Redox States and Associated Interchain Processes of Thienylenevinylene Oligomers

Joke J. Apperloo,[a] Jean-Manuel Raimundo,[b] Pierre Frère,[b] Jean Roncali,*[b] and René A. J. Janssen*[a]

Abstract: The electronic structure of successive redox states of two series of thienylenevinylene oligomers (*n*TVs, $n = 4$, 5, 6, 8, and 12) that carry hexyl substituents at the α- or β-positions in order to increase the solubility was investigated in detail by means of UV/Vis/near-IR and ESR spectroscopy in solution. The *n*TV redox states have been fully characterized up to the dication for the shorter oligomers ($n \leq 6$) and up to the tetracation for the longer oligomers ($n \geq 8$). While the monocation radicals of the *n*TVs exhibit two dipole-allowed electronic transitions in the Vis/near-IR region, all the higher oxidized states invariably show a single strong absorption in the near-IR region. The electronic transitions of the various oxidized states and those of their vibronic replicas shift to lower energies with increasing conjugation length. The ESR spectra, recorded as a function of the degree of oxidation, provide evidence for the presence of electron spin in the odd-charged and the absence of spin in even-charged cations. Variable-temperature UV/Vis/near-IR and ESR spectroscopy establish that the tendency of the *n*TV monocation radicals to form spin-less π dimers in solution strongly depends on the number of solubilizing hexyl groups. While the oligomers that carry two hexyl chains at the α-positions of the terminal thiophenes (α-*n*TVs) readily form π dimers at low temperature, the oligomers that carry hexyl groups on the β- and β'-positions of every thiophene ring (β-*n*TVs) do not form π dimers. Low-temperature UV/Vis/near-IR and ESR experiments on solutions in which neutral and singly oxidized *n*TVs are simultaneously present, reveal the occurrence of interchain interactions between these two species, accompanied by a pronounced change in the existing disproportionation equilibrium.

Keywords: conducting materials • oligomers • pi interactions • radical ions • redox chemistry

Introduction

The alternating single/double bond structure of π-conjugated polymers and the associated possible senses in the alternation of the double bonds give rise to their semiconducting behavior in the pristine state and their electrical conductivity after oxidative or reductive doping.[1–3] These functional properties, combined with their processibility from common organic solvents, have resulted in a number of (opto)electronic applications that use π-conjugated polymers as the active material, such as light-emitting diodes, field-effect transistors, and photovoltaic cells.[1, 2]

Because each of these applications relies in some way on the transport of charges through the polymer, the nature of the charge carriers is of interest. As a consequence, several studies have addressed the redox states in conjugated polymers in relation to the extent of doping.[4] For non-degenerate conjugated polymers, for example, polythiophenes (PTs), polythienylenevinylenes (PTVs), and poly(*p*-phenylenevinylenes) (PPVs), the generally accepted mechanism of charge transport along a polymer chain is by means of rearrangements of the double bonds into polarons (singly charged, $S = ½$) or bipolarons (doubly charged, $S = 0$).[4] Polarons and bipolarons are considered to be selflocalized geometrical deformations of the polymer chain that carry the charge. The polaronic versus bipolaronic nature of the charge carriers and their possible interconversion at intermediate doping levels remains the subject of discussions.[5]

Detailed investigations on small, well-defined oligomeric model compounds have provided unambiguous evidence that oligomer monocation radicals, produced in the first oxidation step, invariably exhibit an ESR signal and two subgap electronic transitions, while the corresponding dications formed in the second oxidation step, show no ESR signal

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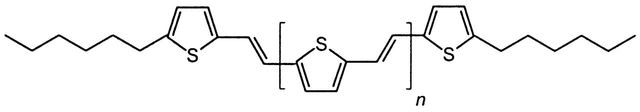
and a single strong subgap transition.[6] This behavior is fully corroborated by theoretical calculations.[7] In contrast, oxidized π-conjugated polymers often exhibit two strong electronic subgap absorptions and either the absence or at the most a very weak, ESR signal.[4] Clearly, a gap exists in our understanding of the redox behavior of short well-defined oligomers and the longer polydisperse polymers, which they should represent.

One possible explanation to overcome this apparent contradiction has been advanced with the discovery that monocation radicals of oligothiophenes,[8–11] oligopyrroles,[12] mixed thiophene–pyrrole oligomers,[13] and oligo(*p*-phenylenevinylenes),[14] have a tendency to form π dimers in solution at high concentrations or low temperatures.[15] These π dimers are spin-less and exhibit two subgap absorptions and a characteristic charge-transfer band.[8c, 12b] The extent of π dimerization in solution depends on a subtle balance between attractive and repulsive interactions, in which the solvent, the nature of the π-conjugated backbone, and the number and nature of backbone substituents (through the van der Waals interactions) play decisive roles.[16] As an alternative to π dimerization, σ dimers have recently been proposed to explain the low electron spin and the hysteresis between charging and discharging of conjugated polymers.[17] Based on a detailed electrochemical study of diphenyloligoenes, there is evidence that their monocation radicals form σ dimers rather than π dimers.[17] The formation of σ dimers from monocation radicals in solution has also been suggested for end-capped bithiophenes and bipyrroles.[18, 19]

Two recent X-ray structures give important insight into the geometrical structure of π dimers of oligomer monocation radicals in the solid state. The hexafluorophosphate salts of substituted diphenyl-terthiophene and diphenyl-bipyrrole monocation radicals reveal that the π dimers can be represented as face-to-face complexes, in which the interaction occurs through the π orbitals of the constituent species.[19, 20] The attractive interaction between the two monocation radicals in the π dimer is evident from the short π-stacking distance (3.2–3.4 Å). The interaction is driven by a gain in energy, caused by double occupation of a lower lying energy level, which results from the splitting of the two degenerate singly occupied energy levels.

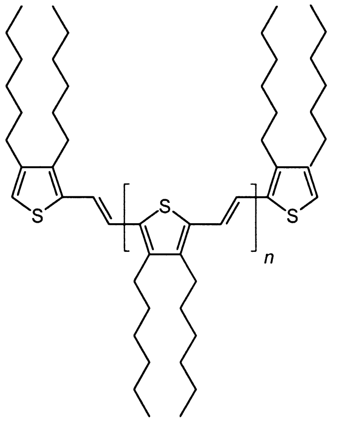
Experimental evidence indicates that dications of long oligothiophenes (*n*T, $n \geq 12$) exhibit two subgap absorptions and no ESR signal, similar to the behavior of polythiophenes.[21] This has been attributed to an electronic structure in which two individual polarons are accommodated on the oligomer chain rather than a single bipolaronic distortion. The rationale for this effect in dications of long oligothiophenes is that the decrease in the Coulomb repulsion, which is obtained by moving the two positive polarons further apart along the chain, outweighs the energy cost required to create two individual geometrical deformations on the chain, instead of a single deformation associated with a bipolaron.

Thienylenevinylenes have received limited attention up to now, despite their attractive properties as NLO chromophores[22] and as the active material in polymeric field-effect transistors.[23] Little is known of the electronic properties of their redox states.[24] Recently, however, the synthesis has been reported of soluble thienylenevinylene oligomers (*n*TVs) up to the hexadecamer and their electrochemical and optical properties have been analyzed.[25, 26] Compared to other series of conjugated oligomers, *n*TVs present the advantage of a much larger effective conjugation which provides access to highly oxidized species, such as the hexacation and even octacation.[25, 27]



n=2: α–4TV

n=3: α–5TV



n=2: β–4TV

n=4: β–6TV

n=6: β–8TV

n=10: β–12TV

Here we present a detailed investigation of the electronic structure of up to five consecutive redox states of two related homologous series of thienylenevinylene oligomers in which the chain lengths increase from the tetramer up to the dodecamer, by means of variable-temperature UV/Vis/near-IR and ESR spectroscopy. In contrast to long oligothiophenes (*n*T, $n \geq 12$), the dication of long thienylenevinylene oligomers possesses a bipolaronic structure, rather than two polarons on one chain. The two series of *n*TVs differ with regard to the number and position of solubilizing side chains present. The first set (α-*n*TVs, $n = 4$ and 5) carries two hexyl groups at the α-positions of the terminal thiophene rings, while the second set (β-*n*TVs, $n = 4$, 6, 8, and 12) has hexyl groups on the β- and β′-positions of every thiophene ring. The influence of the alkyl groups on the electronic properties of the π-conjugated compounds is found to be minor and can readily be explained by the electron-releasing effect of the hexyl substituents. The effect of solubilizing substituents on the extent of intermolecular interactions between the various redox states, in particular the π dimerization of monocation radicals, however, is very significant and will be discussed in terms of steric hindrance and solubility. In addition to π dimerization of monocation radicals, we present evidence for charge-transfer-like interactions between neutral thienylenevinylene oligomers and their monocation radicals. These interchain interactions between different redox states may be of relevance to the understanding of interchain charge transport in π-conjugated materials, which is generally thought to occur by the hopping of charge between chains.

Experimental Section

The synthesis of thienylenevinylene oligomers has been described in detail elsewhere.[25] Solvents were distilled, dried, and deoxygenated before use. The oxidation of neutral oligomers in solution was accomplished by adding solutions of thianthrenium perchlorate ($THIClO_4$)[28] or nitrosonium tetrafluoroborate ($NOBF_4$) from a gas-tight syringe. UV/Vis/near-IR spectra were recorded on a Perkin Elmer Lambda 900 spectrometer equipped with an Oxford Optistat cryostat for variable-temperature experiments. The temperature was kept constant to within ±0.3 K and spectra were corrected for volume changes. The concentrations in optical experiments varied between 10^{-5} and 10^{-3} M, in 10 mm and 1 mm near-IR grade suprasil quartz cells. ESR experiments were carried out with an X-band Bruker ESP 300E spectrometer, operating with a standard cavity, an ER035M NMR Gauss meter, and a HP 5350B frequency counter. The temperature was controlled by means of a Bruker ER4111 variable-temperature unit.

Results and Discussion

Stepwise oxidation of thienylenevinylene oligomers: Table 1 summarizes the oxidation potentials of the *n*TVs previously determined from electrochemical measurements.[25] The longer oligomers are more readily oxidized and the separation between the first and second oxidation potential decreases. The first two waves coalesce into a single two-electron first oxidation process for β-8TV and β-12TV.

Table 1. Oxidation potentials for the *n*TVs determined by cyclic voltammetry measurements in CH_2Cl_2.[25]

	$E_{pa}1$	$E_{pa}2$	$E_{pa}3$	$E_{pa}4$
α-4TV	0.74	0.91		
α-5TV	0.69	0.88		
β-4TV	0.59	0.79		
β-6TV	0.50	0.56		
β-8TV	0.46		0.80	0.92
β-12TV	0.42		0.59	

Since it was found that the coalescence of redox waves gives rise to the formation of a disproportionation equilibrium [Eq. (1)], it is instructive to discuss the short oligomers ($n \leq 6$) and longer oligomers ($n \geq 8$) separately.

$$2n\mathrm{TV}^{+\bullet} \rightleftharpoons n\mathrm{TV} + n\mathrm{TV}^{2+} \qquad (1)$$

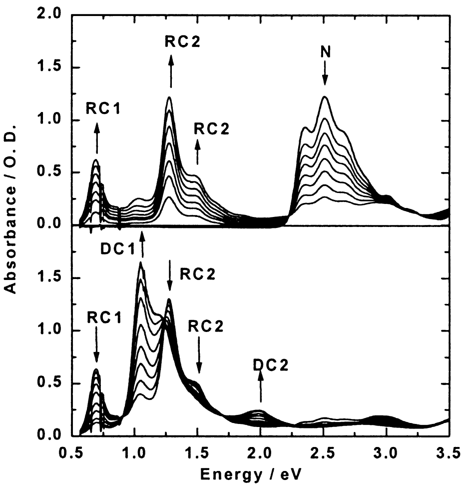


Figure 1. Evolution of the UV/Vis/near-IR spectra of a solution of α-5TV in dichloromethane at 295 K upon stepwise addition of $THIClO_4$. The top spectrum shows the changes upon addition of the first equivalent of oxidizing agent (conversion of neutral compound (N) into monocation radicals (RC)); the bottom spectrum shows the corresponding changes upon addition of the second equivalent (formation of dications, DC). Labels 1 and 2 refer to low-energy and high-energy transitions of the same species.

Table 2. Summary of peak positions (0–0) of neutrals (N), monocation radicals (RC), dications (DC), trications (TrC), tetracations (TeC), dimers (D), and stacked dimers (SD) (labels 1 and 2 refer to low and high energy, respectively) and their vibronic replicas (0–1). Data are given in eV. E_∞ is the transition energy in the limit of effective conjugation length as determined from Equation (2).

	vibronic	α-4TV	α-5TV	β-4TV	β-6TV	β-8TV	β-12TV	E_∞
N	0–0	2.50	2.36	2.39	2.13	2.03	1.97	1.96
	0–1	2.67	2.51	2.54	2.27	2.16	2.10	2.09
RC1		0.82	0.69	0.84	0.62	0.53	0.48	0.47
RC2	0–0	1.43	1.27	1.40	1.13	1.04	1.00	0.99
	0–1	1.62	1.47	1.60	1.32	1.19	1.18	1.16
DC1	0–0	1.32	1.05	1.31	0.90	0.68	0.55	0.50
	0–1	1.45	1.19	1.46	1.04	0.83		
DC2	0–0	2.27	1.98	2.22	1.71	1.44	1.16	1.03
TrC1						0.73	0.62	
TeC						0.83	0.67	
D1		1.12	1.00					
D2		1.77	1.63					
SD1		1.29	1.12					
SD2		2.10	1.82					

As a representative of the shorter thienylenevinylene oligomers (α-4TV, β-4TV, α-5TV, and β-6TV), the UV/Vis/near-IR spectra recorded during the stepwise oxidation of α-5TV in dichloromethane are shown in Figure 1. For the shorter oligomers, the first and second oxidation potentials are well separated. Therefore, the oxidation to the dication is a two-step process starting with the transformation of neutral oligomers into monocation radicals, followed by their conversion into dications (Figure 1). The transformation of α-5TV to the corresponding monocation radical is characterized by the loss of the neutral absorption band at $E = 2.36$ eV (0–0 transition) and the formation of two new bands labeled RC1 and RC2 at $E = 0.69$ and 1.27 eV, respectively (Figure 1, top; Table 2). The RC2 band possesses vibrational fine structure and exhibits a shoulder of a 0–1 transition at $E = 1.47$ eV. The RC1 bands are assigned to a transition from the lowest doubly occupied level to the singly occupied electronic (polaron) level, while the RC2 bands are assigned to a transition from the singly occupied level to the lowest unoccupied electronic

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level. During the addition of the second equivalent of oxidizing agent, the RC1 and RC2 bands of the monocation radical decrease again and are replaced by a strong transition at $E = 1.05$ eV (DC1) and a weak transition at 1.98 eV (DC2) (Figure 1, bottom, Table 2). The DC1 band is assigned to the dipole-allowed transition from the lowest doubly occupied level to the empty lowest polaron level, while DC2 is the dipole-forbidden transition to the highest polaron level. Both oxidation steps are accompanied by the presence of well-defined isosbestic points which indicate the clean interconversion of two species and the absence of a disproportionation equilibrium[21] at intermediate doping levels [Eq. (1)]. All *n*TVs with $n \leq 6$ show essentially the same redox behavior and the spectral characteristics of the monocation radicals and dications are summarized in Tables 2 and 3.

Table 3. Molar absorption coefficients ε [$\text{M}^{-1}\text{cm}^{-1}$] of the different electronic transitions of the β-*n*TV redox states

	β-4TV	β-6TV	β-8TV	β-12TV
N	69500	109000	156000	206000
RC1	56000	65000	94000	103000
RC2	195000	153000	125000	103000
DC	285000	273000	312000	206000

The oxidation process of the short *n*TVs has also been monitored by ESR spectroscopy. Figure 2 (top) shows the well-resolved ESR spectrum of the α-4TV$^{+\bullet}$ monocation radical as an example. The spectrum can be successfully simulated by the use of seven different sets of hyperfine coupling constants with two hydrogen nuclei in each set (Figure 2). The value of $g = 2.00199 \pm 0.00007$, is close to that of a free electron and is consistent with the formation of the α-4TV$^{+\bullet}$ monocation radical. For β-4TV$^{+\bullet}$ (Figure 2, bottom, $g = 2.00198 \pm 0.00005$) some ill-resolved fine structure is observed, while α-5TV$^{+\bullet}$ ($g = 2.00193 \pm 0.00010$) and β-6TV$^{+\bullet}$ ($g = 2.00191 \pm 0.00007$) exhibit a single, featureless, ESR transition. The lack of resolved hyperfine structure for these oligomers is tentatively explained by the increased number of interacting nuclei and the concomitant decrease of the average coupling constant as a consequence of the extended delocalization of the unpaired electron. For the *n*TVs with $n \leq 6$ the ESR intensity, determined by double integration, increases with the addition of the first equivalent of oxidizing agent and subsequently decreases to a very small value with the second equivalent.

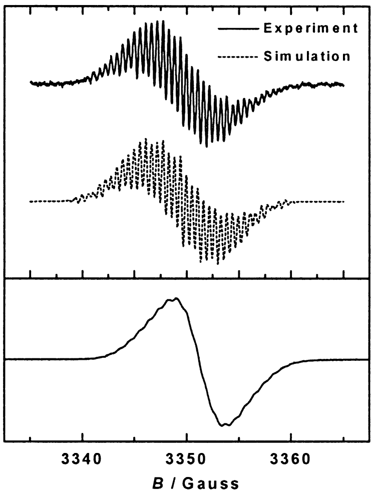

Figure 2. ESR spectra of the monocation radicals of α-4TV (top) and β-4TV (bottom). The spectrum of α-4TV$^{+\bullet}$ is successfully simulated (dotted spectrum) with the following hyperfine coupling parameters: $a(\text{H}) = 0.3332$ mT (2H); $a(\text{H}) = 0.1224$ mT (2H); $a(\text{H}) = 0.0717$ mT (2H); $a(\text{H}) = 0.1482$ mT (2H); $a(\text{H}) = 0.1726$ mT (2H); $a(\text{H}) = 0.1638$ mT (2H); $a(\text{H}) = 0.0587$ mT (2H) with a Lorentzian line shape and a 0.015 mT line width. The splitting in the ESR spectrum of β-4TV$^{+\bullet}$ is ≈ 0.09 mT.

Figure 3 shows the UV/Vis/near-IR spectra recorded during the stepwise oxidation of the longer oligomers, β-8TV and β-12TV, up to their doubly oxidized states. Similar to the shorter oligomers, β-8TV and β-12TV exhibit two strong bands (RC1 and RC2) for the monocation radical and one strong band (DC1) for the dication (Table 2). Figure 3 clearly shows that the RC1 and DC1 absorption bands become increasingly closer in energy as the length of the oligomer increases. In case of β-12TV, the positions of RC1 and DC1 are almost equal, although the latter is significantly broader. This is mainly attributed to the more intense 0–1 vibronic transition. Consistent with the electrochemical data (Table 1), we observe the simultaneous presence of neutral, singly oxidized, and doubly oxidized compounds at doping levels of ≈ 0.75–1.75, especially in the case of β-12TV. This is a clear indication of a disproportionation equilibrium [Eq. (1)]. The disproportionation also occurs for β-8TV, as will be shown in the discussion of the variable-temperature experiments.

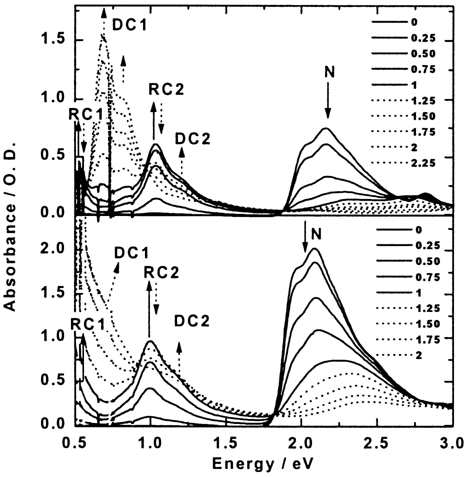

Figure 3. Evolution of the UV/Vis/near-IR spectra of a solution of β-8TV (top) and β-12TV (bottom) in dichloromethane at 295 K upon stepwise addition of two equivalents THlClO_4 (the inset shows the number of equivalents added). The addition of the first and second equivalent of oxidizing agent is represented with a solid and dotted line, respectively.

β-8TV and β-12TV can be oxidized further to produce the trication radical and eventually the tetracation. The spectral features of these higher oxidation states are more difficult to distinguish on account of overlapping positions and vibrational overtone absorptions of the solvent in this energy region. The analysis of solutions of both β-8TV and β-12TV in thin cells made it possible to obtain the individual spectra of the various oxidized states, with clear isosbestic points for the transitions from the second oxidation state to the third, and from the third oxidation state to fourth. The UV/Vis/near-IR spectra of the five consecutive redox states of β-8TV obtained in this way are depicted in Figure 4. The UV/Vis/near-IR spectra of the trication and tetracation radical are characterized by a single strong absorption in the near-IR region, similar to that of the dication. The position of the band shifts to higher energies with increasing oxidation level. Similar results were obtained for β-12TV (Table 2).

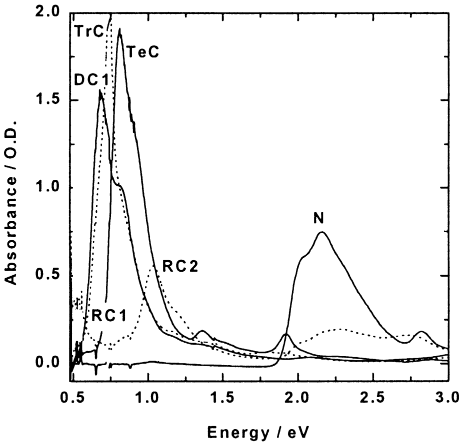

Figure 4. UV/Vis/near-IR spectra of β-8TV in five consecutive redox states; neutral (N), monocation radical (RC), dication (DC), trication radical (TrC), and tetracation (TeC), recorded in dichloromethane at 295 K after oxidation with THIClO$_4$.

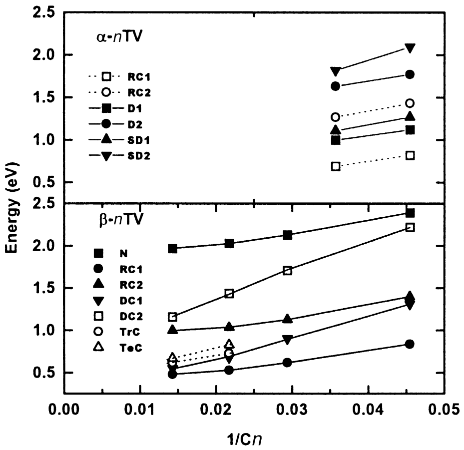

Figure 5. Evolution of the peak positions of the redox states of the thienylenevinylene oligomers (α-nTV ($n = 4$ and 5) and β-nTV ($n = 4$, 6, 8 and 12)) observed in the UV/Vis/near-IR spectra, as a function of 1/Cn, the reciprocal number of carbon atoms in the conjugated chain. The data are summarized in Table 2. For clarity the neutral (N) and dication (DC) positions are only shown for the β-nTV series (the α-nTV results are in full agreement with the observed trends). Solid lines for β-nTV represent fits according to Equation (2).

By combining UV/Vis/near-IR absorption with ESR spectroscopy in a single flat ESR cell, we were able to correlate the changes in the absorption spectrum with those in the ESR spectrum during the stepwise oxidation of β-8TV and β-12TV up to their fourth oxidation states. This correlation revealed that the double integral of the ESR signal initially increases with the formation of the singly oxidized species, and subsequently decreases, followed by another increase until it finally decreases, on the addition of the second, third, and fourth equivalents of oxidizing agent, respectively. For both β-8TV and β-12TV, the intensity of the ESR signal of the singly oxidized state is higher than that of the triply oxidized state.

Table 2 lists the optical transitions of the various redox states of the thienylenevinylene oligomers. The values are plotted against 1/Cn, the reciprocal number of carbon atoms in the conjugated system, in Figure 5. Because of the difference in the number of hexyl substituents, the data for the homologous series of the β-nTV ($n = 4$, 6, 8, 12) and the α-nTV ($n = 4$ and 5) oligomers do not coincide and are therefore plotted separately. In agreement with previous results,[6, 9a, 12a, 21, 29] all transitions (N, RC1, RC2, DC1, and DC2) show a gradual bathochromic shift with increasing conjugation length. While the shift of the transition energies is more or less linear with 1/Cn up to the octamer, a significant leveling-off occurs for the dodecamer, in agreement with the leveling-off of the neutral absorption in long oligothiophenes.[30] The shift of the DC transitions is significantly more pronounced (26 eV per unit 1/Cn in the linear regime) than the N, RC1, and RC2 transitions (13–16 eV per unit 1/Cn in the linear regime). From Figure 5 it can be seen that the RC1 and DC1 transitions and also the RC2 and (forbidden) DC2 transitions are expected to coalesce for oligomers longer than 12TV and probably reach a limiting value instead of exhibiting a continuous decrease with the oligomer length. For the monocation radical and for the dication of the nTVs, the limiting effective conjugation length is reached at $n > 12$, which is long enough to accommodate each of the geometric distortions.

To account for a convergence limit of the conjugation length in oligomers we have adapted a model recently described by Meier et al. which accounts for the energies of the optical transitions.[31] The electronic transition energy of a redox state of the oligomer, $E(Cn)$, with Cn carbon atoms in the conjugated chain, is described by Equation (2), in which

$$E(Cn) = E_\infty + [E_1 - E_\infty]\exp^{[-a(Cn-1)]} \tag{2}$$

E_1 represents the point where $Cn = 1$ and E_∞ is the limiting value of $E(n)$ for $n \rightarrow \infty$. In this equation the difference $E_1 - E\infty$ characterizes the overall effect of conjugation and the parameter a is an indication of how fast the convergence limit is reached. As can be seen from Figure 5 this equation accurately fits the data of the neutral, monocation radical, and dication redox states of the β-nTV oligomers. The limiting values E_∞ are collected in Table 2 and show that the convergence limit has not been reached for $n = 12$ ($Cn = 70$).

Also the electronic transitions of the trication and tetracation (only attainable in case of β-8TV and β-12TV) shift to lower energies with increasing oligomer length. The slope of the transition energies seems somewhat smaller for the trication (≈ 15 eV per unit 1/Cn) than for the tetracation (≈ 22 eV per unit 1/Cn), which is comparable to the different slopes for monocation and dication. These slopes are similar to those for the lower oxidized states in the *shorter* oligomers; however, they are relatively large compared to the leveling-off observed for the lower oxidized states in the *longer* oligomers. It is important to note that individual bands of the trication and tetracation can be observed for β-8TV and β-12TV, while in the case of a PTV polymer only a gradual shift to lower energy with increasing degree of doping is observed.[32]

Interestingly, the changes in the UV/Vis/near-IR spectra of β-12TV upon oxidation show a strong resemblance to the spectra recorded for the oxidation of a number of different π-conjugated polymers (PTs, PPVs, and PTVs).[33] In these cases we observe the presence of two polaron bands (similar to RC1 and RC2) in the spectrum up to levels where one charge is accommodated by five to six monomeric units. At higher doping levels the high-energy polaron (RC2) band disappears from the spectrum, whereas the low-energy polaron band (RC1) evolves into a single strong bipolaron (DC1) band.

π Dimerization of monocation radicals: The π dimerization of α-4TV and β-4TV monocation radicals has recently been analyzed by concentration-dependent and temperature-dependent cyclic voltammetry.[26] For α-4TV, the apparent redox potential corresponding to the formation of the monocation radical was found to shift negatively as the concentration of the substrate increased or when the temperature decreased, as expected for an $EC_{Dim}E$ scheme.[26] Surprisingly, π dimerization was not observed for β-4TV. Here we present a detailed investigation of the π dimerization of the two series, α-*n*TV ($n = 4$ and 5) and β-*n*TV ($n = 4$, 6, 8, and 12), by means of variable-temperature UV/Vis/near-IR and ESR spectroscopy.

Upon cooling solutions that contain monocation radicals of α-4TV or α-5TV, the clear characteristics of π dimerization are observed in the UV/Vis/near-IR absorption spectra: a decrease in the intensity of the monocation radical is accompanied by two new upcoming π-dimer transitions (D1 and D2) at the high energy side of the two monocation radical transitions (RC1 and RC2). Figure 6 (top) shows the spectral changes corresponding to the formation of π dimers from monocation radicals of α-5TV in the range between 240 and 280 K as an example. The π dimerization is fully reversible with temperature and the presence of isosbestic points is a clear indication of the interconversion of two species. The blue shift of the D1 and D2 transitions with respect to RC1 and RC2 is attributed to a Davidov interaction between the transition dipole moments of the two cation radicals in the π dimers.[34] Under the conditions used in the UV/Vis/near-IR experiments, the monocation radicals are predominantly present in the monomeric form at ambient temperature, and fully dimerized at the lowest temperatures.

Apart from the π-dimerization process described above, new features appear in the spectrum at temperatures below 240 K (Figure 6, bottom). Below 240 K the transitions associated with the free monocation radicals continue to decrease, while at the same time the intensity of the D1 and D2 transitions decreases, accompanied by an increase of two new bands at higher energy, labeled SD1 and SD2. The SD1 and SD2 bands are the only features present at 190 K. Although the exact nature of the SD1 and SD2 bands is not clear, we tentatively attribute these transitions to arise from the stacking of π dimers or monocation radicals. Such a stack is expected to give rise to a larger exciton splitting in the Davidov model than a simple π dimer of monocation radicals. The additional blue shift D1 → SD1 and D2 → SD2 is consistent with this explanation because in a nearly parallel stack of monocation radicals, the only dipole-allowed transition is to the upper Davidov level.

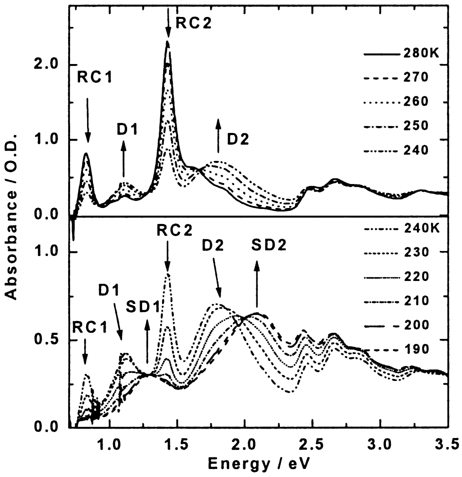

Figure 6. Temperature dependence of the UV/Vis/near-IR spectra of singly oxidized α-5TV in dichloromethane. The changes with temperature are completely reversible. The temperatures [K] are given in the insets. The top spectrum shows the formation of π dimers during the initial cooling from 280 to 240 K (RC1 and RC2 are the two monocation radical transitions, D1 and D2 are the growing π-dimer bands). The bottom spectrum (note the different scale) shows the spectral changes between 240 and 190 K with the decrease of D1 and D2 and an increase of SD1 and SD2.

The transition energies of the π dimers as well as the stacked π dimers are summarized for both α-4TV and α-5TV in Table 2 and plotted as a function of $1/Cn$ in Figure 5. The D1, D2, SD1, and SD2 bands shift to lower energies with a similar slope as their parent monocation radical transitions.

The enthalpy of dimerization ΔH_{dim} can be determined from the decrease of the RC1 and RC2 bands, or from the increase of the D1 and D2 bands by plotting $-\ln K$ versus $1/T$, where K is defined as $(1 - x_M)/(2x_M{}^2[A_T])$ in which x_M is the fraction of monomeric monocation radicals and $[A_T]$ is the total concentration of singly oxidized species. In practice, K is most conveniently determined from the decrease of the RC2 band (Figure 7), since analysis of the RC1, D1, and D2 bands is often hampered by overlapping absorption bands. The ΔH_{dim} values obtained in this way are -47 ± 5 kJ mol^{-1} for the α-4TV monocation radical and -57 ± 5 kJ mol^{-1} for the α-5TV monocation radical. The more negative value for the longer compound implies a higher tendency to dimerize, in agreement with previous results on other oligomers.[8c, 9a, 21] The dimerization enthalpies for the monocation radicals of α-4TV and α-5TV are of the same order of magnitude as those for monocation radicals of oligothiophenes, oligopyrroles, and oligo(*p*-phenylenevinylenes).[8, 9, 12, 14] For the α-*n*TV monocation radicals, the ESR signal intensity gradually disappears upon cooling, consistent with the formation of spin-less

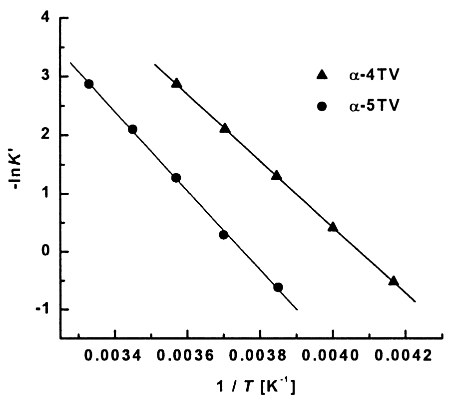

Figure 7. Determination of the enthalpy of dimerization, according to the Van't Hoff equation, in case of α-4TV (▲) and α-5TV (●). Temperature-dependent equilibrium constants for the π dimerization are determined from the change in the intensity of the RC2 transition. Only the temperature regions in which the normal π dimers are formed is used. ΔH_{dim} is -47 ± 5 kJ mol^{-1} and -57 ± 5 kJ mol^{-1}, respectively. Note that the K' is used here, which is defined as $K' = K^*[A_T]$.

π dimers. The quantitative analysis of the decrease in the doubly integrated ESR signal confirms the values for ΔH_{dim} as determined from the absorption spectra.

In contrast, cooling solutions that contain monocation radicals of the β-*n*TV series does not result in a significant change of the UV/Vis/near-IR spectra. The spectra at low temperature are identical to those at ambient temperature, except for a slight narrowing of the bands as a result of increased intramolecular order, and show no sign of π dimerization. Variable-temperature ESR experiments confirm the large differences in the tendency between end-substituted α-*n*TVs and fully substituted β-*n*TVs. For β-4TV (Figure 8, as representative of the β-*n*TV series) an increase in the signal is observed instead of a decrease. The increase is qualitatively consistent with Curie's law (intensity ∝ $1/T$) and in accordance with absence of π dimerization as inferred from UV/Vis/near-IR absorption spectroscopy.

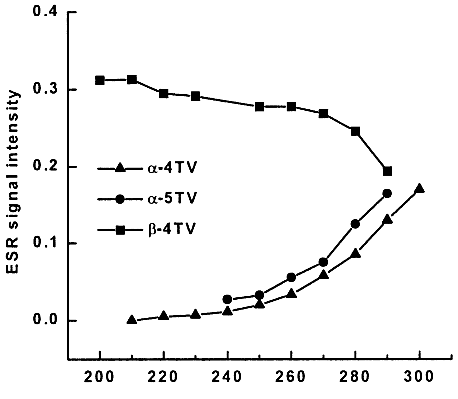

Figure 8. Variable-temperature ESR experiment. Evolution of the doubly integrated intensity of the ESR signal as function of T, for solutions that contain α-4TV, α-5TV, and β-4TV monocation radicals.

The large difference in the tendency of monocation radicals of α-*n*TVs and β-*n*TVs to form π dimers in solution at low temperature must be rationalized in terms of the number and position of solubilizing hexyl chains. One likely explanation is steric hindrance between the hexyl groups which prevents the backbones from coming close together and makes the interaction between the two unpaired π-electrons impossible.

An alternative explanation for the lack of π dimerization could be the high solubility of β-*n*TVs monocation radicals in dichloromethane. Favorable solvation may both entropically and enthalpically outweigh the tendency to form π dimers which can be considered as a solvophobic process. A recent study of solvent effects on the π dimerization of monocation radicals of oligothiophenes and oligopyrroles revealed that π dimerization is favored in less polar solvents, unless aliphatic solubilizing substituents are present.[16] Apparently, van der Waals interactions between apolar substituents in polar solvents are likely to fulfill a significant role in the π dimerization, in addition to the favorable interaction between the unpaired electrons. To check whether π dimerization of β-4TV monocation radicals occurs in solvents more polar than dichloromethane, a 3:1 (v/v) mixture of acetonitrile and dichloromethane was used (β-4TV does not dissolve in pure acetonitrile). The spectral changes that occur upon cooling (Figure 9) reveal that the RC2 transition of the monocation radical at $E = 1.40$ eV looses intensity, consistent with π dimerization. However, there is no distinct concurrent increase of a D2 transition of a π dimer, which is expected at $E \approx 1.75 - 1.80$ eV. Instead, new bands appear at positions higher in energy ($E = 1.91$, 2.09 eV, and 2.22 eV) than those expected for β-4TV monocation radical π dimers. One of the new positions ($E = 2.09$ eV), exactly matches the position attributed to stacked monocation radicals of α-4TV in dichloromethane and might indicate that in acetonitrile/dichloromethane some sort of stacked aggregation of monocation radicals is present.

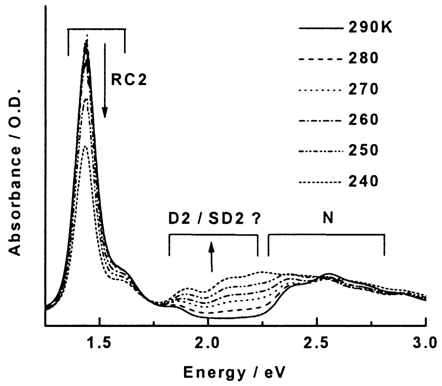

Figure 9. Temperature dependence of the UV/Vis/near-IR spectra of singly oxidized β-4TV in acetonitrile/dichloromethane (3:1 v/v). The temperatures are given in the inset. New transitions appear at $E = 1.91$, 2.09 and 2.22 eV upon cooling. For clarity, only the high-energy region is shown.

Variable-temperature experiments from partially oxidized compounds: Apart from studying the π dimerization of singly oxidized thienylenevinylene oligomers in solution, we investigated the interchain interactions that occur upon lowering the temperature in solutions when the doping level is less than 1. Figure 10 shows the UV/Vis/near-IR absorption spectra of

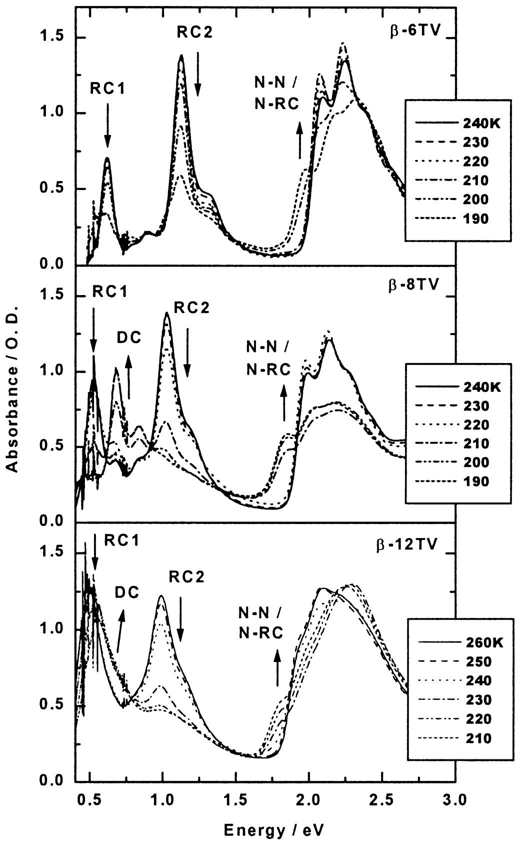

Figure 10. Variable-temperature UV/Vis/near-IR experiments of partially oxidized β-6TV, β-8TV, and β-12TV in dichloromethane solution, recorded in 1 mm cells. Only the temperature ranges in which major changes occur are shown. The following degrees of oxidation are present: 0.42 for β-6TV, 0.56 for β-8TV, and 0.68 for β-12TV.

partially oxidized β-6TV, β-8TV, and β-12TV oligomers in dichloromethane recorded at different temperatures. Figure 11 shows the corresponding changes in the intensity of the ESR signal, determined for the same solutions. The changes with temperature shown in Figure 10 and Figure 11 are completely reversible.

For each thienylenevinylene oligomer shown in Figure 10, there is a decrease of the RC1 and RC2 bands, accompanied by the appearance of new peaks on the low-energy side of the neutral transition and, in case of β-8TV and β-12TV, also at the position of the dication band DC1. In the same temperature range, we observe a decrease of the doubly integrated ESR intensity (Figure 11), consistent with the decrease of the RC1 and RC2 transitions.

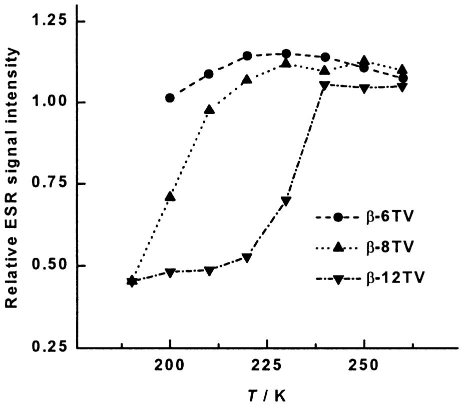

Figure 11. Evolution of the ESR signal intensity as a function of T, for partially oxidized solutions of β-6TV, β-8TV, and β-12TV. The solutions are identical to those used in the UV/Vis/near-IR experiments shown in Figure 10.

These results cannot be explained by π dimerization because the β-nTV monocation radicals do not form π dimers to any extent in dichloromethane and, moreover, because the spectral changes are not consistent with the formation of π dimers. The question arises as to how to explain the decreasing intensities of the monocation radical bands and ESR signals. The new transition at the low-energy side of the neutral band is reminiscent of aggregates of neutral oligomers; however, it might also be attributed to a charge-transfer complex between neutral and monocation radical oligomers, that is $(\beta\text{-}n\mathrm{TV})_2^{+\bullet}$. For β-8TV and β-12TV, the observed phenomena are consistent with a change of the disproportionation equilibrium shown in Equation (1), when a shift to the right-hand side occurs at low temperature. From the absorption spectra in Figure 10 and the molar absorption coefficients in Table 3, it is possible to estimate how much of the disappearing RC2 intensity is transferred to the growing DC1 transition. In case of β-8TV this is a little more than 60 %, and in case of β-12TV it is $\approx$90 %, in general agreement with the proposed disproportionation that follows from the coalescence of $E_{\mathrm{pa}}1$ and $E_{\mathrm{pa}}2$ (Table 1). However, these numbers also indicate that part of the new transition, especially in case of the shorter oligomers, must be attributed to a charge-transfer interaction between a neutral oligomer and its monocation radical. For such an interaction it is not obvious whether we are dealing with a 1:1 complex or that more molecules are involved.

The fact that in β-6TV, for which the disproportionation equilibrium lies on the left-hand side as a consequence of the 60 mV separation between $E_{\mathrm{pa}}1$ and $E_{\mathrm{pa}}2$, the decrease of the RC1 and RC2 bands is *not* accompanied by an upcoming DC1 band, is another indication that the intensity of the new band at the low-energy side of the neutral transition may have a significant contribution from a charge-transfer complex. Neither cooling of an equally concentrated solution of neutral β-6TV, nor cooling a completely singly oxidized β-6TV solution gave any indications for aggregation or π-dimerization processes. This shows that the coexistence of *both* redox types is required in order to observe the new transition. The slight decrease of the ESR signal in case of β-6TV (Figure 11, albeit not as pronounced as for β-8TV and β-12TV), however, cannot be easily understood without invoking some disproportionation because in a charge-transfer complex the electron spin is retained, unless the charge-transfer complex forms stacks in which the unpaired electrons are paired to some extent.

While the interchain interactions between neutral and singly oxidized oligomers can be observed for a range of concentrations, differences in the overall concentration do affect the outcome of these variable-temperature experiments in a rather subtle way. Figure 12 shows that the aggregate band is more pronounced when the total concentration is lower.

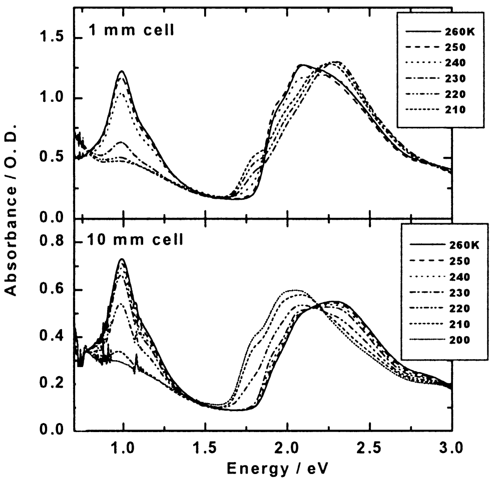

Figure 12. Comparison of the spectral changes with temperature of a concentrated (top) and dilute (bottom) solution of partially oxidized β-12TV. For clarity reasons, only the RC2/N energy region is shown.

Conclusions

The evolution of the energies of the electronic transitions of the successive redox states of thienylenevinylene oligomers (nTV) with increasing chain length has been analyzed and does not show saturation up to the dodecamer, although a significant deviation from a linear behavior with 1/Cn is observed. While the monocation radicals invariably exhibit two strong optical transitions, the dication, trication, and tetracation are characterized by a single strong band in the UV/Vis/near-IR spectrum, which shifts to higher energy with each additional charge added to the oligomer. Odd-charged redox states exhibit an ESR signal while the even-charged cations are ESR silent. In contrast to long oligothiophenes (nT, $n \geq 12$),[21] the dications of long thienylenevinylene oligomers do not show a tendency to give two polaronic deformations on a single chain, instead they possess a bipolaronic structure, as found consistently for shorter oligomers.

The α-nTV monocation radicals form π dimers in dichloromethane solution at low temperature, in a similar manner to many other conjugated oligomer monocation radicals.[8–14] The dimerization enthalpy increases with the length of the oligomer. When the temperature is further reduced the π dimers reorganize into what we propose to be spin-less π-stacks of monocation radicals. In strong contrast, the corresponding β-nTV monocation radicals do not form π dimers under similar conditions, not even for the longest oligomers for which a stronger dimerization could be expected.[8c, 9a, 21] Although the most obvious and likely explanation for this contrasting behavior is the increased steric hindrance of the hexyl chains in the β- and β'-positions, a definitive explanation has not yet been obtained. It must be noted that the π dimerization of oligomer monocation radicals results from a fine balance between attractive and repulsive interactions such as π-bond strength, van der Waals interactions, and Coulomb repulsions. Therefore, the extent of dimerization will depend (in a complex manner) on the nature of the solvent. It has been argued that more polar solvents (e.g. acetonitrile) can disperse the charge and minimize the Coulombic repulsions to result in a higher degree of dimerization than in less polar solvents, such as dichloromethane.[8a, 15] Recently, we obtained evidence that the dimerization enthalpy of monocation radicals of unsubstituted oligopyrroles and oligothiophenes is more negative in less polar solvents (e.g. chloroform and dichloromethane); however, this tendency is reversed when solubilizing alkyl groups are present[16] which indicates that solvophobic interactions of side chains may add to the $\pi-\pi$ interactions in the formation of π dimers. In agreement with this proposition, we found that in a more polar solvent, the electronic spectra (Figure 9) of the β-nTVs are similar to those of the π-stacks of the α-nTV monocation radicals.

For solutions in which both neutral and singly oxidized β-nTVs are present at the same time, we showed that lowering the temperature has a profound effect on the disproportionation equilibrium described by Equation (1), for $n = 8$ or 12. At low temperatures a clean conversion of monocation radicals into neutral and dicationic oligomers takes place. The larger separation of first two redox waves for $n = 6$, inhibits the disproportionation reaction. In addition to the changing disproportionation equilibrium, the reduced temperature also results in the formation of charge-transfer complexes, or the dimer monocation radicals, $(\beta\text{-}n\text{TV})_2^{+\bullet}$, for $n = 6$, 8, and 12.

Together with previous studies,[8–14] the present results demonstrate that the π dimerization of oligomer monocation radicals, as first described by Miller et al. for oligothiophenes,[8] is a general phenomenon for conjugated oligomers, which, however, can be inhibited by the presence of substituents. The result that charge-transfer complexes of mixed redox states are formed at reduced temperatures in solution demonstrates the versatility of the interchain processes that occur in these redox systems.

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