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# Small Band Gap Oligothieno[3,4-*b*]pyrazines

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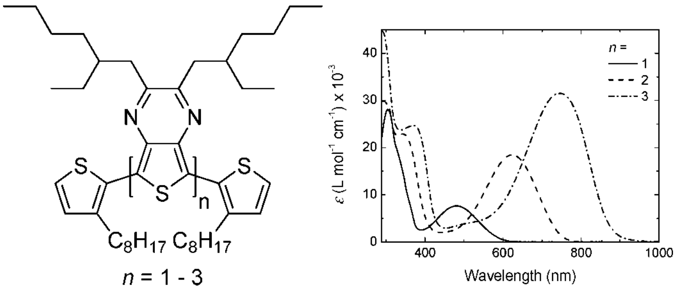
## ABSTRACT



**The synthesis and the optical and electrochemical properties of thiophene end capped oligo(2,3-alkylthieno[3,4-*b*]pyrazine)s are presented. The optical absorption rapidly shifts to lower energies with increasing chain length, caused in almost equal amounts by a rise of the HOMO and a lowering of the LUMO levels. The optical band gap of the polymer is estimated to be 1.13 ± 0.07 eV. Extrapolated redox potentials indicate that the polymer is a small band gap *p*-type material.**

In recent years, various conjugated polymers that absorb both visible and near-infrared light have been developed to increase the energy conversion efficiency of polymer solar cells by collecting a larger part of the solar spectrum.[1,2] These small band gap polymers usually consist of electron-rich and electron-poor units alternating along the chain and feature small optical gaps of 1−2 eV,[3] by exploiting the high-energy HOMO of the donating unit and the low-energy LUMO of the accepting unit. An alternative strategy for creating small band gap polymers is the homopolymerization of heterocyclic units that favor a quinoidal structure. Classical examples here are poly(isothianaphthene)[4] and poly(thieno[3,4-*b*]pyrazine)[5,6] that feature very small band gaps (∼1 eV). Theoretical calculations and IR and Raman studies have shown that the small band gap is caused by their quinoid ground state.[7]

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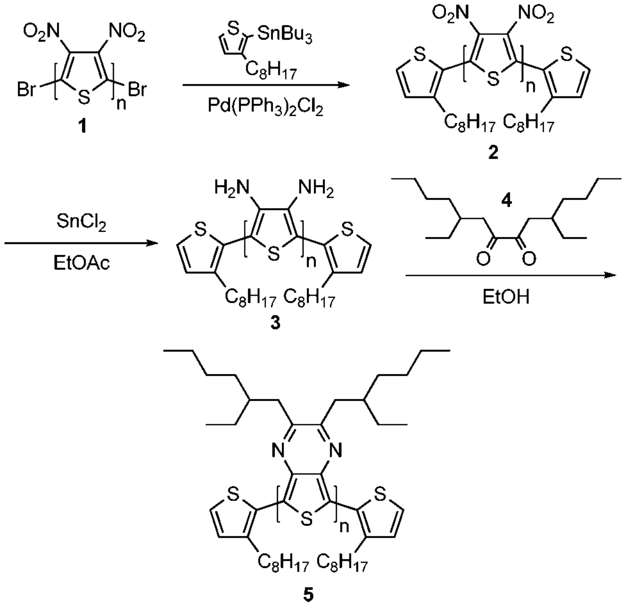
We are interested in considering poly(2,3-dialkylthieno[3,4-*b*]pyrazine)s for use in solar cells. Poly(2,3-dialkylthieno[3,4-*b*]pyrazine)s, however, have so far been prepared in significant amounts only by oxidative polymerization using iron(III) chloride. In these polymers residual iron is complexed to the polymers and cannot be removed.[5,8] This ambiguity on residual doping has led to some discussion in the literature on the actual band gap of poly(2,3-alkylthieno[3,4-*b*]pyrazine)s.[5,8] Moreover, for electrochemically polymerized poly(2,3-alkylthieno[3,4-*b*]pyrazine)s there is a rather unexpected strong dependence of the oxidation and reduction potentials of up to 0.5 V on the length of the alkyl chain.[8] Such large differences can even change the material from electron-donating to electron-accepting in combination with a second semiconductor in a solar cell.

To obtain more insight into the properties of poly(2,3-dialkylthieno[3,4-*b*]pyrazine)s, we prepared a series of well-defined oligomers. The synthesis of trimethylsilyl end capped oligomers of 2,3-dimethylthieno[3,4-*b*]pyrazine has recently been reported by Wen and Rasmussen.[9] In this work, we present a series of well-defined oligothieno[3,4-*b*]pyrazines with thiophene end caps (Scheme 1) and study the electrochemistry and the optical properties of these oligomers as function of chain length. Using these oligomers we are able to resolve some of the existing questions for the corresponding polymer.

**Scheme 1.** Synthesis of the Oligomers ($n = 1-3$)



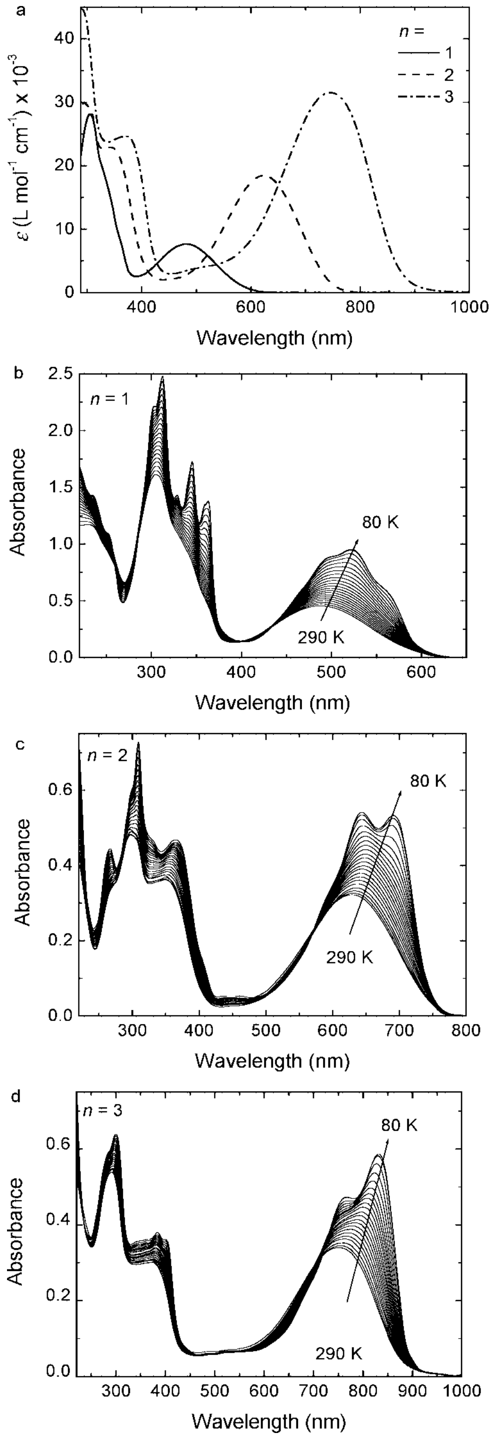


**Figure 1.** UV−vis absorption spectra of compounds **5** ($n = 1-3$) in dichloromethane (a) and low temperature UV−vis absorption in 2-methyltetrahydrofuran (b−d).

The synthesis of the oligomers is outlined in Scheme 1. The α,ω-dibromo-oligo(dinitrothiophene)s **1** ($n = 1-3$) were prepared from the dibromothiophenes (for $n = 1, 2$) or from 5,5″-dibromo-3′,4′-dinitro [2,2′;5′,2″]terthiophene (for $n = 3$), by nitration with either $HNO_3/H_2SO_4$ (for $n = 1$) or $NO_2BF_4$[10,11] (for $n = 2, 3$). The resulting nitro compounds were reacted in a Stille coupling with tributyl-(3-octylthiophen-2-yl)-stannane, followed by reduction of the nitro groups using tin(II) chloride. The final step consisted of the

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**Table 1.** UV−vis Absorption Data and Onset of Redox Potentials ($E_{ox}$ and $E_{red}$ vs Fc/Fc$^+$) in Dichloromethane

| $n$ | $\lambda_{max}$ (nm) | $\lambda_{onset}$ (nm) | $E_g^{opt}$ (eV) | $E_{ox}$ (V) | $E_{red}$ (V) | $E_g^{cv}$ (eV) | $E_{max}^{RC}$ (eV) |
|---|---|---|---|---|---|---|---|
| 1 | 479 | 591 | 2.10 | 0.24 | −1.97 | 2.21 | n.d. |
| 2 | 620 | 745 | 1.66 | −0.06 | −1.71 | 1.65 | 1.59 |
| 3 | 745 | 871 | 1.42 | −0.24 | −1.59 | 1.35 | 1.34 |

condensation of the amine compounds with diketone **4** to give end capped oligomers **5**. The oligomers were characterized by $^1$H NMR, $^{13}$C NMR, and MALDI-TOF mass spectrometry.

UV−vis absorption spectra of the oligomers, both at room temperature and at low temperature (down to 80 K), were measured. Figure 1 clearly shows that adding extra thieno[3,4-*b*]pyrazine units causes a large red shift and an increase of the molar absorption coefficient of the low energy absorption band. The optical band gaps $E_g^{opt}$, as estimated from the onsets of absorption, are summarized in Table 1. When cooling down, the spectra exhibit a gradually enhanced vibronic fine structure on the low-energy absorption. The relative intensity of the 0−0 transition increases with chain length. This points to a lesser degree of structural deformation in the excited-state for the longer oligomers, consistent with an extensive delocalization of both HOMO and LUMO over the whole molecule. As can be clearly seen, the onset of absorption does not shift upon cooling. This indicates that the changes with temperature are due to a reduction of inhomogeneous line-broadening, as a result of less intramolecular motions at lower temperature, rather than aggregation.

The redox behavior of the oligomers was investigated by cyclic voltammetry. The onset potentials of oxidation ($E_{ox}$) and reduction ($E_{red}$) were determined, and the electrochemical band gap was calculated as $E_g^{cv} = E_{ox} - E_{red}$. The values are represented in Table 1. The electrochemical band gaps are close to the optical band gaps.

Chemical oxidation of the oligomers can be accomplished by addition of a strong oxidant. In this case, thianthrenium hexafluorophosphate[12] was added to a solution of the oligomers **5** ($n = 2, 3$) in dichloromethane in small aliquots. The UV−vis−NIR absorption spectra of the radical cations that are produced in solution with increasing equivalents of thianthrenium are shown in Figure 2. For oligomer **5** ($n = 1$), the formed radical cation dimerizes and the spectrum (not shown) exhibits the absorption band of the corresponding cation of the dimer.

It can be seen from Figure 2 that the radical cations have a very intense absorption band located at lower energy, slightly below the onset of the absorption of the neutral molecules, and that additional low intensity bands appear at very low energy. The absorption maxima ($E_{max}^{RC}$) are summarized in Table 1. Compared to the onset of absorption of the neutral oligomer, the new strong absorption of the oxidized state exhibits a relatively small red shift of only around 0.15 eV. Therefore, oxidation of electrochemically polymerized poly(thieno[3,4-*b*]pyrazine) might explain the reported reduction in band gap compared to the same polymer that was made via oxidative polymerization using FeCl$_3$.[5,8]

The evolution of the optical band gap and the oxidation and reduction potentials with the increasing number of thieno[3,4-*b*]pyrazine units is depicted in Figure 3, plotted versus the reciprocal number of rings in the conjugated backbone, $1/(n + 2)$.

The interesting issue is that the dependence of the band gap on chain length is much stronger for these oligothieno[3,4-*b*]pyrazines than for small band gap oligomers based on alternating electron-rich and electron-deficient units.[13] The likely explanation for the much stronger chain length dependence is the stronger dispersion of both HOMO and LUMO in the homo-oligomers, compared to alternating systems where the different units tend to localize the HOMO

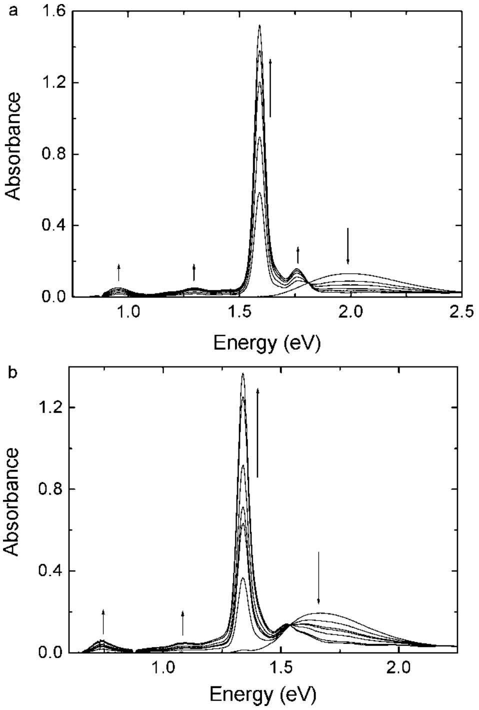

**Figure 2.** Chemical oxidation of oligomers **5** ($n = 2$) (a) and ($n = 3$) (b) in dichloromethane, by adding a solution of thianthrenium hexafluorophosphate. The appearance and disappearance of absorption bands is indicated with arrows.

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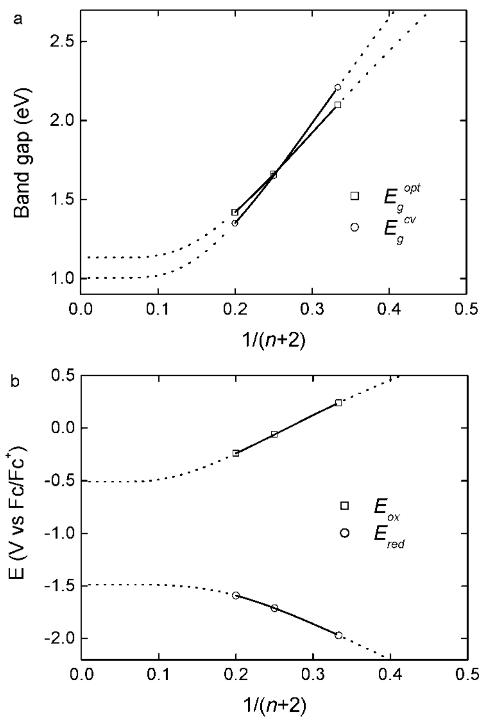

**Figure 3.** Evolution of the optical and electrochemical band gap (a) and oxidation and reduction potentials (b) with the amount of thieno[3,4-*b*]pyrazine. Fits are according to eq 1.

on the electron-rich part and the LUMO on the electron-deficient unit.[13]

It is well-known that for conjugated oligomers the evolution of the optical properties with chain length are described by the following equation:[14]

$$E_m = E_\infty + (E_1 - E_\infty)\exp[-a(m-1)] \qquad (1)$$

In this equation, $E_m$ is the value of the transition energy (e.g., band gap) for the oligomer with length $m$, $E_1$ is the transition energy for the oligomer with $m = 1$, and $a$ is a parameter which describes how fast the optical property saturates toward its polymer value. Fitting the optical band gap to eq 1 using $m = n + 2$ for the end capped oligothieno[3,4-*b*]pyrazines gives a value for $E_\infty$ of 1.13 ± 0.07 eV, which agrees quite well with the literature value of 1.14 eV of poly(2,3-dihexylthieno[3,4-*b*]pyrazine) in chloroform solution.[5] Although the number of data points fitted is equal to the number of parameters in eq 1, we think the extrapolation for the band gap to the polymer is valid, because the optical and electrochemical data provide consistent results.

The electrochemical data clearly demonstrate that the band gap reduction is caused by a rise of the HOMO (lowering of oxidation potential) and a lowering of the LUMO (rise of reduction potential) in almost equal amounts (Figure 3b). Oxidation and reduction potentials can also be fitted to eq 1. This yields values of −0.51 ± 0.08 V for the oxidation potential and −1.49 ± 0.06 V for the reduction potential of the polymer. These values indicate that the polymer would be easily oxidized, but that the electron-accepting properties are not very good. Hence, poly(thieno[3,4-*b*]pyrazine)s are probably not the most viable candidates to function as *n*-type materials in devices like solar cells but are rather *p*-type polymers, although the low oxidation potentials would lead to a low open-circuit voltage in combination with commonly used fullerene derivatives as acceptor.

In conclusion, oligothieno[3,4-*b*]pyrazines with up to three consecutive units and two thiophene end caps were prepared and their optical and electrochemical properties were investigated. As the number of thieno[3,4-*b*]pyrazine units increases, the optical absorption of the compound rapidly shifts to lower wavelengths, having an absorption onset of close to 900 nm for the system with three thieno[3,4-*b*]pyrazines. Extrapolation yields a value of 1.13 ± 0.07 eV for the optical band gap of the corresponding polymer. Electrochemistry reveals that this reduction in band gap is caused by a decrease in LUMO level and a concomitant rise in HOMO level. This points to frontier orbitals that are delocalized over the entire system. This observation is supported by UV−vis absorption experiments at low temperature. Chemical oxidation of the oligomers reduces the optical band gap by ~0.15 eV, compared to the neutral compounds. Extrapolation of the oxidation and reduction potentials to the polymer values gives $E_{ox} = -0.51 \pm 0.08$ V and $E_{red} = -1.49 \pm 0.06$ V. These extrapolated redox potentials lead to the conclusion that poly(thieno[3,4-*b*]pyrazine)s are small band gap *p*-type polymers rather than *n*-type.

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**Supporting Information Available:** Cyclic voltammograms and detailed description of experimental procedures, synthesis, and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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