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Soluble Thienylenevinylene Oligomers End-Capped with 1,3-dithiole-2-ylidene groups

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Abstract: The synthesis of thienylenevinylene oligomers end-capped with 1,3-dithiole-2-ylidene is described. CV analysis shows that these compounds can be oxidized up to their tetracationic state within a narrow potential window Copyright © 1996 Elsevier Science Ltd

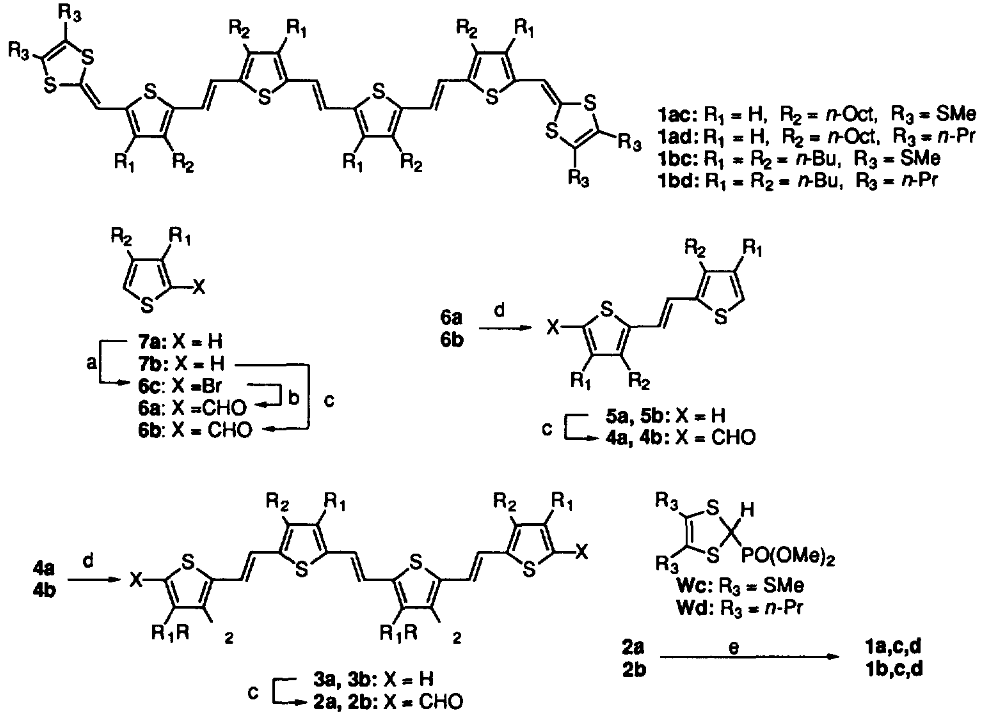
Linear conjugated systems built by combination of a π-conjugating spacer with 1-3 dithiole units have recently become a focus of keen attention.[1-3] In addition to their π-donor properties which make them interesting precursors for the preparation of conducting cation radical salts,[2] these compounds appear as interesting basic structures for the design of push-pull and push-push systems for quadratic and cubic nonlinear optics.[3] In this context, the use of thienylenevinylene oligomers (nTVs) as π-conjugating system[4] appears of particular interest as a good trade-off between the efficient but unstable polyolefinic spacers and the more stable but less efficient poly- (hetero) -aromatic ones.[5]

Recently, we have reported the synthesis of the first members of a series of push-push systems based on nTVs end-capped with 1,3-dithiole-2-ylidene moieties.[6] Despite the promising properties of these compounds such as smaller HOMO-LUMO energy gap than their oligothiophenes (nTs) analogs,[1c] absence of saturation of effective conjugation when increasing chain length and easy access to multiple redox states, the development of longer systems has been hampered by the considerable loss of solubility resulting from the extension of the π-conjugated system.

In an attempt to solve this problem we report here preliminary results on the synthesis and characterization of a new series of longer end-capped nTVs in which the thiophene rings have been substituted by solubilizing 3-octyl (**1a**) and 3,4-dibutyl (**1b**) chains (Scheme).

Aldehydes **6a** and **6b** were obtained by formylation of 3-octylthiophene[7] **7a** and 3,4-dibutylthiophene **7b.**[8] In the case of **7a**, formation of the 5-substituted isomer was avoided by selective 2-bromination by NBS. McMurry reaction of **6a,b** gave dithienylethylenes **5a** and **5b** in 89 and 67% yields. Repetition of this two-step procedure yielded respectively 71 and 78% of oligomers **3a** and **3b.** Vilsmeier formylation of **3a** and **3b** led to the dialdehydes **2a** and **2b** in 83 and 87% yields. The target compounds **1a** and **1b**[9] were then obtained in 80-95% yields by Wittig-Horner olefination of **2a,b** with phosphonates anions of **Wc,d.**[10]

Table 1 lists the main electrochemical and optical data of **1a** and **1b** together with those of the corresponding nTVs **3a** and **3b**. As already observed for nTs analogs,[1c] introduction of the 1,3-dithiole unit at both ends of the π-conjugated oligomer chain leads to a considerable red shift of λ_{max} and to a significant decrease of the HOMO-LUMO energy gap (ΔE) (estimated from the low energy absorption edge). Compared to previous results obtained on the parent compounds containing shorter nTVs spacers,[6] the data show the expected red shift of λ_{max} and narrowing of ΔE. Compounds **b** containing 3,4-disubstituted thiophene rings absorb at longer wavelengths and exhibit smaller ΔE. These variables depend also on the substitution of the 1,3-dithiole ring and replacement of the SMe substituent by *n*-propyl produces a further red shift of λ_{max} and decrease of ΔE. While previous X-ray studies have shown that the rigidity of the end part of the molecule is ensured by the strong intramolecular interactions between the sulfur atoms of the thiophene and dithiole moieties,[1c] the further red shift of λ_{max} and the persistence of a discernable vibronic fine structure in the optical spectrum of compounds **1** (Fig. 1) suggest that the nTV spacer adopts a planar and rather rigid geometry.



Reagents: (a) NBS, AcOH/CHCl$_3$; (b) *n*-BuLi, DMF; (c) POCl$_3$, DMF, DCE; (d) TiCl$_4$, Zn, THF; (e) *n*-BuLi, THF

Scheme

The cyclic voltammetric (CV) behavior of compounds **1** also shows a strong dependence on the structural factors. Thus, whereas the oxidation process of **3a** and **3b** involves two successive one-electron steps with anodic peak potentials Epa$_1$ and Epa$_2$ at 0.70 and 0.88 V for **3a**, these values undergo a 0.10 V negative shift for **3b** due to the +*I* effect of the additional alkyl substituent. As already observed for other linear π-conjugated systems,[1] introduction of the 1,3-dithiole end groups induces a considerable negative shift of Epa$_1$ while the two successive one-electron waves merge into a single-step two electron transfer (Fig. 2). As for the corresponding nTVs spacers **3a** and **3b**, compounds **1b** exhibit lower Epa$_1$ values than **1a**. A further negative shift of Epa$_1$ is also observed when the SMe (R$_3$) substituent is replaced by *n*-propyl, as generally observed in the tetrathiafulvalene series.[1,6] Table 1 and the CV of Fig. 2 show that the first two-electron oxidation step is followed by two reversible one-electron oxidation waves with Epa_2 and Epa_3 in the 0.70 and 1.00 V region thus demonstrating that compounds **1** can be reversibly oxidized up to the tetracationic state. In contrast to Epa_1, Epa_2 and Epa_3 shows only a small dependence on the structural parameters which suggests that electronic structure of the π-conjugated system in the dicationic state is rather similar for all compounds **1**.

Table 1 : Electrochemical[11] and Optical Data for **1** and **2** in CH_2Cl_2.

Compd	Epa_1	Epa_2	Epa_3	λ_{max} (nm)	ΔE (eV)
2a	0.70	0.88		473	2.09
1ac	0.42	0.79	1.08	540	1.90
1ad	0.30	0.74	1.06	548	1.85
2b	0.60	0.78		488	2.13
1bc	0.32	0.79	1.02	554	1.85
1bd	0.19	0.72	0.99	563	1.80

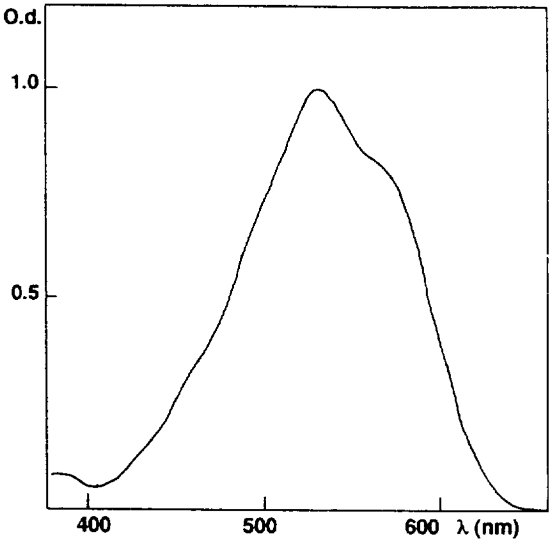


Fig. 1: UV-Vis. Spectrum of **1ad** in CH_2Cl_2

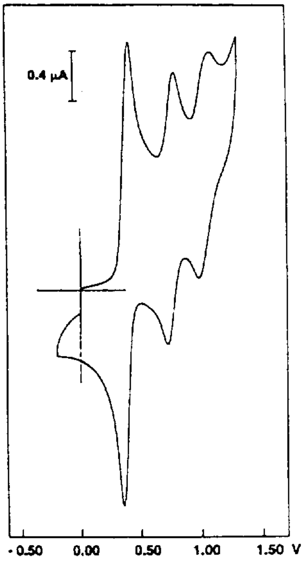


Fig. 2: CV of **1ac**[11]

To summarize we have shown that substitution of the thiophene ring of nTVs by solubilizing alkyl chains allows to synthesize longer hybrid oligomers end-capped with 1,3-dithiole units. This type of structure leads to a large reduction of ΔE wich reaches values as low as 1.80 eV, close the bandgap of the parent polymer poly(thienylenevinylene).[12] On the other hand, these oligomers exhibit strong π-donor ability illustrated by the one-step formation of the dicationic state at low potential and by the easy access to stable tetracations in a narrow potential window.

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9. All compounds show analytical and spectrocopic data in accordance with the proposed structures. Selected data for **1bd:** m.p. 232°C (dec.), ms (FAB) $(M+1)^+$ 1253, ^1H NMR ($CDCl_3$): 7.03 (d,2H, ^3J = 15.5 Hz, 2H ethyl.); 6.97 (s, 2H, 2H ethyl. centr.); 6.95 (d, 2H, ^3J = 15.5 Hz, 2H ethyl.); 6.67 (s, 2H, $2S_2C{=}CH$); 2.62-2.60 (s, broad signal, 16H, $8CH_2$ butyl); 2.50-2.34 (m, 8H, $4CH_2$ propyl); 1.68-1.34 (m, 40H, 8 $(CH_2)_2$ butyl and 4 CH_2 propyl); 1.04-0.89 (m, 36H, 8 CH_3 butyl and 4 CH_3 propyl). ^{13}C NMR ($CDCl_3$) 141.4, 140.9, 140.7, 136.9 (C-5', C-2, C-5, C-2'); 135.6, 134.7, 133.9, 132.3 (C-3', C-3, C-4, C-4'); 128.5 ($S_2C{=}CH$-); 127.6, 125.5 (Pr-$\underline{C}{=}\underline{C}$-Pr); 119.7, 119.1, 177.7 (-CH=CH-); 104.6 ($S_2C{=}CH$-); 33.5, 33.3, 33.1, 30.7, 30.0, 26.9, 26.7, 26.6, 23.1, 23.0, 22.9, 22.8, 22.7, 14.0, 13.9, 13.8, 13.6, (butyl and propyl).
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