Assembly of TTF in modified layered zirconium phosphate under controlled oxidation conditions

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Tetrathiafulvalene reacts with γ-zirconium phosphate doped with Cu^{II} to give intercalation compounds in which the extent of electron transfer and the electrical properties are a function of the degree of copper doping in the host matrix.

Of the structural and electronic criteria required for the synthesis of electronically conducting organic compounds the presence of segregated stacks of electron donors and acceptors and partial (non-integral) charge transfer between the stacks are of key importance.[1] Organic π donors can crystallise in segregated two-dimensional arrangements with electron acceptors,[2–6] where coordination and crystal packing considerations lead to crystallisation in a two-dimensional arrangement in a one-step reaction. Another approach, developed by Averill and coworkers[7–9] and others,[10–11] uses pre-formed layered solids having negatively charged inorganic layers. The success of this route is illustrated by the highly conducting bis(ethylenedithio)tetrathiafulvalene/FeOCl[9] and TTF/$FePS_3$[11] intercalation compounds. Here, as in the above one-step syntheses, the ultimate electrical properties are conferred only by the electrochemical characteristics of the donor and acceptor species. We propose an original method which makes use of two of the properties of layered solid acids, cation exchange and assembly of organic molecules, which allows some control of the extent of charge transfer. We have previously reported the use of copper(II)-exchanged α- and γ-zirconium phosphates for the *in situ* polymerisation of aniline,[12] a strategy which has also been effective for the polymerisation of organic electron donor molecules in the three-dimensional channels of zeolites.[13] These reactions were 'all or nothing' in that no modulation of the degree of oxidation by the concentration of oxidant was attempted. In fact limited cation doping of layered solids often gives rise to multiphasic systems, the extent of which was reduced in the present study by the use of γ-zirconium phosphate, $ZrPO_4(H_2PO_4)\cdot 2H_2O$ (γ-ZrP).[14] Even so, charge transfer could possibly lead only to the presence in varying proportions of neutral and fully ionised TTF. We show that, on the contrary, this method allows the stabilisation of non-integral valence states and a degree of modulation of the extent of charge transfer, which also influences the electrical properties of the resulting bidimensional nanocomposite.

When γ-ZrP, prepared according to published methods,[15] is contacted with solubilised TTF (acetonitrile), no reaction occurs even after several days. However, by suspending γ-ZrP in an acetonitrile solution of $(TTF)_3(BF_4)_2$,[16,17] direct ion-exchange occurs to give a new material of interlayer spacing 19.7 Å and stoichiometry $ZrH_{1.2}(PO_4)_2(TTF)_{0.8}\cdot 2H_2O$ in which TTF is fully ionised.

Partial ion exchange of Cu^{II} on γ-ZrP was achieved using copper acetate (100 ml, 0.005–0.0125 mol dm^{-3}) such that $ZrPO_4(H_{2-2x}PO_4)Cu_x\cdot nH_2O$ (x = 0.035, 0.11, 0.21, 0.33 and 0.50; n = 2–4) was prepared. The exchange of Cu^{II} on γ-ZrP has been studied in detail; the copper-exchanged material is monophasic for x = 0.035, 0.33 and 0.50 and biphasic in an intermediate region including x = 0.11 and 0.21. Samples of copper(II)-exchanged γ-ZrP were then suspended in acetonitrile to which a TTF solution was added. After stirring at 40 °C for 6 days the solution was recovered by centrifugation and washed. Fig. 1 compares the powder XRD patterns of γ-ZrP, its copper(II)-exchanged derivative, and the intercalation compounds prepared by redox insertion and direct ion exchange. The interlayer distance is invariant for all TTF intercalates, independent of the synthesis route or the amount of TTF adsorbed, and corresponds to a free height of *ca.* 10.5 Å (the thickness of the inorganic sheets in γ-ZrP is *ca.* 9 Å). Considering the dimensions of the TTF molecule (long axis 10.7 Å; short axis 6.7; depth 3.7 Å) a number of orientations of intercalated TTF are possible based on these data alone, including (*i*) TTF oriented perpendicular to the host layer with the long axis parallel to the *c* direction, (*ii*) a single layer of TTF perpendicular to the layers and with the central C=C bonds parallel to the layers, (*iii*) a double or triple layer of TTF molecules lying parallel to the host layers. Of these possibilities, (*iii*) is considered unlikely, in view of the small quantities of TTF which, when intercalated, still give rise to the 19.7 Å basal spacing. Chemical analysis shows the organic entity to be intact (S/C ≈ 1.75) and the TTF content to vary between 6 and 37% organic matter, increasing as the Cu^{II} in the precursor phase increases. Complete analyses are given in Table 1. No Cu could

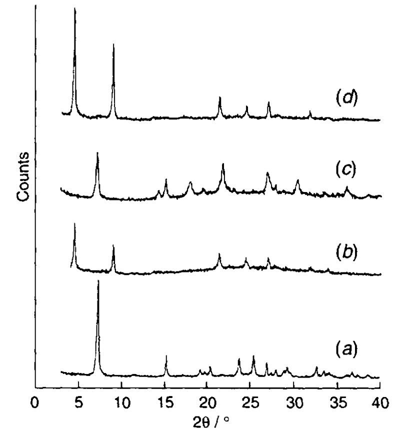

Fig. 1 Powder XRD patterns of (*a*) γ-ZrP, (*b*) intercalate prepared by direct ion exchange with $(TTF)_3(BF_4)_2$, (*c*) $ZrHPO_4Cu_{0.5}PO_4\cdot 4H_2O$ and (*d*) intercalate obtained by redox insertion in $ZrH_{1.78}PO_4Cu_{0.11}PO_4\cdot H_2O$. For (*b*) and (*d*), interlayer distance = 19.7 Å.

Table 1 Chemical analysis of precursor phases and TTF intercalates

x[a]	Partial charge[b]	TTF content[c]	Charge ratio[d]
0.035	0.77	0.10	1.09
0.11	0.90	0.24	0.98
0.21	0.93	0.46	1.04
0.33	0.96	0.72	1.06
0.50	0.98	1.05	1.04

[a] For precursor $ZrH_{2-2x}Cu_x(PO_4)_2\cdot yH_2O$ as determined by AAS. [b] Determined by Raman spectroscopy. [c] Determined from C, H, S elemental analysis. [d] (TTF content × partial charge/2) × Cu^{II} content in precursor.

be detected in the solid products after intercalation, and it is concluded this is eliminated as colloidal Cu^0. A general equation for the reaction may then be written [eqn. (1)] where n^+

$$\mathrm{ZrH_{2-2x}Cu^{II}}_x\mathrm{(PO_4)_2{\cdot}}y\mathrm{H_2O(s)} + z\mathrm{TTF\ (soln)} \rightarrow \mathrm{ZrH_{2-nz}(TTF^{n+})}_z\mathrm{(PO_4)_2{\cdot}H_2O(s)} + x\mathrm{Cu^0} \quad (1)$$

is the partial charge on TTF and $x = nz/2$.

IR studies (KBr disc, Bomem DA8 FTIR) show the superposition of bands arising from the phosphate backbone and intercalated TTF. Perturbation of the baseline in the form of a progressively increasing background absorption towards higher wavenumbers is evidence for the presence of electronically conducting domains. The extent of oxidation of intercalated TTF can be inferred from the positions of key lines in the Raman spectra, in particular that resulting from the central C=C stretch at 1515 cm^{-1} in the neutral molecule, which shifts to 1415 cm^{-1} in fully ionised TTF^+. The partial charge is a linear function of the wavenumber of the Raman line between these two limits.[18] The Raman spectra shown in Fig. 2 were recorded on two materials prepared from Cu pre-exchanged phases with $x = 0.21$ (0.45 mol TTF intercalated) and 0.035 (0.1 mol intercalated) using grazing incidence on pressed discs (Dilor spectrometer, Ar laser, $\lambda = 514.3$ nm, 50 mW). The Raman line at 1438 cm^{-1} for $x = 0.035$ (0.1 mol TTF intercalated) corresponds to a predominant partial oxidation state of 0.77+. For the TTF intercalate prepared from the precursor with $x = 0.21$ (biphasic precursor), more than one partial oxidation state is stabilised, since a maximum at 1422 cm^{-1} and a shoulder at *ca.* 1435 cm^{-1} are simultaneously observed, corresponding to partial oxidation states of 0.93+ (major) and 0.77+ (minor).

The electrical resistivity was measured by the dc four-probe technique on pressed discs. The dc current was applied over an extended time in order to monitor the polarisation effect (no change over 30 min). The electrodes are blocking to ionic transport and any possibility that the transport properties are due to proton transfer under the experimental conditions can therefore be excluded. These measurements are averaged over all crystallographic orientations in the anisotropic arrangement. The resistivities determined are observed to be a function of the initial level of Cu doping. At room temp., $\mathrm{ZrH_{1.2}(PO_4)_2(TTF)_{0.8}{\cdot}2H_2O}$ (prepared by ion-exchange, charge +1 on TTF) has a conductivity of $10^{-5.5}$ S cm^{-1}. For samples prepared by redox intercalation, the conductivity is higher by up to two orders of magnitude, and increases with decreasing degree of charge transfer. $\mathrm{ZrH_{1.92}(PO_4)_2(TTF^{0.77+})_{0.1}{\cdot}0.9H_2O}$ has the lowest resistivity, $10^{-3.5}$ S cm^{-1}. These values are in the semiconductor range, but it is significant that the conductivity is higher for compounds containing little intercalated organic electron donor suggesting that the conductivity conferred on the (insulating matrix + conducting guest) composite by $TTF^{0.77+}$ is particularly high. Furthermore, note that the amount of intercalated TTF with its partial charge as deduced from the Raman spectra corresponds almost quantitatively to the total Cu^{II} content, if complete reduction to the zero-valent state occurs. The maximum uptake of *ca.* 1 TTF per mol Zr corresponds to close packing of organic molecules in the interlayer region. At lower uptake, the charge is compensated by non-exchanged protons and the electronic conductivity implies that islets of TTF ions are stacked at short enough distances to result in appreciable orbital overlap between adjacent molecules. Any further description of the interlayer arrangement of TTF at this stage would be speculative.

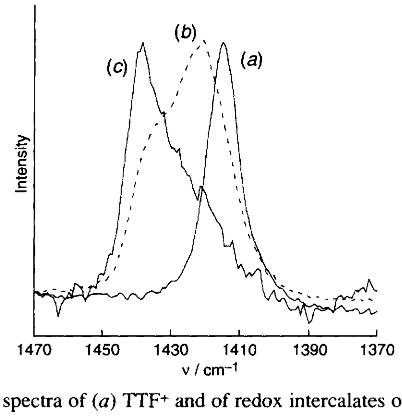

Fig. 2 Raman spectra of (*a*) TTF^+ and of redox intercalates obtained using copper(II)-exchanged precursors with $x = 0.21$ (*b*) and 0.035 (*c*). Partial charges are 1+, 0.93+ and 0.77+ respectively. (Intensities have been rescaled according to the TTF content.)

We therefore conclude that the pre-insertion of varying amounts of Cu^{II} into the interlayer space of layered (and otherwise electrically inactive) solids is a route to the modulation of the extent of charge transfer within a certain range and that this is, therefore, directly responsible for the electrical properties of the solids. This is the first time that such a relation has been shown for an intercalation compound.

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