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Hydroxyphenyl substituted tetrathiafulvalene vinylogues affording stable cation radical salts with unusual crystal structures

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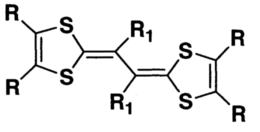
Abstract—TTF vinylogues containing hydroxyphenyl groups were newly prepared. They are stronger electron donors than BEDT-TTF and afforded their cation radical salts as single crystals upon electrochemical oxidation. X-Ray structure analysis has revealed their unusual crystal structures, where π-overlapping and hydrogen bonding play a crucial role in constructing them. © 2001 Elsevier Science Ltd. All rights reserved.

Crystal structure control as well as molecular design is of importance for the development of organic conductors. Tetrathiafulvalene (TTF) bearing hydroxy groups have been prepared to induce intramolecular hydrogen bonding.[1–3] Some derivatives afforded the charge transfer complexes[4] and cation radical salts[5–8] whose structures have hydrogen bonding networks. On the other hand, TTF vinylogues have attracted much attention since they are strong electron donors with small Coulombic repulsion owing to the extended π-conjugation.[9] We have recently found that the TTF vinylogues containing *o*-substituted phenyl groups at the vinyl positions afford cation radical salts with unusual crystal structures such as a two-dimensional columnar structure.[10–12] The formation of the structures could be attributed to the steric effect of the phenyl groups as well as the π-overlapping. As an extension of this work, we have now prepared TTF vinylogues with hydroxy groups at the phenyl groups and have succeeded in obtaining the cation radical salts as single crystals. We report here the unusual crystal structures, where hydrogen bonding in addition to the π-overlapping is involved in the intermolecular interactions.

We have found a facile synthetic method for TTF vinylogues involving oxidative coupling reaction of 1,4-dithiafulvenes.[10,11] According to this method, the dibenzo derivatives **1a**,**b** were prepared in moderate yields from 1,4-dithiafulvenes **2a**,**b**, which were obtained by Wittig reaction of a phosphonium salt with the corresponding benzaldehydes. On the other hand, bis-ethylenedithio derivatives **1c**,**d** were prepared by reaction of benzyloxy substituted derivatives **1e**,**f**, which were obtained from **2e**,**f**, with BBr_3, since **2c**,**d** could not be synthesized by the direct Wittig reaction of the corresponding benzaldehydes.



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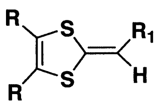

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a; R, R = $(CH=CH)_2$, R_1 = *o*-HOC_6H_4
b; R, R = $(CH=CH)_2$, R_1 = *p*-HOC_6H_4
c; R, R = SCH_2CH_2S, R_1 = *o*-HOC_6H_4
d; R, R = SCH_2CH_2S, R_1 = *p*-HOC_6H_4
e; R, R = SCH_2CH_2S, R_1 = *o*-$BzOC_6H_4$
f; R, R = SCH_2CH_2S, R_1 = *p*-$BzOC_6H_4$

Table 1. The oxidation potentials[a] of donors **1**

Donor	$E^1_{1/2}$ (V)	$E^2_{1/2}$ (V)	ΔE (V)[b]
1a	0.44	0.64	0.20
1b	0.50	0.61	0.11
1c	0.31	0.51	0.20
1d	0.38	0.49	0.11
1e	0.28	0.50	0.22
1f	0.40	0.50	0.10
BEDT-TTF	0.50	0.85	0.35

[a] 0.1 mol dm^{-3} $^nBu_4NPF_6$ in C_6H_5CN, Pt electrode, scan rate 100 mV s^{-1}, V versus SCE.
[b] $\Delta E = E^2_{1/2} - E^1_{1/2}$.

Keywords: electron donors; electrical conductors; thiafulvalenes; hydrogen bonding; X-ray crystal structures.

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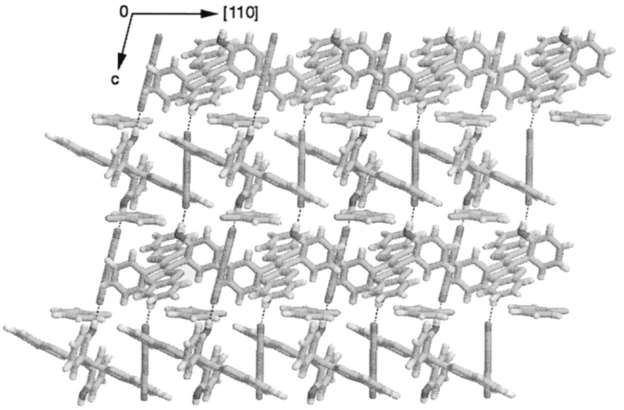

Figure 1. Crystal structure of **1a**·Au(CN)$_2$·PhCl viewed along the [1–1 0] direction. Dotted lines show the O–H···N hydrogen bonds.

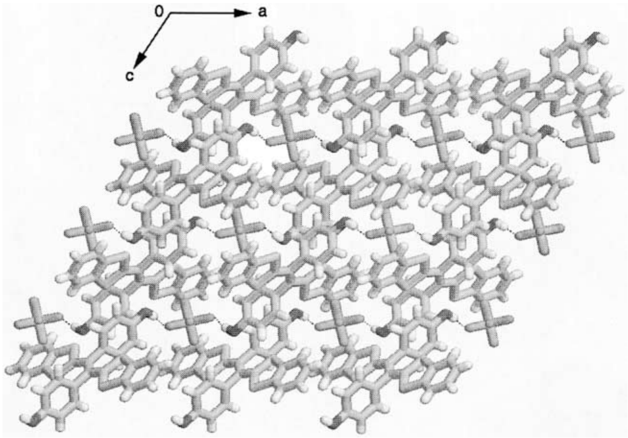

Figure 2. Crystal structure of **1b**·PF$_6$ viewed along the *b* axis. Dotted lines show the O–H···F hydrogen bonds.

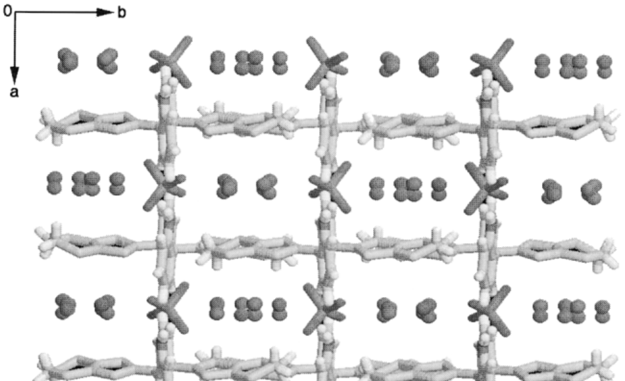

Figure 3. Crystal structure of **1c**·ReO$_4$·(H$_2$O)$_8$ viewed along the *c* axis.

The oxidation potentials of donors **1** measured by cyclic voltammetry are listed in Table 1. The first oxidation potentials are lower than that of BEDT-TTF, indicating that they are stronger electron donors than BEDT-TTF. The differences between the first and second oxidation potentials (ΔE) of the *o*-substituted phenyl derivatives are larger than those of *p*-substituted ones, indicating that the cation radical states of the former are more stable than those of the latter, as pointed out previously.[10]

The cation radical salts **1a**·Au(CN)$_2$·PhCl, **1b**·PF$_6$, and **1c**·ReO$_4$·(H$_2$O)$_8$ were obtained as single crystals by electrochemical oxidation of the donors in chlorobenzene. The stoichiometry of the donor and counter ion is all 1:1, indicating that the donor molecules are completely charged. The salts of **1a** and **1c** contain the solvent and water molecules, respectively. The salt of **1b** is the first example of single crystals of the cation radical salts of *p*-substituted phenyl derivatives. They exhibited semiconductive behavior due to the 1:1 composition [**1a**·Au(CN)$_2$·PhCl; $\sigma=5\times10^{-4}$ S cm^{-1} ($E_a=$ 0.21 eV), **1b**·PF$_6$; $\sigma=1\times10^{-3}$ S cm^{-1} ($E_a=0.15$ eV)].

The X-ray crystal structure analyses of the three salts were carried out.[†] The molecular structures of the donor molecules are similar to each other, where the TTF vinylogue skeleton is planar and the phenyl groups are almost orthogonal to it. The dihedral angles between the phenyl groups and 1,3-dithiole groups are 84.9, 89.9 and 85.5° for **1a**, **1b** and **1c**, respectively. It is noteworthy that the *para*-substituted derivative has a similar structure to those of the *ortho*-substituted ones. On the other hand, there is a diversity of crystal structures. In **1a**·Au(CN)$_2$·PhCl[‡] one donor molecule bridges the two molecules to avoid the steric hindrance of the phenyl groups (Fig. 1). Although the overlap pattern is similar to the two-dimensional columnar structure found in the *o*-fluoro substituted derivative,[10] the two 2D columns stacked toward different directions exist alternately, where solvent molecules are located between the columns. Hydrogen bonding between the

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[†] Reflection data for **1a**·Au(CN)$_2$·PhCl and **1c**·ReO$_4$·(H$_2$O)$_8$ were collected on a Rigaku R-AXIS IV imaging plate area detector with Mo Kα radiation ($\lambda=0.71070$ Å) at 296(2) K, and reflection data for **1b**·PF$_6$ were collected on an Enraf–Nonius CAD4 diffractometer using Cu Kα radiation ($\lambda=1.54178$ Å) at 296(2) K. No absorption correction was applied. All structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELX-97.[13] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in geometrically calculated positions and refined by using a riding model. Crystallographic data (excluding structure factors) for **1a**·Au(CN)$_2$·PhCl, **1b**·PF$_6$ and **1c**·ReO$_4$·(H$_2$O)$_8$ have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 160089–160091. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

[‡] Crystal data for **1a**·Au(CN)$_2$·PhCl: $C_{30}H_{18}AuN_2O_2S_4{\cdot}ClC_6H_5$, $M=$ 876.22, dark green plate, monoclinic, space group $C2/c$, $a=$ 17.880(6), $b=11.543(3)$, $c=17.752(15)$ Å, $\beta=112.13(4)°$, $V=3394(3)$ Å^3, $Z=4$, $D_c=1.715$ g cm^{-3}, $F(000)=1716$, $\mu=4.695$ mm^{-1}, crystal dimensions 0.50×0.10×0.05 mm, 7547 reflections collected, 2595 independent ($R_{int}=0.1066$), $R_1=0.0884$, $wR_2=0.2351$ for $I>2\sigma(I)$, $R_1=0.1149$, $wR_2=0.2665$, $S=1.131$ for all data.

OH and CN groups (O···N distance: 2.74 Å) is formed to lead to an infinite network. The **1b**·PF_6[§] structure is more complicated. While no π-overlapping of the donor molecules is observed, a network based on hydrogen bonding between the OH group and the F atom of the anion is formed (Fig. 2). The O···F distance is 2.86 Å. The *para*-position of the OH group seems to be important to construct such an infinite network. In contrast, **1c**·$ReO_4\cdot(H_2O)_8$[¶] has a one-dimensional columnar structure (Fig. 3). As pointed out previously, the ethylenedithio group is unfavorable for π–π overlap compared with the benzo one.[12] In this case the steric interaction between the phenyl groups produces a space with molecular distances of 8.6 and 9.7 Å, where water molecules are included. Hydrogen bonding is observed between the OH group and the O atom of the counter anion (O···O distance: 2.69 Å).

These results indicate that the TTF vinylogues containing OH groups afford cation radical salts with unusual crystal structures, where hydrogen bonding is formed between the OH groups and the counter ions.

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[§] Crystal data for **1b**·PF_6: $C_{28}H_{18}F_6O_2PS_4$, $M=659.63$, green prism, monoclinic, space group $C2/c$, $a=21.747(4)$, $b=9.5285(10)$, $c=15.212(3)$ Å, $\beta=118.061(12)°$, $V=2781.6(7)$ Å^3, $Z=4$, $D_c=1.575$ g cm^{-3}, $F(000)=1340$, $\mu=4.297$ mm^{-1}, crystal dimensions 0.25×0.10×0.05 mm, 2957 reflections collected, 2842 independent ($R_{int}=0.0251$), $R_1=0.0515$, $wR_2=0.1249$ for $I>2\sigma(I)$, $R_1=0.1236$, $wR_2=0.1630$, $S=1.013$ for all data.

[¶] Crystal data for **1c**·$ReO_4\cdot(H_2O)_8$: $C_{24}H_{18}O_{14}ReS_8$, $M=973.06$, dark green plate, monoclinic, space group $C2/c$, $a=17.839(5)$, $b=19.805(8)$, $c=13.868(3)$ Å, $\beta=121.641(16)°$, $V=4171(2)$ Å^3, $Z=4$, $D_c=1.549$ g cm^{-3}, $F(000)=1908$, $\mu=3.366$ mm^{-1}, crystal dimensions 0.35×0.15×0.05 mm, 5510 reflections collected, 2620 independent ($R_{int}=0.0756$), $R_1=0.0976$, $wR_2=0.2405$ for $I>2\sigma(I)$, $R_1=0.1506$, $wR_2=0.2859$, $S=1.106$ for all data.