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Strong π-electron donors based on a self-rigidified 2,2′-bi(3,4-ethylenedioxy)thiophene–tetrathiafulvalene hybrid π-conjugated system

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Abstract—Strong π-donors based on the association of TTF and 2,2′-bi(3,4-ethylenedioxy)thiophene conjugating unit have been synthesised; optical and an X-ray data show that intramolecular interactions lead to full rigidification of the conjugated system.
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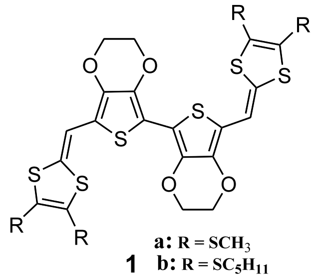
Organic semi-conductors based on extended linear π-conjugated systems are a focus of considerable current interest motivated by their technological applications in field effect transistors or organic light-emitting diodes.[1,2] Tetrathiafulvalene (TTF) is one of the strongest π-electron donating system widely used for the elaboration of conducting and superconducting materials.[3] In order to combine these two approaches extended TTFs incorporating a large variety of π-conjugated spacer have been developed.[4] The electronic properties of the π-conjugated systems are modulated by the strong π-donor properties of 1,4-dithiafulvenyl groups and their well-known propensity to strengthen intermolecular interactions.[5] On the other hand, the overlapping mode of hybrid molecules in the structure of cation radical salts or neutral compounds is strongly orientated by the nature of the heteroatoms in the spacer.[6]

In previous studies, we have shown that the covalent rigidification of π-conjugated systems allows a strong enhancement of π-electron delocalisation and thus a decrease of the HOMO–LUMO gap due to the combined effects of planarisation and/or reduction of bond-length alternation.[7] An interesting further step in this direction would consist in the development of full self-rigidification for extended TTFs through non-covalent interactions. In this context intramolecular S···X interactions (with X = S, O and N atoms) stabilising planar conformations have been observed in conjugated oligomers based on thiophene units.[8] On the other hand, for extended TTF analogues, similar S···X interactions between the sulfur atoms of the end dithiafulvenyl groups and heteroatoms of the spacer strongly contribute to ensuring the coplanarity of the 1,3-dithiole rings with the central conjugated systems for both the neutral and oxidised states.[6,9]



1 **a:** R = SCH_3
b: R = SC_5H_{11}
c: R = C_3H_7

We report here the synthesis and characterisation of extended conjugated systems consisting in a 2,2′-bi(3,4-ethylenedioxy)thiophene (bi-EDOT) unit end-capped with dithiafulvenyl groups (**1**). Crystallographic, optical and electrochemical data show that the combination of the electron-releasing effect of the ethylenedioxy groups with the full self-rigidification of the molecule by intramolecular interactions lead to a new series of extended conjugated systems with strong π-donor properties.

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The synthesis of compounds **1** is depicted in Scheme 1. The bi-EDOT unit, obtained by copper–catalyzed coupling of the lithiated derivative of EDOT, was treated by an excess of Vilsmeier reagent ($POCl_3$–DMF) leading to the 5,5′-diformyl-2,2′-bi(3,4-ethylenedioxy)thiophene **2** in 60% yield. The last step consisted in a twofold Wittig–Horner olefination with phosphonates **P**. The very low solubility of dialdehyde **2** led to the adoption of an unconventional procedure involving dropwise addition of ^{n}BuLi to a suspension of the dialdehyde in the presence of an excess of phosphonate **P** under ultra-sound at room temperature. Sonication favoured the solubilisation of the dialdehyde and the fast nucleophilic addition of the anion onto the carbonyl group afforded the target molecules **1a–c** in 20–35% yield.[10]

Single crystals of **1b**, obtained by slow evaporation from a $CHCl_3$–EtOH solution, have been analysed by X-ray diffraction.[11] The structure of compound **1b** (Fig. 1) reveals the perfect planarity of the conjugated system. The two EDOT units adopt an *anti* conformation and short S···O distances $d_{S\text{–}O} = 2.914(5)$ Å are observed. This value, considerably shorter than the sum of the van der Waals radii of sulfur and oxygen (S: 1.85 Å+O: 1.50 Å = 3.35 Å), clearly shows that intramolecular interactions rigidify the central part of the molecule. Further rigidification of the conjugated system occurs between the dithiafulvalene groups and thiophene units which adopt a δ_{syn} conformation stabilised by S···S intramolecular interactions, as shown by the short distances $d_{S\text{–}S} = 3.098(4)$ Å. The molecules stack with a lateral displacement allowing minimisation of steric hindrance, hence close S···S contacts ($d = 3.58$ Å) between the sulfur atoms of dithiole and thiophene cycles are observed.

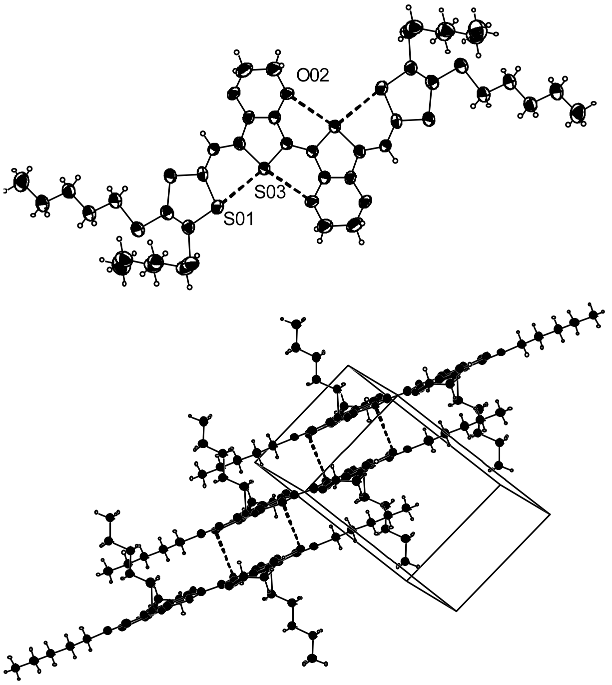
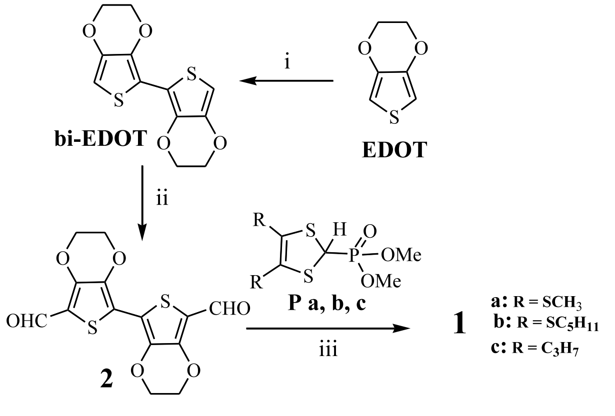
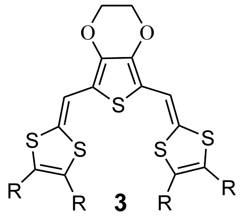


Figure 1. X-Ray molecular structure of compound **1b**. Intramolecular and intermolecular interactions are indicated by dotted lines.

The optical and electrochemical properties of compounds **1** gathered in Table 1 are compared to their analogues incorporating EDOT (**3**)[12] or 2,2′-bithiophene (**4**)[13] as π-conjugated spacer.



Scheme 1. Synthesis of **1**. *Reagents and conditions*: (i) BuLi, $CuCl_2$; (ii) $POCl_3$, DMF, reflux in $ClCH_2CH_2Cl$; (iii) 4 equiv. of **P**, BuLi/THF, sonic activation, 20°C.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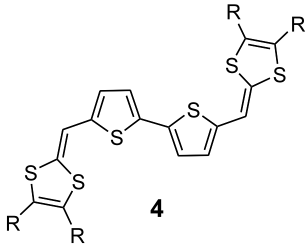
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Table 1. Optical[a] and electrochemical[b] data for **1–3**

Compounds	λ_{max} (nm)	$\lambda_{0\text{-}0}$ (nm)	$E°_1$ (V)	$E°_2$ (V)	$\Delta E = E°_2 - E°_1$ (mV)	K^c
1a	472	505	0.17	0.34	170	1.33×10^{-3}
1b	474	509	0.16	0.34	180	0.9×10^{-4}
1c	477	513	0.01	0.18	170	1.33×10^{-3}
3a[12]	446	474	0.30	0.51	210	2.8×10^{-4}
3c[12]	446	476	0.08	0.35	270	2.7×10^{-5}
4a[13]	462	488 (sh)	0.55	0.60	50	1.47×10^{-1}
4b[13]	463	490 (sh)	0.52	0.57	40	2.1×10^{-1}

[a] 10^{-5} mol L^{-1} in CH_2Cl_2.

[b] 5×10^{-4} mol L^{-1} in Bu_4NPF_6/CH_2Cl_2 (10^{-1} mol L^{-1}), scan rate 100 mV s^{-1}, $E°$ versus SCE, determinate from deconvoluted voltammogram.

[c] Calculated from the potential difference with the equation $K = \exp[(F/RT)\times(-\Delta E)]$.

Compared to derivatives **3**, the lengthening of the conjugated spacer by insertion of an additional EDOT ring produces a red shift of λ_{max} (31 nm between **3c** and **1c**) indicating a decrease of the HOMO–LUMO gap. Comparison with compounds **4** with the same number of carbon atoms in the conjugated chain as **1** shows the strong effects of the ethylenedioxy groups grafted on the thiophene cycles. Electronic absorption spectra of **1b** and **4b** are presented in Figure 2. The spectra of **4** present large broad absorption bands with only a slight fine vibronic structure indicating rotational disorder of the bithiophene unit. The replacement of bithiophene by bi-EDOT produces both a red shift of the absorption bands associated to a shorter gap and a strong enhancement of the fine structure with the emergence of two main absorbance bands. Such behaviour, observed for extended TTF with covalently bridged π-conjugated spacers, is characteristic of a rigidification of the conjugated systems.[7] This result indicates that the chalcogen–chalcogen interactions observed in the crystallographic structure persist in solution, thus contributing to the full rigidification of the molecule in a planar conformation.

As shown in Figure 3, the cyclic voltammogram (CV) of compounds **1** exhibits two one-electron oxidation waves corresponding to the formation of the cation radical and dication. Comparison with data for compounds **1** and **3** bearing the same substituents R on the 1,3-dithiole rings, shows that the insertion of a second EDOT moiety produces a 40–60 mV negative shift of $E°_1$ and a decrease of the difference $\Delta E = E°_2 - E°_1$ indicative of a diminution of the intramolecular coulombic repulsion between positive charges in the dication. It is worth noting that for unsubstituted thiophene and bithiophene spacers the lengthening of the spacer from one to two rings leads to the opposite effect due to the rotational disorder of the conjugated chain.[13] For compound **1c** with the more electron-releasing propyl groups, $E°_1$ reaches a value close to 0.0 V versus SCE which is one of the lowest value reported to date for a TTF analogue.[14]

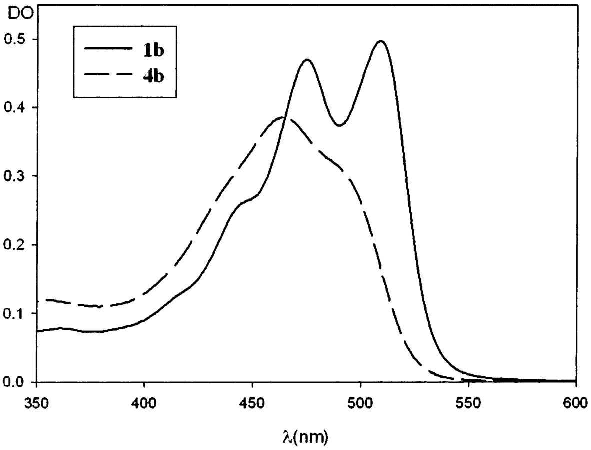

Figure 2. Electronic spectra of **1b** and **4b** (10^{-5} M in CH_2Cl_2).

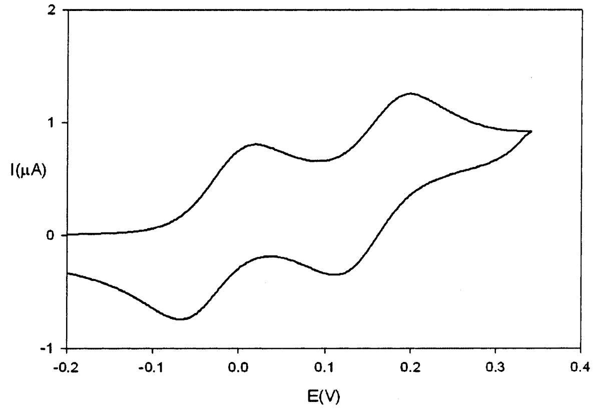

Figure 3. CV of **1c** (5×10^{-4} M in CH_2Cl_2).

Comparison of the electrochemical data for compounds **1** and **4** shows that, in addition to the expected enhancement of the π-donor ability, the replacement of the bithiophene (BT) spacer by bi-EDOT induces a marked increase of ΔE from 40–50 to 170–180 mV. Such evolution corresponds to a lower value of the equilibrium constant K for the disproportionation of the cation radical into neutral and dication species. Thus, the value of K which is two orders of magnitude lower than that of **4** reveals a strong enhancement of the thermodynamic stability of radical cation $\mathbf{1}^{+\bullet}$. This result, indicative of a dramatic increase of the coulombic repulsion between positive charges in the dication $\mathbf{1}^{2+}$, suggests that replacement of the BT spacer by the strong electron-donating bi-EDOT leads to a relocalisation of the positive charges of the dication from the end dithiafulvenyl group to the middle of the conjugated system, thus resulting in an increase of the on-site coulombic repulsion.

To summarise we have shown that the use of bi-EDOT as π-conjugating spacer in extended TTF analogues gives rise to the development of intramolecular chalcogen–chalcogen interactions which stabilise a fully planar rigid conformation of the molecule, thus contributing to strongly enhance the π-donor ability of the molecule. In view of their electronic properties, these new extended π-conjugated systems could lead to interesting active materials for the realisation of field effect transistors. Work in this direction is now in progress.

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10. ^{1}H NMR and mass spectrometry of new compounds gave satisfactory results. Selected data:

    2: white powder; mp >250°C; EI MS $M^{+\bullet}$ 338 for $C_{14}H_{10}O_6S_2$; IR (KBr) 1635 cm^{-1} (strong, CO); solubility too low for NMR experiment.

    1a: red powder; mp 126°C (decomp.); ^{1}H (CDCl$_3$) 6.61 (s, 2H), 4.37 (br s, 4H), 4.28 (br, s, 4H), 2.82 (s, 6H); MALDI-TOF M+. Found 693.72, calcd 693.84 for $C_{24}H_{22}O_4S_{10}$.

    1c: red powder; mp 208°C (decomp.); ^{1}H (CDCl$_3$) 6.59 (s, 2H), 4.35 (br s, 4H), 4.25 (br, s, 4H), 2.38–2.30 (m, 8H), 1.60–1.51 (m, 8H), 0.97–0.93 (m, 12H); MALDI-TOF M+. Found 677.92, calcd 678.11 for $C_{32}H_{38}O_4S_6$.
11. Crystal data of **1b**: $C_{20}H_{27}O_2S_5$, $M=459.72$, triclinic, P-1, $a=9.183(1)$, $b=9.393(1)$, $c=13.644(2)$ Å, $\alpha=102.19(2)$, $\beta=92.84(2)$, $\gamma=102.79(2)°$, $V=1116.1(2)$ Å^3, $Z=2$, μ(MoKα)$=0.533$ mm^{-1}, 10827 reflections collected ($2<\theta<26$) from which 4003 ($R_{\mathrm{int}}=0.081$) were independent, 1885 reflections with $I>2\sigma(I)$, 244 refined parameters, $R_1=0.041$, wR_2 (all data)$=0.062$. Data were collected on a STOE-IPDS diffractometer at 293 K. The structure was solved by direct methods (SIR) and refined on F^2 by full-matrix least-squares method, using SHELXL-97 (Sheldrick, G. M., 1997). Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated. Crystallographic data excluding structure factors have been deposited with the Cambridge Crystallographic Data Centre under reference CCDC: 195335.
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