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Oxidation of TTF Derivatives Using (Diacetoxyiodo)benzene: a General Chemical Route toward Cation Radicals, Dications, and Nonstoichiometric Salts

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For the past three decades, tetrathiafulvalene (TTF) derivatives have been the subject of intensive studies, mainly owing to their ability to form conducting and superconducting nonstoichiometric cation radical salts $R_4TTF_n\ X_m$.[1]

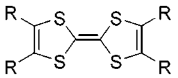
A vast majority of the nonstoichiometric TTF derived salts were prepared by the electrocrystallization technique.[1] Here we describe a general nonelectrochemical synthetic approach toward cation radical salts of the TTF derivatives, which provides unlimited quantities of the products and an efficient stoichiometry control. The utility of this method is demonstrated, in particular, by the chemical synthesis of the superconducting κ-$ET_2Cu(NCS)_2$ salt.

Whereas the electrochemical method is widely employed for producing monocrystalline nonstoichiometric salts, it involves several disadvantages, such as long reaction times (several weeks) and drastic limitations imposed on solvents and the amount of the target product (a few mg). In contrast, the chemical approach does not suffer from these restrictions and can theoretically afford unlimited quantities of materials.

To date, however, the nonelectrochemical syntheses of TTF salts are mostly based on the direct oxidation process: $TTF + ox \rightarrow TTF^{\cdot +} + red^-$, which implies the availability of the oxidized form ox corresponding to the desirable anion red^-. This approach is mostly limited to oxidation by halogens[2] and a number of salts of transition metal in their higher oxidation state (e.g., oxidation by $Cu^{II}(NCS)_2$,[3] giving the anion $[Cu^I(NCS)_2]^-$ or by Fe^{III} salts[4]).

A more general approach would involve oxidation of the TTF derivatives by an external oxidizing agent in the presence of an anion, ensuring formation of a highly soluble salt, from which a desirable product can be obtained by metathesis.

To our knowledge, the only known example of this approach is synthesis and further metathetical conversions of the moderately soluble $(TTF)_3(BF_4)_2$ salt, which was prepared by oxidation of **1a** with hydrogen peroxide in the presence of tetrafluoroboric acid.[5] A number of other TTF fluoroborates and perchlorates have also been synthesized by chemical oxidation, but these salts have not been used in metathesis reactions.[2,6] Cation radicals can also be generated by $AlCl_3$ or protic doping, but these methods have been used only for spectroscopic observations and not for isolation purposes.[7]



1a, R = H (TTF)
1b, R = Me (TMTTF)
1c, R = SMe (TMT-TTF)
1d, R+R = SCH_2CH_2S (ET)

Oxidation of TTFs using (hydroxytosyloxyiodo)benzene[8] is the most convenient for the preparative purposes since no solid byproducts form in the reaction. (Diacetoxyiodo)benzene was shown to be in equilibrium with phenylacetoxyiodonium ions, and in the presence of strong acids the equilibrium is shifted toward the ionic species.[9] Indeed, the CV of $PhI(OAc)_2$, recorded in acidic conditions[10] exhibited an irreversible reduction peak at ~0.9 V, and therefore, this reagent should be able to oxidize the TTF derivatives up to their dications. The following reactions (eq 1−3) were mainly used:

$$(1)\ R_4TTF + 1/2PhI(OAc)_2 + CF_3SO_3H \longrightarrow R_4TTF^{\cdot +}\ CF_3SO_3^- + 1/2PhI + AcOH$$

$$(2)\ R_4TTF^{\cdot +}CF_3SO_3^- + nR_4TTF + Q^+X^- \longrightarrow \underline{(R_4TTF_{n+1})^+}, X^- + Q^+CF_3SO_3^-$$

$$(3)\ R_4TTF + PhI(OAc)_2 + 2CF_3SO_3H \longrightarrow R_4TTF^{2+}2CF_3SO_3^- + PhI + 2AcOH$$

The optimal yields of the stoichiometric triflates were achieved using 0.5 mol of $PhI(OAc)_2$ and 2 mol of the acid, whereas 1−3 mol of the oxidizer and acids in larger excess were employed for the synthesis of the dications. Thus, oxidation in acetonitrile at room temperature in the presence of triflic acid (eq 1) afforded the stoichiometric triflates $(R_4TTF)CF_3SO_3$ **2a**−**d** in high isolated yields. These salts were characterized by their elemental analyses, UV/vis/NIR[11] and IR spectra.[12] In addition, the crystal structure of compound **2a**, which crystallized from benzonitrile as a semihydrate upon slow aerial evaporation, was determined.[13]

Salts **2a** and **2c** are highly soluble in acetonitrile and dichloromethane. In contrast, like their parent neutral precursors, salts

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(1) (a) Ferraro, J. R.; Williams, J. M. *Introduction to Synthetic Electrical Conductors*; Academic Press: New York, 1987. (b) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, U. Geiser, K. D.; Wang, H. H.; Kini, A. M.; Whangbo, M. H. *Organic Superconductors*; Prentice Hall: Englewood Cliffs, 1992.

(2) (a) Wudl, F.; Smith, G. M.; Hufnagel, E. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1453. (b) Scott, B. A.; La Placa, S. J.; Torrance, J. B.; Silverman, B. D.; Welber, B. *J. Am. Chem. Soc.* **1977**, *99*, 6631. (c) Hünig, S.; Kieβlich, G.; Quast, H.; Scheutzow, D. *Liebigs Ann. Chem*. **1973**, *1973*, 310. (d) Hinh, L. V.; Schukat, G.; Fanghänel, E. *J. Prakt. Chem.* **1979**, *321*, 299.

(3) Müller, H.; Ueba, Y. *Bull. Chem. Soc. Jpn.* **1993**, *64*, 32.

(4) Kim, Y. I.; Hatfield, W. E. *Inorg. Chim. Acta* **1993**, *204*, 261

(5) Wudl, F. *J. Am. Chem. Soc.* **1975**, *97*, 1962.

(6) (a) Starodub, V. A.; Batulin, V. P.; Babiichuk, V. P. *Elektron. Org. Mater.* **1985**, 386 (*Chem. Abstr.* **1988**, *109*, 37760). (b) Yamashita, Y.; Tanaka, S.; Tomura, M. *J. Chem. Soc., Chem. Commun.* **1993**, 652. (c) Kokar, V. R.; Kampar, V. E.; Neilands, O. *Zh. Org. Khim.* **1983**, *19*, 1224.

(7) See, e.g.: (a) Cavara, L.; Gerson, F.; Cowan, D. O.; Lerstrup, K. *Helv. Chim. Acta* **1986**, *69*, 141. (b) Giffard, M.; Alonso, P.; Garin, J.; Gorgues, A.; Nguyen, T. P.; Richomme, P.; Robert, A.; Roncali, J.; Uriel, S. *Adv. Mater.* **1994**, *6*, 298.

(8) (a) Kreicberga, Y. N.; Neilands, O. *Zh. Org. Khim.* **1985**, *21*, 2009. (b) Neilands, O.; Belyakov, S.; Tilika, V.; Edzina, A. *Chem. Commun.* **1995**, 325. (c) Neilands, O.; Tilika, V. Zh.; Supe, A. A.; Edzhinya, A. S. *Chem. Heterocycl. Compd.* **1996**, *32*, 112.

(9) (a) Varvoglis, A. *Chem. Soc. Rev.* **1981**, *10*, 377. (b) Kokkinidis, G.; Papadopoulou, M.; Varvoglis, A. *Electrochim. Acta* **1989**, *34*, 133.

(10) In CH_3CN, $PhI(OAc)_2$: 2 mmol L^{-1}, CF_3SO_3H: 8 mmol L^{-1}, vs SCE.

(11) For a discussion of UV/vis/NIR and EPR spectra of **2a**−**d** see: Khodorkovsky, V.; Shapiro, L.; Krief, P.; Shames, A.; Giffard, M.; Gorgues, A.; Mabon, G., submitted.

(12) Three strong bands at ~1255, 1025, and 635 cm^{-1} arise from vibrations of the $-SO_3^-$ moiety: Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 2nd ed.; Methuen: London, 1958; p 364.

(13) Crystal data for **2a**, 0.5 H_2O: $C_7H_5F_3O_{3.5}S_5$, $M_w = 362.43$, monoclinic, $P2_1/c$, black, $a = 21.530(7)$ Å, $b = 7.954(1)$ Å, $c = 15.846(6)$ Å, $\beta = 72.79(4)°$, $V = 2592(1)$ Å^3, $T = 293$ K, Z = 8, $R = 0.047$, $R_w = 0.064$, G.O.F. = 1.25.

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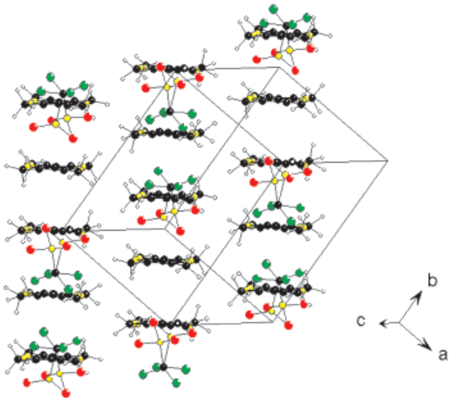

Figure 1. Crystal structure of $TMTTF_2CF_3SO_3$ (**3b**).

2b,**d** possess lower solubility that, nevertheless, was sufficient for further transformations; benzonitrile was found to be a solvent of choice for both salts.

The nonstoichiometric triflates **3b**,**c**,**d** were prepared from the stoichiometric triflates **2b**,**c**,**d** and the corresponding neutral derivatives. Thus, slow cooling a benzonitrile solution of equimolecular amounts of **1d** and **2d** down from 100 °C resulted in crystallization of the salt $ET_2CF_3SO_3$ (**3d**) which is identical to the material obtained by electrocrystallization,[14] as proven by the powder and monocrystal X-ray determinations of its unit cell. Previously unknown $TMTTF_2CF_3SO_3$ (**3b**) was prepared from **1b** and **2b** using the same procedure and characterized by the X-ray diffraction experiment.[15] The TMTTF units in **3b** adopt a β-like packing pattern,[1] and similarly to $ET_2CF_3SO_3$,[14] the anions $CF_3SO_3^-$ are disordered at room temperature (Figure 1). The salt $TMT\text{-}TTF_2CF_3SO_3$ precipitated from ethanolic solution of a **1c** and **2c** mixture upon slow evaporation.

Stoichiometric triflates are convenient precursors for metathetic conversions and, upon addition of a suitable onium ($Q = R_4N$ or R_4P) salt, either stoichiometric ($n = 0$) or nonstoichiometric ($n \neq 0$) salts can be obtained (eq 2). Thus, we prepared the stoichiometric chloride $TTF^{\bullet +}Cl^-$ (**4a**) by metathesis using **2a** and benzyltriethylammonium chloride in acetonitrile at room temperature.[16] The same reaction, performed in the presence of **1a** (**1a**/**2a** ratio = 0.6) resulted in precipitation of the nonstoichiometric salt $TTFCl_{0.68}$ (**5a**). The selenocyanate $TTF(SeCN)_{0.58}$ (**6a**) was similarly obtained by anion exchange from **2a** and tetraphenylphosphonium selenocyanate, in the presence of **1a**. Noteworthily, unlike TTF halides, **6a** cannot be obtained by direct oxidation, since selenocyanogen $(SeCN)_2$ is not available. The composition of salts **4a**, **5a**, and **6a** was confirmed by the elemental analysis, and their X-ray powder diffractions were indexed according to the literature data.[2b,17]

The above procedure also allowed the synthesis of $\kappa\text{-}ET_2Cu(NCS)_2$ (**4d**) using $(C_6H_5)_4PCu^I(NCS)_2$[18] and (**3d**) in benzonitrile at room temperature.[19] Compound **4d** was shown to be identical to the electrogenerated material[20] by the powder X-ray diffraction.

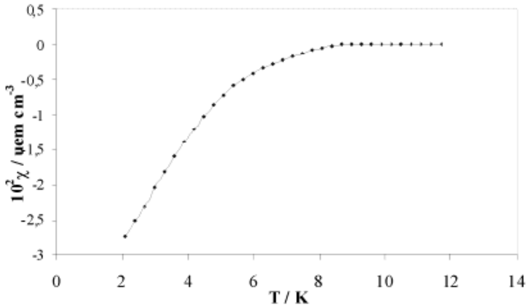

Figure 2. Temperature dependence of the volume magnetic susceptibility of **4d**.

Furthermore, **4d** also undergoes a superconducting transition evidenced by the SQUID magnetic measurements (Figure 2). Two independently prepared samples of **4d** showed T_c (onset) at 8.5 and 9 K. The T_c value observed from the resistance measurements of electrocrystallized 4**d** was 10.4 K.[20] The values determined from the magnetic measurements are known to be lower by 1−2 K.[1b,20]

Formation of the TTF-derived dications (reaction 3) occurs quantitatively at room temperature as evidenced by the electronic absorption spectra. The absorption bands of the TTF derivatives (**1a**−**d**) disappeared within minutes, and the characteristic bands of the corresponding cation radicals[11] were absent. The longest wavelength bands at 352 nm (TTF^{2+}), 415 nm ($TMTTF^{2+}$), 701 nm ($TMT\text{-}TTF^{2+}$), and 711 nm (ET^{2+}) were observed. These salts, especially those derived from **1c** and **1d**, are moisture-sensitive, and their solutions, exposed to air, slowly, and upon addition of water, instantly, are converted into **2a**−**d**. Instant formation of the cation radicals **2a**−**d** was observed also when the corresponding neutral **1a**−**d** were added to solutions of the dications. Solid dications are somewhat more stable, and isolated ET^{2+}, $2BF_4^-$, identical to the electrogenerated compound,[21] according to the powder diffraction data, has been isolated.

In summary, the described approach, based on oxidation of the TTF derivatives by (diacetoxyiodo)benzene in the presence of triflic acid and further metathetical conversions, provides a general and flexible synthetic methodology for the synthesis of a variety of TTF-derived cation radicals and dications, which is free of limitations imposed by the electrochemical technique. The regular crystallization can afford monocrystals possessing the same electrophysical properties as those obtained by electrocrystallization. This approach can be extended to other electron donors as well, and our preliminary experiments show that $PhI(OAc)_2$ in the presence of strong acids can be used for oxidation of ferrocenes and oligothiophenes.

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Supporting Information Available: Experimental synthetic procedures, analytical data and crystallographic data (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Chasseau, D.; Watkin, D.; Rosseinsky, M. J.; Kurmoo, M.; Talham, D. R.; Day, P. *Synth. Met.* **1988**, *24*, 117.

(15) Crystal data for **3b**: $C_{21}H_{24}F_3O_3S_9$, $M_W = 669.99$, triclinic, $P\text{-}1$, black, $a = 8.598(2)$ Å, $b = 12.995(3)$ Å, $c = 13.081(2)$ Å, $\alpha = 75.36(2)°$, $\beta = 87.35(2)°$, $\gamma = 82.30(2)°$, $V = 1401.2(7)$ Å^3, $T = 293$K, Z = 2, $R = 0.047$, $R_w = 0.069$, G.O.F. = 1.15. Low-temperature structural and electrical properties of **3b** will be reported elsewhere.

(16) Alternatively, **4a** was also obtained in one step through direct oxidation of TTF (**1a**) by $PhI(OAc)_2$ in the presence of HCl.

(17) Somoano, R. B., Gupta, A.; Hadek, V.; Novotny, M.; Jones, M.; Datta, T.; Deck, R.; Hermann, A. M. *Phys. Rev. B* **1977**, *15*, 595.

(18) Hehl, R.; Thiele, G. *Z. Anorg. All. Chem.* **1998**, *624*, 1736.

(19) Noteworthy, an attempt of direct preparation of this salt from stoichiometric triflate **2d**, $(C_6H_5)_4PCu(NCS)_2$ and **1d** failed probably because high temperature (100 °C) was required to ensure complete dissolution of **1d** in benzonitrile.

(20) Uramaya, H.; Yamochi, H.; Saito, G.; Nozawa, K.; Sugano, T.; Kinoshita, M.; Sato, S.; Oshima, K.; Kawamoto, A.; Tanaka, J. *Chem. Lett.* **1988**, 55.

(21) Chou, L. K.; Quijada, M. A.; Clevenger, M. B.; de Oliveira, G. F.; Abboud, K. A.; Tanner, D. B.; Talham, D. R. *Chem. Mater.* **1995**, *7*, 530.