Electrocrystallisation of Conductive Nonstoicheiometric Adducts of Tetrathiafulvalene with Inorganic or Organic Anions, and of Similar Adducts of Tetracyanoquinodimethane

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Summary Growth of single crystals of TTFX$_n$ by electrocrystallisation on a platinum anode in acetonitrile solutions of TTF^0 and X$^-$ gives unidimensionally metallic nonstoicheiometric ($n \neq 1$) adducts (TTF is tetrathiafulvalene, X$^-$ is NO$_3^-$, Cl$^-$, Br$^-$, I$^-$, HCO$_3^-$, BF$_4^-$, HSO$_4^-$, C$_2$O$_4$K$^-$, OAc$^-$, maleate, fumarate, *p*-MeC$_6$H$_4$SO$_2^-$, N$_3^-$, or B$_4$O$_7^-$, the last three giving powders or microcrystals); conductivities at *ca.* 300 K are 10^{-3}—$20\ \Omega^{-1}\ \text{cm}^{-1}$, and (NO$_2$)$_{0\cdot1}$TCNQ (TCNQ = tetracyanoquinodimethane) and other TCNQ adducts were likewise prepared cathodically.

Pyrene, perylene, and azulene perchlorates have been prepared by electrocrystallisation,[1] as have single crystals of perylene nickel dithiolate.[2] Tetrathiafulvalenium bromide (TTFBr) was also prepared electrochemically,[3] and non-stoicheiometric halides TTF(Hal)$_n$ ($n<1$) were prepared by NEt$_4$Hal diffusion into electrochemically generated TTF–TTF$^+$ solution in MeCN.[4] Stoicheiometric TTFCl from synthesis[5] contrasts with TTFCl$_{0\cdot68\pm0\cdot03}$ prepared photochemically.[6] We have now used direct electrocrystallisation on a Pt anode in TTF^0 solution also containing R$_4$N$^+$X$^-$, to obtain TTFX$_n$ crystals, where usually $n<1$. X represents a variety of anions not hitherto complexed with TTF, or, otherwise, not complexed in the stoicheiometry that we have obtained. Thus, the N$_3^-$ adduct has not been hitherto preparable,[7] and the generation of TTF$^+$ in the presence of TTF^0 together with such anions as HSO$_4^-$ [not readily obtainable in the uncharged form, contrasting with, *e.g.*, tetracyanoquinodimethane (TCNQ)] at a growth-supporting electrode surface, provides a new general technique for preparing TTF adducts with such stable anions. The conductivities, σ, are anisotropic and unidimensionally metallic in the cases tested.

The electrocrystallisations were conducted under nitrogen in acetonitrile at controlled potentials determined by preliminary cyclic voltammetry, in the region of 0·75 V (w.r.t. S.C.E.), a potential sufficient[8] to generate TTF^{2+}. $\mathrm{LiClO_4}$ was used as supporting electrolyte when needed to enhance the solution conductance. The crystals took 9—15 h to grow and were usually black and needle shaped (*ca.* 3 × 0·1 × 0·1 mm^3), but occasionally were powder, micro-crystalline, or blocklets (see Table).

Table. Properties of TTFX_n

Compound	X	n	$\sigma/\Omega^{-1}\,\mathrm{cm}^{-1}$
Ref. 5	Cl	1	0·27
Ref. 6	Cl	0·68 ± 0·03	0·63, powder
(**1**)	Cl	1·1	0·06[a], 4
(**2**)	$\mathrm{BF_4}$	0·55	0·6[a], 0·08
(**3**)	$\mathrm{NO_3}$	0·55	20[a], 4
(**4**)	Br	0·7	1·4[a], 0·3
(**5**)	$\mathrm{HCO_3}$	3/2	0·9
(**6**)	$\mathrm{HSO_4}$	1·2	0·03
(**7**)	$\mathrm{C_2O_4K.3/2H_2O}$	1	0·005
(**8**)	$\mathrm{MeCO_2}$	*ca.* 0·7	3
(**9**)	I	0·7	10
(**10**)	Maleate		0·02
(**11**)	Fumarate	*ca.* 0·25	0·002
(**12**)	Tosylate	1	Powder
(**13**)	$\mathrm{B_4O_7}$	0·5	,,
(**14**)	$\mathrm{N_3}$	0·74	Microcrystals

[a] Four probe; otherwise 2-probe.

Conductivities are given in the Table together with values of n, which were constant for successive preparations or for different crystals of the same batch, which indicates that the compositions are specific rather than adventitious. *X*-Ray diffraction on $\mathrm{TTFCl}_{1\cdot1}$ and $\mathrm{TTF(NO_3)}_{0\cdot55}$ clearly establishes their single crystallinity. It may be surmised that for a particular substance the most conductive composition is in part favoured (selected) by the method, since resistive (*e.g.* stoicheiometric) material could inhibit the progress of the surface redox reactions giving rise to crystal growth.

Preliminary temperature dependence measurements on the adducts (**1**) and (**3**) show enhanced conductivity along the needle axes on cooling, with maxima at *ca.* 271 K for (**1**) and 291 K for (**3**), but at 341 K for (**2**) [*i.e.* (**2**) is metallic only above 341 K]. Below 220 K such conductivities dropped below $10^{-3}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. The metal–semiconductor transition temperatures are unusually high, and the values of $\sigma_{\mathrm{max}}/\sigma_{\mathrm{RT}}$ can be large, 134 for one sample of (**1**), but more usually 1·5—15. Four probe conductimetry in an Oxford Instruments CF100 Cryotip was employed. $\mathrm{TTF(BF_4)}_{0\cdot55}$ showed an unusual second conductivity maximum at 180 K, implying a semiconductor–metal transition at 200 K with the reverse again at 180 K.

Crystals of $\mathrm{(NO_2)}_{0\cdot1}\mathrm{TCNQ}$ having σ(needle) = 0·01 Ω^{-1} cm^{-1} have been grown cathodically in a solution of TCNQ^0 and $\mathrm{NO_2{}^+PF_6{}^-}$, as have stoicheiometric crystals of $\mathrm{NEt_4(TCNQ)_2}$ (rectangular blocklets) and acridinium-TCNQ. Powders of Methylene Blue-TCNQ and $\mathrm{ZnI(TCNQ)}_{1\cdot6}$ have likewise been obtained. Wide extensions of the technique can be foreseen, such as the growing of mixed (doped) crystals, and employment of other donor and acceptor units.

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