


Figure 5. ESR spectra of $BT_2B/NOBF_4$ solution at 133 K (**2**, 4.2×10^{-4} M) with different ratios of NO^+/**2**: (a) 0, (b) 1.03, (c) 2.31, and (d) 3.37.

Upon the addition of excess $NOBF_4$ to compound **2**, bands due to both cation radical and π-dimer diminished, but the peak at 1.97 eV increased slightly as shown in Figure 4. Therefore, a peak with a maximum at 1.97 eV is assigned to the dication, $\mathbf{2}^{2+}$. This peak accidentally overlaps the position of the 1.97-eV peak of the π-dimer, $(\mathbf{2}^{+})_2$. Further evidence for the formation of cation radical and spinless dication during the oxidation of compounds **1** and **2** is given by ESR spectra. As illustrated in Figure 5, the chemical oxidation of compound **2** to the cation radical produced a strong ESR signal at $g = 1.9981 \pm 0.0001$. Interestingly, no hyperfine structure was observed from the ESR signal, suggesting that the positive charge was mainly localized on the EDOT rings in which the protons on the ethylene group are too far away from the spin loci to produce observable hyperfine splitting. The peak intensity de-

---

(34) McCrae, E. G.; Kasha, M. *J. Chem Phys.* **1958**, *28*, 721.

(35) Kasha, M. *Radiation Res.* **1963** *20*, 55.

(36) Munroe, O. Q.; Marques, H. M. *Inorg. Chem.* **1996**, *35*, 3768, and references therein.

(37) Brédas, J.-L.; Beljonne, D.; Cornil, J.; Calbert, J. Ph.; Shuai, Z.; Silbey, R. *Synth. Met.* **2002**, *125*, 107.

(38) van Haare, J. A. E. H.; van Boxtel, M.; Janssen, R. A. J. *Chem. Mater.* **1998**, *10*, 1166.

(39) Jiang, X.; Harima, Y.; Zhu, L.; Kunugi, Y.; Yamashita, K.; Sakamoto, M.; Sato, M. J. *Mater. Chem.* **2001**, *11*, 3043.

(40) Harima, Y.; Tang, H.; Zhu, L.; Yamashita, K.; Oshita, J.; Kunai, A. *J. Electroanal. Chem.* **1999**, *472*, 157.

(41) Casado, J.; Miller, L. L.; Mann, K. H.; Pappenfus, T. M.; Kanemitsu, Y.; Orti, E.; Viruela, P. M.; Pou-Amerigo, R.; Hernandez, V.; Lopez, Navarrete, J. T. *J. Phys. Chem. B* **2002**, *106*, 3872.

(42) Frère, P.; Allain, M.; Elandaloussi, E. H.; Levillain, E.; Sauvage, F.-X.; Riou, A.; Roncali, J. *Chem. Eur. J.* **2002**, *8*, 784.

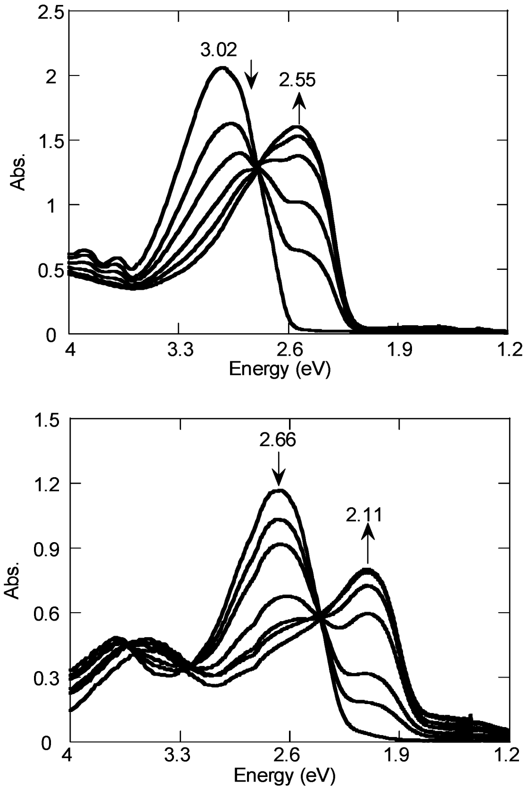


Figure 6. (Top) UV−vis−NIR spectra recorded during the chemical oxidation of **3** (8.0×10^{-5} M) by $NOBF_4$ (7.8×10^{-4} M). The mole ratios of $NOBF_4$/**3** are 0.0, 0.56, 0.91, 1.26, 1.61, 1.00, and 2.00. (Bottom) UV−vis−NIR spectra recorded during the chemical oxidation of **4** (5.3×10^{-5} M) by $NOBF_4$ (6.5×10^{-4} M). The mole ratios of $NOBF_4$/**4** are 0.0, 0.14, 0.25, 0.52, 0.80, 1.00, and 1.21.

creased significantly after adding excess oxidant, an indication of forming diamagnetic dications. The ESR signal almost disappeared after complete conversion of cation radical to the dications.

In contrast to compounds **1** and **2**, no reversible cation dimerization was observed for compounds **3** and **4** during chemical oxidation as shown in Figure 6. Instead, a peak emerged with the maximum at 2.11 or 2.55 eV for compound **3** or **4**, respectively. In addition, the observation of an isosbestic point in both spectra suggests that only two species are present in the solution during the chemical oxidation. The UV−vis−NIR spectra may be analyzed to provide an estimate of the stoichiometric coefficient, *a*, defined in eq 1.

$$\mathrm{M} + a\mathrm{NO}^{+} \rightarrow \mathrm{M}^{+a} + a\mathrm{NO} \qquad (1)$$

Chemical oxidation of compounds **3** and **4** using $NOBF_4$ as the oxidant decreases the absorbance of the neutral species at its $\lambda_{\max}^{(1)}$ as shown in Figure 6. The total absorbance at $\lambda^{(1)}$ can be described as in eq 2,

$$A(\lambda_{\max}^{(1)}) = f_1 A_1 + f_2 A_2 \qquad (2)$$

where f_1 and f_2 are the mole fractions of neutral and oxidized species, respectively. A_1 is the corresponding absorbance of neutral species before oxidation ($f_1 = 1$) at its wavelength maximum, $\lambda_{\max}^{(1)}$, and A_2 is the corresponding absorbance of the oxidized species after oxidation ($f_1 = 0$) at the same wavelength. If f is defined as

$$f = \frac{\text{mol of NOBF}_4\text{ added}}{\text{mol of the neutral oligomer before oxidation}} \qquad (3)$$

then eq 2 may be written as eq 4,

$$A(\lambda_{\max}^{(1)}) = \left(1 - \frac{f}{a}\right)A_1 + \frac{f}{a}A_2 = A_1 + f\frac{A_2 - A_1}{a} \qquad (4)$$

where a is the stoichiometric coefficient defined above. The coefficient a can be obtained from the slope of a least-squares fit to a plot of $A(\lambda_{\max}^{(1)})$ vs f. Similarly, the growth of the oxidized peak can also be used to extract the a value, but now the absorbances at the wavelength maximum of the oxidized species, $A(\lambda_{\max}^{(2)})$, are used.

Tables S1 and S2 in the Supporting Information list the absorbance of the UV−vis−NIR spectra of compounds **3** and **4** during the oxidation as a function of the mole fraction of added oxidant. Plots of absorbance vs f are shown in Figure S1 (Supporting Information). For compound **3**, A_2 and A_1 at $\lambda_{\max}^{(1)}$ are 0.71 and 2.09, and |slope| is 0.687. Thus, the stoichiometric coefficient, a, is equal to 2.01. Similarly, a is equal to 1.96 based on the absorbance at $\lambda_{\max}^{(2)}$. For compound **4**, A_2 and A_1 at $\lambda_{\max}^{(1)}$ are 0.513 and 1.353, respectively, and the |slope| is equal to 0.411, giving the two values of a equal to 2.03 and 2.01, respectively. These data indicate that compounds **3** and **4** are oxidized directly to the dication without the intermediacy of the monocation. In other words, the polarons of **3** and **4** are unstable with respect to disproportionation into a neutral molecule and the bipolaron. ESR experiments also confirm this conclusion. As demonstrated in Figure S2, only very weak ESR signals were recorded during the oxidation of **3** in CH_2Cl_2 with $NOBF_4$, implying the formation of diamagnetic dications. Strong ESR signals were also absent during the oxidation of **4** in CH_2Cl_2 solution, even after large excess of $NOBF_4$. We therefore suspect that the two oxidation waves observed in the CV of **4** (see above) is an artifact produced by the same processes that render the CV oxidations of **3** and **4** irreversible.

Discussion

Over the years, there has been a vigorous debate over the role of polarons and bipolarons as the charge carriers in doped poly(thiophene)s.[43] Polarons possess a spin of $^1/_2$ and are paramagnetic, whereas bipolarons are diamagnetic, and this distinction has been the primary means of distinguishing the two. Some investigations revealed that the spin concentration paralleled the degree of doping up to relatively high levels,[44,45] whereas other measurements showed that the spin concentration increased at low levels of doping and then rapidly dropped as the dopant concentration increased above a few percent.[46,47] The situation became even more unsettled when Miller et al. showed that spin-

---

(43) Brédas, J.-L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309.

(44) Schärli, M.; Kiess, H.; Harbeke, G. *Synth. Met.* **1988**, *22*, 317.

(45) Christensen, P. A.; Hamnett, A.; Hillman, A. R.; Swann, m. J.; Higgins, S. J. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 595.

(46) Colaneri, N.; Nowak, M.; Spiegel, D.; Hotta, S.; Heeger, A. J. *Phys. Rev. B* **1987**, *36*, 7964.

(47) Chen, J.; Heeger, A. J.; Wudl, F. *Solid State Commun.* **1986**, *58*, 251.

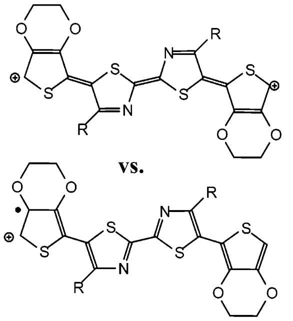
paired π-aggregates are an alternative explanation for the decrease in spin concentration as the concentration of polarons increases.[48] Furthermore, the interpretation of the optical spectra of oxidized (p-doped) polymers often rested on models derived from band theories applicable to inorganic semiconductors, but with little relevance to the behavior of excitons in molecular materials. It was not until the spectra of discrete oligomeric cationic species were reported that good models for optical spectra of polarons and bipolarons in polymeric materials became available.[49] More recently, a good theoretical description of the energetics and wave functions associated with polarons and bipolarons on a single, conjugated chain has appeared.[33] The best description of a bipolaron is that it consists of two charges associated with a common lattice deformation, whereas each polaron has its own lattice deformation.

It is now well-established that polarons are characterized by two strong absorptions of lower energy than the absorption of the neutral material. A third, weak absorption, ascribed to a charge-transfer transition, is seen in some cases.[13] On the other hand, bipolarons are characterized by a single strong absorption, usually located at an energy intermediate between those of the absorptions of the neutral molecule and the polaron. The spectra of the oxidized bithiazole/EDOT oligomers reported here conform to this pattern. Oligomers of the A−D−A (acceptor−donor−acceptor) type, **1** and **2**, are sequentially oxidized to the polaron, followed by further oxidation to the bipolaron. Because the positive charge is concentrated on the EDOT_2 portion of the molecule, the second oxidation potential is increased relative to the first by about 400 mV. Thus, the equilibrium constant for the disproportionation of two A−D−A polarons into a bipolaron and a neutral molecule, eq 5, is $K_d = \exp(-F\Delta V/RT) = \exp(-\Delta V/25.7) = 2 \times 10^{-7}$. Thus, dications are not formed until all the neutral molecules have been oxidized to the monocation.

$$2\mathrm{M}^{+1} \rightarrow \mathrm{M}^{+2} + \mathrm{M} \qquad K_d = [\mathrm{M}^{+2}][\mathrm{M}]/[\mathrm{M}^{+1}]^2 \quad (5)$$

The D−A−D compounds, **3** and **4**, on the other hand, are oxidized in a single step directly to the respective bipolaron. This observation means that the D−A−D polarons undergo the disproportionation reaction represented by eq 5. Under the influence of electrostatic forces alone, removal of an electron from a molecule that already possesses a positive charge requires more energy than removal of an electron from the neutral molecule. In condensed media, this increase is tempered by the increase in the solvation or polarization energy of the dication and by the relaxation of the molecular structure (lattice deformation) to accommodate the change in electron distribution in the molecule. If we assume that in the D−A−D type molecules the positive charge is more or less localized on the donor sites, then a crude estimate of the increased electrostatic energy required for the second ionization is simply $\Delta V = e/4\pi\epsilon\epsilon_o\langle r\rangle = 4.8V/\langle r\rangle$, where $\langle r\rangle$ is the average distance between the loci of positive charge in Å and a value of 3.0 was assumed for the effective dielectric constant, ϵ.

Scheme 3



The bithiazole ring is about 8-Å long, so if a value of 10 Å is assumed for $\langle r\rangle$, then $\Delta V \approx 0.5$ V. Thus, if the decrease in total energy due to the polarization and lattice deformation associated with the bipolaron exceeds about 0.5 eV, the $\mathrm{D{-}A{-}D}^{+1}$ polaron will disproportionate to the bipolaron and neutral molecule. A larger separation between the donor portions of the molecule decreases the difference between potentials of the first and second oxidations, so a lower stabilization energy, $e\Delta V$, is required for the formation of a dication. The question that then arises is the following: Is the dication a bipolaron or two polarons on the same chain?

Van Haare et al. have presented an excellent analysis of the electronic states and energetics of the mono- and dications of thiophene oligomers, T_6, T_9, and T_{12}.[33] Experimentally, they find that the hexamer and nonamer are oxidized sequentially through the polaron to the dication, and the ground state of the dication corresponds to a bipolaron; that is, the two charges share a common, quinoidal lattice deformation. In the T_{12} oligomer, however, the monocations disproportionate into dications, the ground state of which appears to be that of a spin-coupled diradical. In other words, the T_{12}^{+2} oligomer has two polarons on it, located at opposite ends of the chain, and each polaron has its own distinct lattice deformation.

In contrast, the dications of the D−A−D molecules, **3** and **4**, consisting of only 4 and 6 heteroatom rings, respectively, are already stabilized with respect to the polaron. We believe that this occurs because localization of the positive charge occurs on the donor groups consisting of only one or two EDOT rings. The degree of stabilization that can be provided to the polaron by any reasonable lattice deformation confined primarily to one or two rings is probably so small that the energy gained by spreading the deformation out over the entire molecule is sufficient to tip the energy balance in favor of the bipolaron (Scheme 3).

Our data also confirm previous suggestions that formation of π-dimers is an alternative to bipolarons as an explanation for both spectral changes and loss of spin concentrations, especially for the type of molecules that have been shown to form π-stacks in the solid state.[10,12,13,19,32] The absorption bands of the π-dimer arise as a consequence of exciton coupling and imply that the dimer has a face-to-face structure that leads to a hypsochromic shift of the absorption ("H-type" aggregation), and the exciton coupling constant, J, is obtained directly from the difference in the energies of the dimer and monomer absorptions. It is interesting to note that the values obtained for J are similar to

---

(48) Miller, L. L.; Mann, K. R. *Acc. Chem. Res.* **1996**, *29*, 417.
(49) Fichou, D.; Horowitz, G.; Xu, B.; Garnier, F. *Synth. Met.* **1990**, *39*, 243.

those extracted from the spectra of π-stacked neutral molecules.[24,26] In an infinite one-dimensional π-stack, the width of the exciton band is given by $4J$, so these values predict exciton bandwidths of 1−2 eV for π-stacked radical cations of thiophene-type compounds. This is a relatively large bandwidth for molecular materials and is a consequence of the large oscillator strength of the $\pi-\pi^*$ transition and the relative alignment of the molecular transition dipole moments in the solid state.

The CVs of compounds **1** and **2** were reversible and showed the two waves corresponding to the chemical oxidations to mono- and dication, but the CVs of **3** and **4** were not at all indicative of the simplicity or nature of the chemically oxidized materials. Thus, electrochemical oxidations, exemplified by the CV scans, are not necessarily good predictors of the behavior of conjugated oligomers upon chemical oxidation and should be used with caution in determining the charge state of oxidized materials.

Finally, one should be wary of broad generalizations concerning the relative stabilities of polarons vs bipolarons, as it appears that relatively minor changes in molecular structure can reverse their relative energies. In fact, their relative stabilities can be reversed even by changing the phase from solution to the solid state.[42]

Acknowledgment. The authors thank the National Science Foundation for support of this work through Grant No. DMR 9986123.

Supporting Information Available: UV−vis−NIR absorbances of compounds **3** and $\mathbf{3}^{+2}$ and **4** and $\mathbf{4}^{+2}$. Plots of absorbance vs the mole ratio *f*; ESR measurement of the chemical oxidation of compounds **3** and **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM034484K