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Oligothiophene Cation Radicals. π-Dimers as Alternatives to Bipolarons in Oxidized Polythiophenes

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Three oligomers of thiophene, 2,5″-dimethylterthiophene (3Th-Me), 2,5′-(dithiomethyl)-5,2′-bithienyl (2Th-SMe), and 2,5″-(dithiomethyl)-5,2′,5′,2″-terthienyl (3Th-SMe), were prepared to model polythiophene. In these compounds, the thiophene rings were α-linked and the terminal α-positions were blocked with methyl or thiomethyl substituents to prevent polymerization. Electrochemical methods were used to generate cationic solution analogues of these postulated in oxidized polythiophenes. UV–vis–near-IR spectroelectrochemistry, in situ ESR, and cyclic voltammetry (CV) provided a sufficiently short time scale to characterize one- and two-electron oxidation products without incursion of further, multielectron, chemistry. Variable-temperature spectroelectrochemistry at potentials corresponding to the first CV oxidation peaks of the oligomers revealed the formation of cation radicals and their diamagnetic π-dimers at equilibrium. At more positive potentials, dications were formed and characterized. These results are compared to previously characterized oligothiophene cations and oxidized polythiophene. It is suggested that the radical dimerization phenomena enucleated here may be common for oxidized oligo- and polythiophenes and can explain previous observations attributed to bipolarons.

Introduction

Although conducting polymers have received considerable attention, there is still much to be learned about their structure and properties. One approach to understand the behavior of complex, polymeric materials is to prepare and study oligomeric analogues. Because conducting polymers are usually composed from partially oxidized or reduced, highly conjugated π-systems, this approach involves several steps: the preparation of an oligomer; the characterization of the oxidized or reduced oligomer in solution; and the study of the conductivity and other properties of the solid ionic oligomer for comparison with the conducting polymer. This approach is appealing because it addresses the difficulties associated with unravelling *intra*molecular effects from the *inter*molecular effects which are necessarily present in the solid. As a specific example of the model oligomer approach, we chose to study the spectroscopic properties of oligothiophene cation radicals and dications in solution, as they should be interesting models for the polaron and bipolaron states proposed in oxidized polythiophenes.[1] Paramagnetic polarons and diamagnetic bipolarons now form the theoretical cornerstone for understanding the structure and properties of many conducting polymers,[2] but this stone has rested on infirm ground, as experimental characterization of the spectroscopic properties of these species was not definitive.

Although a large number of α-coupled oligothiophenes have been reported, their facile oxidative polymerization[3] usually prevented characterization of the cation radicals and dications. An exception discovered in this laboratory is the oxidized oligomers of 3-methoxythiophene, which could be reduced, purified, and studied. The major component in this mixture was shown to be the 2,5-bonded pentamer.[4,5] Reoxidation of this pentamer gave stable acetonitrile solutions with ESR and vis–near-IR properties of diamagnetic dications. Oxidation of water-insoluble thin films of the neutral gave a material with spectroscopic properties similar to those of oxidized polythiophene and dry film conductivities of 10^{-2}–10^{-3} S cm^{-1}.[4,6] These results suggested that we could use the model oligomer approach and prepare stable cation radicals and dications of properly selected oligothiophenes.

Recently, the cation radicals of terthienyl and several derivatives have been prepared photolytically and characterized by transient Vis absorption spectroscopy.[7] Under these conditions, the cation radical is rapidly consumed by back electron transfer and/or other reactions. In other contemporary reports, Fichou and co-workers[8] documented the spectra of quatra-, quinque-, and sexithienyl, (four, five, or six rings) oxidized with FeCl$_3$ in CH$_2$Cl$_2$. Before intractable solids precipitated, optical and ESR spectra of the solutions documented the presence of cation radicals. For sexithienyl, the dication could also be formed.

The instability of oligothiophene cations is curious because oxidized polythiophenes can have one charge for every five or six thiophene rings,[1] similar to the charge on an oligomer cation radical. We thought that the polymerization of oligothiophene cation radicals could be overcome if the terminal positions of a 2,5-linked oligomer were blocked to slow down the coupling. We have demonstrated

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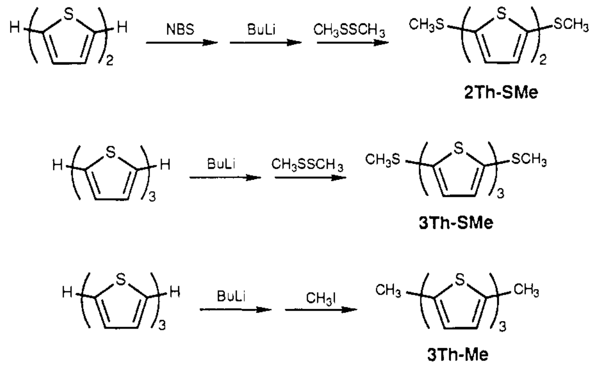
Scheme I



the efficacy of this approach in a preliminary communication where we report CV, ESR, and vis–near-IR studies of oxidized 2,5″-dimethylterthiophene.[9] Caspar et al.[10] have also circumvented the polymerization problem by encapsulating 2,5″-dimethylterthiophene, as well as uncapped oligothiophenes (bi-, ter-, quatra-, and sexithienyl), in the channels of oxidizing pentasil zeolites. While they observe oxidative coupling at unblocked α-positions at elevated temperatures, the zeolite cages provided sufficient stabilization to allow the generation and spectroscopic (vis–near-IR and ESR) characterization of several cation radicals and dications.

Until recently there was little electrochemical evidence for oligothiophene cation radicals in solution. Now Diaz, Tour, and co-workers have presented CV results on a series of end-capped oligothiophenes that form cation radicals and dications without polymerization on the CV time scale.[11] They also report optical and ESR spectra of the cation radicals and dications using $FeCl_3$ in CH_2Cl_2. Their results compare well with those of Fichou and co-workers, and they are able to correlate optical transition energies with conjugation lengths.

Herein, we report the spectroscopic characterization of the cation radicals and dications formed when terminally blocked oligothiophenes are electrochemically oxidized in CH_3CN. Variable-temperature spectroelectrochemistry and ESR spectroscopy were used to characterize cation radicals, dications, and cation radical π-dimers. The formation of π-dimers has been further authenticated in a study which used photooxidation to generate stable cation radicals and dications from the oligomers studied here.[12] *The formation of π-dimers in dilute solution suggests that the polaron/bipolaron model for the chemistry and physics of oxidized polythiophene is too simple and should take into account favorable interchain interactions that give diamagnetic products (π-dimers or π-stacks) that are not bipolarons.* Further, we suggest that these intermolecular π-interactions among polarons will be important structural interactions in thin films and provide a mechanism for electrical conductivity.

Results

Synthesis of Oligomers. The three oligomers of interest here are the dimethylterthiophene (3Th-Me), bis(thiomethyl)dithiophene (2Th-SMe), and bis(thiomethyl)terthiophene (3Th-SMe). The rings of each oligomer are bonded at the 2,5-positions and the terminal 2- and 5-positions are blocked. We chose the π-donor thiomethyl groups as they might stabilize the cations electronically, as well as sterically block the polymerization reaction.

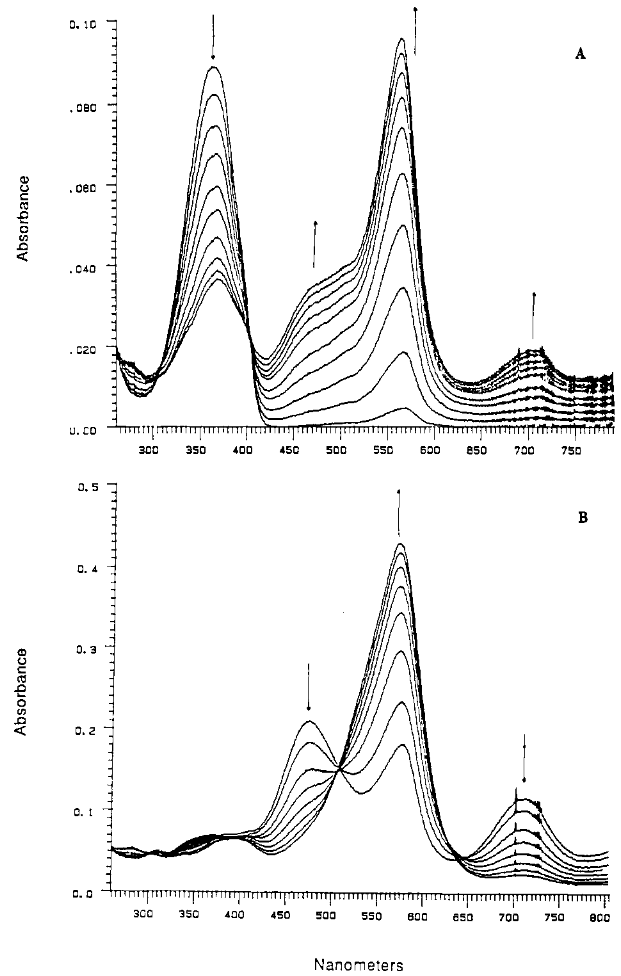


Figure 1. UV–vis spectra measured during the spectroelectrochemical oxidation of 3Th-Me in CH_3CN, 0.1 M Bu_4NBF_4. Spectra recorded every 5 s (a) during the passage of $1e^-$/molecule at 1.0 V ($[\text{3Th-Me}]_{\text{initial}}$ = 0.7 mM; T = 21 °C), (b) during passage of a second 1 e^-/molecule at 1.1 V ($[\text{3Th-Me}]_{\text{initial}}$ = 1.5 mM; T = −10 °C).

Our synthetic approach followed the literature[5,13] as outlined in Scheme I.

Cation Radicals. *3Th-Me*$^+$. In a preliminary communication, we reported that 3Th-Me undergoes a chemically reversible $1e^-$ oxidation (E_{pa} = 1.02 V, E_{pc} = 0.96 V vs SCE at 100 mV s^{-1}) in CH_3CN with 0.1 M $Bu_4N^+BF_4^-$ as the supporting electrolyte.[9] This electrochemical response is quite unlike that of terthiophene, which shows currents that increase on repetitive anodic sweeps due to polymerization. We conclude that blocking the terminal α-positions was successful. The UV-vis spectroelectrochemical oxidation of 3Th-Me at 21 °C (Figure 1) shows that as neutral 3Th-Me is oxidized in the thin-layer cell, the initial band at 360 nm gives way to four new bands at longer wavelengths. If the electrolysis is discontinued, the spectrum does not change for several minutes.

Several experimental observations indicate that the absorbances at 572 nm and >800 nm (beyond the spectrometer range) are due to one species (assigned as the

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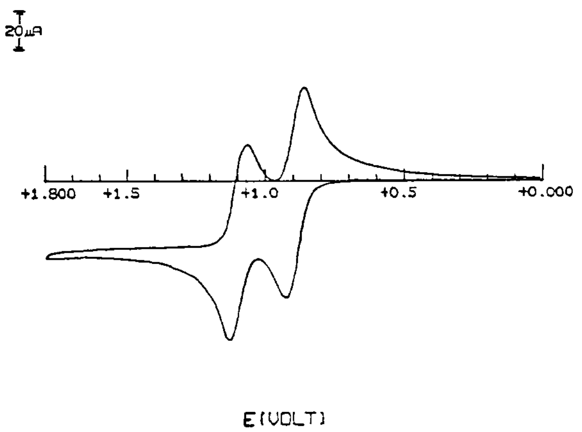

Figure 2. Cyclic voltammogram for 2Th-SMe (3 mM) in CH_3CN, 0.1 M BuN_4BF_4. Sweep rate = 100 mV s^{-1}.

Table I. Cyclic Voltammetry Data[a]

compound	$E^{\circ\prime}_{+/0}$	$E^{\circ\prime}_{2+/+}$
3Th-Me	0.99	
2Th-SMe	0.93	1.17
3Th-SMe	0.89	1.02

[a] Measured at 100 mV s^{-1} in CH_3CN at room temperature. All potentials vs SCE (volts).

Table II. Absorption Maxima for Oligothiophene Species[a]

	3Th-Me	2Th-SMe	3Th-SMe
T	360	345	383
T^+	572, 880	560, 879	655, 1100
$(T^+)_2$	466, 708, 868	457, 662, 8*xx*	524, 838, 1094
T^{2+}	570[b]	505, 530	625, 685

[a] Spectroelectrochemical data in nanometers measured as described in the text. [b] Unstable.

Table III. Visible Band Absorption Ratios of $2Th\text{-}SMe^+/(2Th\text{-}SMe^+)_2$[a]

temp (°C)	A_{560}/A_{450}	temp (°C)	A_{560}/A_{450}
+5	0.87	−23	1.61
−8	0.94	−30	2.10
−15	1.15		

[a] Measured as described in the text on a solution that was originally 1.2 mM in 2Th-SMe.

monomeric cation radical, $3Th\text{-}Me^+$), while the bands at 466 and 708 nm are due to a second species (assigned as the cation radical dimer $(3Th\text{-}Me^+)_2$): First, upon one electron oxidation of 3Th-Me at constant temperature, higher initial concentrations of 3Th-Me favored the peaks at 466 and 708 nm relative to the peak at 572 nm; lower concentrations favored the 572-nm peak relative to those at 466 and 708 nm. Second, at fixed concentrations of one-electron-oxidized 3Th-Me, lowering the temperature of the solution increased the absorbances at 466 and 708 nm at the expense of the absorbance at 572 nm; restoring these cold solutions to their initial temperatures restored all of the absorbances to their initial intensities. Significantly, these temperature-dependent spectra showed that no neutral 3Th-Me was generated at any temperature, abrogating the possibility of a disproportionation of cation radicals to dications and neutrals. Finally, at all temperatures and concentrations studied, plots of log A_{572} vs log A_{460} yielded straight lines with slopes of 2. This strongly implies that oxidation of 3Th-Me generates an equilibrium mixture of monomer cation radicals, $3Th\text{-}Me^+$ (572 nm) and cation radical dimers, $(3Th\text{-}Me^+)_2$ (460 and 708 nm).

The ESR signal of an electrochemically oxidized 3Th-Me solution exhibited an analogous temperature dependence. Cooling the sample decreased the signal intensity dramatically, so that at about −20 °C the doubly integrated signal was only 15% as intense as the that observed at 23 °C. Consistent with the UV–vis experiments, these ESR changes were completely reversible. An analysis and simulation of the ESR spectrum is presented elsewhere.[12] On the basis of the ESR data, we conclude that the monomer cation radical is ESR active, but the dimer has no ESR signal and is presumably diamagnetic.

Oxidations of 3Th-Me at several temperatures and concentrations were studied, and in each case good fits to the equilibrium expression, $K = [\text{dimer}]/[\text{monomer}]^2$ were obtained. At room temperature, we found that K was equal to approximately 250 M^{-1}.[14] van't Hoff plots of the various K values were made, giving $\Delta H = -10$ kcal/mol and $\Delta S = -25$ eu, values quite compatible with the proposed equilibrium.

$2Th\text{-}SMe^+$. In acetonitrile solution, with 0.1 M Bu_4NBF_4 as the supporting electrolyte, 2Th-SMe shows (Table I, Figure 2) a room-temperature CV with two reversible couples. At scan rates between 10 and 200 mV s^{-1} the anodic–cathodic peak separation is 60 mV for each of the processes. The anodic–cathodic peak currents are equal to within ±10%. Similar voltammograms are observed in benzonitrile and in methylene chloride solutions. These voltammograms indicate that the cation radical ($2Th\text{-}SMe^+$) is stable on the CV time scale. Repetitive cycling did not give the increasing currents characteristic of polymerization.

Slow, preparative electrooxidations (tens of minutes) of $2Th\text{-}SMe^+$ in acetonitrile did not give solutions with stable visible spectra and ultimately resulted in the passage of more than 4 electrons/molecule. However, in situ spectroelectrochemistry allowed the spectroscopic characterization of $2Th\text{-}SMe^+$. Figure 3a shows the low-temperature spectroelectrochemical oxidation of 2Th-SMe at 0.87 V (vs a Pt pseudo-reference electrode). This potential was just positive enough to produce a significant anodic current, corresponding to the first peak of the CV. The initial absorbance at 356 nm (due to 2Th-SMe) diminishes while new bands grow in at 461, 570, 688, and >800 nm. During this process the current dropped to about 10% of its original value. The charge consumed for this process corresponds approximately to 1 electron/molecule. After this oxidation, if the potential is then stepped back to 0.7 V, the spectrum of neutral 2TH-SMe is regenerated with more than 95% of its original intensity. The process is fully reversible on the time scale of a few minutes at −30 °C, in agreement with expectations from the CV.

In accord with our observations for 3Th-Me, solutions of oxidized 2Th-SMe also gave temperature-dependant spectra (Table III). These measurements were made with no current flowing and were completely reversible. The monomer $2Th\text{-}SMe^+$ is assigned to peaks at 570 and 879 nm; the dimer to peaks at 461, 688, and beyond 800 nm (Table II).

In situ ESR spectra of oxidized 2Th-SMe (acetonitrile/Bu_4NBF_4 or benzonitrile/Bu_4NBF_4 solutions) were measured by potentiostatic electrogeneration in the cavity of the spectrometer. The spectrum of the oxidized product grew in when anodic current was passed, but when the potential was made more cathodic, it disappeared. At long electrolysis times, the instability of the cation radical caused the signal to decay. The computer-simulated

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(14) See ref 12 for details.

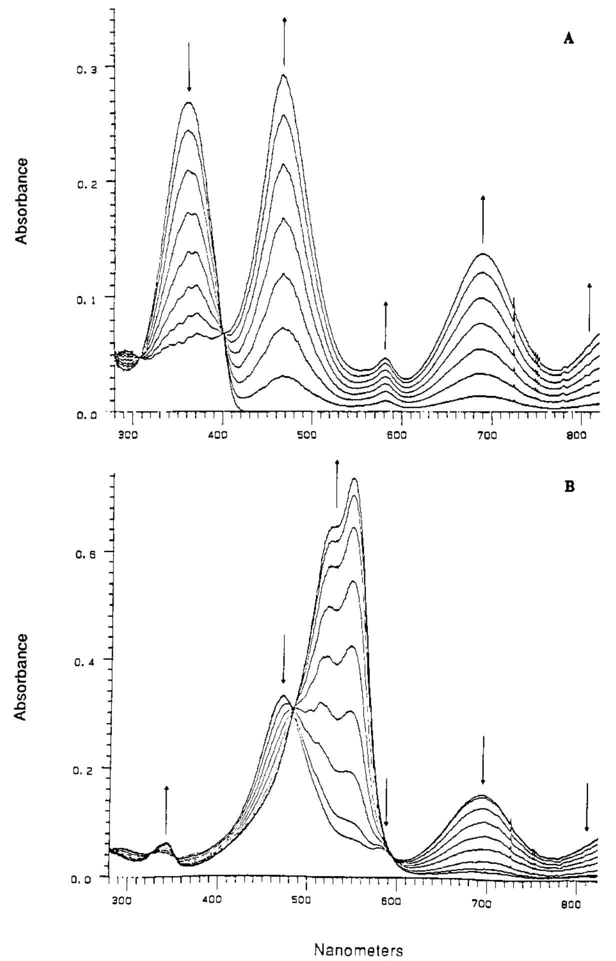


Figure 3. UV–vis spectra measured during the oxidation of 2Th-SMe (1 mM) in CH_3CN, 0.1 M Bu_4NBF_4 at −35 °C. Spectra recorded every 10 s (a) during the passage of 1 electron/molecule at 0.9 V, (b) during passage of another 1 electron/molecule at 1.3 V (vs Pt pseudo-reference).

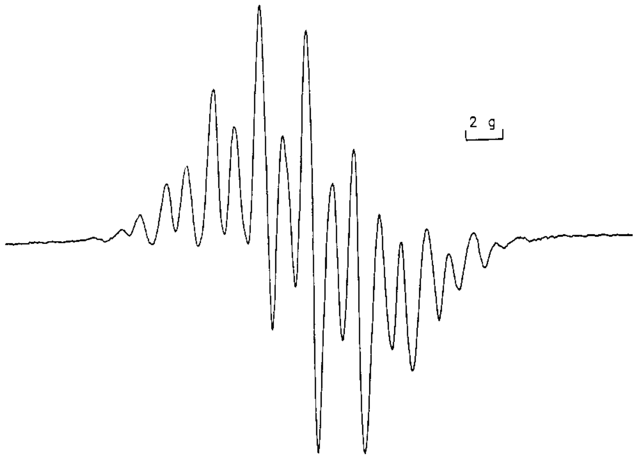


Figure 4. ESR spectrum of 2Th-SMe$^+$ in CH_3CN, 0.1 M Bu_4NBF_4 generated in situ at room temperature.

spectrum is consistent with the experimental spectrum (Figure 4) of 2Th-SMe$^+$ and shows coupling of the electron spin with six hydrogens a_H = 2.35 G, two hydrogens a_H = 2.65 G, and two other hydrogens a_H = 1.40 G.

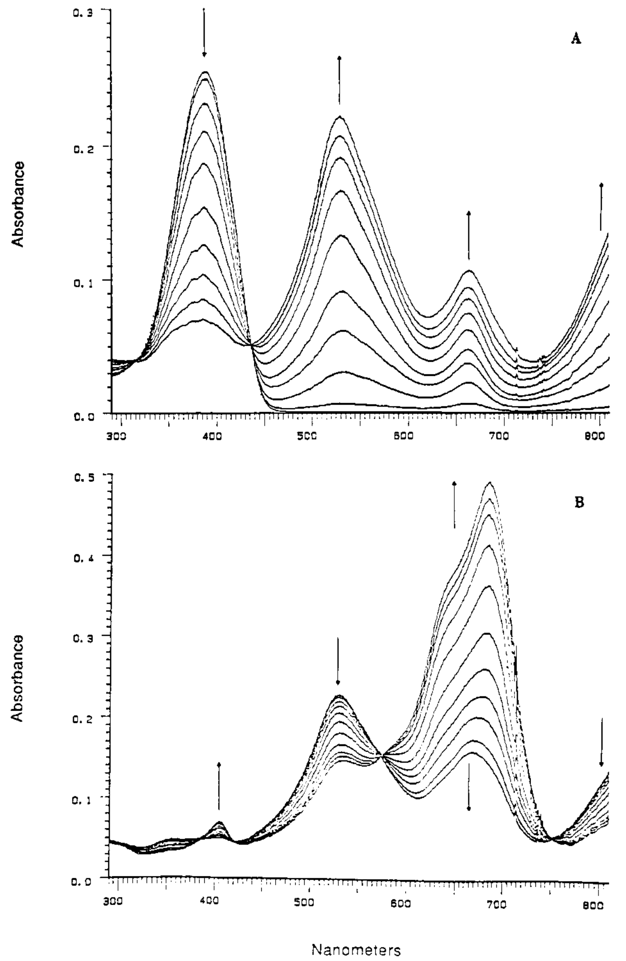


Figure 5. UV–vis spectra measured during the oxidation of 3Th-SMe (1 mM) in CH_3CN, 0.1 M Bu_4NBF_4 at −30 °C. Spectra recorded every 10 s during the passage of approximately 1 electron/molecule at 0.85 V. Spectra recorded every 18 s during the passage of a second electron/molecule at 0.95 V (vs Pt pseudo-reference).

3Th-SMe$^+$. At a platinum electrode, two closely spaced, cleanly reversible oxidation processes were observed for 3Th-SMe by CV at 10–200 mV s^{-1} (Table I) in acetonitrile or benzonitrile solutions with Bu_4NBF_4 as the supporting electrolyte. The anodic–cathodic peak separations for these two processes were 60 ± 5 mV, suggesting that the cation radical and dication are stable on this time scale.

Slow (tens of minutes) preparative scale oxidations at the first oxidation potential gave from 5 to 10 times the expected current. The exclusion of air and light, as well as careful solvent and electrolyte purification did not change this behavior. The low-temperature UV–vis spectroelectrochemical oxidation of 3Th-SMe in acetonitrile is shown in Figure 5; the UV–vis spectrum of the cation radical exhibited a similar temperature dependence as those observed for 3Th-Me and 2Th-SMe.

Although the electrogenerated mixture of 3Th-SMe$^+$ and (3Th-SMe$^+$)$_2$ does not exhibit long-term stability at room temperature, we were able to record its spectrum in the NIR beyond 800 nm. A divided cell with a large anode area to analyte volume ratio was employed to rapidly oxidize 3Th-SMe. After passage of 1 electron/molecule for 20 s, the solution was transferred to the spectrometer. The visible spectrum of this solution was identical to that spectroelectrochemically generated for the 3Th-SMe$^+$-(3Th-SMe$^+$)$_2$ equilibrium mixture. A set of high-temperature peaks at 665 and 1100 nm was assigned to 3Th-SMe$^+$, and a set of low-temperature peaks at 524, 838, and 1094 nm were assigned to (3Th-SMe$^+$)$_2$.

To confirm the 3Th-SMe$^+$–(3Th-SMe$^+$)$_2$ monomer–dimer equilibrium, two different concentrations of 3Th-SMe were used. One-electron oxidation of 1.0 mM 3Th-SMe at room temperature gave mainly the peaks assigned to (3Th-SMe$^+$)$_2$, while oxidation of a 0.5 mM solution of

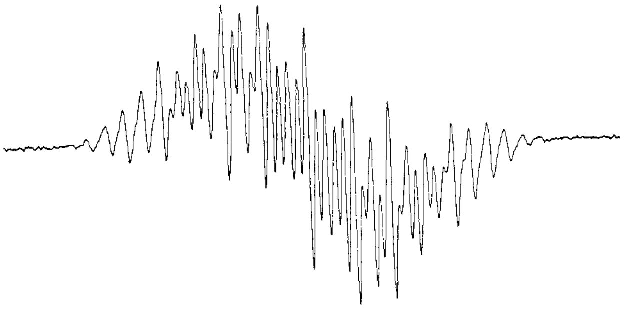


Figure 6. ESR spectrum of 3Th-SMe in CH_3CN, Bu_4NBF_4 generated in situ at room temperature.

3Th-SMe gave spectra enhanced in the peaks assigned to 3Th-SMe^+. Unfortunately, the spectroelectrochemical cell design made a more thorough concentration study impractical.

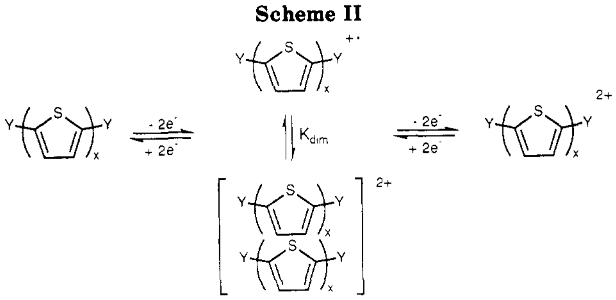
Electrooxidation of 3Th-SMe in the ESR cavity gave the spectrum shown in Figure 6. This spectrum was stable and reproducibly formed in acetonitrile. It disappeared upon reduction and seems to be due to 3Th-SMe^+, but we were unable to simulate the spectrum. Several trial combinations of coupling constants gave spectra in rough but imperfect accord with the experimental results. In a further attempt to understand this spectrum, the bis(trideuteriomethyl)terthienyl was prepared and oxidized. The resulting spectrum had five broad lines that we attribute to coupling the unpaired electron with four protons (a_H = 2.3 G). Even armed with this information, we were unable to obtain a unique simulation and did not pursue the analysis further.

However, it was of interest to measure the intensity of the ESR spectrum at high- and low-temperature to establish that 3Th-SMe^+ is paramagnetic and the dimer (3Th-SMe^+)$_2$ is diagmagnetic. Solutions of 0.5 mM 3Th-SMe were oxidized by 1 electron/molecule and at 30 °C gave a doubly integrated spectrum with approximately the intensity expected for 1 unpaired spin/molecule in comparison to a DPPH standard. The intensity of this spectrum was about 10 times that of the spectrum at −30 °C. This result strongly supports the dimerization theory and is in excellent accord with the UV–vis–near-IR spectra.

A final observation also supports a monomer–dimer equilibrium for the one-electron oxidation level in these molecules. A monomer–dimer equilibrium of this type should affect the separation between the first and second oxidation peaks in the cyclic voltammogram. Qualitatively, consider that dimerization stabilizes 3Th-SMe^+ compared to 3Th-SMe or 3Th-SMe^{2+} so that at high concentrations, the peak separation should be larger. Qualitatively, this is observed. At 1.8 mM the peak separation is 125 mV, while at 0.6 mM the separation is 80 mV. The difference, 45 mV, is within experimental error of the 38-mV value calculated from the Nernst equation.[15] It was not possible to obtain better data over a larger concentration range because the peaks merge at low concentration and the solubility is limited.

Dications. Room-temperature spectroelectrochemical oxidations of 3Th-Me at potentials more positive than the first anodic process result in the initial appearance of a species (absorbance centered at 570 nm) that rapidly decays and causes passivation of the Pt electrode. At low temperatures this product is somewhat more stable. Figure 1B shows the spectroelectrochemical oxidation of 3Th-Me^+/(3Th-Me^+)$_2$ at −10 °C. An intense absorption, presumably due to 3Th-Me^{2+}, grows in at 570 nm at the expense of the bands at 572, 466, and 708 nm. Even at −20 °C, re-reduction of this solution yields only about 70% of the original neutral starting material.

Scheme II



Preparative oxidation of 2Th-SMe at the second CV peak potential to form 2Th-SMe^{2+} leads to the passage of more than 4 electrons/molecules. However, it was possible during these spectroelectrochemical experiments to identify a new species present throughout this process. Upon oxidation of the cation radical solution, the peaks assigned to 2Th-SMe^+ and (2Th-SMe^+)$_2$ diminished and two new peaks at 505 and 530 nm due to 2Th-SMe^{2+} grew in intensity (Figure 3B). The relative intensities of these new peaks are constant, and there are two sharp isosbestic points. If the potential was stepped negatively after the passage of 2 electrons/2Th-SMe molecule, 2Th-SMe^{2+} was reduced and the spectrum of 2Th-SMe was regenerated with 85% of its original intensity. During the reduction the peaks previously attributed to 2Th-SMe^+ and (2Th-SMe^+)$_2$ were seen transiently. Finally, a cyclic voltammogram of a bulk electrolyzed solution containing 2Th-SMe^{2+} shows the expected reversible couples plus a small, new couple near 0.2 V which slowly increases as more than two electrons are passed. Clearly, new chemical species are formed in the further oxidation of this compound. Further characterization of these overoxidized species is beyond the scope of this current work.

Figure 5B shows the spectroelectrochemical oxidation of a 3Th-SMe^+/(3Th-SMe^+)$_2$ mixture. Isosbestic points are again apparent as the singly oxidized species are further oxidized to the dication. The spectrum of the resulting 3Th-SMe^{2+} ion, with maxima at 625 and 685 nm, is similar to those of 3Th-Me^{2+} and 2Th-SMe^{2+}. When 3Th-SMe^{2+} was generated in a controlled 2-electrons/molecule oxidation from 3Th-SMe, it could then be re-reduced to 3Th-SMe in high yield.

Discussion

This investigation was undertaken because we believed the current paradigm for understanding the properties of oxidized polythiophene was incomplete and could be articulated by studies of model oligomeric cations. This and other recent studies have provided definitive spectroscopic information about cation radicals and dications of oligothiophenes, which should be models for polarons and bipolarons. The special significance of the present investigation is the identification of cation radical dimers. After comparisons of the present results with the literature, we discuss the structure of these dimers and then speculate on their importance for understanding oxidized polythiophene.

To summarize the results and clarify the discussion, consider Scheme II. The evidence presented here and in an accompanying paper[12] unequivocally supports this set of equilibria. In this study the three oligomers gave results that are completely internally consistent.[16] Moreover, the

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[15] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications.*; John Wiley and Sons: New York, 1980.

trends in the data are completely expected. Thus, 3Th-SMe oxidizes most easily, has the most stable ions, the smallest separation of $E°$ values, and the longest wavelength absorptions for both the cation radical and dication. This is expected in that 3Th-SMe has more thiophene rings than 2Th-SMe and has SMe groups, which delocalize charge better than Me groups.

The solvent acetonitrile, which was used here, gave cationic species which are less stable than those formed in methylene chloride. This is expected, and it is of particular importance for the small oligomers of interest here. Indeed, this made the use of spectroelectrochemistry necessary.

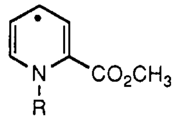
The optical spectra of monomeric cation radicals reported here correlate well with several literature reports.[7,8,11,12] In the separate study from this laboratory[12] identical spectra were recorded of photochemically generated cations from these oligomers. The wavelength range was also extended to the NIR. The more extensive study of Diaz, Tour, and co-workers[11] showed that a variety of oligomeric monocations had two electronic transitions, one in the visible and one in the near-infrared regions. Each of these bands showed vibrational structure with a spacing of about 1400 cm^{-1}. Because the oligomers are differently substituted than those reported here, a direct comparison is not possible. Considering the predicted substituents effects, however, the agreement is quite good.

The optical spectra of dications reported here are in agreement with previous reports of $FeCl_3$-produced dications.[8] Thus small oligomers show a pair of closely spaced (ca. 1400 cm^{-1}) bands in the visible region. It is indeed expected that dications will absorb at shorter wavelength than cation radicals. The dication ground state is stabilized compared to the excited state by the pairing energy which results from putting two electrons in one orbital. Cation radicals have no change in the pairing energy.

Another recent report of cation radical and dication spectra concerns oxidatively doped oligothiophenes generated within the channels of the pentasil zeolites Na-ZSM-5 and/or Na-β.[10] Our results (and those of Diaz, Tour, et al.[11]) are not in the complete accord with these findings. As described above, all of the monomeric cation radicals we studied have one visible and one NIR band, separated by approximately 6000–6500 cm^{-1} (Table II). Additionally we, and others, find that dications of small oligomers (2–4 thiophene rings) exhibit an intense visible transition within ±1500 cm^{-1} of the higher energy cation radical band. For oligomers of comparable chain length, however, ref 10 lists the dication transitions in the near-IR region, 6500–7000 cm^{-1} lower in energy than the high-energy bands found for the cation radicals. For the compound common to both studies, our spectroelectrochemical experiments show that 3Th-Me$^+$ absorbs at 572 and 880 nm (see Table II), while ref 10 suggests that when encapsulated within the zeolite Na-β, 3Th-Me$^+$ shows only a single band (at ca. 580 nm) with no low-energy features. Importantly, ref 10 also demonstrates that encapsulation of 3Th-Me in a different zeolite (Na-ZSM-5) produces oxidized 3Th-Me that exhibits two bands, at 580 and 875 nm. It was suggested that only the cation radical (with a single band at 580 nm) was formed in Na-β, while both cation radical (580 nm) and dication (875 nm) were formed in Na-ZSM-5. Given that the spectrum of the proposed mixture of radical and dication in Na-ZSM-5 is nearly identical to our spectrum of 3Th-Me$^+$, however, we offer an alternative explanation of the Du Pont data. We suggest that in Na-ZSM-5, 3Th-Me exists primarily as the cation radical but in Na-β 3Th-Me is oxidized to the dication. The excellent agreement between the Na-β spectrum and our 3Th-Me^{2+} spectrum (Figure 1b) strongly supports this conclusion.

Turning now to the cation radical dimers, we assign the structures as π-dimers. In such a structure (Scheme II) one or more cationic thiophene rings forms a π-complex in which the spins are paired. While the exact conformational details of this system remain in question, we note that cation radical dimer complexes of this type are well known. Two typical and pertinent examples are the diamagnetic dimers of ethylviologen cation radical and of Wurster's blue.[17,18] For example, the monomeric ethylviologen cation radical has π–π^* bands at about 600 nm and the dimer has bands at 533 and 870 nm. This dimer is favored at higher concentrations or lower temperature. The 533-nm band is a π–π^* band, shifted to slightly higher energy than the corresponding monomer band. The 870-nm band results from charge transfer between the rings of the dimer. This spectral pattern is quite characteristic of ion radical π-dimers. *Our cation radicals show entirely analogous spectral features and behavior.* Thus, each cation radical shows two π–π^* bands while each cation radical π-dimer shows analogous π–π^* bands shifted to the blue, plus the charge-transfer band at longer wavelengths.

The properties of the dimers we observe here are consistent with π-dimers because they are readily formed (even at millimolar concentrations) and the equilibrium with the monomer is rapidly reestablished when the temperature is changed. Alternative dimer structures with covalent bonds have been considered because oligothiophene cations are known to polymerize. It seems unlikely, however that an equilibrium between monomers and a covalent dimer would be so rapidly established. The near-IR bands we observe for the dimer species are also inconsistent with the expected thiol-stabilized carbocation structure of a covalent dication because delocalized carbocations absorb in the UV–vis. In this regard analogy can be made to the neutral pyridinyl radical shown here:



which forms both a π-dimer and a σ-dimer.[19] The π-dimer has a long-wavelength (645 nm) charge-transfer band. In contrast, the σ-dimer (345 nm) has no absorption peak at such long wavelengths. These observations and interpretations are consistent with our assignment of π- and not σ-dimers.

An earlier report concerning the oxidized products of oligomerized methoxythiophene (mainly pentamers) clearly showed the presence of two types of oxidized species.[4] These two species were assigned as cation radicals and dications based on the small integrated ESR signal. It now seems quite an attractive alternative to reassign these species as cation radical and π-dimer.

The polythiophene oxidation literature is dominated by concerns of paramagnetic polarons and diamagnetic bi-

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[16] A fourth oligomer, 2,5″-dibromoterthiophene, was studied and found to behave similarly. However, the unstable ions could be characterized only at −22 °C in CH_2Cl_2.

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polarons.[1,2] These species are polymeric analogs of cation radicals and dications. It has been proposed that oxidation leads first to polarons, and as the extent of oxidation increases along one chain, these polarons combine to form bipolarons. The evidence for bipolarons is sparse and comes mainly from an interpretation of ESR spin count measurements. This argument says that at constant potential, paramagnetic polarons form initially but do not build up in concentration as more charge is passed. Thus, some (it seems to depend on the sample (see refs 2a,b,e vs 2c) conducting materials contain a low percentage of spins and are considered to be mainly bipolaronic. *Our results for oligomer oxidation demonstrate that oligothiophene cation radicals rapidly form diamagnetic π-dimers even in dilute solution. This illustrates that the small ESR signal intensity in oxidized polythiophene may be due to interchain π-dimers instead of bipolarons.* Indeed, we suggest that as more charge is passed and the concentration of polarons increases, more cation radical π-dimers and perhaps π-stacks should be expected in polythiophene thin films. The high concentration in the film compared to the solution will favor aggregation. These important interactions should have major structural consequences and provide a mechanism for intermolecular charge transfer and conductivity. Because stack conductivity is well recognized in the field of charge-transfer complexes,[20] it provides an attractive mechanism for interchain conduction in conducting polymers.

In conclusion, this study, as well as other recent reports, has shown that terminal blocking groups do stabilize oligothiophene cations. This has allowed the characterization of cation radicals, cation radical π-dimers, and dications from three blocked oligothiophenes. It provides the first evidence for the formation of cation radical dimers. As discussed in the accompanying papers[11,12] the vis–near-IR and ESR spectra of these species provide structural information and could serve as a spectral signature for polarons, π-dimers of polarons, and bipolarons in oxidized polythiophene. The close spacing of the $E°$ values gives some insight into the complexity of understanding the π-dimer (or stack), polaron, bipolaron problem in thin films.

Experimental Section

Instruments used for ESR, NMR, IR, near-IR, and mass spectrometry have been previously identified, as has the equipment used for cyclic voltammetry and bulk electrolysis.[21] Starting materials for synthesis were purchased from Aldrich Chemical Co.

2,2′:5′,2″-Terthienyl (3Th) was prepared according to the literature using 2-bromothiophene, magnesium metal, and then 1,3-bis(diphenylphosphino)propane nickel(II) chloride and 2,5-dibromothiophene.[22] The product was recrystallized and had properties consistent with the literature.

2,5″-Dimethylterthiophene (3Th-Me). A solution of 3Th (0.2 g, 0.81 mmol) in 25 mL of dry THF was degassed and cooled to −78 °C. *n*-BuLi (0.65 mL, 2.5 M; 1.63 mmol) was then added dropwise, causing the solution to turn from light yellow to rust to bright green. The resulting solution was quenched with 0.1 mL of CH_3I (1.61 mmol) and allowed to warm to room temperature, causing the solution to appear pale yellow. The product was poured into a mixture of Et_2O/H_2O and extracted into the ether. After the solvent was stripped off under vacuum, recrystallization of the resulting solid from ethanol afforded 0.07 g (31% yield) of 3Th-Me as long needles.

2,5′-Bis(methylthio)-2,5′-bithienyl (2Th-SMe). 2,5′-Dibromobithiophene (2.9 g, 9.6 mmol) was put into a dry 250-mL round-bottom flask, and the flask purged with argon. After 15 min, 50 mL of freshly distilled THF was syringed into the flask. The flask was cooled to −78 °C in a cold bath for 15 min, and then BuLi (2.1 M in hexane, 4.6 mL, 9.6 mmol) was syringed into the solution slowly. The solution was warmed to 0 °C for 5 min, then returned to −78 °C. Dimethyl disulfide (1.9 g, 20 mmol) was syringed into the solution, which was then allowed to warm to room temperature. The solution was then poured into a mixture of ether and water, the organic layer separated, the aqueous layer extracted a second time with ether, and the combined ether layers were washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the resulting yellow solid was recrystallized from methanol. 200-MHz ^1H NMR ($CDCl_3$) d 6.95 (s, 4 H), 2.50 (s, 6 H). 50-MHz ^{13}C NMR ($CDCl_3$) d 139.51, 136.710, 131.744, 123.84. MS: $M^{\bullet+}$ 258.

2,5″-Bis(methylthio)-5,2′:5′,2″-terthienyl (3Th-SMe). Terthiophene (124 mg, 0.5 mmol) was put into a dry 10-mL round-bottomed flask. The flask was purged with nitrogen, and the solid dissolved in 5 mL of THF. The solution was cooled in a −78 °C bath for 20 min, and then BuLi (2.5 m in hexane, 0.5 mL, 1.25 mmol) was syringed into the solution. Within 30 s of addition, the color had changed from rust to dark brown to bright yellow, with solid present. The flask was warmed to 0 °C for 10 min and then cooled back to −78 °C, and after 10 min the reaction was quenched with dimethyl disulfide (0.2 mL, 2 mmol) and allowed to warm to room temperature for 30 min. The solution was then poured into a mixture of ether and water, the organic layer separated, the aqueous layer extracted a second time with ether, and the combined ether layers were washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the resulting yellow solid was recrystallized twice from methanol to give the desired product, (no mono adduct present). 200-MHz ^1H NMR ($CDCl_3$) d 7.00 (s, 2 H), 6.98 (m, 4 H), 2.51 (s, 6 H). 50.3-MHz ^{13}C NMR ($CDCl_3$) d 139.1, 133.6, 131.8, 124.4, 123.9, 22.1. MS: 340, 325, 310. UV-vis: $\lambda_{max} = 390$ nm.

Electrochemical and ESR Experiments. CV was performed with a polished glassy carbon disk working electrode ($A = 0.07$ cm^2), and a AgCl/Ag (containing 1.0 M KCl) or a SCE reference electrode. The working compartment of the electrochemical cell was separated from the reference compartment by a modified Luggin capillary. All three compartments contained a 0.1 M solution of supporting electrolyte. Bulk electrolyses employed a carbon sponge anode. In situ ESR experiments employed a previously described cell,[23] which had platinum wire working and auxiliary electrodes and a silver wire reference electrode.

The acetonitrile and dichloromethane (Burdick and Jackson) used for all electrochemical and spectroelectrochemical experiments were distilled from P_2O_5. Tetrabutylammonium tetrafluoroborate (Southwestern Analytical) was used as received. Electrolyte solutions were prepared and stored over 80–200 mesh activated alumina (Fisher Scientific Co.) and activated 4-Å molecular sieves prior to use. The working compartment of the cell was bubbled with solvent-saturated argon to deaerate the solution.

UV-Vis Spectroelectrochemical Experiments. Ambient temperature UV–vis spectroelectrochemistry was carried out in an optically transparent flow-through thin-layer cell (100- or 200-μm path length), as previously described.[24] Data were collected on a Tracor Northern TN-6500 rapid-scan diode-array apparatus, employing a Xe arc lamp as the light source. Electrolyses were controlled by a BAS-100 thin-layer bulk electrolysis program. For variable-temperature work, the entire spectroelectrochemical cell was mounted in an insulated box with two sets of double-sided quartz windows. Temperature was controlled by adjusting the flow of a liquid nitrogen cooled stream of nitrogen into the box and monitored by a thermocouple in contact with the cell wall. During the course of an experiment, the temperature

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inside the box remained constant to within ±1 °C.

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Registry No. 3Th, 1081-34-1; 3Th-Me, 59949-61-0; 2Th-SMe, 99119-58-1; 3Th-SMe, 118824-88-7; 2Th-SMe$^+$, 143332-30-3; MeSSMe, 624-92-0; 2,5′-dibromodithiophene, 4805-22-5; terthiophene, 111744-23-1.

Photochemical Formation of Oligothiophene Cation Radicals in Acidic Solution and Nafion

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Three α-coupled terthiophenes, substituted on the terminal positions with methyl, thiomethyl, or bromo substituents, were photooxidized in a solvent mixture of methylene chloride and trifluoroacetic acid to form cation radicals. Visible, near-IR, and ESR spectra are reported. It is shown that the photooxidation requires oxygen and is acid catalyzed. In acetonitrile/trifluoroacetic acid, cation radical π-dimers are formed. Using Nafion, stable films of the cation radical dimer or dication of 2,5″-bis(thiomethyl)terthiophene could be formed.

Introduction

The cation radicals and dications of oligothiophenes have become interesting as models for the polarons and bipolarons proposed to be present in oxidized polythiophene.[1] As reviewed in the two accompanying papers, polarons and bipolarons form the theoretical basis for understanding the conducting polymer, and it would be useful to have some spectroscopic handle to clarify their role in the structure and conductivity. Because unsubstituted oligothiophenes, such as terthiophene, polymerize upon oxidation and the larger oligomers are rather insoluble, it has only recently become possible to study the oxidized species. This was made possible by blocking the terminal positions to prevent, or at least slow down, the polymerization process. Thus, Tour, Diaz, and co-workers,[2] following Fichou and co-workers[3] who studied unsubstituted sexithienyl, 1, have prepared a series of terminally blocked oligothiophene cation radicals, e.g., **2**$^+$, and dications by ferric chloride oxidation in methylene chloride, and recorded the vis–near-IR and ESR spectra. Caspar and co-workers have further stabilized the cations by incorporating them in zeolites.[4] Again vis–near-IR spectra were recorded. Studies from this laboratory showed that terminally blocked terthiophenes could be oxidized to cation radicals and dications in acetonitrile.[5] Because of the short lifetime of the ions in this solvent, the vis–near-IR spectra were recorded with spectroelectrochemistry and in situ ESR experiments were used.

Although cyclic voltammetry (CV) has provided definitive evidence[2,5] for anodic formation of the cation radicals and dications as somewhat stable species, the spectroscopic results seem particularly important. The reported cation radical vis–near-IR spectra[2–5] are, with one exception, in good agreement. Cation radicals in this series have a closely spaced pair of peaks in the vis and a second pair in the NIR. The bands for the substituted terthiophene cation radicals are near 600 and 1100 nm. Longer oligomers show these bands at longer wavelength, e.g., sexithienyl cation radicals have bands near 800 and 1500 nm. Dications show only one closely spaced pair of bands; these appear near 600 nm for terthienyl and 1100 nm for sexithienyls. Although we have some concern about previous interpretations of the spectra in terms of polaron–bipolaron theory, it is theoretically reasonable that dications absorb at shorter wavelength than the cation radicals, and the results suggest that bipolarons should absorb at shorter wavelengths than polarons.

ESR studies[2–5] are in agreement in that all the cation radicals show strong spectra in methylene chloride. There is, however, an unresolved question concerning the hyperfine coupling (or lack of it). In all cases the dications showed no ESR spectra as expected.

An observation of particular interest for the structure of oxidized polythiophene is that in acetonitrile solution the cation radicals form π-dimers.[5] These otherwise unreported dimers were identified by optical and ESR spectra, as well as by changes in the CV. Because they are diamagnetic the π-dimers are interesting as alternatives to bipolarons.

We set out in the present investigation to solidify our understanding in this area and to develop a useful chemical method for the generation of oligothiophene cation radicals and dications. We report on a photooxidation method which, since it works well for small oligomers, should have

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