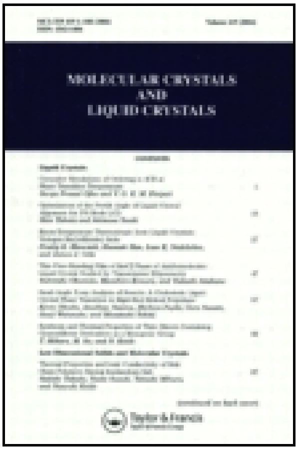

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# Two-dimensional organic-inorganic intercalation hybrids of tetrathiafulvalene in zirconium phosphate

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Two methods have been developed for intercalating partially charged tetrathiafulvalene (TTF) into zirconium phosphate (ZrP). The first is based on an oxidative intercalation using $\gamma$-ZrP modified by partial pre-exchange with Cu(II). In the second, TTF is oxidised *ex situ* and assembled in $\alpha$- or $\gamma$-ZrP expanded with surfactants or long chain alcohols. The latter method leads to materials of conductivity higher by *ca.* $10^6$ that of the starting matrices. Factors favourable to the development of electronic conductivity in a non-redox matrix like ZrP are discussed.

Keywords: zirconium phosphate; TTF; electronic conductor

## INTRODUCTION

Self-organisation of organic molecules such as dyes, polyaromatic hydrocarbons and other electron donors within the confining environment of layered hosts is an excellent means towards the development of physical properties including the generation of second harmonics or anisotropic electronic conductivity. This association into stacks leads to the formation of so-called aggregates, the spatial organisation of which is not necessarily commensurate with that of the inorganic host system. Optimisation of the properties demonstrated by intercalation hybrids depends clearly on the nature of the guest, but also on control of its uptake and orientation within the interlayer region, factors which depend on the charge density of the layers and on eventual host - guest interactions, *via* hydrogen bonding for example. Tetrathiafulvalene (TTF) demonstrates such tendency to self-organise into stacks, an arrangement which increases orbital overlap and leads to high electronic conductivity when the TTF units are partially charged. In the results described below on the intercalation of TTF in α- and γ-zirconium phosphates (α-ZrP, γ-ZrP), our efforts have been directed towards exercising a degree of control over the partial oxidation state of TTF whilst, at the same time, maximising the uptake of TTF, aspects which have not been considered in previous reports of intercalation of TTF in other layered hosts, such as FeOCl[1] or $FePS_3$.[2]

## EXPERIMENTAL SECTION

### Host and Precursor Phases

Host α-ZrP and γ-ZrP were prepared following published methods. γ-ZrP (0.2 g) was partially loaded with Cu(II) by exchange with solutions (100 mL) of $Cu(OAc)_2$ of concentration 0.005 - 0.0125 mol $dm^{-3}$ to give γ-$ZrPO_4.(H_{2-2x}PO_4)Cu_x.nH_2O$, with x = 0.035 - 0.50 and n = 2 - 4 (Cu determined by atomic absorption spectrometry on the solid dissolved in dilute HF). α and γ-ZrP were also expanded with trimethyldodecylammonium (TMDDA) bromide and with octanol respectively. For the former, this necessitated the use of a propylammonium-α-ZrP precursor prepared by contacting α-ZrP with propylamine vapour overnight. Chemical (CHN) analysis enabled the formulae α-$Zr(PO_4)_2H_{1.3}(TMDDA)_{0.7}.1.3H_2O$ and γ-$ZrPO_4(octanol)_{0.87}(H_2PO_4).1.2H_2O$ to be derived.

### Intercalation of TTF

Oxidative intercalation reactions were performed using γ-ZrP loaded to different degrees with Cu(II). γ-$ZrPO_4.(H_{2-2x}PO_4)Cu_x.nH_2O$ was reacted with TTF (Aldrich) dissolved in acetonitrile (40°C) for 4 days. Direct ion exchange of $TTF^+$ with γ-ZrP was performed using $(TTF)_3(BF_4)_2$.

In a second approach, TTF was oxidised *ex situ* using an acetonitrile solution of $Br_2$ until a ratio Br : TTF of 1 was reached. Under these conditions, the dominant species in solution is $TTFBr_{0.76}$ which was extracted into an ethanolic suspension of expanded α or γ-ZrP. All compounds were recovered by centrifugation, washed with acetonitrile and/or ethanol, and were dried in air.

### Characterisation

The uptake of TTF was determined from elemental and thermogravimetric analyses. IR and Raman spectra were recorded using a BOMEM DA8 FTIR and a Spectraphysics Ar laser (5145 Å) respectively. Transmission UV-VIS-NIR spectra were recorded between 310 and 2500 nm on KBr discs. Electrical conductivity measurements were performed on thin (< 1mm) pressed discs, between -150 and 50°C using the "4-point method". Electron spin resonance spectra were measured from liquid helium to room temperature using a Bruker spectrometer operating at 9 GHz.

## RESULTS AND DISCUSSION

### Direct Intercalation/Ion-Exchange of TTF

Zirconium phosphate readily undergoes both intercalation reactions, generally based on an acid - base type interactions between the host and guest, and ion exchange. Possibly the most obvious route to the assembly of partially charged TTF in the solid acid matrix of ZrP is to make use of a substituted TTF carrying basic groups, and attempt partial oxidation of the TTF core in a second stage. Results obtained using this strategy are described elsewhere in this volume. Direct ion-exchange with $TTF^+$ from a solution of $(TTF)_3(BF_4)_2$ occurs both with α- and γ-ZrP to give phases with an interlayer distance given by the $d_{002}$ diffraction line of 19.7 and 15.0 Å respectively. For the former, this new basal spacing is compatible with an orientation of TTF more or less perpendicular to the zirconium phosphate plane (long axis of TTF is *ca.* 10.7 Å); for the latter the interlayer spacing observed implies a greater tilt angle.Chemical analysis shows *ca.* 1 mole $TTF^+/Zr$, but in neither case is the ZrP-TTF compound so-prepared conducting ($\sigma_{RT} < 10^{-6}$ $Scm^{-1}$). This observation clearly demonstrates the essential condition, for any enhancement in this system of the inherent conduction properties of ZrP, of partial charge transfer from TTF in addition to contiguous stacking of TTF units.

### Intercalation with Control of the Degree of Charge Transfer

**Oxidative intercalation into Cu(II)-doped γ-ZrP**

Following reaction of $\gamma$-$ZrPO_4.(H_{2-2x}PO_4)Cu_x.nH_2O$ (x = 0.035, 0.11, 0.21, 0.33 and 0.5) with TTF, elemental analysis shows the resulting compounds to be free of copper, and TTF uptake to depend on the initial copper loading. The interlayer distance is invariant for the five samples, with $d_{002}$ = 19.4 Å. Raman spectroscopy was used to determine the degree of charge transfer from TTF, using the known relation between the position of the stretching vibration $\nu_s(C{=}C)$ and the partial charge on TTF.[3] The results showed that the amount of copper pre-exchanged on to the host matrix defines both the uptake of TTF and its partial charge, the former ranging from 0.1 to 1 and the latter from 0.78 to 0.98, with lowest uptake and partial charge being observed for the precursor phase with x = 0.035. The conductivity also clearly depends on the synthetic conditions; over the range of initial compositions studied, the conductivity increases linearly from $4.10^{-5}$ to $3.10^{-4}$ $Scm^{-1}$ at room temperature.

Although successful as a strategy for the oxidative intercalation of TTF, and despite providing a degree of control over the partial charge on the occluded species, the method is limited by the low TTF uptakes, which can only form isolated aggregates in the interlayer space, that result from the use of weakly copper-loaded γ-ZrP. The ideal situation must combine both the assembly of TTF of least partial charge, with maximisation of the packing density of the incoming molecules.

## Simulaneous Partial Oxidation of TTF *ex situ* and Insertion in an Expanded Host

The long chain alcohol or surfactant molecules play two key roles in the precursor phase *viz.* (i) by greatly increasing the interlayer distance and facilitating entry of TTF, and (ii) by activating a defined number of surface -OH groups, either by hydrogen bonding or ion-exchange, which then represents the ion-exchange capacity of the precursor. The importance of the latter connot be over-emphasised, since it is the parameter which provides a means of control of the uptake of partially charged TTF. $Br_2$ acts as oxidant for TTF and gives, in the bulk phase under the same conditions, the mixed valence salt $TTF^{\delta+}Br_{\delta}$, with $\delta = 0.69 - 0.79$.

Reconstruction of expanded α- or γ-ZrP around bromine-oxidised TTF gives new materials of interlayer distance 14.3 and 19.4 Å respectively, close to those already reported above. In this case however, the TTF uptake is notably higher reaching, for the α-ZrP intercalate, 0.93 TTF/Zr and, for the γ-ZrP phase, 1.2 TTF/Zr. These values do not, of course, represent the level of cation exchange, since they must be moderated by the partial charge on interlayer TTF. The Raman spectrum in the region 1400 - 1500 $cm^{-1}$ is shown in Figure 1. The position of of the $\nu_s(C{=}C)$ vibration at 1447 $cm^{-1}$ corresponds to a charge $\delta+$ of 0.72 (neutral TTF:1515; $TTF^+$: 1418 $cm^{-1}$). Using this value and the stoichiometries of the intercalates given above, the total charge taken up by each matrix is equal to that "activated" in the respective immediate precursor, *e.g.* for $\alpha\text{-}ZrP(TTF^{0.72+})_{0.93}$, total charge taken up = 0.67+, practically equal to the number of exchanged protons in the TMDDA-expanded precursor (0.70+).

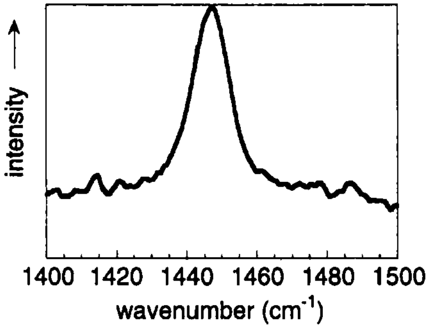

FIGURE 1 Raman spectrum in the region of the $\nu_s(C{=}C)$ vibration of $\alpha\text{-}ZrP(TTF^{0.72+})_{0.93}$

The higher packing densities of partially charged TTF authorised by this method is expected to be conducive to the formation of larger aggregates, which would be no longer isolated into islets but form contiguous stacks. Indeed, the conductivities observed support this hypothesis, Figure 2.

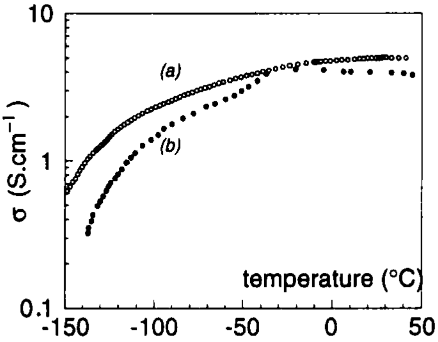

FIGURE 2 Conductivity of ZrP-TTF hybrids measured on heating using the "four-point" method (a) α-ZrP-$(TTF)^{0.72+}$ (b)γ-ZrP-$(TTF)^{0.72+}$

The room temperature conductivity, between 3 and 5 $Scm^{-1}$ for the α- and γ-ZrP/TTF intercalates respectively, is some 6 orders of magnitude higher than that of the starting materials. Although they have similar room temperatures values, the behaviour of the two phases as a function of temperature is different. Thus whereas α-ZrP-$(TTF)^{0.72+}$ shows a smooth asymptotic increase as the temperature is raised, γ-ZrP-$(TTF)^{0.72+}$ shows metallic behaviour between -20 and 50°C. Differences in the nature of the transport properties are also seen in the results of thermopower measurements made over the same temperature range. Both show semiconductor temperature-dependent values of the Seebeck coefficient to around room temperature, but the sign of the coefficient indicates p-type behaviour for α-ZrP-$(TTF)^{0.72+}$ and n-type behaviour for the γ-ZrP congener.

This might, at first, seem surprising. However, similar differences are known in bulk mixed valence salts, even for closely related systems such as $TTFBr_{0.76}$ and $TTFI_{0.71}$, which are respectively n- and p-type conductors. One likely origin lies in different packing arrangements of TTF within the interlayer region of γ-ZrP and α-ZrP; we have already noted above that the expansion of the former following intercalation of TTF is compatible with a quasi-perpendicular arrangement of TTF, whilst a more tilted arrangement is required in the latter. It can readily be estimated from the known structure of mixed valence halides[4] that the average surface area occupied per TTF unit is *ca.* 28 Å$^2$, which implies a theoretical maximum uptake of 1.25 TTF/Zr, using the charge density of γ-ZrP (1/35 Å$^{-2}$).The closeness of this value to that observed experimentally (1.22) supports the idea of a similar packing arrangement of TTF in the γ-ZrP matrix as in mixed valence halides: alternate stacks of perpendicular and edge-on TTF units. In contrast, similar reasoning leads us to consider that the packing of TTF in α-ZrP may involve only tilted, end-on TTF ions.

Finally, it should be noted that the accident in the conductivity/temperature plot seen only for γ-ZrP-$(TTF)^{0.72+}$ is also seen in the variation of the EPR linewidth with temperature, and would seem to indicate a phase transition at -38 ± 10 °C.

## Intercalation of Other Electron Donors

In fact the second approach developed above is not limited to TTF but can be extended to other π-donor molecules susceptible to oxidation by bromine. The method is therefore a generalisable strategy for the insertion of "neutral", electroactive organic molecules into an ion-exchanging but inherently non-redox active layered matrix. Optimisation of the electrical properties of the final material depends closely on the expanded precursor phase used, and this is chosen as a function of the partial charge on the oxidised molecule. In this way, we have recently achieved the ion-exchange of tetramethyltetraselenafulvalene and of polyaromatics such as perylene in both α- and γ-ZrP. The variation of the conductivity with temperature of the perylene intercalates is shown in Figure 3.

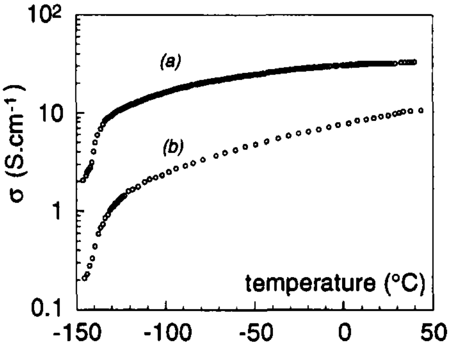

FIGURE 3 Conductivity of ZrP-perylene hybrids (a) α-ZrP (b) γ-ZrP

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