Small Bandgap Molecular Semiconductors based on Rigidified Tetrathiafulvalene–Bithiophene Hybrid Conjugated Systems

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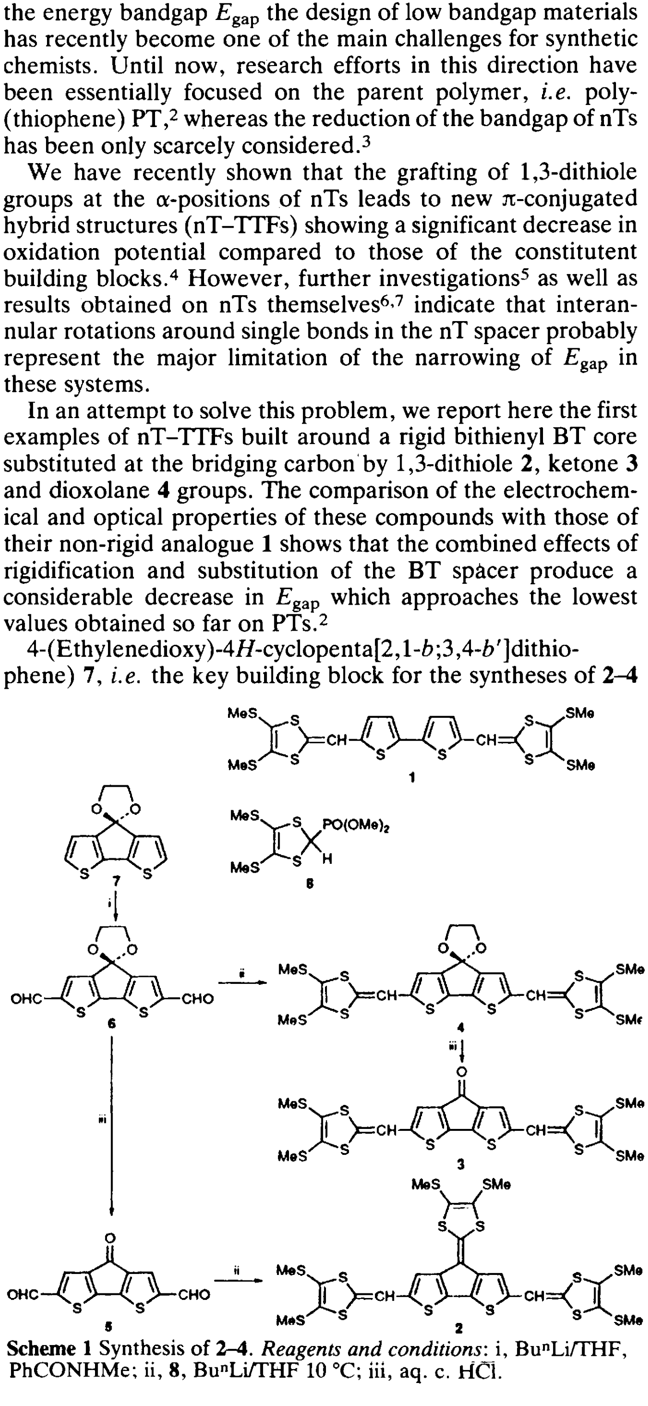
Rigidified tetrathiafulvalene–bithiophene hybrid systems with multi-step oxidation and reduction stages and bandgaps <1.5 eV have been synthesized.

The emergence of new applications such as non-linear optics, electronic devices or, more recently, electroluminescent diodes has caused a renewal of interest in conjugated thiophene oligomers (nTs).[1] However, the first developments of these applications have also shown the need for new specifically tailored organic semiconductors. In particular, since the intrinsic optical, electronic and electrochemical properties of these materials are governed by the magnitude of the energy bandgap E_{gap} the design of low bandgap materials has recently become one of the main challenges for synthetic chemists. Until now, research efforts in this direction have been essentially focused on the parent polymer, *i.e.* poly(thiophene) PT,[2] whereas the reduction of the bandgap of nTs has been only scarcely considered.[3]

We have recently shown that the grafting of 1,3-dithiole groups at the α-positions of nTs leads to new π-conjugated hybrid structures (nT–TTFs) showing a significant decrease in oxidation potential compared to those of the constitutent building blocks.[4] However, further investigations[5] as well as results obtained on nTs themselves[6,7] indicate that interannular rotations around single bonds in the nT spacer probably represent the major limitation of the narrowing of E_{gap} in these systems.

In an attempt to solve this problem, we report here the first examples of nT–TTFs built around a rigid bithienyl BT core substituted at the bridging carbon by 1,3-dithiole **2**, ketone **3** and dioxolane **4** groups. The comparison of the electrochemical and optical properties of these compounds with those of their non-rigid analogue **1** shows that the combined effects of rigidification and substitution of the BT spacer produce a considerable decrease in E_{gap} which approaches the lowest values obtained so far on PTs.[2]

4-(Ethylenedioxy)-4*H*-cyclopenta[2,1-*b*;3,4-*b*′]dithiophene) **7**, *i.e.* the key building block for the syntheses of **2**–**4** (Scheme 1), was prepared according to literature procedure.[8] Formylation of **7** using *N*-methylformanilide afforded the dicarbaldehyde **6**. Compound **4** was then obtained by double olefination of **6** using the methylthio-substituted 1,3-dithiole Wittig–Horner reagent **8**[9] under already described conditions.[10] Methylthio-substituted dithiole units were used for solubility reasons, and also because intramolecular S···S interactions with the thiophene rings contribute to increase the rigidity of the system.[5] Hydrolysis of **4** by aqueous HCl afforded **3**. The same procedure applied to **6** led to ketone **5** which was subsequently converted to **2** by a triple Wittig–Horner reaction.†



Scheme 1 Synthesis of **2**–**4**. *Reagents and conditions*: i, Bu^{n}Li/THF, PhCONHMe; ii, **8**, Bu^{n}Li/THF 10 °C; iii, aq. c. HCl.

Whereas the electronic absorption spectrum of **1** shows a single absorption band with λ_{max} at 462 nm,[5] the spectra of **2**–**4** exhibit additional spectral features on the low energy side. Thus for **2** a new absorption band emerges in the 1.5–2.5 eV region with a maximum at 2.20 eV (563 nm). For **3** and **4** this new absorption band appears as a broad shoulder and undergoes a further extension towards low energies while its intensity decreases. However, the spectra recorded at higher magnification clearly show that the absorption threshold occurs at much lower energy for **3** and **4** than for **2**. These absorption onsets lead to estimated E_{gap} values[11] of *ca.* 1.2–1.3, 1.3–1.4 and 1.5–1.6 eV for **3**, **4** and **2** respectively. The comparison of these results with the 2.2–2.3 eV value obtained for **1**[5] shows that the combined effects of the rigidification and substitution of the BT spacer lead to a considerable reduction of E_{gap}.

These modifications of the electronic spectrum are strongly reminiscent of those observed with the PTs obtained by electropolymerization of cyclopenta[2,1-*b*;3,4-*b*′]dithiophen-4-one (CDT), 4-dicyanomethylene-4*H*-cyclopenta[2, 1-*b*; 3,4-*b*′]dithiophene (DCM) and **7**.[2b,c,f] In the case of poly(CDT) and poly(DCM) the reduction of E_{gap} was attributed to a strong decrease of the energy of the LUMO caused by the introduction of electron-withdrawing groups on the sp^2 bridging carbon.[2b,c] However, the fact that the grafting of a dioxolane group at an sp^3 bridging carbon produces similar effects[2f] strongly suggests that rigidification of BT also plays a determining role in the decrease of E_{gap}. This conclusion, recently demonstrated on a rigid terthienyl model,[7] is further supported by the results obtained with **2**, which show that despite the presence of the electron-donating 1,3-dithiole group at the bridging carbon, a considerable reduction of E_{gap} occurs in this case too.

Table 1 lists the cyclic voltammetric data of **1**–**4**. As previously observed, nT–TTFs containing more than one thiophene ring exhibit a complex CV response with multiple oxidation stages. This electrochemical behaviour is further complicated here by the overlap of the effects of rigidification and substitution. The CV of **2** shows two well-resolved reversible oxidation waves with peaks at 0.18 and 0.50 V (E_{pa} 1 and E_{pa} 2), assigned to the successive generation of the cation radical and dication. The 0.36 V negative shift of E_{pa} 1 compared to **1** appears consistent with the strong electron-donating effect of the 1,3-dithiole group, although rigidification is also likely to play an important role. On the other hand, the increase in the difference E_{pa} 2 − E_{pa} 1 from 0.09 to 0.32 V indicates a large enhancement of the coulombic repulsion between positive charges in the dication state.[12] Although

Table 1 Electrochemical data for **1**–**4** (10^{-3} mol l^{-1}) in Bu_4NPF_6/CH_2Cl_2 (10^{-1} mol l^{-1}), scan rate 100 mV s^{-1}. All potentials in V *vs* SCE.

Compound	E_{pa} **1**	E_{pa} **2**	E_{pa} **3**	E_{pa} **4**	E_{pr} **1**	E_{pr} **2**	E_{pa} **2** $- E_{pa}$ **1**	E_{pa} **1** $- E_{pr}$ **1**
1[a]	0.54	0.64	0.74		−0.84		0.09	1.38
2	0.18	0.50	0.61	0.87	−0.90	−1.10	0.32	1.08
3	0.38	0.56	0.65	0.90	−0.56	−1.14	0.18	0.94
4	0.38	0.46	0.68	0.96	−0.52	−1.12	0.08	0.90

[a] From ref. 5.

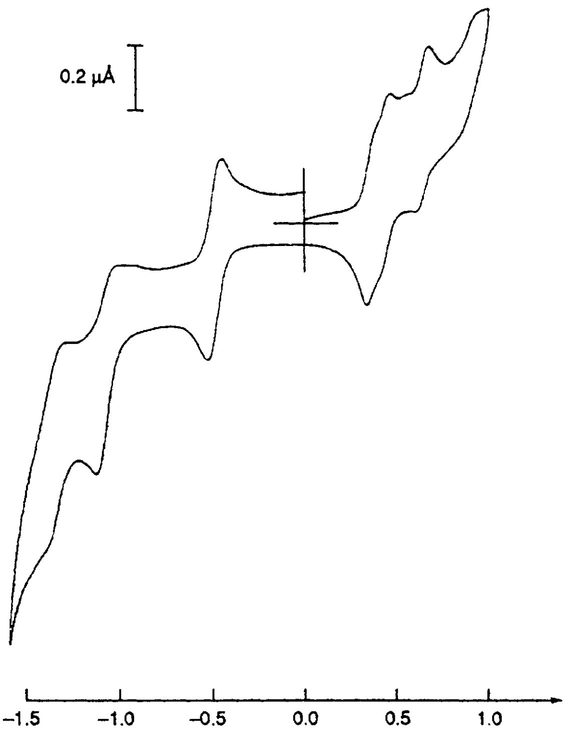


Fig. 1 Cyclic voltammogram of **4** (10^{-3} mol l^{-1}) in Bu_4NPF_6/CH_2Cl_2 (10^{-1} mol l^{-1}) scan rate 100 mV s^{-1}

comparison with the data obtained for **3** and **4** shows that this result is related to the electronic effects of the 1,3-dithiole group, we have up to now no definitive explanation for this phenomenon. Finally, the fact that the potential of the first reduction peak (E_{pr} **1**) is rather insensitive to the electronic effects of the 1,3-dithiole group (−0.90, *cf.* −0.84 V for **1**) confirms that the rigidity of the conjugated system is a determining factor for efficient reduction.[2f,7,13]

As expected from the optical data, the introduction of a ketone or dioxolane group at the bridging carbon considerably affects the electrochemical behaviour of the BT–TTF π-conjugated system. Thus, compared to **2**, E_{pa} **1** shifts positively by 0.20 V, whereas E_{pa} **2** is much less affected. This results in a decrease of E_{pa} **2** − E_{pa} **1** to 0.18 and 0.08 V for **3** and **4** respectively. This reduction of the coulombic repulsion in the dication state appears consistent with the enhanced quinonoidic character of the conjugated BT spacer.[2b,c,f] As expected, the electron-withdrawing effects of the substituents in **3** and **4** induce a positive shift of E_{pr} **1** up to *ca.* −0.50 V, whereas a second and even a third reduction wave assigned to the di- and tri-anion states occur at more negative potentials. These changes are accompanied by a considerable increase in the electrochemical reversibility of the reduction processes (Fig. 1).§

Although the E_{gap} values indicated by the potential difference between hole and electron injection[11] follow the sequence already indicated by electronic absorption spectra, the values estimated from cyclic voltammetry are significantly lower than the optical bandgaps. Although we have no definitive explanation for these discrepancies, they may reflect rather large differences between the solvation energies of the oxidized and reduced states.[11]

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Footnotes

† ^1H NMR and mass spectrometry of all new compounds gave satisfactory results.

§ Whereas all compounds can be electrodeposited in the form of dication salts by repetitive positive potential scans,[4] in the case of **3** electrodeposition of the dianion salt can also be achieved by recurrent scans in the cathodic potential region. The corresponding electrochemical study will be published elsewhere.

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