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Synthesis of tetrahydroxy-π-extended tetrathiafulvalenes as new supramolecular redox building blocks

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Abstract—A novel *p*-quinonoid π-extended tetrathiafulvalene (exTTF) endowed with four hydroxy groups with different reactivity (phenol and alcohol) has been synthesized as a supramolecular redox building block. The redox properties, studied by cyclic voltammetry, reveal a strong donor ability and, despite the different substitution pattern on the 1,3-dithiole rings, only one oxidation wave involving two electrons to form the dication species. © 2003 Elsevier Science Ltd. All rights reserved.

One of the most appealing challenges in materials science is the creation of supramolecular materials in which the constituent units are highly regular molecular nanostructures. In this regard, learning how to create large supramolecular units, and the rules that mediate their macroscopic organization into functional materials, represents a fascinating prospect for technology.[1]

Among the different known strategies to construct supramolecular assemblies by using intermolecular interactions, hydrogen bonding is at the forefront due to its relative strength, high directionality and selectivity.[2]

Tetrathiafulvalene (TTF) derivatives endowed with substituents (hydroxy, amido, etc.) able to form intermolecular hydrogen bonding have been used for the construction of redox-active supramolecular systems with application in different areas.[3,4]

In contrast, suitably functionalized *p*-quinodimethane analogues of TTF (exTTF) have been much less studied for the construction of redox-active supramolecular ensembles despite the interesting electron donor properties they display.[5] This fact can be accounted for by the lack of available procedures for the synthesis of exTTFs bearing groups which can participate in intermolecular hydrogen bonding interactions.

To the best of our knowledge, only recently the chemical functionalization of extTTFs has been undertaken and some derivatives bearing a functional group on the central hydrocarbon skeleton (**1**)[6] or on the 1,3-dithiole ring (**2**[7], **3**[8]) have been reported (Chart 1).

Previously, hydroxy containing exTTF molecules were reported bearing one or two hydroxy groups on either the 1,3-dithiole ring or the hydrocarbon skeleton (**1**–**3**).

In this communication we describe the multistep synthesis of a novel tetrahydroxy-9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (**11**) as a suitable building block endowed with four hydroxy groups, located simultaneously on the carbo and heterocyclic rings, for further applications in the construction of exTTF-based supramolecular ensembles.

In order to gain a better understanding of electroactive compound **11**, the electrochemical properties as well as the molecular geometry determined by semiempirical calculations at the semiempirical PM3 level were carried out.

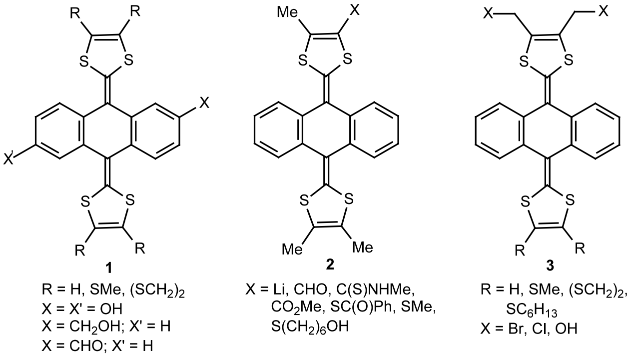

Chart 1.

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The synthesis of the exTTF-tetraol (**11**) was carried out as depicted in Scheme 1. Thus, dihydroxy substituted anthrone (**5**) was prepared from commercially available 2,6-dihydroxyanthraquinone (**4**) (anthraflavic acid) by refluxing in a solution of tin dichloride in hydrochloric acid as reducing system.[9] Compound **5** precipitates quantitatively in the reaction medium with a high purity.

Olefination reaction of the anion of the dihydroxyanthrone (**5**) with bis-hydroxymethyldithiolium salt (**6**), which was in turn prepared in a three-step synthetic procedure,[10] led to the tetrahydroxy derivative **7** in 54% yield. Introduction of the second dithiole ring in **7** requires protection of the hydroxy groups which was achieved by reaction with *tert*-butyldiphenylsilyl chloride. Further Wittig–Horner reaction of the tetrakis-protected tetraol **8** with phosphonate ester **9**[11] under basic conditions (LDA/THF) afforded the protected quinonoid-exTTF (**10**) as a stable yellow solid in 65% yield. Deprotection of **10** was carried out by treatment with tetrabutylammonium fluoride to give the 2,6-dihydroxy-9-(4,5-dihydroxymethyl-1,3-dithiol-2-ylidene)-10-(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (**11**) in 65% yield, which was purified by flash chromatography (silica gel) using hexane:ethyl acetate (1:9) as eluent.

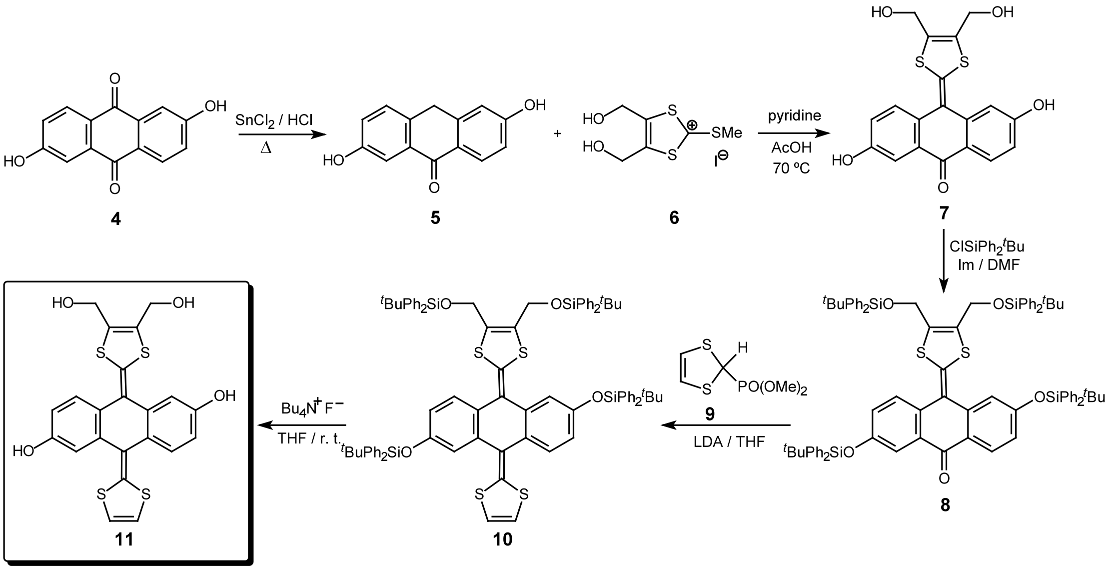
Compound **11** was poorly soluble in non-polar common organic solvents. All attempts to obtain a single crystal of **11** were unsuccessful and revealed the relatively low stability of this compound on air.

Tetrahydroxy TTF **11** and its precursors were fully characterized by using analytic and spectroscopic methods.[12] Thus, compounds **5**, **7** and **11** bearing hydroxy groups showed a broad band at around 3420–3215 cm^{-1} in the FTIR spectra which disappears in the hydroxy protected compounds **8** and **10**. The ^{1}H NMR spectrum of tetraol **11** showed, in addition to the expected aromatic signals, the protons of the dithiole ring as a singlet at 6.33 ppm and the methyleneprotons as two singlets at 4.23 and 4.24 ppm. The hydroxy protons were not observed in the spectrum registered in CD_3OD. However, these protons were observed when the spectrum was recorded in deuterated acetone, the phenolic hydroxy groups appearing as a broad signal at 8.7 ppm and the hydroxymethyl OH protons at 4.58 ppm. The OH groups were also detected in the precursor **7** registered in DMSO-d_6 at 10.65 and 9.98 ppm for the phenolic protons and as a broad signal at around 5.5 ppm for the remaining OH groups. The ^{13}C NMR spectrum of **11** showed as significant signals the methylene groups at 56.0 ppm.

The UV–vis spectrum of **11** shows the λ_{max} at 422 nm (CH_2Cl_2) similarly to the parent unsubstituted exTTF (**1**: $R=X=X'=H$, $\lambda_{max}=415$ nm, CH_2Cl_2). However, compound **7** showed a strong bathochromic shift ($\lambda_{max}=469$ nm) which corresponds to a charge-transfer transition from the donor 1,3-dithiole moiety to the acceptor carbonyl group, similarly to that observed for other related systems.[13]

Due to the interest of compound **11** as an electron donor building block for the preparation of electrically conducting materials with high dimensionality, as well as for the construction of supramolecular ensembles based on hydrogen bonding and π–π interactions, we determined the redox properties of **11** by cyclic voltammetry at room temperature. Table 1 shows the redox properties of **11** together with **7** and the parent exTTF (**1**: $R=X=X'=H$) for comparison purposes.

In contrast to the parent TTF, *p*-quinonoid π-extended TTFs showed the presence of a quasireversible oxidation wave involving a two-electron process to form the dication species.[14]



Scheme 1.

Compound **11** bearing the hydroxymethyl and hydroxy groups shows a quasireversible oxidation wave with the oxidation potential at 0.55 V. This value is anodically shifted 80 mV in comparison with the unsubstituted exTTF (Table 1). Thus, although a different substitution pattern is present in both 1,3-dithiole rings in **11**, only one oxidation wave is observed, which indicates that the presence of two hydroxymethyl groups do not alter significatively the electrochemical behaviour of the 1,3-dithiole ring.

Compound **7** showed an amphoteric redox behaviour exhibiting a quasireversible oxidation wave at remarkable more positive potential values, since only one 1,3-dithiole ring is present in the molecule, and a quasireversible reduction wave at −0.99 V, corresponding to the reduction of the carbonyl group.

Theoretical calculations carried out at semiempirical PM3 level on donor **11** predict a molecular geometry quite similar to other previously reported exTTF molecules with a butterfly-shaped structure with the central ring adopting a boat conformation.[15]

Distorsion from planarity (Fig. 1) can be described in terms of the angles α and γ (α corresponds to the angle formed by the outer benzene rings, and γ to the tilting of the dithiole units). These calculated angles (α=139.6° and γ=33.8°) are in good agreement with that observed experimentally for the X-ray data determined for the related tetramethylthio substituted exTTF (α=143.8° and γ=33.3°).[14]

Table 1. Cyclic voltammetry of novel compounds **7** and **11**[a]

Comp.	$E^1_{\text{ox (p a)}}$	$E^1_{\text{ox (p c)}}$	$E^1_{\text{red (p c)}}$	$E^1_{\text{red (p a)}}$	$\lambda_{\max}$ (nm)[b]
1	0.47	0.20	–	–	415
7	0.98	0.73	−0.99	−0.83	469
11	0.55	0.10	–	–	422

[a] Experimental conditions: THF as solvent, V versus SCE, GCE as working electrode, Bu_4NClO_4 (0.1 M) as supporting electrolite; 200 mV s^{-1}.

[b] In CH_2Cl_2.

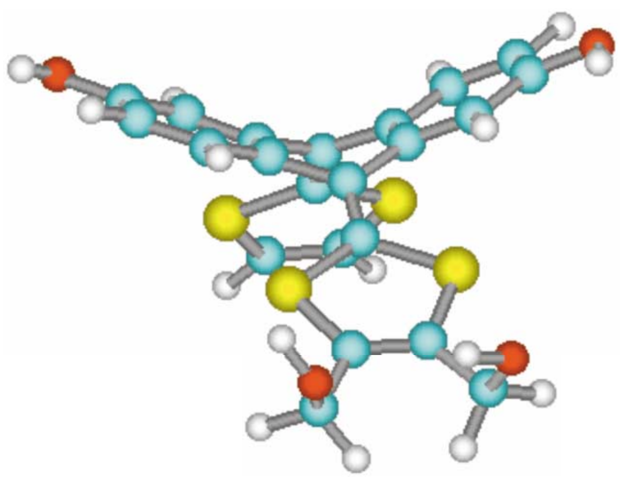


Figure 1. Minimum energy molecular geometry calculated (PM3) for compound **11**.

In summary, we have synthesized a novel exTTF system bearing four hydroxy groups with different nature and reactivity (alcohol and phenol) in a multistep synthetic procedure, as an appealing redox active building block for further applications in supramolecular and materials science. The redox properties determined by cyclic voltammetry show a good electron donor ability which can be used for the preparation of novel salts and charge-transfer complexes exhibiting a strong hydrogen bonding network in the solid state. Work is currently in progress in these directions.

Acknowledgements

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12. Selected spectroscopic data for **7**: 54% yield; mp 257–259°C; ^{1}H NMR (DMSO, 300 MHz) δ 10.65 (s, 1H, OH), 9.98 (s, 1H, OH), 7.96 (d, 1H, $J=8.6$ Hz, ArH), 7.73 (d, 1H, $J=8.5$ Hz, ArH), 7.45 (d, 1H, $J=2.7$ Hz, ArH), 7.16 (d, 1H, $J=2.2$ Hz, ArH), 7.11 (dd, 1H, $J_1=8.5$ Hz, $J_2=2.7$ Hz, ArH), 6.84 (dd, 1H, $J_1=8.6$ Hz, $J_2=2.2$ Hz, ArH), 4.33 (s, 4H, 2CH$_2$); ^{13}C NMR (DMSO, 75 MHz) δ 182.0 (CO), 144.4, 140.2, 138.3, 132.2, 130.5, 129.5, 126.4, 126.3, 115.5, 55.9 (2CH$_2$); FTIR (KBr) 3385 (OH), 2924, 2852, 1570 (CO), 1506, 1466, 1319, 1238, 1159, 1051, 1009, 822, 673 cm^{-1}; UV–vis/λ_{max} (nm, CH$_2$Cl$_2$): 249, 363, 469. Anal. calcd for $C_{19}H_{14}O_5S_2$: C, 59.05; H, 3.65. Found: C, 58.95; H, 3.99%.

    Selected spectroscopic data for **11**: 65% yield; mp 247–249°C; ^{1}H NMR (CD$_3$OD, 200 MHz) δ 7.37 (d, 1H, $J=8.3$ Hz, ArH), 7.31 (d, 1H, $J=8.3$ Hz, ArH), 6.98 (d, 1H, $J=2.4$ Hz, ArH), 6.93 (d, 1H, $J=2.4$ Hz, ArH), 6.58 (dd, 2H, $J_1=8.3$ Hz, $J_2=2.4$ Hz, ArH), 6.33 (s, 2H, 2CH), 4.24 (s, 2H, CH$_2$), 4.23 (s, 2H, CH$_2$); ^{1}H NMR (CD$_3$COCD$_3$, 200 MHz) δ 8.68 (bs, 2H, 2OH), 7.52 (d, 1H, $J=8.2$ Hz, ArH), 7.44 (d, 1H, $J=8.2$ Hz, ArH), 7.17 (d, 1H, $J=2.2$ Hz, ArH), 7.08 (d, 1H, $J=2.2$ Hz, ArH), 6.79 (dd, 2H, $J_1=8.2$ Hz, $J_2=2.2$ Hz, ArH), 6.56 (s, 2H, 2CH), 4.59 (s, 2H, 2OH), 4.37 (s, 4H, 2CH$_2$); ^{13}C NMR (DMSO, 75 MHz) δ 136.4, 134.6, 134.3, 129.3, 126.0, 125.1, 124.6, 123.5, 121.1, 118.0, 56.0; FTIR (KBr) 3385 (OH), 3067, 2922, 2345, 1724, 1655, 1551, 1518, 1444, 1280, 1049, 781, 756, 675, 644 cm^{-1}; UV–vis/λ_{max} (nm, CH$_2$Cl$_2$): 233, 356, 422. Anal. calcd for $C_{19}H_{14}O_5S_2$: C, 55.91; H, 3.41. Found: C, 56.31; H, 3.81%.

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