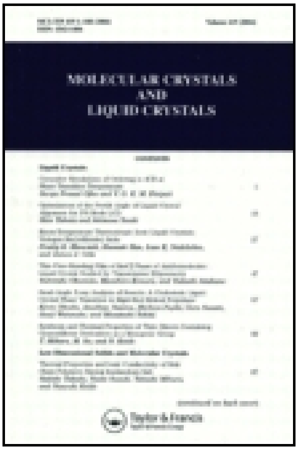

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Intercalation and Post-synthesis Oxidation of Basic Electroactive TTF-type Molecules in Zirconium Phosphate

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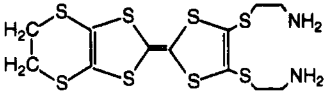
Bis(amino)-functionalised tetrathiafulvalenes **4a** and **4b** intercalate easily into γ-zirconium phosphate to give phases in which the interlayer distance is expanded to *ca.* 25 Å from 12.2 Å in the host material. As-prepared compounds are poorly conducting, but the electrical properties can be improved by a factor 10^3 by *in situ* oxidation of the TTF core. The conductivity depends strongly both on the amount of TTF taken up, and on its partial charge. Compounds have been characterised using electron paramagnetic resonance, infrared and Raman spectroscopies.

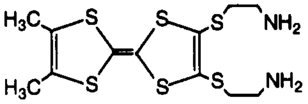
Keywords: zirconium phosphate; bis(amino)-TTF; electronic conductor

INTRODUCTION

The development of synthetic organic (non-polymeric) metals is, in large part, based on salts and charge transfer complexes containing electroactive molecules of the tetrathiafulvalene (TTF) type. The electrical perfomance of these materials is associated with partial oxidation of the TTF species and their regular structural organisation within the salts, for example as stacks. In order to induce such structural organisation favourable to the metal-like properties of the material, we have developed an intercalation chemistry of TTF and TTF derivatives within two-dimensional inorganic host matrices[1-3]. We recently reported the redox intercalation of TTF in γ-$ZrPO_4.H_2PO_4.2H_2O$ (γ-ZrP) pre-exchanged with Cu(II)[2], and the assembly of partially oxidised TTF by ion-exchange[3]. A further route to the preparation of conducting TTF zirconium phosphate systems lies in the intercalation of amine- or alcohol-substituted TTFs *via* an acid - base reaction with the matrix, followed by a post-synthesis oxidation step. We present here the intercalation of bis(amino) TTFs **4a** and **4b** in γ-ZrP, and the spectroscopic and electrical characterisation of the resulting hybrid organic-inorganic compounds.



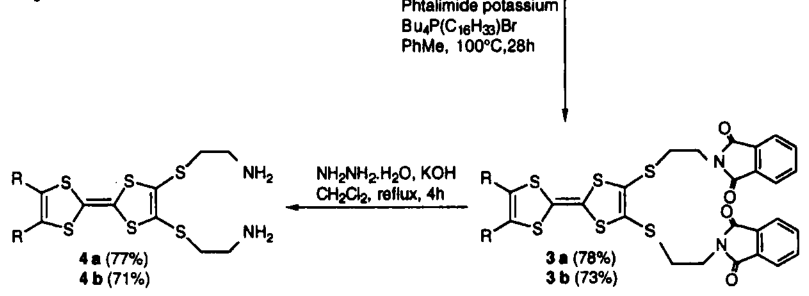
4a



4b

EXPERIMENTAL SECTION

2,3-bis(2-aminoethylthio)-6,7-(ethylenedithio)tetrathiafulvalene **4a** and 2,3-bis(2-aminoethylthio)-6,7-dimethyltetrathiafulvalene **4b** were prepared from the corresponding hydroxy TTF derivatives **1a** and **1b** respectively *via* a three-step sequence as previously described[4] (scheme 1). Bis(mesylates) **2a** and **2b** were obtained quantitatively from bis(hydroxy) TTFs **1a** and **1b** respectively by treatment with methanesulfonylchloride and triethylamine. Compounds **2a** and **2b** were treated with potassium phthalimide in the presence of hexadecyltributylphosphonium bromide. The bis(phthalimido)TTFs **3a** and **3b** obtained, were then converted into bis(amino) TTFs **4a** and **4b** by a basic hydrolysis (NH_2-NH_2-H_2O/KOH) with good overall yield (60 % and 52 % respectively).



Scheme 1

Intercalation reactions were performed on γ-ZrP (prepared using the "HF" method[5]) which had been pre-expanded using octanol. $\gamma\text{-ZrPO}_4{\bullet}\text{H}_2\text{PO}_4(\text{CH}_3(\text{-CH}_2)_7\text{OH})_{0.85}.1.3\ \text{H}_2\text{O}$ is metastable, and has an interlayer distance (given by the d_{002} reflection) of 30 Å. Bis(amino)-TTFs **4a** and **4b** (50 mg) were dissolved in octanol (80 ml), and γ-ZrP added to give a mole ratio **4a** (or **4b**) / Zr = 2. This suspension was stirred for one week at room temperature, after which time the solid products of the reactions were carefully recovered by centrifugation, washed three times with ethanol and dried in air. γ-ZrP - **4a** is orange in colour; γ-ZrP - **4b** is dark green.

RESULTS AND DISCUSSION

Powder X-ray diffraction provides clear evidence for intercalation of bis(amino)-TTFs **4a** and **4b** in γ-ZrP, Fig. 1. Intercalation is accompanied by some loss of crystallinity, and adjustment of the interlayer distance to 24.5 Å for γ-ZrP - **4a** and to 24.9 Å for γ-ZrP - **4b**. The latter compound is biphasic, a second phase of interlayer spacing 21.0 Å being clearly distinguishable.

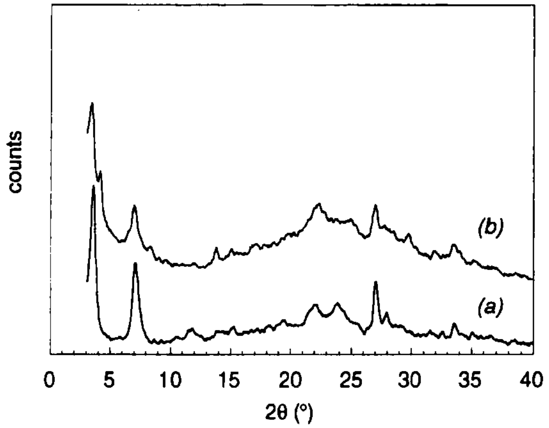


FIGURE 1 Powder X-ray diffraction patterns of (*a*) γ-ZrP-**4a** (*b*) γ-ZrP-**4b**

Various orientations of the substituted-TTF guests are possible in view of their diamino functionality and the asymmetry of the molecule. A perpendicular orientation (long axis perpendicular to the layers) implies interaction of both amino groups with the same layer, and an interdigitating arrangement in the interlayer region. The long dimension of the rigid moiety of **4a** is approximately that of bis(ethylenedithio)TTF, 15.9 Å, which would infer a minimum interlayer distance on intercalation in γ-ZrP of *ca.* 26 Å [for bis(amino)-TTF rigorously perpendicular to the phosphate layers].

Alternatively, an "edge-on" orientation would involve interaction of the amino groups with the layers above and below and, by comparison with diamine intercalates of γ-ZrP, an interlayer distance of *ca.* 20 Å is expected. The biphasic character of γ-ZrP - **4b** may indicate both of these orientations to be present in different regions.

Thermogravimetry shows the pattern of weight loss to 200°C to be strikingly different, representing 3.5 % of the initial mass of γ-ZrP-**4a**, and 21 % of that of γ-ZrP-**4b**. It is concluded that only water is co-intercalated in the former, whilst octanol is present in the latter. In addition, the weight loss in the region between 200 and 600°C allows the following formulae to be deduced: γ-ZrP-(**4a**)$_{0.22}$•0.8H$_2$O and γ-ZrP-(**4b**)$_{0.20}$•0.7(octanol).

During the intercalation process, proton transfer is expected to occur from the host layers [-P(OH)$_2$] groups to the amino groups of the guests. Indeed, this provides the driving force for intercalation, since no electron transfer with the zirconium phosphate matrix is possible. Examination of the infrared spectra in the region 1500 - 1650 cm^{-1} shows absorptions at 1511 and 1624 cm^{-1}, characteristic of δ_{as} and δ_s(NH$_3^+$). Under these conditions, the TTF-core of the occluded molecules is effectively neutral, and the requirements for developing electronic conduction properties are not, in consequence, satisfied. The conductivity of the as-prepared intercalates is 1.10^{-6} Scm^{-1} for both γ-ZrP-(**4a**)$_{0.22}$•0.8H$_2$O and γ-ZrP-(**4b**)$_{0.20}$• 0.7(octanol). Rather significant increases in these values are obtained by post-synthesis oxidation. Samples were exposed to Br$_2$ vapour in closed vessels, and the conductivity monitored as a function of time. This result is shown in Fig. 2. For both bis(amino)-TTF intercalates, the conductivity rises rapidly over the first 24 hours, before stabilising at a maximum value of 3.10^{-3} Scm^{-1} for γ-ZrP-(**4a**)$_{0.22}$•0.8H$_2$O and 2.10^{-3} Scm^{-1} for γ-ZrP-(**4b**)$_{0.20}$•0.7(octanol). Comparison may be made with the conductivity of radical cation salts prepared in solution by electrocrystallisation: 6.10^{-4} S cm^{-1} for **4a**-(ClO$_4$)$_2$ and 1.10^{-3} Scm^{-1} for **4a**-(PF$_6$)$_2$.

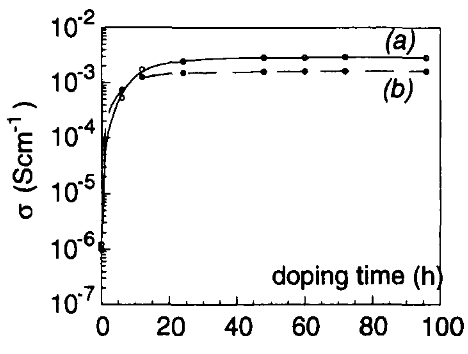


FIGURE 2 Conductivity of (a) γ-ZrP-(**4a**)$_{0.22}$•0.8H$_2$O/Br$_2$(g) (b) γ-ZrP-(**4b**)$_{0.20}$•0.7(octanol)/Br$_2$(g) as a function of the time of exposure to Br$_2$(g)

Raman and electron paramagnetic resonance spectroscopies were used to identify the change which had occured in the intercalated bis(amino)-TTFs in the presence of bromine. Firstly, EPR spectroscopy demonstrates oxidation of intercalated bis(amino)-TTFs after contact with bromine vapour, since both γ-ZrP-(**4a**)$_{0.22}$•0.8H_2O/Br_2(g) and γ-ZrP-(**4b**)$_{0.20}$•0.7(octanol)/Br_2(g) give EPR signals, indicating the presence of radical cations. Notably, the non-oxidised precursors, as well as bulk, non-intercalated **4a** and **4b**, are inactive in EPR [a vanishingly weak signal was obtained for γ-ZrP-(**4b**)$_{0.20}$•0.7(octanol)].

The degree of charge transfer in tetrathiafulvalene-type molecules can be quantified using Raman spectroscopy, since the position of the symmetric stretching vibration of the central C=C bond is directly related to the partial oxidation state of TTF [6]. Thus non-substituted TTF gives a line at 1515 cm^{-1}, and the fully oxidised species, TTF^+, a line at 1420 cm^{-1}. Raman spectra recorded of **4a**, **4b** and of the intercalates γ-ZrP-(**4a**)$_{0.22}$•0.8H_2O and γ-ZrP-(**4b**)$_{0.20}$•0.7(octanol) before and after exposure to bromine were recorded and those of the **4a** series are shown in Fig. 3. Here, it may be seen that the position of ν_s(C=C) is little displaced in **4a** and its direct intercalate (**4a**: 1488 cm^{-1}, intercalated **4a**: 1482 cm^{-1}). The position for the neutral molecule lies at lower frequency than that in non-functionalised TTF.

After contact with bromine vapour, Raman spectroscopy provides clear evidence that the intercalated species have undergone oxidation, so demonstrating the accessibility of the interlayer region in such materials. For γ-ZrP-(**4a**)$_{0.22}$•0.8H_2O exposed to bromine, ν_s(C=C) is shifted to 1428 cm^{-1}. The Raman spectrum given by bulk salts of known stoichiometry

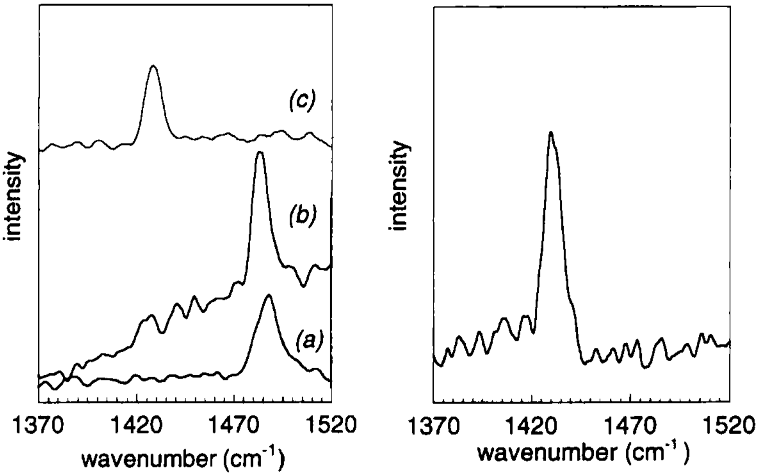


FIGURE 3 Raman spectra of (a) **4a** (b) γ-ZrP-(**4a**)$_{0.22}$•0.8H_2O (c) γ-ZrP-(**4a**)$_{0.22}$•0.8H_2O/Br_2(g) (d) **4a** - $(PF_6)_2$

prepared by electrocrystallisation provides a means of estimating the degree of electron transfer from the TTF core in the corresponding intercalate. Thus for **4a** - $(PF_6)_2$, $\nu_s(C{=}C)$ is observed at 1430 cm^{-1}, suggesting the intercalated bis(amino)-TTF **4a** to have a charge close to 0.5+ after bromine treatment.The system prepared using **4b** shows a similar evolution in the Raman spectrum: **4b**: 1473; intercalated **4b**: 1470 cm^{-1}; intercalated **4b**/Br_2(g): 1409 cm^{-1}. These spectra were recorded on samples giving the highest conductivities described above.

Oxidation of the TTF units within the interlayer region requires an accompanying process in order that charge balance be maintained. In the present case, insertion of Br^- or partial elimination of protons can be envisaged. In support of the former, a slow drop in conductivity with time (a factor *ca.* 10 after 1 month) is observed, possibly caused by loss of bromide from the interlayer region through reaction with interlayer protons or atmospheric moisture, and consequent partial reduction of the TTF core. Infrared spectra recorded after bromine treatment show the increasing background absorption towards high wavenumbers characteristic of electronically conducting domains.

In conclusion, the possibility of intercalating functionalised TTF-type molecules into layered hosts has been demonstrated. Although protonation of the end-groups occurs on intercalation, the "TTF" core remains electrically neutral, and the intercalates electrically insulating. Most interestingly however, the bis(amino)-TTFs between the phosphate layers are chemically accessible and can be oxidised post-synthetically, under which conditions radical cations form. Following bromine treatment, a decrease in the interlayer distance shown by X-ray diffraction provides evidence for structural rearrangement. The conduction properties then observed are compatible with reorganisation of the substituted TTF units into non-contiguous electronically conducting islets. Previous studies on the oxidative insertion of TTF in Cu(II) exchanged γ-ZrP have shown that both a partial oxidation state and high packing density of occluded TTF are required if the conductivity of the composites is to be maximised[2]. In this context, optimisation of the nature of the functionalised TTF is essential, since its uptake is controlled by the charge density on the layers inherent to the matrix, and its orientation on proton transfer/hydrogen bonding interactions between host and guest.

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