

Spectra and Reactivity of Methoxyoligothiophene Cation Radicals

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Abstract: A set of α -coupled oligothiophenes, dimer through hexamer, was studied. Each oligomer was terminated with two methyl groups and was substituted with two or four methoxy groups. Electrochemical studies showed that methoxy groups substituted at “inside” β -positions on the terminal rings (positions toward the center of the chain) gave stable cation radicals. The E^0 values for the reversible couples were 0.24–0.52 V (SCE). The changes in E^0 with structure were explained using PPP molecular orbital calculations. Cation radicals were generated using either chemical or electrochemical oxidation, and in several cases stable salts were isolated. The vis–near-IR spectra of the cation radicals were recorded. In CH_2Cl_2 solvent the cation radicals were monomeric and showed two π – π^* -bands, which shifted to longer wavelength with oligomer length. In CH_3CN solvent the cation radicals were primarily in the form of π -dimers, which showed two π – π^* -bands and a charge transfer band at longer wavelength in the near-IR. All three bands shifted to longer wavelength with oligomer length. The equilibrium constant for dimerization increased by a factor of 10^3 on going from a terthiophene to a quinquethiophene. Spectra of oligomers terminated with hydrogens or dimethylphenylsilyl groups showed that steric effects of the small hydrogen and bulky silyl group on π -dimerization were very small. Methyl-terminated oligomers substituted with “outside” methoxy in the terminal rings gave rather positive oxidation potentials and unstable cation radicals. In one case, the cation radical decomposition products were studied and it was shown that reactions had occurred on a terminal methyl group.

The recent spate of publications^{1–7} concerning oligothiophenes has focused on the optical and electrical properties of alkyl-substituted oligomers. Fundamental data have accumulated concerning electrochemistry and the spectra of neutral, cation radical and dication species, and these data have been used to model neutral and oxidized polythiophenes. The electrical, nonlinear optical, and electrooptical properties of oligothiophenes have also been developed.⁸ Our interest has been directed toward cation radicals and dications formed by

oxidation, and monocations formed by protonation.⁷ Of special interest here is the formation of cation radical π -dimers^{7a,b} from such oligomers. These aggregates have important implications for the mechanisms of charge transport in conducting polymers where the important unsolved problem concerns interchain electron transport. There is increasing theoretical⁹ and experimental^{10,11} evidence that such dimers or stacks may be present in oxidized polythiophenes. It is commonly held that diamagnetic bipolarons, dications confined to a segment of one chain, are responsible for the conductivity of materials like polythiophene.^{12,13} However, if π -dimers and stacks are present, this 1-D theory cannot be adequate. We have suggested that the spectroscopic evidence for bipolarons in conducting polymers might also be interpreted in terms of diamagnetic π -aggregates of cation radicals (polarons). Sorting out these alternatives might be possible if one has legitimate models for the spectra of the different species. The cation radical and dication spectra of a number of unsubstituted and alkyl-substituted oligomers have been reported,^{1–7} but until now only limited information has been available concerning the spectra of their cation radical π -dimers. Here we document the vis–near-IR spectra of a set of such dimers and discuss the changes in the extent of dimerization as a function of the structure and medium.

Although a number of efforts have been made to stabilize oligothiophene cation radicals and dications by blocking the

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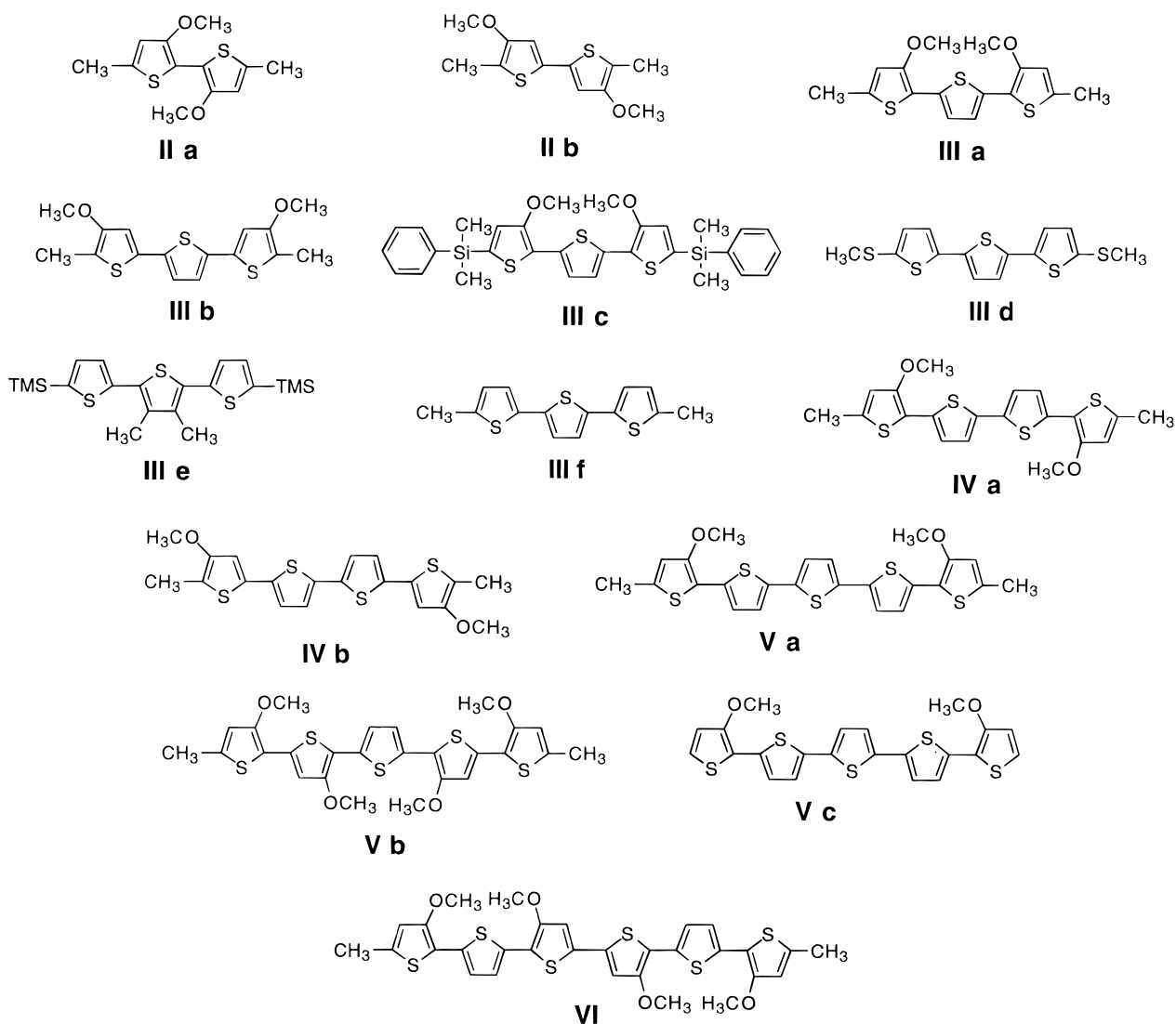
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Chart 1



terminal positions¹⁻⁷ to prevent dimerization and polymerization, we have become aware of the limited stability of such species. Stability is clearly important for conducting devices where cationic species are present, but it may also play a role in devices utilizing nominally neutral oligomers in which current is passed through the device, giving the possibility of irreversible oxidation. The present investigation explores stabilization of oligothiophene cation radicals, using methyl-terminated oligomers substituted either "inside" or "outside" with methoxy groups.^{7d} These were chosen on the basis of the electron donor capacity of alkoxy groups which seems to stabilize cation radicals derived from oxidatively oligomerized methoxythiophene,¹⁴ and oxidized poly(alkoxythiophenes)¹⁵ as well as the stabilizing effects of terminal substituents which impede cation radical dimerization and polymerization.

Results and Discussion

The synthesis and characterization of all the oligomers except **IIIc** (Chart 1) have been described elsewhere.^{6,7d} Here we report cyclic voltammetry (CV), Coulometric oxidations, optical spectra of cation radicals, cation radical π -dimers, and dications, molecular orbital calculations, and the oxidative decomposition products from one compound. In the following, inside substitu-

tion refers to methoxy groups symmetrically attached to β -positions nearer the center of the molecule, while outside refers to substitution on β -positions nearer the ends of the molecule.

Electrochemistry. Methyl-terminated oligothiophenes with two (**IIa**, **IIIa**, **IVa**, **Va**) or four (**Vb**, **VI**) inside methoxy groups were studied. These were electrochemically oxidized in methylene chloride/0.1 M tetraethylammonium fluoroborate or hexafluorophosphate solution or in acetonitrile/lithium perchlorate solution at a glassy carbon electrode. CV (see Figure 1 for an example) showed two reversible couples for **IIIa**, **IVa**, **Va**, and **Vb** in either solvent (60–90 mV anodic/cathodic peak separation for each couple with equal peak currents). Clearly, both the cation radicals and dications from these inside oligomers are stable on this time scale. Dimer **IIa** gave one reversible couple and one irreversible couple in CH_2Cl_2 . Hexamer **VI** formed a precipitate on the electrode when oxidized. Cation radical stability was confirmed in several cases by Coulometric oxidation. **IIa**, **IIIa**, and **IVa** in CH_2Cl_2 underwent repetitive 1.0 faraday/mol oxidations and 1.0 faraday/mol rereductions, regenerating the original oligomers in high yield. Complete stability in methylene chloride solution or as isolated salts for more than one month was confirmed for the cation radicals **IIIa**⁺ and **IVa**⁺ and is, therefore, expected for the longer analogs.

This stability is greater than that of other small oligomers

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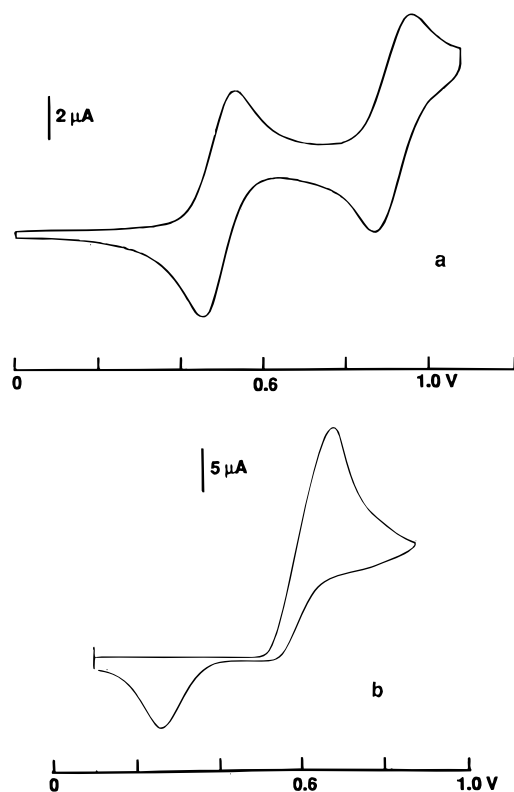


Figure 1. Cyclic voltammograms measured using 0.1 M $\text{Et}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$, a 3 mm glassy carbon electrode, and an SCE: (a) 1 mM **IIIa**, 20 mV/s; (b) 1 mM **IIIb**, 100 mV/s.

Table 1. E^0 Values^a

compound	E_1^0	E_2^0	compound	E_1^0	E_2^0
IIa	0.52	(1.24) ^b	Va	0.48	0.70
IIIa	0.50	0.92	Vb	0.24	^c
IVa	0.49	0.77	IIIc	0.64	1.09

^a $\text{CH}_2\text{Cl}_2/0.1$ M Et_4NPF_6 , scan rate 100 mV s^{-1} , glassy carbon electrode, SCE, $E^0 = (E_{\text{pa}} + E_{\text{pc}})/2$. ^b Anodic peak potential, irreversible oxidation. ^c Adsorption distorts the peak shape.

lacking the methoxy groups. α,ω -Dimethylbithiophene gives an irreversible first oxidation peak, and α,ω -dimethylterthiophene cation radical **IIIc** is only stable for minutes at room temperature.^{7b} Similarly, the silyl-terminated dialkylterthiophene **IIIe** gives only one reversible couple at 50 mV s^{-1} ⁶ while **IIIa** gives evidence for a somewhat stable dication.

Apparent E^0 values are shown in Table 1. Most interesting are the E_1^0 values for the inside dimethoxy series **IIa–Va**, which shift less than a hundred millivolts to more negative values with increasing oligomer length. The expectation from the literature was for a larger shift, but clearly the methoxy and methyl groups on the end rings effectively stabilize the cation radical charge, regardless of the number of intervening rings. Two methoxys

shift E_1^0 to about 0.5 V compared to, for example, 0.99 V for dimethylterthiophene **IIIc**.^{7a} Two more methoxys give a further shift to 0.24 V for **Vb**. As previously noted for silyl-terminated oligomers,⁶ there is a more substantial shift in E_2^0 with oligomer length. The stability of dications depends on reducing the Coulombic repulsions, and longer oligomers are more effective in this way. In total the electrochemical data confirm our expectations that inside β -methoxy groups have an important stabilizing effect on cation radicals and dications.

Surprisingly, the isomeric outside dimethoxyoligothiophenes **IIb**, **IIIb**, and **IVb** did not produce stable cation radicals. CV (Figure 1) showed an irreversible first oxidation even in poorly nucleophilic methylene chloride solvent at 100 mV s^{-1} . The anodic peak potentials were around 0.7 V for **IIb**, **IIIb**, and **IVb**. Coulometric oxidation of **IIIb** consumed approximately one electron per molecule, but re-reductions did not regenerate the original oligomer. UV-vis spectra of the oxidized product showed peaks at 407, 590, and 634 nm, but not near-IR peaks characteristic of cation radicals. The 590 nm peak appeared to be due to the cation **IIIbH⁺**⁷ arising from protonation of **IIIb** with electrogenerated acid. To facilitate product isolation, a preparative oxidation was performed in acetonitrile in the presence of the base 2,6-lutidine. After passage of 2.2 faradays/mol workup and chromatographic separation, the alcohol and aldehyde shown in Scheme 1 below were isolated and identified spectroscopically.

Both of these products come from reaction on the “blocking” methyl group. This is understandable in the sense that oxidation activates the methyl group in a fashion quite analogous to electrooxidation of toluene and methoxytoluene,¹⁶ leading to loss of a proton from the methyl, further one electron oxidation, and trapping by nucleophilic water. Importantly, the “benzylic” radical and cation are resonance stabilized by the neighboring outside methoxy group, lowering the activation energy for deprotonation of the methyl group. We suspect that other alkyl-terminated oligothiophene cation radicals and dications are reactive at that terminal blocking group.

Molecular Orbital Calculations. In order to understand the E^0 values for cation radical formation, PPP calculations¹⁷ were performed. These π -electron calculations are parameterized for spectra, but like the results from any MO calculation the HOMO energies can be correlated with E^0 values. The structures calculated lack the methyl groups on the terminal positions. A linear, all-trans geometry with all the rings in the same plane was used. Essentially this geometry was found by X-ray crystallography for tetramer **IVa** without terminal methyls.^{7d} In one run precise bond lengths and angles from this X-ray structure were input. As expected the small changes in geometry,^{8,9} from perfect planarity, had a <10% effect on the orbital energies.

The calculated E_{HOMO} values (Table 2) increase only slightly as oligomer length increases on going from **IIa** to **Va**. This correlates well with the experimental observations. Furthermore,

Scheme 1

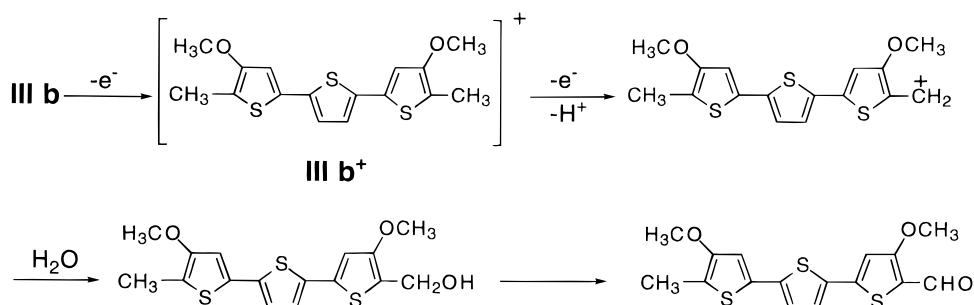
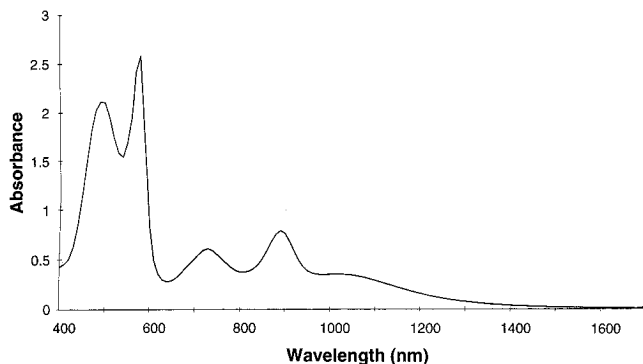
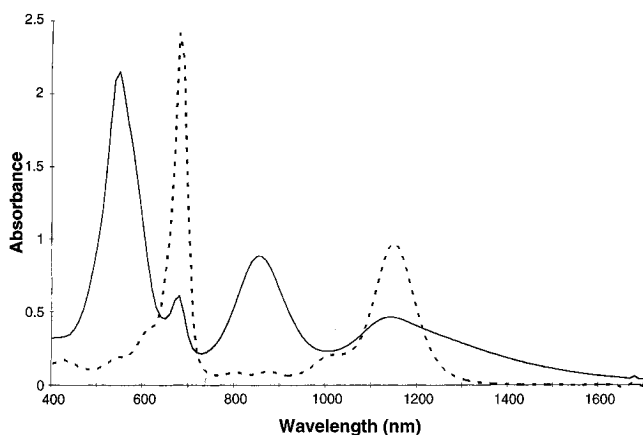


Table 2. PPP Calculations

compound	$-E_{\text{HOMO}}$ (eV)	$-E_{\text{LUMO}}$ (eV)	λ_{max}^a (nm)
IIa	7.62	1.70	370
IIIa	7.47	2.19	439
IIIb	7.73	2.33	445
IVa	7.38	2.49	490
Va	7.34	2.68	529
Vb	7.00	2.43	549

^a Calculated with CI.**Figure 2.** Vis-near-IR spectra of **IIIa**⁺: (—) 1.04 mM in CH₃CN/2% TFA; (---) 0.26 mM in CH₂Cl₂/2% TFA.**Figure 3.** Vis-near-IR spectra of **IVa**⁺: (---) 0.26 mM in CH₂Cl₂/2% TFA; (—) 0.57 mM in CH₃CN/HBF₄.

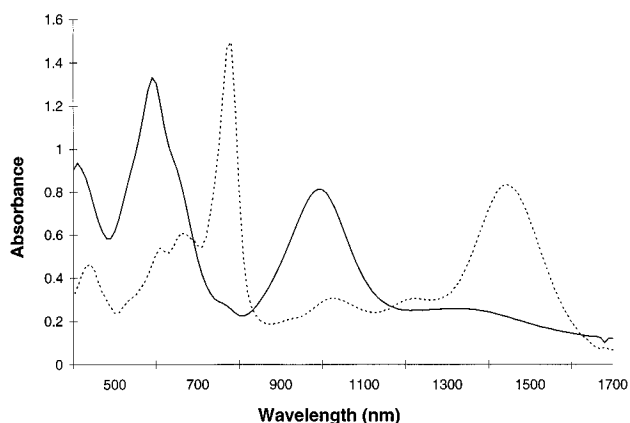
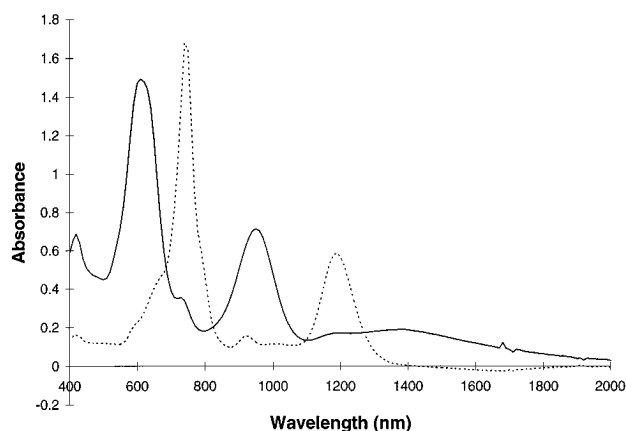
the coefficients of this orbital are substantial on the position substituted by methoxy, explaining the methoxy stabilization. Compound **Vb** with four methoxy groups has a less stable E_{HOMO} as expected from the experimental E^0 .

In contrast, the E_{HOMO} for outside-substituted **IIIb** is relatively low and the coefficients of the HOMO on the outside position, the position substituted with methoxy in the outside methoxy isomers, shows a small value. This explains the lack of stabilization by this methoxy and the relatively high oxidation potential of the outside isomers.

These PPP calculations also give the λ_{max} values for neutral oligomers, which were correlated with the spectra below. The

Table 3. UV-Vis and Near-IR Data [λ_{max} (nm), $h\nu_{\text{max}}$ (eV)]

oligomer	neutral	radical cation ^a		π -dimer ^b			dication ^a
		1	2	1	2	3 (CT band)	
IIIa	384 (3.23)	580 (2.14)	890 (1.39)	495 (2.51)	730 (1.70)	1015 (1.22)	643 (1.93)
IIIc	393 (3.16)	590 (2.10)	910 (1.36)	515 (2.41)	743 (1.67)	1010 (1.23)	
IVa	414 (3.00)	680 (1.82)	1150 (1.08)	550 (2.25)	855 (1.45)	1140 (1.09)	703 (1.76)
Va ^a	438 (2.83)	777 (1.60)	1444 (0.86)	593 (2.09)	1001 (1.24)	1335 (0.93)	838 (1.48)
Vb ^a	455 (2.73)	740 (1.68)	1190 (1.04)	611 (2.03)	948 (1.31)	1391 (0.89)	810 (1.53)
Vc ^a	431 (2.88)	756 (1.64)	1370 (0.91)	591 (2.10)	984 (1.26)	1330 (0.93)	821 (1.51)
VI ^a	486 (2.55)	861 (1.44)	1695 (0.73)	709 (1.75)	1268 (0.98)		1033 (1.2)

^a In CH₂Cl₂ solution. ^b In CH₃CN solution.**Figure 4.** Vis-near-IR spectra of **Va**⁺: (---) 0.34 mM in CH₂Cl₂/2% TFA; (—) 0.24 mM in CH₃CN/HBF₄.**Figure 5.** Vis-near-IR spectra of **Vb**⁺: (---) 0.19 mM in CH₂Cl₂/2% TFA; (—) 0.40 mM in CH₃CN/2% TFA.

calculations show that as the oligomer length increases E_{LUMO} decreases while E_{HOMO} is rather constant, explaining the trend to longer λ with oligomer length.

Optical Spectra. Visible spectra of the neutral oligomers were recorded in CH₂Cl₂ and CH₃CN solution. The λ_{max} values in Table 3 show the expected¹⁻⁷ progression to longer wavelength as the oligomer length increases. These shifts are qualitatively mirrored by the PPP calculations (Table 2). Dimethoxy substitution gives an about 20 nm shift in the λ_{max} to longer wavelength compared to the unmethoxylated analogs, i.e., **IIIa** (384 nm) compared to **IIIc** (364 nm).

Spectra of oxidized species were measured in CH₂Cl₂ and CH₃CN solutions. The formation of cation radicals and dications was controlled stoichiometrically or by monitoring the extent of oxidation spectroscopically. The spectra in Figures 2-6 and the data in Table 3 were obtained using either trifluoroacetic acid or fluoroboric acid.^{7b} For the longer oligomers the oxidation was rapid; for the shorter ones photolysis was used. Very similar spectra were obtained, however,

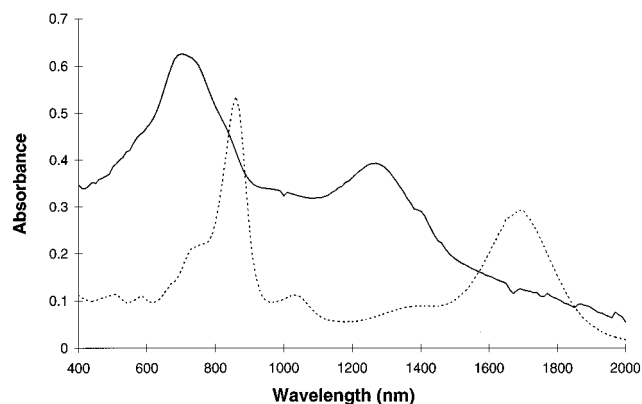


Figure 6. Vis-near-IR spectra of **VI**⁺: (---) 0.32 mM in CH₂Cl₂/2% TFA; (—) 0.023 mM in CH₃CN/2% TFA, 1 cm cell.

when oxidation was performed with iodine or FeCl₃ in CH₂Cl₂ or iodine in CH₃CN or when anodic oxidation was performed in either CH₂Cl₂ or CH₃CN. We note that iodine is not a sufficiently strong oxidant for **IIa** or **IIIc**. When cation radicals formed, triiodide peaks appeared in the spectra. In general the cation radical spectra were stable for days or months. Dications were generated in CH₂Cl₂ by acid photooxidation, by FeCl₃, or anodically.

The spectra of cation radicals in CH₂Cl₂ were dominated by the two peaks of the unaggregated species, while CH₃CN gave spectra dominated by three peaks of the cation radical π -dimers. Often it is possible to discern the peaks from both species in one spectrum. For **IIIa**, which does not π -dimerize strongly, it is possible to see nearly equivalent absorbances from the two species in acetonitrile (Figure 2). Further confirmation of the spectral assignments was obtained by increasing the concentration or lowering the temperature to increase the relative intensity of π -dimer peaks. As previously discussed^{7ab} the different behavior in the two solvents results because the more polar acetonitrile can disperse the charge and minimize the Coulombic repulsions that result when two cation radicals come together in a π -dimer. Similar effects have been observed for other ion radicals¹⁸ and for cationic dyes.¹⁹

The unaggregated cation radicals have spectra (Table 3) quite similar to those of unmethoxylated analogs, but shifted to slightly longer wavelengths. This is reasonable since the donor methoxy groups are in conjugation with the π -system and interact strongly to stabilize the positive charge in the oxidized species. These cation radicals show bands due to π - π^* -excitations from HOMO to SOMO and from SOMO to LUMO as expected. Usually these bands show vibronic structure.^{7a,b} (In Table 3 only the position of the most intense vibronic band is listed.) As the oligomer length increases the bands shift to longer wavelength due to the greater delocalization lengths.

In CH₃CN solutions three bands are observed for all the cation radical π -dimers, except for the hexamer which was so insoluble in acetonitrile that a good spectrum did not result (Figure 6). We found no evidence for mixed π -dimers⁴ formed from cation radicals and neutrals present in partially oxidized solutions. Following our previous assignments of cation radical π -dimer

Table 4. π -Dimerization Equilibrium Constants

cation radical	K_{Dim} (mM ⁻¹)	cation radical	K_{Dim} (mM ⁻¹)
IIIa ⁺	0.72	Va ⁺	>10 ³
IIIb ⁺	10 ^a	Vb ⁺	>10 ³
IVa ⁺	79	Vc ⁺	>10 ³

^a From ref 7b.

spectra, two bands are assigned to π - π^* -transitions. They are shifted to shorter wavelengths and are significantly broader than the corresponding peaks of the monomeric species. The third, longest wavelength π -dimer band is assigned to the "charge transfer" (CT) transition, an excitation polarized along the axis joining the two cation radicals. This band has proven illusive in previous reports of π -dimers. The reason is now clear. The band is relatively broad with a smaller A_{max} than those of the π - π^* -bands, and it lies quite close to the long-wavelength band of the monomeric cation radical. A broad band shape at wavelengths beyond the π - π^* -bands is often observed for charge transfer bands.¹⁹

The data for **IIIa**, **IVa**, **Va**, and **Vb** demonstrate that longer oligomers dimerize more. To quantitate this effect, the ϵ values determined in CH₂Cl₂ were used as the ϵ values for the monomeric cation radicals in CH₃CN. This allows an estimate of the undimerized cation radical concentration in CH₃CN. We assume only monomer and dimer are present in CH₃CN, which then allows a calculation of the relative concentrations of the two species and the equilibrium constant, $K_{\text{Dim}} = [\pi\text{-dimer}]/[\text{cation radical}]^2$. It is found (Table 4) that the trimer is the least prone to dimerization, $K_{\text{Dim}} < 1$, while the pentamers are the most dimerized, $K_{\text{Dim}} > 10^3$ (the monomer peaks are very small). The K_{Dim} for **IVa** was checked using the ESR spin count, giving $K_{\text{Dim}} = 66 \text{ mM}^{-1}$ in approximate agreement with the vis-near-IR value of 79 mM^{-1} . K_{Dim} values are determined by a number of factors including (a) the π -bond strength, (b) van der Waals effects, (c) Coulombic effects, (d) steric effects, and (e) solvent effect. We have not attempted to dissect the effects. The CT transition energies (Table 3) become smaller as the oligomer length increases. This indicates that oligomer length stabilizes the CT excited state even more than the π -dimer ground state. One explanation of this excited state stabilization is that it results from electronic configurations in which charge transfer gives dication/neutral valence bond structures. The E^0 values (Table 1) show that longer oligomers would stabilize such structures. There are, however, a number of other explanations involving the variations of π -bonding and dimer geometry as oligomer length changes.

Consideration of π -dimer geometry led us to measure the spectra of two other oligomers. Trimer **IIIc** has two inside methoxy groups, but bulky dimethylphenylsilyl terminating groups replace the methyls of **IIIa**. Cation radical **IIIc**⁺ was generated electrochemically since oxidation in the presence of acid gave an unstable product, presumably from protodesilylation. The **IIIc**⁺ spectra in both CH₂Cl₂ and CH₃CN (Table 3) were nearly identical to those of **IIIa**⁺. Notable is the λ_{max} of the charge transfer band. **IIIa** has a band at 1015 nm, **IIIc** at 1010 nm. We further note that the equilibrium constant for dimerization has not been substantially diminished by the bulky group. To study the smallest terminating substituent, hydrogen, we chose unmethylated pentamer **Vc**. The cation radical **Vc**⁺ proved to be sufficiently stable in CH₃CN (the unmethylated precursors of **IIa**–**IVa** were not stable when oxidized), and comparing its spectrum with **Va**⁺ again showed very small differences.

These data demonstrate that the structure of π -dimers and the strength of their π -bond are not much affected by the size

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of the terminating group. It seems that the size of the dimethylphenylsilyl terminal group in **IIIc** must prevent a coaxially aligned π -dimer of linear cation radicals. Therefore, it may be that all these dimers have noncoaxially aligned molecular components. The data can be accommodated by structures in which two linear cation radicals form a twisted dimer, the involvement of nonlinear cation radicals (for example, from an *s-cis* geometry between rings), or similar distortions. It may be true that such distortions have only a small effect on the spectra, but we note a recent study on stacks of neutral imides which describes the changes in intermolecular bonding and spectra that accompany small variations in stack geometry.²⁰ The structure and spectra of cation radical π -dimers clearly deserve attention from a computational perspective.

Turning briefly to dications, longer exposure to UV light or oxidation with more FeCl₃ in CH₂Cl₂ allowed the formation of oligomer dications. These dications were stable for hours or days in CH₂Cl₂. In particular the sexithiophene dication **VIa**²⁺ was stable for weeks. As reported for unmethoxylated analogs,^{6,7a,b} these dications have one absorption band (Table 3) with vibronic structure. As expected, these bands are shifted to slightly longer wavelength than the bands for analogous unmethoxylated dications and the bands are at longer wavelength for longer oligomers. Importantly, dication bands are always at shorter wavelength than the long-wavelength near-IR band of the corresponding cation radical. The difference in these transition energies is about 0.5 eV.

Comparisons with Conducting Polymers. We start from the observation that π -dimers form from cation radicals (polaron models) at millimolar concentrations in solution and are, therefore, likely to form in oxidized polymer solids where polaron concentrations in highly oxidized samples could be as high as several molar. Indeed each polaron will find itself near a polaron on an adjacent chain. Since longer oligomers π -dimerize more strongly than short ones, the oxidized polymer is an especially good candidate for the formation of interchain π -dimers and, at high oxidation levels, π -stacks.^{7e,f,11}

This is not an appropriate forum to discuss in detail the spectra of oxidized polythiophene in comparison with oxidized oligomer aggregates, but we iterate⁷ that interchain π -dimers and stacks formed from polaron aggregation will give vis–near-IR and ESR results which are consistent with the observations made for oxidized polymers. It is also important to iterate that the spectra of cation radicals and dications formed on the same oligomer demonstrate that bipolarons localized over the same number of rings as polarons should absorb at shorter wavelength.^{6,7a,b} This conclusion from oligomer experiments has

been reinforced by theory.⁹ We note that oxidized polythiophenes absorb more and more strongly in the near-IR–IR near 2500 nm as oxidation proceeds.^{10,13,21} There is no evidence of a shift to shorter wavelengths. Thus, if bipolarons are present, they must not be confined to the same number of rings as the polarons.^{5a}

The conductivity of conducting polymers depends on electrons moving from chain to chain, and theoretical treatments of interchain interactions have indicated that even weak bonding destabilizes polarons.²² The data we provide suggest that chains may be bound together by specific π -dimer or stack structures. Such structures delocalize electrons between chains, and this corresponds to making the conducting structure two- or three-dimensional. In essence, to the extent that π -dimers or stacks exist in oxidized conducting polymers, 1-D polaron–bipolaron theory is not adequate.

Experimental Section

The synthesis and characterization of the oligomers have been reported^{7d} except for those for **IIIc**. The electrochemical, molecular orbital, and spectroscopic methods and the equipment have been previously reported as well.¹⁸

5,5''-Bis(dimethylphenylsilyl)-3,3''-dimethoxy-2,2':5',2''-terthiophene (IIIc). At –78 °C *n*-butyllithium (0.36 mL, 0.90 mmol) was added dropwise to a solution of 3,3''-dimethoxy-2,2':5',2''-terthiophene (136 mg, 0.44 mmol) in 20 mL of THF. The reaction mixture was then stirred at 0 °C for 0.5 h and then recooled to –78 °C, and dimethylphenylsilyl chloride was added (154 mg, 0.9 mmol). The mixture was stirred for 3 h at –78 °C, warmed to room temperature, for 1 h and then poured into water. The aqueous layer was extracted with ether, and the combined organic extracts were washed with brine and dried with Na₂SO₄. Solvent was removed by rotary evaporation, and the residue was purified by flash chromatography to yield 214 mg (85%) of **IIIc** as yellow crystals: UV–vis λ_{max} 393 nm (ϵ 2.5 × 10⁴); IR (KBr) 2934, 1561 cm⁻¹; ¹H NMR (300 MHz, CD₃CN) δ 7.60 (m, 4H), 7.38 (m, 6H), 7.16 (s, 2H), 7.10 (s, 2H), 3.92 (s, 6H), 0.58 (s, 12H); ¹³C NMR (300 MHz, CD₃CN) δ 155.9, 138.1, 135.1, 134.8, 134.2, 130.6, 129.0, 125.6, 124.0, 121.3, 59.7, –1.8; HRMS for C₃₀H₃₃O₂S₂Si₂ (M + H⁺), calcd 571.0171, found 571.1112.

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