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Synthesis and Electrochemistry of Soluble Double-Bridged Tetrathiafulvalene (TTF)-*p*-benzoquinone Dyads

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Abstract : The synthesis of novel soluble unsymmetrically substituted TTF derivatives as precursors for the preparation of novel TTF-based donor-bridge-acceptor dyads is reported. Substitution on the acceptor *p*-benzoquinone moiety has a strong influence on the reduction potentials in compounds **18** which, however, do not show the presence of a charge transfer band in the electronic spectra. The cyclic voltammetry measurements reveal two oxidation waves for the TTF moiety and a third oxidation wave assigned to the hydroquinone moiety in **16** and **17**. Compounds **18** show, in addition to the TTF oxidation waves, the presence of the reduction wave corresponding to the quinone moiety. The spectroelectrochemical study indicates the step formation of cation-radical and dication of the TTF fragment.

1. Introduction

Organic molecules containing both electron donor and acceptor moieties constitute a very promising field of study due to the interesting optical and electronic properties they exhibit. Molecular electronic devices,[1] nonlinear optical materials (NLO),[2] and artificial photosynthetic models[3] have been proposed as potential applications for these donor-acceptor compounds.

We have recently reported the synthesis, together with a detailed study of the structural, optical and electrochemical properties of novel donor-acceptor systems derived from tetracyano-*p*-quinodimethane (TCNQ) and dicyano-*p*-quinonediimine (DCNQI) containing benzo[b]dithiin (**1**), benzo[b]oxathiin (**2**) and benzo[b]phenoxazine (**3**) as weak donor moieties.[4] (Figure 1)

These compounds give rise to both stable cations and anions and show semiconducting behavior. Their donor-acceptor nature is further evidenced by the low energy absorption band present at around 500-600 nm.

In order to improve the donor-acceptor properties exhibited by the previously reported compounds[4] (**1-3**), the heterocyclic benzo[b]dithiin, benzo[b]oxathiin and benzo[b]phenoxazine donor moieties in **1**, **2**, and **3**, respectively, were substituted by the stronger donor tetrathiafulvalene (TTF). We have recently reported our preliminary results on this type of compounds.[5] In this paper we report the synthesis and electrochemistry of novel *p*-benzoquinone-TTF containing single-component donor-acceptor organic compounds. Substitution on

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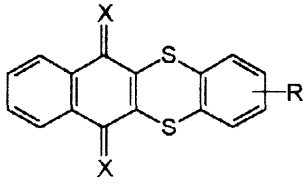
the *p*-benzoquinone ring has a striking influence on the acceptor ability of this moiety and, consequently, on the donor-acceptor interactions in these compounds.



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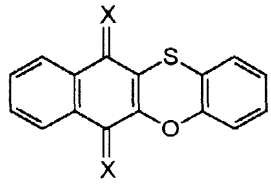
1b: X = $C(CN)_2$
1c: X = N-CN



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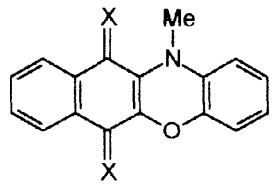

3a: X = O
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3c: X = N-CN

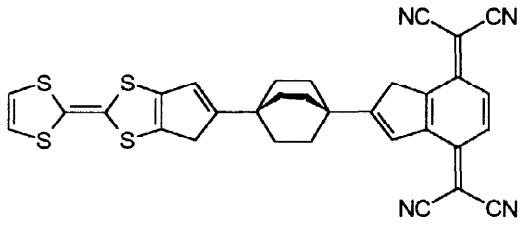

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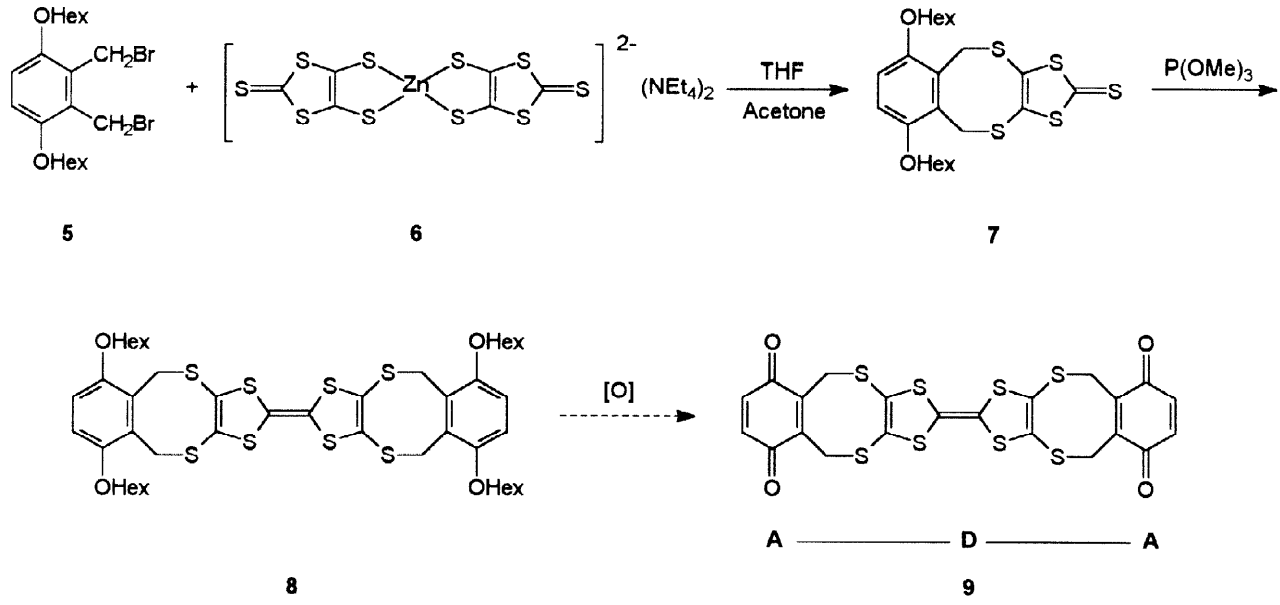
Figure 1

TTF derivatives are among the most widely used donors in the preparation of two-component conducting and superconducting organic charge-transfer complexes and ion-radical salts.[6] However, the synthesis of covalently linked donor-σ-acceptor systems bearing the TTF unit as the donor moiety has been less studied despite the interest they have for the preparation of molecular electronic devices.[7] Thus, the Aviram-Ratner molecular rectifier formed by TTF-σ-TCNQ (**4**) (Figure 1) which was proposed over twenty years ago has not yet been synthesized[8] although some related analogues with different sigma bridges and more accessible donors have been reported.[9] In this regard, the first experimental evidence of rectification in a molecule has just been described.[10]

Our synthetic plan towards the synthesis of covalently linked donor-σ-acceptor systems involves the preparation of molecules which contain the TTF molecule attached to a quinone moiety which, in turn, can be used as precursors for other stronger acceptor moieties, e.g. the TCNQ and DCNQI units.[11]

2. Synthetic strategies

In the beginning of our project, we designed the four step synthesis depicted in Scheme 1 in order to obtain the acceptor (A) - donor (D) - acceptor (A) molecule 9 which contains two quinone moieties covalently linked to a TTF unit. Thiones of type 7 are available by reaction of 1,4-bis(alkoxy)-2,3-bis(bromomethyl)benzene (5)[12] with bis(tetraethylammonium)bis(2-thioxo-1,3-dithiole-4,5-dithiolate)zincate (6).[13] In the following reaction, it is necessary to use derivatives of the thione 7 with solubility-improving substituents in order to perform the triethyl phosphite-induced coupling reaction. Thus, it was not possible to obtain the TTF derivative 8 from the dimethoxisubstituted thione 7 while the employment of the dihexyloxy substituted thione allowed the obtention of TTF derivative 8 as it was previously reported by Müllen et al.[12]



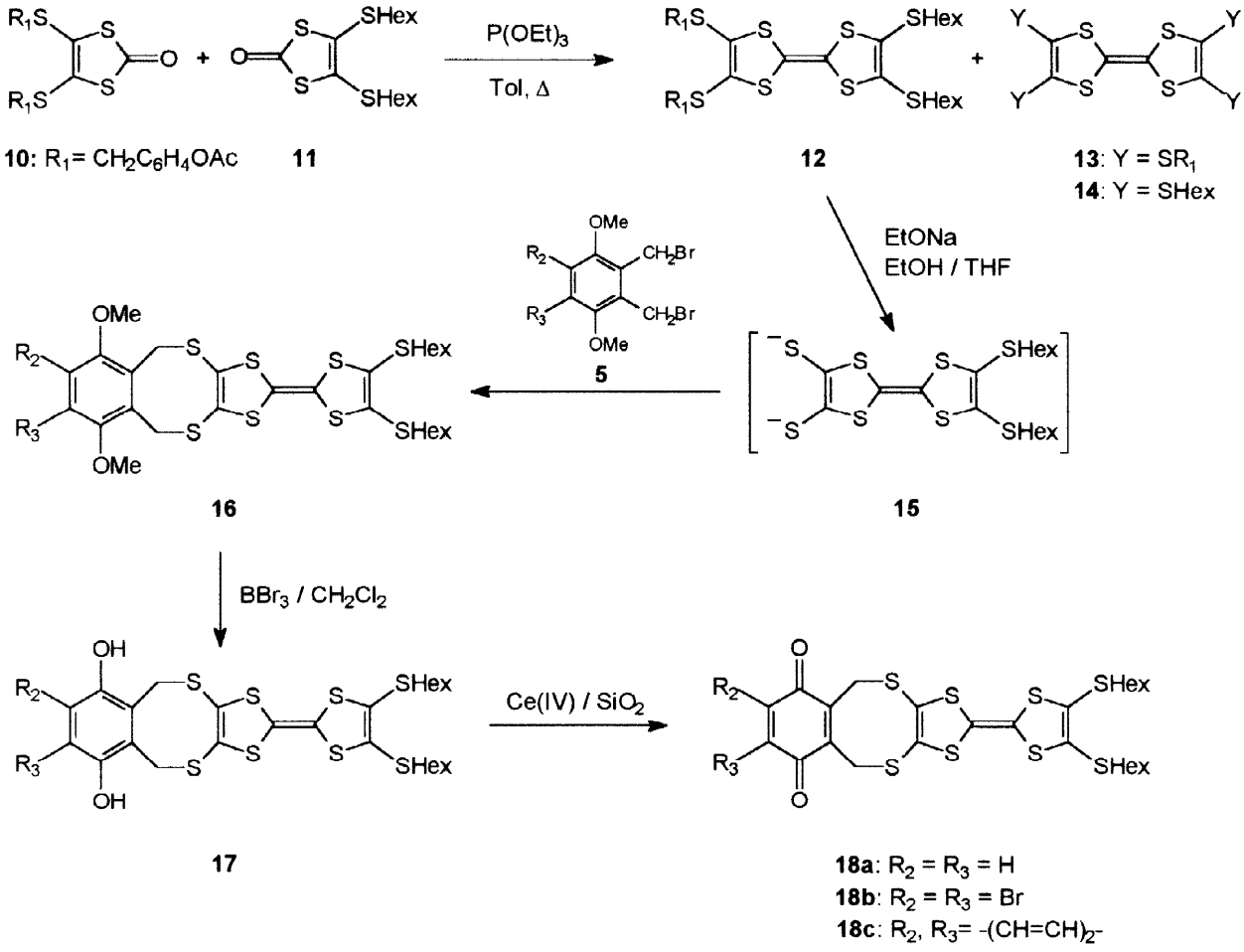
Scheme 1

We did not succeed in the isolation and characterization of 9 by further oxidation of the dihexyloxysubstituted 8, probably as a consequence of the lack of solubility of the target molecule (9) when the solubilizing hexyloxy substituents are removed. Thus, treatment of 8 with different oxidizing agents such as ceric ammonium nitrate (CAN),[14] silver oxide in nitric acid[15] or manganese(IV) oxide[16] afforded to complex mixtures from which no characterizables product could be isolated.

In an attempt to solve the solubility problems, we decided to incorporate solubilyzing alkoxy chains in a different position of the molecule in order to avoid its further elimination in the oxidation process. With this

aim, we designed the synthetic route depicted in Scheme 2 in which the target molecules contain a quinone moiety covalently linked to a dihexylthio-substituted tetrathiafulvalene.

In contrast to the above acceptor-donor-acceptor system **9**, the obtention of the new target molecules **18** involves the preparation of unsymmetrical TTFs. The synthesis of this type of compounds is difficulted by the lack of general routes to them[17] in addition to the difficulties in the preparation of 1,3-dithiole-2-one or 1,3-dithiole-2-thione bearing suitable protecting groups compatible with the available cross-coupling methods.[18]



Scheme 2

We have overcome these difficulties by using the *p*-acetoxybenzyl protecting group which has been reported to be stable during the cross-coupling reaction and easily removed under mild basic conditions.[19] Thus, the desired unsymmetrical TTF derivative **12**, together with the two symmetrically substituted derivatives **13** and **14**, were prepared from a phosphite mediated cross-coupling reaction of equimolecular amounts of the *p*-

acetoxybenzyl diprotected oxone **10**[19] and 4,5-dihexylthio-1,3-dithio-2-one **11**[20] which had been previously obtained from the $[Zn(dmit)_2](Et_4N)_2$ complex (**6**) according to previously described procedures. These three TTF derivatives (**12**, **13** and **14**) could be conveniently separated by flash column chromatography and isolated analytically pure.

Treatment of compound **12** with a sodium ethoxide solution in dry ethanol and THF under inert atmosphere at -10 °C yielded the free dithiolate **15** which was successfully trapped with differently substituted 2,3-bis(bromomethyl)-1,4-dimethoxybenzene **5** to afford the novel TTF derivatives **16a-c**.

Further treatment of TTF derivatives **16** with boron tribromide in dry dichloromethane at room temperature led to the cleavage of the alkyl ethers while the TTF moiety remains unaltered. Finally, hydroquinone derivatives **17** can be easily oxidized either with commercial bleach (5 %) or with CAN to yield the target molecules **18** with a D-A pattern. Compounds **18** were purified by flash chromatography on silica gel. The hydroquinone derivative **17c** could not be isolated since treatment of the dimethoxisubstituted derivative **16c** with boron tribromide yielded directly the quinonic system **18c**.

In contrast to other carbonyl-bridged TTFs,[21] the presence of the hexyl chains attached to the TTF moiety in **18a-c** led to highly soluble compounds in common organic solvents which can be completely characterized by IR, NMR spectroscopy, cyclic voltammetry and UV-Vis spectroscopy.

The redox properties of the new molecules were determined by cyclic voltammetry measurements carried out in methylene dichloride at room temperature with tetrabutylammonium perchlorate as the supporting electrolyte. The half-wave redox potentials measured are listed in Table 1. Redox potentials of bis-ethylenedithiotetrathiafulvalene (BEDT-TTF) and *p*-benzoquinone measured under identical conditions are included for comparison purposes.

All compounds show the presence of two oxidation waves to form the cation radical and dication of the TTF fragment. The oxidation potential values confirm the expected anodic shift, related to TTF, caused by the presence of the alkylthio groups linked to the TTF moiety.[22] Compounds **16** and **17** show an additional irreversible oxidation wave corresponding to the dimethoxybenzene and hydroquinone moiety respectively. Compared with the dimethoxybenzene derivative **16a**, fusing a benzene ring to the dimethoxybenzene system in **16c** provokes a shift to less positive value of the third oxidation wave as a consequence of the more electron rich character of the naphthalene moiety in comparison with the benzene ring. On the other hand, introduction of two bromine atoms in the dimethoxybenzene ring lowers this third oxidation wave to such an extent that it can not be observed within the window of the solvent.

Table 1. Redox Potentials of Novel Compounds **16-18**

Compound	$E^1_{1/2}$ ox[a]	$E^2_{1/2}$ ox[a]	E^3 ox[a]	$E_{1/2}$ red[a]
16a	0.529	0.835	1.606	-
16b	0.571	0.848	-	-
16c	0.554	0.858	1.434	-
17a	0.481	0.742	1.420	-
17b	0.532	0.854	-	
18a	0.595	0.860	-	-0.394
18c	0.596	0.872	-	-0.424
BEDT-TTF	0.524	0.906	-	-
***p*-benzoquinone**	-	-	-	-0.466

[a] In volts *vs.* SCE ; solvent : CH_2Cl_2 ; supporting electrolite : NBu_4ClO_4 ; working electrode : GCE ; scan rate : 0.2 Vs^{-1}

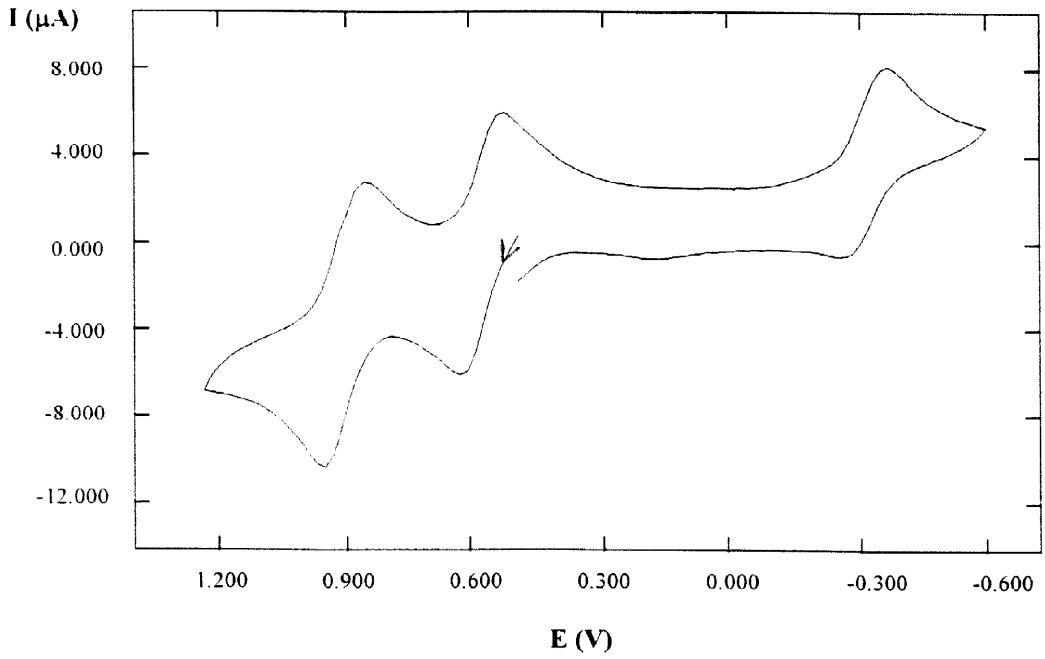


Figure 2. Voltammogram of compound **18a** at 0.2 $V.s^{-1}$

This third oxidation wave is not observed in the quinone containing analogues **18**. Instead, they exhibit a reversible wave at a negative potential value corresponding to the reduction of the *p*-benzoquinone (in

18a, Figure 2) and 1,4-naphthoquinone (in **18c**) moieties. Due to its extremely low solubility it was not possible to obtain good voltammograms of the dibromine substituted derivative **18b**. This fact contrasts with the cyclic voltammetry study of other previously reported TTF quinones which did not show the oxidation waves corresponding to the donor fragment[18] and is in agreement with the redox behavior observed by Müllen and Frenzel for Donor-Acceptor-Donor systems in which two TTF moieties are directly fused to a *p*-benzoquinone system[23] in which both the quinonic and the TTF moieties preserve their own electroactive character within the molecule.

We have also carried out the spectroelectrochemical study of compound **18a** (CH_2Cl_2 / 0.1 M tetrabutylammonium perchlorate) using a Pyrex cell and ITO electrodes in a sandwich configuration of the general type described by De Angelis and Heineman[24] with a potential range from 0 to 1500 mV. During the spectroelectrochemical investigation, over the potential range of the first oxidation wave observed in the CV for the TTF moiety, new absorptions at 450 and 800 nm appears while the absorption at 332 nm corresponding to the neutral molecule decreases. These new absorptions can be reasonably assigned to the radical cation. The redox couple was converted from one oxidation state to another by a series of incrementally applied potentials (potential steps of 100 mV) ; each potential was maintained for 30 seconds so that no further absorption change occurred.[25] By further increasing the potential, the new absorptions become 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 occur. This new and intensive absorption is assigned to the formation of the dication of the TTF moiety, being the sole band above 1100 mV.

Thus, during the oxidation process the spectrum of the neutral TTF derivative is converted first to the radical cation spectrum with isosbestic point at 360 nm and second to the dication spectrum with isosbestic points at 517 and 754 nm. In Figure 3 are depicted the electronic spectra of the neutral molecule, the radical cation and dication.

If the applied potential is then varied in the negative direction, first the radical cation spectrum is completely restored, and finally the spectrum of the neutral TTF is obtained as correspond to the two reversible one-electron processes observed in the CV measurements. Spectra were recorded over the range of 300-1500 nm, but beyond 800 nm no absorption change occur.

It is worth to mention that no charge transfer band has been observed in the electronic spectrum carried out for the quinone bridged TTF systems. This fact contrasts with the results that we obtained with the *p*-benzoquinone, TCNQ and DCNQI systems that contain benzo[b]dithiin (**1**), benzo[b]oxathiin (**2**) and benzo[b]phenoxazine (**3**) (Figure 1) in which charge transfer bands in the region between 500 and 760 nm could be observed.[3, 4] Müllen and Frenzel also observe a charge transfer band between 780 and 880 nm in Donor-Acceptor-Donor systems in which two TTF moieties are directly fused to a *p*-benzoquinone system[26] when measurements are carried out in solution and at 1040 nm in the solid state.

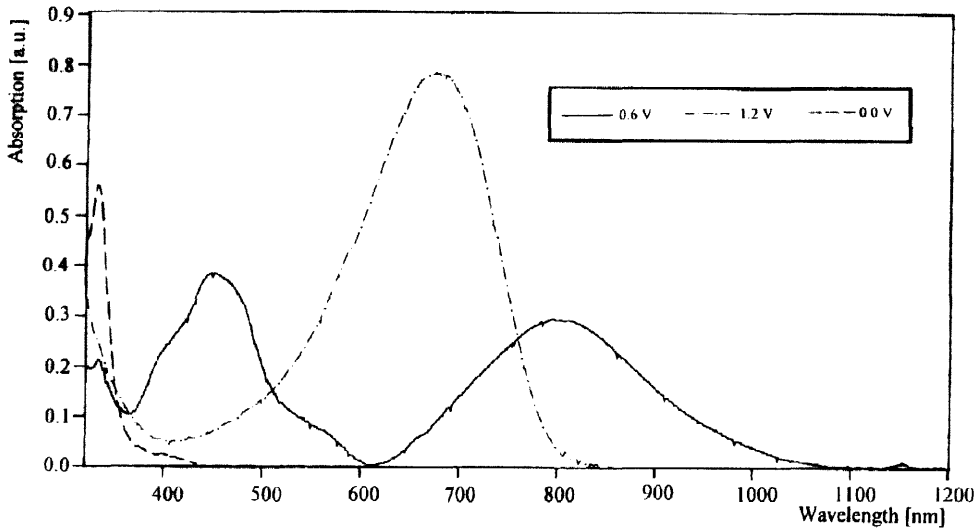


Figure 3. Electronic spectra of neutral (– – –), radical cation (——) and dication (– · – ·–) of **18a** (CH_2Cl_2 / 0.1 M tetrabutylammonium perchlorate with a Pyrex cell and ITO electrodes).

Considering that our previously reported molecules (**1**, **2** and **3**) and those reported by Müllen have both donor and acceptor moieties directly attached with no spacer in between, the presence of the methythio bridge in donor-σ-acceptor systems **18** removing far away both donor and acceptor units of a through space interaction, could be the reason for the absence of a charge transfer band in the electronic spectra of these compounds in the region below 1500 nm.

In summary, we have carried out the synthesis and study of the electrochemical properties of novel donor-acceptor dyads formed by soluble TTF molecules covalently attached through two methylthio bridges to differently substituted *p*-benzoquinones. The synthetic strategy for the preparation of the target molecules is based on the construction of the unsymmetrical TTF derivative **12** bearing *p*-acetoxybenzyl protecting groups, from which generation of dithiolate **15** allows the further preparation of novel unsymmetrical TTFs which can be transformed into the respective donor-acceptor dyads.

The CV data reveal the presence of both donor and acceptor chromophores which behave independently preserving their own redox character. The spectroelectrochemical study show the consecutive formation of cation-radical and dication of the TTF moiety of **18a** by application of variable potentials. Interestingly, no charge transfer interaction is observed in the electronic spectra of compounds **18**. In this regard, stronger electron-acceptors would be needed in order to decrease the difference between the reduction and oxidation potentials of both moieties. Work is in progress directed to the preparation of the respective TCNQ and DCNQI derivatives.

Experimental section

All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 257 spectrometer. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 3 instrument. NMR spectra were determined with a Varian XL-300 spectrometer, and elemental analyses were performed on a Perkin-Elmer CHN 2400 apparatus.

Cyclovoltammetric measurements were performed on a EG & PAR Versastat potentiostat using 250 Electrochemical Analysis software. A Metrohm 6.0840.C10 glassy carbon electrode was used as indicator electrode in voltammetric studies.

1,4-Bis(alkoxy)-2,3-bis(bromomethyl)benzene (**5**),[9] bis(tetraethylammonium)bis(2-thioxo-1,3-dithiole-4,5-dithiolate)zincate (**6**),[10] 4,5-(*o*-xylylendithio)-2-thioxo-1,3-dithiole derivatives (**7**),[9] tetrathiafulvalene derivative **8**,[9] *p*-acetoxybenzyl diprotected 4,5-dithiole-1,3-dithiol-2-one (**10**)[15] and 4,5-dihexylthio-1,3-dithiol-2-one (**11**)[17] were synthesized by following methods previously reported in the literature.

Phosphite mediated cross-coupling reaction of p-acetoxybenzyl diprotected oxone (10) and 4,5-dihexylthio-1,3-dithiol-2-one (11)

5.48 g (14.2. mmol) of 4,5-dihexylthio-1,3-dithiol-2-one (**11**) and 6.788 g (14.2 mmol) of the diprotected oxone (**10**) were dissolved in 14 mL of dry toluene. Triethyl phosphite (9.72 mL) was added and the reaction mixture was heated to reflux under nitrogen atmosphere for 24 hours. After cooling, the reaction mixture was filtered off, the solvent was removed under vacuum and the crude product was chromatographed (silica gel). The first fractions of the column (silica gel, eluted with 20 % CH_2Cl_2 in hexane) contained 4,4',5,5'-tetrakis(hexylsulfanyl)tetrathiafulvalene **14** (2,803 g, 59 %) as a red oil. The next fraction contained the desired 4,5-bis(*p*-acetoxybenzylsulfanyl)-4',5'-bis(hexylsulfanyl)tetrathiafulvalene **12** (3.059 g, 27 %) as a red solid. Finally (eluting with CH_2Cl_2) tetraprotected TTF **13** (2,486 g, 38 %) was obtained as an orange solid.

4,5-Bis(p-acetoxybenzylsulfanyl)-4',5'-bis(hexylsulfanyl)tetrathiafulvalene (*12*) : M.p. : 90 °C ; IR (KBr) : ν = 2924, 2854, 1763, 1508, 1373, 1230 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.25 (d, 4H, arom.), 7.03 (d, 4H, arom.), 3.85 (s, 4H, -S-$\underline{CH_2}$-arom), 2.82 (t, 4H, -S-$\underline{CH_2}$-CH_2), 2.27 (s, 6H, $\underline{CH_3}$-CO-), 1.61 (m, 4H, -CH_2-), 1.46-1.26 (m, 12H, -CH_2-CH_2-CH_2-), 0.89 (t, 6H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 169.2, 150.1, 134.2, 130.1, 129.2, 127.7, 121.7, 111.4, 109.2, 40.1, 36.3, 31.3, 29.7, 28.8, 22.5, 21.1, 14.0. M.S., m/z (%) : 796 (M^+, 100), 710 (4), 647 (18), 614 (39), 498 (75), 411 (34). Anal. calcd. for $C_{36}H_{44}S_8O_4$ (%) : C = 54.27 ; H = 5.53 ; S = 32.16 ; Found : C = 54.50 ; H = 5.40 ; S = 32.43. UV-Vis (CH_2Cl_2) : λ_{max} = 392, 331, 315 nm.

Compound 16a : A solution of sodium ethoxide in ethanol (0.319 g of Na in 28 mL of ethanol) was added to a solution of the diprotected TTF **12** (3.138 g, 3.94 mmol) in dry THF (56 mL) at -10 °C under nitrogen. The mixture was stirred for 30 min during which time a deep red solution was formed. Then, a solution of 1.28 g (3.94 mmol) of the dibromomethylderivative **5a** in THF (28 mL) was added and the reaction was allowed to warm to room temperature. The mixture was concentrated under reduced pressure, redissolved in dichloromethane ,washed with water and dried over Na_2SO_4. After removal of the solvent, the crude product was chromatographed (silica gel, eluting with 20 % CH_2Cl_2 in hexane) to yield 1.72 g (66 %) of **16a** as a yellow solid. M.p. : 130 °C ; IR (KBr) : ν = 2951, 2926, 2856, 2829, 1485, 1464, 1261, 1204 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 6.83 (s, 2H, arom.), 4.32 (s, 4H, -S-$\underline{CH_2}$-arom), 3.83 (s, 6H, OMe), 2.77 (t, 4H, -S-$\underline{CH_2}$-CH_2), 1.57 (m, 4H, -CH_2-), 1.36-1.18 (m, 12H, -CH_2-CH_2-CH_2-), 0.88 (t, 6H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 151.3, 130.8, 127.6, 124.9, 111.5, 110.4, 109.3, 56.7, 36.3, 31.5, 31.3, 29.7, 28.2, 22.5, 14.0. M.S., m/z (%) : 662 (M+, 12), 464 (6), 378 (12), 366 (79), 322 (33), 266 (75) 197 (100), 179 (86). Anal. calcd. for $C_{28}H_{38}S_8O_2$ (%) : C = 50.76 ; H = 5.74 ; S = 38.77 ; Found : C = 51.05 ; H = 5.46 ; S = 38.75. UV-Vis (CH_2Cl_2) : λ_{max} = 411, 332, 312 nm.

By following the same experimental procedure **16b** and **16c** were prepared from diprotected TTF **12** by reaction with the respective dibromomethylderivatives **5b** and **5c**.

Compound 16b: Yield: 70 %. M.p. : 154 °C ; IR (KBr) : ν = 2953, 2923, 2851, 1449, 1383, 1026, 944, 888 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 4.35 (s, 4H, -S-$\underline{CH_2}$-arom), 3.93 (s, 6H, OCH_3), 2.77 (t, 4H, -S-$\underline{CH_2}$-CH_2), 1.64-1.26 (m, 16H, -CH_2-$(CH_2)_2$-CH_2-), 0.88 (t, 6H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 160.3, 152.8, 130.5, 127.6, 121.6, 117.5, 112.7, 62.4, 36.2, 32.6, 31.2, 29.6, 28.1, 22.4, 13.9. Anal. calcd. for $C_{28}H_{36}Br_2S_8O_2$ (%) : C = 40.97; H = 4.42; Found : C = 41.22; H = 4.18. UV-Vis (CH_2Cl_2) : λ_{max} = 416, 336,282, 232 nm.

Compound 16c: Yield : 76 %. M.p. : 108 °C ; IR (KBr) : ν = 2960, 2940, 2870, 1770, 1510, 1380, 1225, 1200 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 8.07 (q, 2H, arom.), 7.55 (q, 2H, arom), 4.53 (s, 4H, -S-$\underline{CH_2}$-arom), 4.04 (s, 6H, OMe), 2.75 (t, 4H, -S-$\underline{CH_2}$-CH_2), 1.57-1.26 (m, 16H, -CH_2-$(CH_2)_2$-CH_2-), 0.86 (t, 6H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 150.0, 134.1, 130.4, 130.1, 129.1, 127.7, 121.7, 112.5, 109.2, 40.0, 36.2, 31.3, 29.7, 28.2, 22.5, 21.2, 14.0. Anal. calcd. for $C_{32}H_{40}S_8O_2$ (%) : C = 53.90; H = 5.65; S =; Found : C = 54.23; H = 6.05. UV-Vis (CH_2Cl_2) : λ_{max} = 398, 332, 312, 234 nm.

General procedure for the cleavage of ethers 16

Compound **17a**: A solution of boron tribromide (1M in dichloromethane, 1.51 mmol, 1.51 mL) was added to a solution of the dimethoxyderivative **16a** (500 mg, 0.76 mmol) in dry dichloromethane (15 mL) at room temperature. After 24 hours the mixture was shaken with water to hydrolize the excess reagent and boron

complexes. The mixture was extracted three times with 10 mL of diethyl ether, the combined organic layers were dried over magnesium sulfate and the solvent was removed under vacuum. Flash chromatography (silica gel, eluting with dichloromethane) of the residue thus obtained yielded 194 mg (40 %) of **17a**. M.p.: 140 °C ; IR (KBr) : ν = 3270, 2950, 2925, 2850, 1485, 1455, 1250, 1150, 970, 890, 810 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 9.07 (s, 2H, OH), 6.61 (s, 2H, arom.), 4.32 (s, 4H, -S-$\underline{CH_2}$-arom) , 2.79 (t, 4H, -S-$\underline{CH_2}$-CH_2), 1.59 (q, 4H, -CH_2-), 1.41-1.29 (m, 12H, -CH_2-CH_2-CH_2-), 0.89 (t, 6H, CH_3). M.S. (F.D.) : 633.9. Anal. calcd. for C_{26} $H_{34}S_8O_2$ (%) : C = 49.21 ; H = 5.36 ; S = 40.38 ; Found : C = 49.45 ; H = 5.28 ; S = 40.15. UV-Vis (CH_2Cl_2) : λ_{max} = 411, 331, 317 nm.

Compound 17b : Following the above general procedure and using compound **16b** as starting material, tetrathiafulvalene derivative **17b** was obtained as a red solid. Yield : 30 %. M.p. : 170 °C ; IR (KBr) : ν = 3490, 2970, 2940, 2860, 1440, 1275, 890, 740 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 5.45 (s, 2H, OH), 4.37 (s, 4H, -S-$\underline{CH_2}$-arom), 2.77 (t, 4H, -S-$\underline{CH_2}$-CH_2), 1.57-1.19 (m, 16H, -CH_2-$(CH_2)_2$-CH_2-), 0.83 (t, 6H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 145.5, 137.8, 128.3, 124.0, 112.1, 37.0, 33.3, 32.0, 30.4, 28.9, 23.2, 14.7. Anal. calcd. for C_{26} $H_{32}Br_2S_8O_2$ (%) : C = 39.39; H = 4.07. Found : C = 38.98; H = 4.39. UV-Vis (CH_2Cl_2) : λ_{max} = 428, 332, 313, 230 nm.

General procedure for the oxidation of hydroquinone-TTF derivatives **17** *:*

Method a : 63.4 mg (0.1 mmol) of the hydroquinone-TTF derivative **17a** were suspended in 1 mL of dry ethanol and 1 mL of 5 % commercial bleach were added. The solution was stirred vigorously for 30 min. After this time the solvent was removed under vacuum and the residue thus obtained was chromatographed (silica gel, eluting with dichlorometane) to yiel 34 mg (54 %) of **18a** as a green solid. M.p. : 60 °C ; IR (KBr) : ν = 2950, 2925, 2880, 1955, 1585, 1485, 1305, 1115, 1024 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 6.87 (s, 2H, quin.), 4.19 (s, 4H, -S-$\underline{CH_2}$-arom), 2.78 (t, 4H, -S-$\underline{CH_2}$-CH_2), 1.59 (m, 4H, -CH_2-) 1.37-1.19 (m, 12H, -CH_2-CH_2-CH_2-), 0.89 (t, 6H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 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 . M.S. (F.D.) : 631.8. Anal. calcd. for C_{26} $H_{32}S_8O_2$ (%) : C = 49.37; H = 5.06; S = 40.41; Found : C = 49.44; H = 4.89; S = 40.58. UV-Vis (CH_2Cl_2) : λ_{max} = 411, 332, 312 nm.

Method b: To a solution of 50 mg (0.08 mmol) of **17a** in 15 mL of dichloromethane were added 921 mg of the Ce(IV)/SiO_2 reagent (0.168 mmol of CAN). The mixture was stirred for 4 hours and during this period, three additional ammounts of 921 mg of the Ce(IV)/SiO_2 reagent were added. After this time the solid was filtered off and the residue was washed twice with 15 mL of dichloromethane. The crude product

obtained after evaporation of the solvent was chromatographed (silica gel, eluting with dichloromethane) to afford 12 mg (19 %) of **18a** as a green solid identical with the sample prepared by method a.

Compound 18b: Following the general procedure described for the synthesis of **18a**, and using **17b** as starting material, the dibromosubstituted quinone-TTF derivative **18c** was isolated as a green solid. Yield : 20 %. M.p. : 110 °C ; IR (KBr) : ν = 2960, 2940, 2860, 1675, 1565, 1265, 1145 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 4.41-4.05 (m, 4H, -S-$\underline{CH_2}$-arom), 2.87-2.52 (m, 4H, -S-$\underline{CH_2}$-CH_2), 1.58-1.18 (m, 16H, -CH_2-$(CH_2)_2$-CH_2-), 0.89 (t, 6H, CH_3). Anal. calcd. for $C_{26}H_{30}Br_2S_8O_2$ (%) : C = 39.49; H = 3.82; Found : C = 39.78; H = 3.97. UV-Vis (CH_2Cl_2) : λ_{max} = 410 (sh), 330 (sh), 260 nm.

Compound 18c : Following the above general procedure for the cleavage of ethers and using compound **16c** as starting material quinone derivative **18c** was isolated as a red solid. Yield : 30 %. M.p. : 96 °C ; IR (KBr) : ν = 2953, 2923, 2852, 1662, 1592, 1295, 729 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 8.14 (q, 2H, arom.) 7.79 (q, 2H, arom.), 4.33 (s, 4H, -S-$\underline{CH_2}$-arom), 2.76 (t, 4H, -S-$\underline{CH_2}$-CH_2), 1.57-1.26 (m, 16H, -CH_2-$(CH_2)_2$-CH_2-), 0.87 (t, 6H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 182.9, 142.3, 134.2, 131.6, 130.8, 127.5, 126.8, 36.3, 31.4, 31.3, 29.6, 28.2, 22.5, 14.0. M.S. (F.D.) : 681.8. Anal. calcd. for $C_{30}H_{34}S_8O_2$ (%) : C = 52.75; H = 5.02; Found : C = 52.99; H = 5.33 . UV-Vis (CH_2Cl_2) : λ_{max} = 430, 334, 306, 258, 252 nm.

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