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Synthesis and Electrochemistry of a Soluble Double-Bridged Tetrathiafulvalene (TTF)-*p*-benzoquinone from Novel Unsymmetrical TTFs

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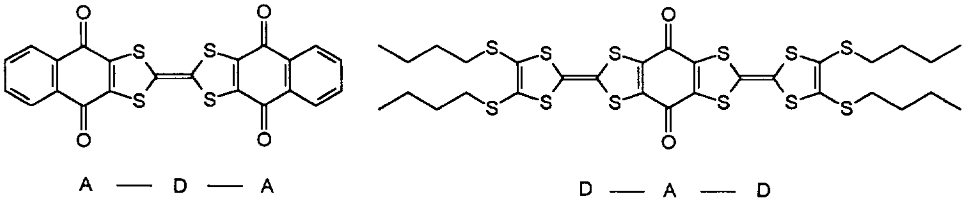
Abstract: The synthesis of novel unsymmetrically substituted TTFs and the subsequent transformation into a donor-σ-acceptor system is reported; The CV and the spectroelectrochemical studies reveal the presence of both electroactive moieties.

Tetrathiafulvalene (TTF) has attracted much interest for its electron-donating ability which has been used in the preparation of electrically conducting compounds.[1] Although different approaches have been developed for the structural control in the TTF-based systems, selective functionalization of the parent TTF molecule is still currently under investigation.[2] In this regard, the synthesis of unsymmetrical TTFs has been scarce due to the lack of a general synthetic procedure[3] and the difficulties in the preparation of 1,3-dithiole-2-one or 1,3-dithiole-2-thione bearing suitable protecting groups on one of the fragments compatible with the cross-coupling methods available.[4]

On the other hand, a big effort has been devoted to the synthesis of dimeric and oligomeric homologes of TTF and its derivatives.[1, 5] However, the synthesis of covalently linked donor-σ-acceptor systems bearing the TTF unit as the donor moiety has been less studied despite their interest for the preparation of molecular electronic devices.[6] Thus, the Aviran-Ratner molecular rectifier formed by TTF-σ-TCNQ (TCNQ = tetracyano-*p*-quinodimethane) which was proposed over twenty years ago has not yet been synthesized[7] although some related analogues have been reported.[8]

To the best of our knowledge, only the TTF-quinones **1** and **2** have been recently reported as donor (D) and acceptor (A) units in full conjugation. However, the poor solubility of **1** prevented its further functionalization and also the structural study of this A-D-A system. In addition, and surprisingly, the cyclic voltammetry (CV) study did not show the oxidation waves corresponding to the TTF donor fragment.[9]



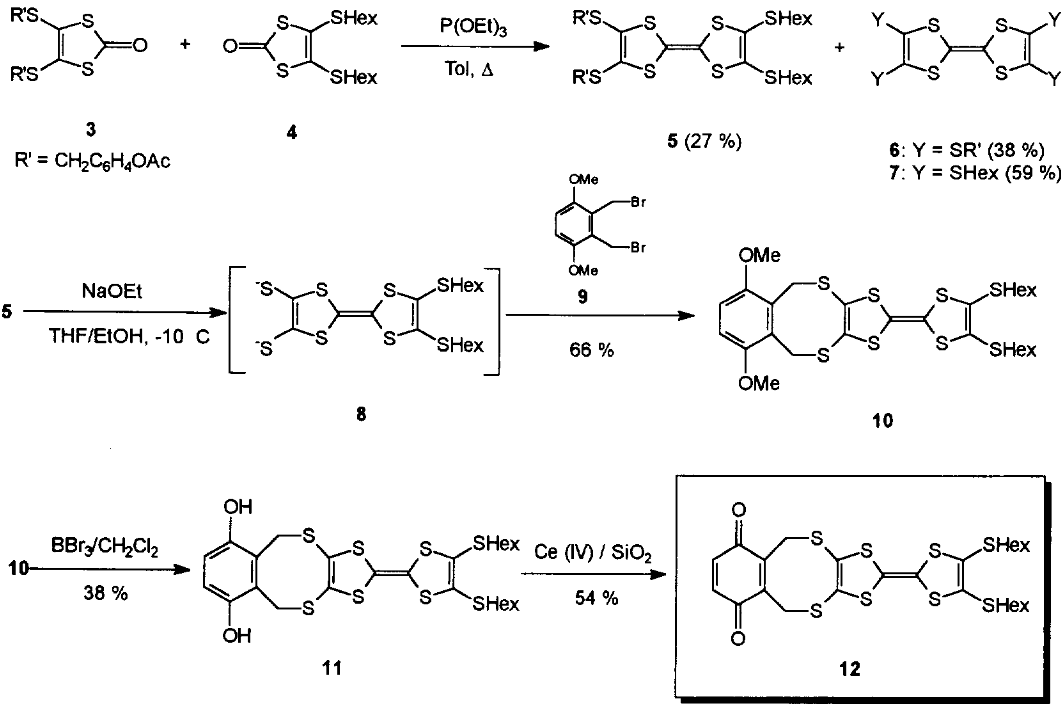
1

2

Figure

In contrast to **1**, compound **2** formed by two donor units and one acceptor, resulted to be soluble in tetrachloroethane and could be charaterized by UV and NMR spectroscopy. Interestingly, the CV reveals only two two-electron oxidation waves anodically shifted, related to the parent TTF, due to the electron withdrawing effect of the quinone moiety.[10] However, no data were reported on the electrochemical behaviour of the *p*-benzoquinone acceptor fragment.

In this comunication we present our preliminary results on the preparation of a novel and soluble donor-σ-acceptor (D-σ-A) molecule in which the TTF fragment is linked to the *p*-benzoquinone ring by two methylenethio (CH_2-S-) spacers (**12**). These bridges allow a minimal conjugation between the D and A fragments, so that each component retains its original identity.



Scheme

The synthesis of the target molecule **12** was carried out as is depicted in the Scheme. Thus, the precursors **3**[11] and **4**[12] were prepared in two steps respectively from the $[Zn(dmit)_2](Et_4N)_2$ complex according to the previously described procedures. It is worth of mention that the use of conventional protecting groups such as benzoyl or acetyl in **3** is incompatible with most of the cross-coupling methods available. The *p*-acetoxybenzyl protecting group has been recently reported to be stable during the cross-coupling reaction and easily removed under mild basic conditions.[11]

The desired unsymmetrical TTF derivative **5**, together with the two symmetrically substituted derivatives **6** and **7**, were prepared from a phosphite mediated cross-coupling reaction of equimolecular amounts of the diprotected oxone **3** and 4,5-dihexylthio-1,3-dithiol-2-one (**4**). These three TTF derivatives (**5**, **6** and **7**) could be conveniently separated by flash column chromatography and isolated analitically pure. Treatment of compound **5** with a sodium ethoxide solution in dry ethanol in THF under inert atmosphere at -10 °C yielded the free dithiolate (**8**) which was succesfully traped with 2,3-di(bromomethyl)-1,4-dimethoxybenzene (**9**)[13] to afford the novel TTF derivative **10**. (Scheme)

Although oxidation of alkyl ethers of hydroquinones are commonly performed using ceric ammonium nitrate (CAN)[14], silver oxide[15] or manganese dioxide in nitric acid[16], the reaction of **10** with these reagents led solely to extensive decomposition. However, the ether cleavage could be easily carried out by treating **10** with boron tribromide in dry dichloromethane at room temperature. Only the oxoalkyls ethers are attacked and the TTF moiety remains unaltered. Finally, oxidation of the obtained hydroquinone (**11**) either with commercial bleach (5 %) or with CAN yielded the target molecule **12** with a D-A pattern, [17] which was purified by flash column chromatography on silica-gel using dichloromethane as eluent.

The electrochemical behaviour of the novel unsymmetrical TTF derivatives (**10**, **11**) and the donor-σ-acceptor molecule (**12**) were studied by cyclic voltammetry (CV) and the data are summarized in the Table. The oxidation potential values confirm the expected anodic shift, related to TTF, caused by the presence of the alkylthio groups linked to the TTF molecule.[18] Compounds **10** and **11** exhibit two oxidation waves to form the cation radical and dication of the TTF fragment and a third oxidation wave corresponding to the oxidation of the substituted benzene ring. In contrast to donors **10** and **11**, compound **12** showed, in addition to the two reversible one-electron oxidation waves, a reversible wave at a negative potential value corresponding to the reduction of the *p*-benzoquinone ring.

Table. Cyclic Voltammetry Data of Novel Donors (V *vs* SCE)[a]

Compound	$E_{1/2}^{1,\,ox}$	$E_{1/2}^{2,\,ox}$	$E_{a.p}^{3,\,ox}$	$E_{1/2}^{1,\,red}$
10	0.529	0.835	1.606	-
11	0.481	0.742	1.420	-
12	0.595	0.860	-	-0.394
***p*-benzoquinone**	-	-	-	-0.466
TTF[b]	0.372	0.672	-	-

[a] Glassy carbon, CH_2Cl_2/ 0.1 M $TBAClO_4$. Scan rate: 100 mvs^{-1}. [b] Measured at the same experimental conditions.

In contrast to other recently reported D-A systems, compound **12** did not show the photoinduced intramolecular charge transfer in the UV-Vis spectrum from the donor TTF fragment to the acceptor *p*-benzoquinone moiety.[8]

However, the electroactive character of both donor and acceptor partners can be clearly observed in the CV measurements.

We have also carried out the spectroelectrochemical study of compound **12** (CH_2Cl_2/ 0.1 M $Bu_4N^+ClO_4^-$) using a Pyrex cell and ITO electrodes with a potential range from 0 to 1500 mV and potential steps of 100 mV. At a potential of 400 mV, the absorption of the neutral molecule at 332 nm decreases and two new weak absorptions appear at 450 and 800 nm which can be reasonably assigned to the radical cation. Increasing the potential, the absorptions became more intensive, reaching a maximum at 800 mV. Above this potential, a new band appears at 650 nm and a decrease of the absorptions at 450 and 800 nm occurr. This new and intensive absorption is assigned to the formation of the dication, being the sole band above 1100 mV. The isosbestic points were located at 360 nm for the formation of the cation radical and 517 and 754 nm for the dication

In summary, we have prepared a single-component TTF containing donor-σ-acceptor electroactive molecule, in which both D and A moieties preserve their identity, from novel unsymmetrically substituted TTFs. The electrochemical data reveal an attractive system as precursor for the preparation of intramolecular charge-transfer complexes. Work is in progress for the preparation of the hitherto unknown TCNQ-σ-TTF and DCNQI-σ-TTF (DCNQI = dicyano-*p*-quinodiimine) analogues.

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References and Notes

1. *Organic Conductors: Fundamentals and Applications*, Farges, J.P. Ed. Marcel Decker, New York, **1994**.
2. Bryce, M.R., *J. Mater. Chem.*, **1995**, *5*, 1481. Garin, J., *J. Adv. Heterocycl. Chem.*, **1995**, *62*, 249.
3. Hellberg, J.; Moge, M.; Schmitt, H.; von Schütz, J.-U., *J. Mater. Chem.*, **1995**, *5*, 1549.
4. Gemmell, C.; Kilburn, J.D.; Ueck, H.; Underhill, A.E.; *Tetrahedron Lett.*, **1992**, *33*, 3923.
5. See for example the Special Issue on Molecular Conductors, *J. Mater. Chem.*, **1995**, *5*.
6. *Molecular Electronics in Granular Nanoelectronics*, Ferry, D.K.. Ed. Plenum Press, New York (1991)
7. Aviram, A.; Ratner, M.A., *Chem. Phys. Lett.* **1974**, *29*, 277.
8. Metzger, R.M.; Panetta, C.A., *J. Molec. Elect.*, **1989**, *5*, 1. Panetta; C.A., Heimer; N.E.; Hussey, C.L.; Metzger, R.M., *Synlett.*, 301 (1991). Bando, P.; Martín, N.; Segura, J.L.; Seoane, C.; Ortí, E.; Viruela, P.M.; Viruela, R.; Albert, A.; Cano, F.H., *J. Org. Chem.*, **1994**, *59*, 4618.
9. Watson, W.H.; Eduok, E.E.; Kashyap, R.P.; Krawiec, M., *Tetrahedron*, **1993**, *49*, 3035.
10. Adam, M.; Müllen, K. *Adv. Mater.* **1994**, *6*, 439.
11. Gemmell, C.; Janairo, G.C.; Kilburn, J.D.; Ueck, H.; Underhill, A.E., *J. Chem. Soc. Perkin Trans. 1*, **1994**, 2715.
12. Charlton, A.; Hill, C.A.S.; Underhill, A.E.; Malik, K.M.A.; Hursthouse, M.B.; Kraulov, A.I.; Moller, J., *J. Mater. Chem.*, **1994**, *4*, 1861.
13. McHale, D.; Mamalis, P.; Marzinkiewicz, S.; Green, J., *J. Chem. Soc.*, **1959**, 3358.
14. Jacob, P.; Calley, P.S.; Shulgin, A.T.; Castagnoli, N.; *J. Org. Chem.*, **1976**, *41*, 3627.
15. Snyder, C.D.; Rappoport, H, *J. Am. Chem. Soc.*, **1976**, *41*, 3627.
16. Errauriz, B.; Tapia, R.; Valderrama, J.A., *Tetrahedron Lett.*, **1985**, *26*, 819.
17. Analytical and spectroscopic data are in full agreement with the proposed structures. Selected spectroscopic data for **12**: M.p. (°C): 60. IR (KBr): ν = 2951, 2925, 2878, 1655, 1590, 1483, 1306, 1024 cm^{-1}. ^1H-NMR (250 MHz, $CDCl_3$): δ = 6.79 (s, 2 H), 4.12 (s, 4 H), 2.71 (t, 4 H), 1.51 (quint, 4 H), 1.37-1.19 (m, 12 H), 0.82 (t, 6 H). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 184.9, 140.1, 136.6, 130.5, 127.7, 110.3, 109.1, 36.4, 31.3, 30.5, 29.7, 28.2, 22.5, 14.0. Anal. Calcd. for $C_{26}H_{32}S_8O_2$ (%): C 49.37, H 5.06, S 40.51. Found: C 49.44, H 4.89, S 40.58.
18. Ikeda, K.; Kawabata, K.; Tanaka, K.; Mizutani, M. *Synth. Met.*. **1993**, *56*, 2007.

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