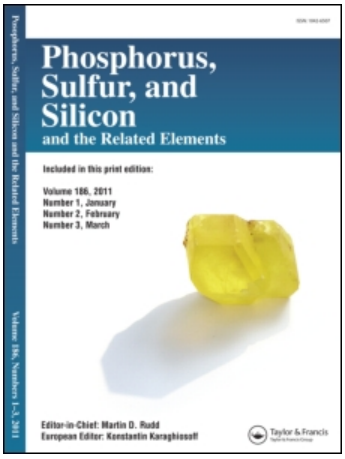

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ALDEHYDE FUNCTIONALIZATION IN THE TETRATHIAFULVALENE SERIES : TOWARDS NEW HIGHLY DIMENSIONAL ORGANIC MATERIALS DERIVED FROM SULFUR-RICH EXTENDED π-DONORS

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Abstract We describe the synthesis of giant analogs of TTF. Their powerful donor ability has been characterized by thin layer cyclic voltammetry. An unprecedented type of 2-D cation-radical salt has been obtained by electrooxidation.

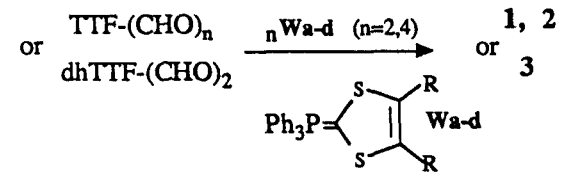
The ability of tetrathiafulvalene (TTF) derivatives to generate monodimensional (1-D) electroconductive salts is now well established.[1] In order to stabilize their metallic state at low temperature, chemists have to design new organic systems suitable to increase the dimensionality in the corresponding materials. The most famous case is the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) from which more than 15 different superconducting salts have been electrochemically grown.[2]

With this aim we have particularly focused on the introduction of i) S-rich substituents onto the TTF moiety, in order to quantitatively increase the intermolecular S...S contacts in the corresponding cation-radical salts, ii) $-CH_2OH$ functional groups which is prone to enhance the dimensionality thanks to H-bonds development.[3]

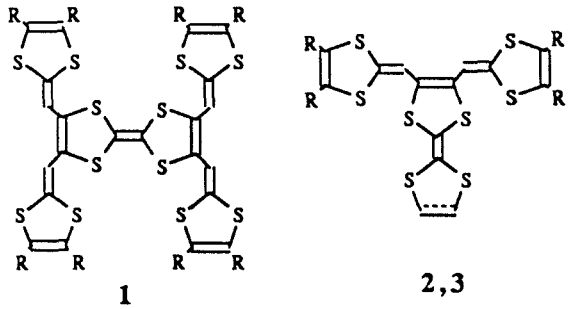
Our synthetic stategy involves the introduction of the aldehyde functionality onto the TTF framework.[4] Thanks to its high reactivity, this key function has allowed to reach a wide range of TTF derivatives,[4-5] and specially a very easy substitution by the above-mentioned substituents.

Compounds **1-2** [5a,b] were straight prepared thanks to fourfold or twofold Wittig olefinations of the corresponding polyformyl-TTF (or diformyl dihydro-TTF (dhTTF)-$(CHO)_2$ for **3**) with the P-ylids **Wa-d** bearing the 1,3-dithiol-2-yliden moiety [6] (Scheme).

The exceptional strong π-donor ability of these giant analogs of TTF has been evidenced by cyclic voltammetry i) both of the two successive $1e^-$ reversible redox processes of compounds **2** and **3** (i.e. **2a**; E^1_{ox}=0.22, E^2_{ox}=0.30 V/ SCE) are found at lower potentials than the first one of TTF itself; ii) compound **1** presents three successive $1e^-$, $1e^-$ and $2e^-$ reversible oxidation peaks (i.e. **1d**; E^1_{ox}=0.08, E^2_{ox}=0.17, E^3_{ox}=0.51V/ SCE; 1,1,2-trichloroethane as solvent), which implies a good stability of the cationic species up to $\mathbf{1}^{4+}$, quantitative coulometric determinations being run by thin layer cyclic



a : R = H; **b** : CO_2Me; **c**: R-R = $(CH=CH)_2$; **d**: $(CH_2-CH_2)_2$



1 2,3

SCHEME

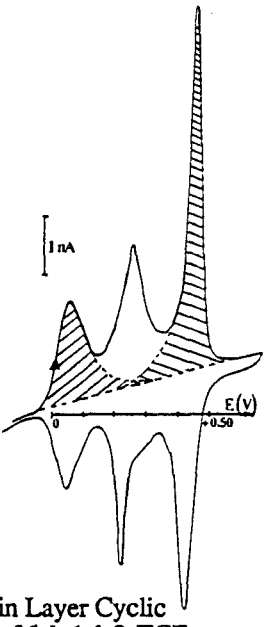


FIGURE Thin Layer Cyclic Voltammetry of **1d**, 1,1,2-TCE, Bu_4NPF_6 (1M), 5mV/sec; (/SCE).

voltammetry[7](figure). We have obtained nice black needles of (**3a**)(ClO_4) by electrocrystallization with Bu_4NClO_4 as supporting electrolyte. Crystallographic data of this salt are fully consistent with the formation of an unprecedented type of 2-D network characterized by an accumulation of *intra*- and *inter*chains contacts.[8]

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