

## $\pi$ -dimers of pyrrole-thiophene oligomer cation radicals

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## $\pi$ -Dimers of pyrrole-thiophene oligomer cation radicals

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### Abstract

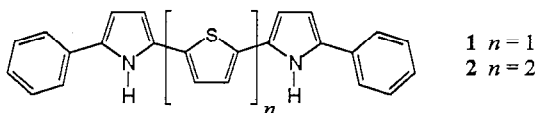
The redox states of phenyl end-capped oligomers containing pyrrole and thiophene units are characterized with optical absorption and EPR spectroscopy. The spectra give direct evidence for the  $\pi$ -dimerization of the corresponding cation radicals in solution.

*Keywords: Pyrrole-thiophene oligomers, In-situ electrochemical spectroscopy, Electron spin resonance,  $\pi$ -Dimers*

### 1. Introduction

The redox states of oligothiophenes have been intensively studied in recent years [1-4]. It has been established that oxidation of oligothiophenes in solution produces in addition to cation radicals and dications also the spinless  $\pi$ -dimers of the cation radicals. Recently we demonstrated that similar redox states are formed from phenyl end-capped oligopyrroles [5].

Various mixed oligoheterocycles have been prepared and studied using electrochemical techniques [6-7]. We found that for phenyl end-capped mixed pyrrole-thiophene oligomers (PhPT<sub>n</sub>PPH,  $n = 0 - 3$ ) the first oxidation potential increases with the number of thiophene rings ( $n$ ) while the second oxidation potential shows the usual decreasing trend with increasing conjugation length [8]. This unusual redox behavior was explained using a Hückel-type band model which indicated that in the oxidized states the positive charges tend to localize on the pyrrole units. Here we report on nature of the oxidized species and the electronic structure of these mixed oligomers with  $n = 1$  and  $n = 2$  as studied using optical absorption and EPR spectroscopy.



### 2. Experimental

The preparation of 1 and 2 and their electrochemical properties have been described elsewhere [8]. All experiments were performed under inert conditions. UV/Vis/NIR spectra were recorded with a Perkin Elmer Lambda 900 spectrophotometer with a thin layer electrochemical cell [5], a 10 mm cuvette, or an Oxford optical cryostat. EPR spectra were recorded on a X-band Bruker ER 200D spectrometer with a ER 4111 variable temperature unit.

### 3. Results and discussion

The phenyl end-capped oligomers 1 and 2 exhibit two reversible one-electron oxidations (1:  $E^\circ = 0.42$  and  $0.81$ ; 2:  $E^\circ = 0.47$  and  $0.72$  V vs SCE) [8]. The electrochemical oxidation of the oligomers to cation radicals and dications at controlled potentials was followed with in-situ UV/Vis/NIR spectroscopy. Alternatively, chemical oxidation in dichloromethane was accomplished by adding small aliquots of thianthrenium perchlorate ( $\text{THI}^+\text{ClO}_4^-$ ) as an oxidizing agent.

Fig. 1 shows the successive formation of the redox states in more detail for 2 as an example. Initially two bands (M1 and M2) are found at low and high energy, respectively. Each of these two bands has an associated second transition (D1 and D2) at higher energy (shifted by about 0.3 eV) attributed to the transitions of a spinless  $\pi$ -dimer of the cation radical. The D1 and D2 transitions are more intense than M1 and M2, suggesting already a significant dimerization at room temperature.

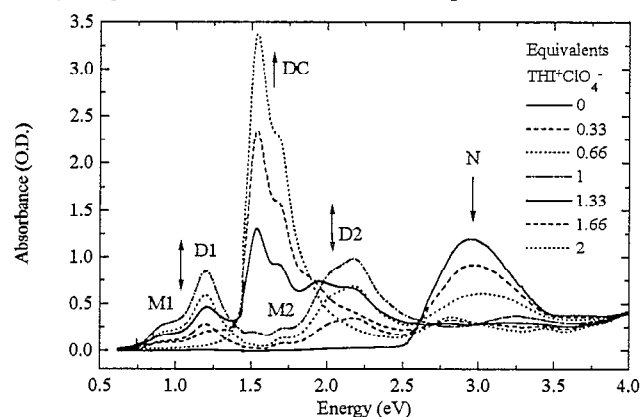


Fig. 1. Absorption spectra of the oxidation of 2 in dichloromethane ( $5 \times 10^{-5}$  M) using  $\text{THI}^+\text{ClO}_4^-$  at room temperature. Spectra were corrected for dilution.

Table 1  
Optical transition energies (eV) of redox states of **1** and **2**.<sup>a</sup>

	N	M1	M2	D1	D2	D3	DC
<b>1</b>	3.11	1.14	1.99	1.45	2.35	1.21	1.85
					2.45		2.01
<b>2</b>	2.95	0.92	1.72	1.20	2.02	0.98	1.54
					2.18		1.69

a For D2 and DC shoulders appearing on the main absorption bands are included.

The M and D bands reach their maximum intensity after addition of one equivalent of  $\text{THI}^+$ . Further oxidation results in a new band (DC) between the M1/D1 and M2/D2 absorptions. This band is attributed to the dication of **2** and shows one or two associated vibrational replicas at higher energy.

The energies of the various optical transitions of the neutral and oxidized states of **1** and **2** show the normal decreasing trend with increasing conjugation length (Table 1). The unusual trend in the first oxidation potential is not reflected in the trend of the transition energies.

The formation of cation radicals and subsequently of diamagnetic dications upon addition of  $\text{THI}^+$  to solutions of **1** and **2** is also evidenced from EPR spectroscopy which exhibits a strong, but unresolved, signal for the cation radical, which decreases upon further oxidation to the dication.

Supporting evidence for the formation of  $\pi$ -dimers of cation radicals of **1** and **2** has been obtained from variable temperature UV/Vis/NIR and EPR experiments. The experimental results for **2** are shown in Figs. 2 and 3. Upon lowering the temperature the intensities of the M1 and M2 bands diminish, while the D1 and D2 bands increase (Fig. 2). In addition, this experiment reveals the appearance of a new band, labeled D3, which is tentatively assigned to a charge-transfer band in analogy with the spectra of oligothiophene cation radical  $\pi$ -dimers [9]. This charge transfer band is associated with a transition polarized along the short axis connecting the two cation radicals in the  $\pi$ -dimer. Lowering the temperature also results in a decrease of the EPR signal intensity of the cation radical which gives direct evidence of the formation of a diamagnetic species (Fig. 3).

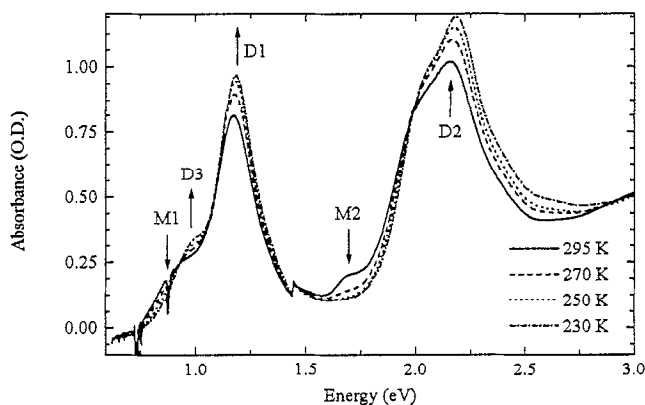


Fig. 2. Electronic spectrum of the cation radical of **2** at variable temperatures.

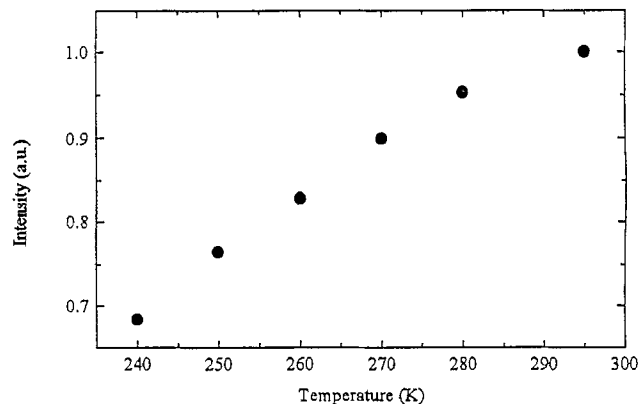


Fig. 3. Temperature dependence of the EPR signal intensity of the cation radical of **2** as a function of temperature.

All spectral changes with temperature are completely reversible and consistent with an equilibrium between cation radicals and their spinless  $\pi$ -dimers.

#### 4. Conclusion

We have shown that phenyl end-capped mixed oligoheterocycles containing pyrrole and thiophene units can be reversibly oxidized to their cation radicals and dications. In full analogy with oligothiophenes and oligopyrroles, the cation radicals of these mixed oligomers have a strong tendency to form  $\pi$ -dimers in solution already at room temperature.

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