Extensively π-conjugated soluble oligothienylenevinylenes

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Soluble oligothienylenevinylenes are synthesized; the longest oligomers exhibit small bandgaps and can be oxidized to the dication by a two-electron transfer.

Conjugated oligomers are subject to considerable current interest related to their potential applications in diodes,[1] field-effect transistors,[2] light-emitting diodes,[3] or molecules for non-linear optics (NLO).[4] From a fundamental viewpoint, π-conjugated oligomers are widely investigated as models for the electronic and electrochemical properties of the parent polymers.[5] While these two fields of research have been extensively developed for thiophene oligomers (nTs),[1–5] oligothienylenevinylenes (nTVs) have attracted less attention. Due to the presence of ethylene linkages, nTVs are expected to exhibit less rotational disorder and lower aromatic character than nTs and hence enhanced electron delocalization. Although advantage has been taken of these efficient electron-transmission properties for the design of NLO molecules,[6] attempts to prepare nTVs of well defined structure have remained scarce.[7] Thus, Nakayama and Fujimori synthesized nTVs containing up to seven thiophene rings,[7b] but their electrochemical properties were not analysed.

Here, we report preliminary results on the synthesis of the first examples of alkyl substituted nTVs, that are also the longest ever reported. The solubility of these nTVs allowed the analysis of their electrochemical properties providing a first evidence for direct two-electron generation of a dication on a conjugated oligomer.

Oligomers containing two (**2a,b**), four (**4a,b**) and eight thiophene rings (**8a,b**) have been synthesized from 3-octyl-thiophene and 3,4-dibutylthiophene using an iterative strategy involving formylation of a nTV of degree *n* followed by McMurry dimerization. Compounds **6a** and **10b** were prepared by double Wittig–Horner alkenation of the appropriate dialde-hyde and with thienylmethylphosphonate (TP), while **6b** was prepared from 3,4-dibutyl-2,5-thiophenedicarbaldehyde by

Table 1 Electrochemical[a] and optical[b] data for nTVs

Compound	E_{pa_1}	E_{pa_2}	$E_{pa_2} - E_{pa_1}$	λ_{max}/nm	ΔE^c/eV
2a	1.06	1.39	0.33	354	2.94
4a	0.70	0.88	0.18	473	2.09
6a	0.60	0.70	0.10	526	1.93
8a	0.56		0.00	552	1.84, 1.70[d]
2b	0.97	1.32	0.35	360	2.94
4b	0.60	0.78	0.18	488	2.13
6b	0.57	0.69	0.12	522	1.99
8b	0.45		0.00	572	1.78
10b	0.43		0.00	586	1.72

[a] 10^{-4} **m** in 0.1 **m** NBu₄PF₆–CH₂Cl₂, scan rate 100 mV s⁻¹, reference SCE (*E* in V). [b] In CH₂Cl₂. [c] Estimated from the absorption edge. [d] On film.

6a

6b

8a R¹ = H, R² = C₈H₁₇
b R¹ = R² = Buⁿ

10b
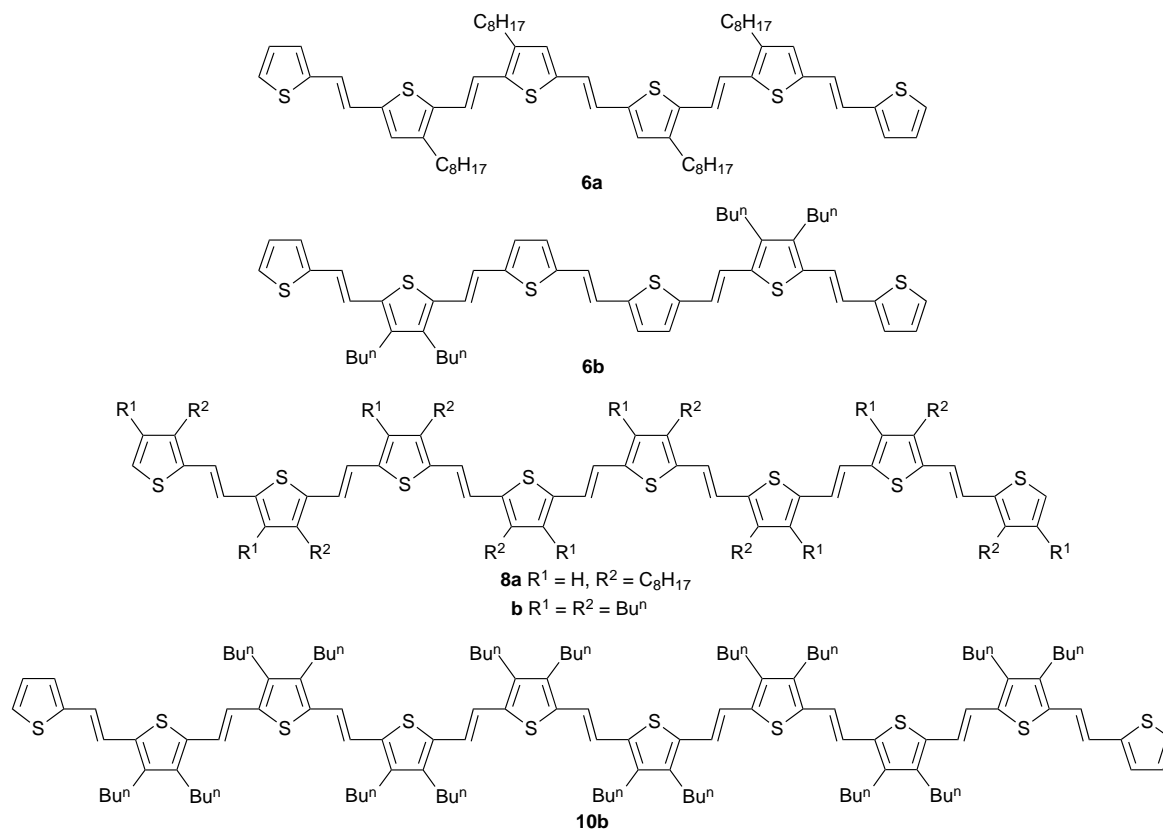
double Wittig–Horner alkenation with TP followed by mono-formylation and McMurry coupling.

Table 1 lists the main electrochemical and optical data of the new nTVs. Due to the +I effect of the two butyl chain, nTVs **b** show lower oxidation potentials and absorb at longer wavelengths than nTVs **a**. The CV of **2a** and **2b** shows two irreversible oxidation waves with peak potentials E_{pa_1} and E_{pa_2} around 1.00 and 1.30–1.40 V corresponding to the successive generation of the radical cation and dication. Extension of the conjugation length in **4a**,**b** and **6a**,**b** leads to a negative shift of the peak potentials and to a decrease of their difference $E_{pa_2} - E_{pa_1}$ indicative of a weaker coulombic repulsion between
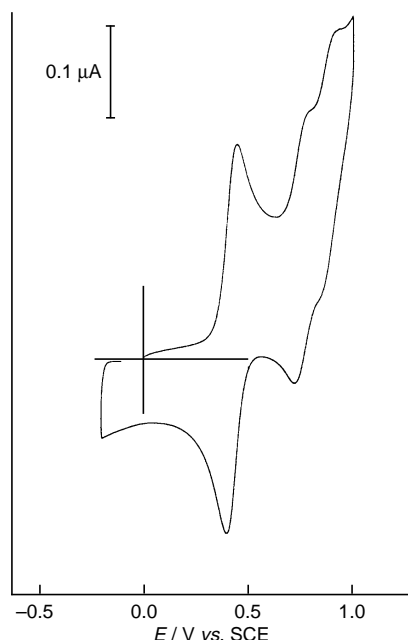

Fig. 1 Cyclic voltammogram of **8b**, 10^{-4} **m** in 0.1 **m** NBu$_4$PF$_6$–CH$_2$Cl$_2$, scan rate 100 mV s^{-1}, reference SCE
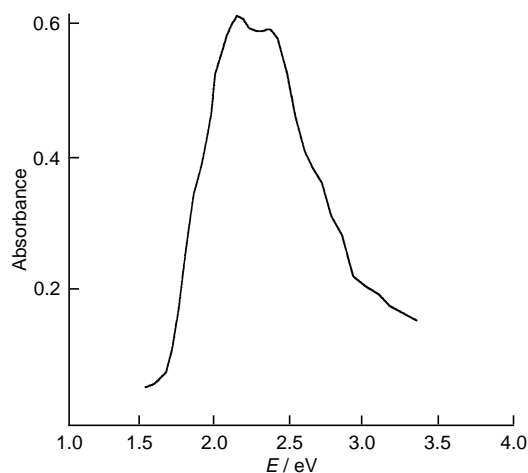

Fig. 2 Optical spectrum of a film of **8a** cast from a CH$_2$Cl$_2$ solution

positive charges in the dication. In parallel, both oxidation waves become reversible. For **8a**,**b**, the dication is formed directly through a single-step two-electron transfer. Furthermore, two additional reversible one-electron waves occur around 0.80 and 1.00 V showing that the system can be charged up to the tetracationic state (Fig. 1). Further chain extension to **10b** produces a further decrease of E_{pa_1} to 0.43 V. However, the combined effects of chain extension and of the absence of alkyl chains on the terminal thiophenes produce a dramatic decrease of the solubility.

Although two-electron oxidations have already been reported,[8] it is to our knowledge the first time that such a process is observed for oligomers based on the repetition of a single basic unit. This result suggests that soluble nTVs could be of great interest for modelling bipolarons in conjugated polymers.

The solution optical spectra of all nTVs exhibit a well defined vibronic fine structure consistent with an all *trans* rigid geometry. Optical data (Table 1) show that chain extension leads to the expected red shift of λ_{max} which reaches 586 nm for **10b** while the HOMO–LUMO gap (ΔE) decreases to 1.72 eV. The optical spectrum of a solution-processed film of **8a** (Fig. 2) reveals the persistence of the vibronic fine structure and a bandgap of *ca.* 1.70 eV. This value, slightly smaller than that of the parent poly(thienylenevinylene) (PTV),[9] suggests that for PTV prepared by thermal elimination the mean conjugation length is limited to *ca.* 8 TV units. On the other hand, the steady decrease of ΔE with chain extension and the absence of saturation observed for both series of nTVs strongly suggest that longer nTVs could exhibit even lower gaps. Further support to this conclusion is provided by the extrapolation of the plot of ΔE *vs.* the reciprocal number of conjugated carbons for nTVs **b** which leads to a predicted bandgap of 1.45 eV for PTV.

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