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Extensively Conjugated Tetrathiafulvalene (TTF) π-Electron Donors with Oligothiophenes Spacer Groups

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New extended p-donors combining the tetrathiafulvalene (TTF) system with the conjugated backbone of substituted terthienyls are described.

The development of new π-electron donors by manipulation of the basic TTF structure is presently subject to intensive research efforts. The main objectives of these studies are an improved control of the charge transport and in some cases superconducting properties of the corresponding cation radical salts (CRSs) as well as a better knowledge of the structural parameters which determine these properties.[1] In this context, the increase of the material dimensionality by modifying the spatial extension of the π-donor and thus the intermolecular interstack bonding has been acknowledged as a crucial factor. Among other strategies, a recent approach involves the insertion of a conjugated spacer between the two 1,3-dithiole rings in order to (*i*) lower the symmetry of the donor molecule (*ii*) decrease the oxidation potentials (*iii*) stabilize the corresponding cation radical or dication and (*iv*) minimize the on-site coulombic repulsion in the di- or poly-cationic states. Besides conjugated polyolefinic bridges,[2] TTF systems involving benzenic or heterocyclic spacers have been recently described.[3]

As a further step in this direction, we report here the synthesis of extended π-electron donors of the TTF series containing substituted terthienyl spacers. In addition to the

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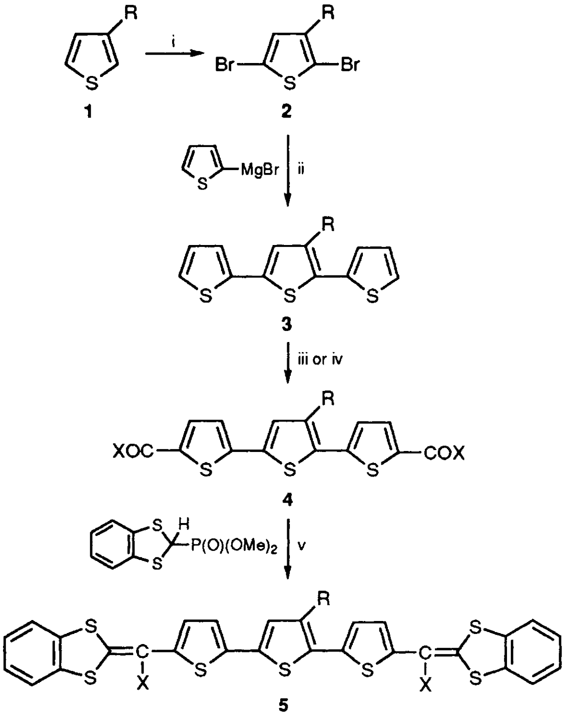

5	X	R
a	H	H
b	H	Me
c	Me	Me
d	H	$(CH_2)_7Me$
e	H	$(CH_2CH_2O)_2Me$

Scheme 1 *Reagents and conditions*: i, Br_2, $CHCl_3$, reflux; ii, Et_2O, $Ni(DPP)PCl_2$, room temp.; iii, lithium diisopropylamide −78 °C, PhMeNHCO; iv, Ac_2O, H_3PO_4 100 °C; v, Bu^nLi, dry tetrahydrofuran, 10 °C; DPP = 1,3-bis(diphenylphosphino)propane

above rationale which directly concerns the field of electroconductive CRSs, these new structures can be considered also from the viewpoint of conjugated oligo- and poly-(thiophenes),[4] and thus as first examples of oligothiophenes derivatized by a TTF system. In this work, the effects of substitution of the conjugated spacer have been analysed and it is shown that this substitution can significantly contribute to control the properties of the donor molecule.

The new compounds **5a–e** have been prepared using the five-step synthetic route depicted in Scheme 1. 3-Octyl and 3-(3,6-dioxaheptyl)thiophene **1d** and **e** were obtained as already described.[5] Bromination of the monomers afforded the corresponding 2,5-dibromo derivatives **2** in 80–85% yield. Cross-coupling of **2** with 2-thienylmagnesium bromide in the presence of $Ni(DPP)PCl_2$[6] [$DPP{\equiv}Ph_2(CH_2)_3PPh_2$] led to the corresponding terthienyls **3** (yields 60–95%). 2,5″-Diformylterthienyls **4** were prepared in 50–60% yield by reaction of *N*-methylformanilide on the dilithiated derivatives of **3** using the procedure already described for the formylation of TTF.[7] In the case of **4b** acylation was performed by reaction of acetic anhydride in the presence of catalytic amounts of phosphoric acid[8] (yield 35%). Wittig–Horner olefination of **4** with the phosphonate anion bearing the 1,3-dithiol-2-ylidene moiety afforded the title compounds **5a–e** in 40–80% yield based on **4**. ^1H NMR and mass spectroscopy of all new compounds gave satisfactory results.

The substitution of the median thiophene ring at the 3-position controls to a large extent the solubility of the molecule. Thus, whereas **5a** is only sparingly soluble in common solvents (Et_2O, CH_2Cl_2), the introduction of methyl groups (**5b, c**) increases the solubility which becomes high enough to allow solution film-casting in the case of **5d, e** bearing long alkyl or oxyalkyl substituents. As shown in Table 1, the substitution of the conjugated spacer exerts significant effects on the electronic absorption spectrum of the donors. Thus, the introduction of a methyl group at the 3-position of the central thiophene ring produces a *ca.* 30 nm bathochromic shift of λ_{max}. This result appears rather surprising since, in the case of terthienyl, the same substitution has opposite effect and produces a blue shift of λ_{max} from 355 to 336 nm.[9] On the other hand, when X = Me in **5c**, a 4 nm blue shift occurs which may be attributed to the slight deviation from planarity caused by the steric interactions between the methyl groups and the dithiole moieties. Increasing the length of the 3-substituent from one to eight carbons in **5d** leads to a further red shift of λ_{max} up to 450 nm, whereas the bathochromic shift observed with the grafting of the oxyalkyl chain in **5e** is inferior to that produced by alkyl substituents.

Table 1 Cyclic voltammetric[a] and UV-VIS absorption[b] data of **5a–e**

	$E1_{1/2}$/V	$E2_{1/2}$/V	Epa3/V	$E2_{1/2}-E1_{1/2}$/mV	λ_{max}/nm
5a	0.50	0.69	0.92	190	417
5b	0.46	0.64	0.82	180	444
5c	0.45	0.61	1.00	160	440
5d	0.50	0.62	0.82	120	450
5e	0.52	0.66	0.82	140	438

[a] In 0.1 mol dm^{-3} Bu_4NClO_4–CH_2Cl_2, Pt electrode, 50 mV s^{-1}. $E_{1/2}$ = (Epa + Epc)/2. All potentials refer to the saturated calomel electrode (SCE). [b] In CH_2Cl_2.

The interpretation of these results is not straightforward since the magnitude of the observed shifts largely exceeds what can be expected from a simple inductive effect. Furthermore, since the $+I$ effects of the substituent are roughly equivalent for **5b**, **5d** and **5e**, the observed spectral changes must have another origin. In the case of poly(thiophene), the large red shifts observed with long alkyl and oxyalkyl chains {λ_{max} = 500, 540 and 556 nm for poly(thiophene), poly(3-nonylthiophene) and poly[3-(3,6-dioxaheptylthiophene)] respectively}[10] were attributed to an enhancement of planarity of the conjugated backbone resulting from the interactions between substituents on adjacent monomers,[10a] or between the substituents and their chemical environment.[10b] Since such an intramolecular mechanism is rather unlikely here, owing to the presence of a single substituted thiophene ring, possible explanations could be conformational changes resulting from the interactions between the side-substituents and the solvent, or the aggregation of donor molecules. Further work is still required to clarify this point.

The analysis of the electrochemical behaviour of **5a–e** reveals several common features *i.e.* two reversible one-electron oxidation waves at *ca.* 0.5 and 0.7 V, followed by a third less-defined one-electron oxidation process in the 0.8–1 V region. The comparison of the potentials corresponding to the cation radical and dication states with those of the parent dibenzo-TTF (0.72 and 1.06 V *vs.* SCE),[3a] shows that the insertion of the terthienyl spacer leads to a marked decrease of the oxidation potentials. Furthermore, the smaller difference between the first and the second oxidation steps ($E2_{1/2} - E1_{1/2}$) (120 mV for **5d** instead of 340 mV for dibenzo-TTF) indicates a significant reduction of the on-site coulombic repulsion between positive charges in the dication state. However, compared with the results recently obtained on the parent compound containing a single thiophene spacer,[3e] these results indicate only a moderate increase of the donor ability in regard to what could be expected from the insertion of a conjugated terthienyl spacer.

Previous works have shown that a three-double bonds polyenic bridge leads to the coalescence of the two first redox waves which occur as a single two-electron wave.[2] The differences between the effects of olefinic and aromatic

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spacers have been discussed by several authors who attributed the persistence of two distinct one-electron waves for compounds containing aromatic bridges to the excess of energy required to dearomatize the spacer group upon formation of the dication.[3a,b] In our case, this charge localization may be further favoured by the conformational changes associated with the *cis-trans* isomerisation about the interannular bonds in the terthienyl cation radical.[11] These factors conjunction could lead to a situation where the terthienyl bridge behaves as a distinct entity. Such behaviour has already been reported for the severely twisted anthracene-bridged TTF for which electrooxidation of the anthracene system could be observed after the formation of the TTF dication.[12]

Preliminary experiments on the electrical properties of the conducting adducts obtained by iodine doping of **5d** and **e** yielded two-probe conductivities in the range of 10^{-3}–10^{-4} S cm^{-1}. Experiments aimed at the electrochemical preparation of high quality single CRSs of these new donors are now underway.

Received, 17th November 1992; Com. 2/06103A

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