

Original Research Article

## A New Organic-inorganic Hybrid Nanocomposite, BEDT-TTF Intercalated into Layered FePS<sub>3</sub>

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### Abstract

A new inorganic–organic hybrid compound, Fe<sub>0.76</sub>PS<sub>3</sub>(BEDT-TTF)<sub>0.48</sub> (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene), has been synthesized by the reaction of the pre-intercalate Fe<sub>0.90</sub>PS<sub>3</sub>(Phen)<sub>0.41</sub> (phen = 1,10-phenanthroline) with (BEDT-TTF)<sub>2</sub>I<sub>x</sub>. The powder X-ray diffraction (XRD) results show that the expansion of the lattice spacing ( $\Delta d$ ) is about 4.0 Å compared with the pristine FePS<sub>3</sub>, indicating that the molecular ring plane of the guest is parallel to the layer of the host. The infrared spectrum of the intercalate shows the existence of BEDT-TTF as a guest between the interlayer region of the layered FePS<sub>3</sub>. The room-temperature electrical conductivity of the compressed pellet of Fe<sub>0.76</sub>PS<sub>3</sub>(BEDT-TTF)<sub>0.48</sub> is about 10<sup>-7</sup> S/cm, which is in the same order of magnitude as that of the pristine FePS<sub>3</sub> (~10<sup>-7</sup> S/cm). The magnetic properties measured with a SQUID-magnetometer indicate that Fe<sub>0.76</sub>PS<sub>3</sub>(BEDT-TTF)<sub>0.48</sub> exhibits the paramagnetism from 120 to 300 K and Curie-Weiss Law was obeyed above 140 K, but a strong antiferromagnetic phase transition occurs at T<sub>N</sub> of 100 K.

### Introduction

In recent years, intercalated MPS<sub>3</sub> compounds have attracted considerable attention of scientists due to interesting electronic and magnetic properties [1–4]. Transition metal phosphorous trisulfides (hexathiohypodiphosphates) MPS<sub>3</sub>, (M = Mn, Fe, Co, Ni, Zn and Cd, etc.) are layered compounds and crystallize to space group C2/m, a monoclinic unit cell related to CdCl<sub>2</sub>-type structure with metal ions and phosphorus-phosphorus pairs occupying the cadmium positions and sulfur ions occupying the chloride positions, so M ions construct a honeycomb lattice in the *ab* plane and they are separated by Van der Waals gap between hexagonal layers of sulfur ions [5, 6]. Many MPS<sub>3</sub> phases showed paramagnetism at high temperature range and become antiferromagnets below the Neel temperature (78 K for MnPS<sub>3</sub>, 120 K for FePS<sub>3</sub> and 153 K for NiPS<sub>3</sub>, respectively) [7]. Several MPS<sub>3</sub> compounds such as M = Mn, Fe, etc. possess a unique non-redox intercalation reaction based on the cation-exchange between the intralamellar M<sup>2+</sup> ions of the host and the guest cations in the solution where the inserted guests can compensate the intralamellar M<sup>2+</sup> ion vacancies to

maintain the charge balance [8, 9]. After intercalation, the magnetic property of some intercalates can be dramatically changed [10–12].

Tetrathiafulvalene (TTF) and its derivatives such as bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), as the excellent organic electron-donors, have constituted a series of organic conductors and superconductors [13–16]. The inorganic–organic hybrids based on the inorganic anions and BEDT-TTF salts have been extensively studied and some novel solid-state physical properties such as paramagnetic superconductivity and metallic-like conductive ferromagnetism have been exhibited [17, 18]. In addition, the intercalates of TTF into some layered hosts, such as FeOCl, Montmorillonite (MT) or MPS<sub>3</sub> etc, exhibit much higher conductivity than that of the corresponding pure host compounds owing to their column stacking arrangement of the mixed-valence TTF molecules between the layers of the host [19–22]. However, since Bringley *et al.* firstly reported BEDT-TTF-FeOCl intercalation compound in 1990 [23], few inorganic–organic hybrid intercalation nanocomposites based on BEDT-TTF molecules inserted into layered inorganic materials have been reported, and we had synthesized the intercalate of BEDT-TTF into layered MnPS<sub>3</sub> [24]. Compared with MnPS<sub>3</sub> and its intercalates the FePS<sub>3</sub> host showed

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higher conductivity and especially some  $\text{FePS}_3$  intercalation compounds exhibited ferromagnetism with higher Curie temperature ( $T_C = 70\sim 90$  K) than those of  $\text{MnPS}_3$  [25]. Therefore, it deserves more study on the intercalation of BEDT-TTF into layered  $\text{FePS}_3$ , which may produce new physical properties. In this paper, we present synthesis, structural characterization and some physical properties of the resulting intercalation material.

## Experimental

X-ray powder diffraction (XRD) patterns were obtained with Dmax rA X-ray diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418$  Å). Infrared spectra were performed on a Nicolet-170SX Fourier transform spectrometer. UV-vis spectra were conducted on Shimadzu UV-1206 spectrometer. Elemental analysis of carbon, hydrogen and nitrogen was performed with a Carloerba-1106 micro-analyzer. The content of iron and phosphorus were measured by the method of ICP-AES with an Atomscan-2000 instrument. The conductivity was measured with classical two-probe method. Thermogravimetric analysis (TGA) was conducted in a Rigaku Thermoflex TG 8110 at a heating rate of  $10$  °C/min. The magnetic property was studied by SQUID-magnetometer (MPMS, Quantum Design).

Pure  $\text{FePS}_3$  was synthesized as described by Taylor *et al.*, which was identified by means of XRD and indexed in a monoclinic unit cell (space group  $\text{C2/m}$ ,  $d = 6.439$  Å,  $a = 5.934$  Å,  $b = 10.280$  Å,  $c = 6.722$  Å,  $\beta = 107.16$  °) [26].

$\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  was synthesized according to the literature method [27].  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  was obtained by treating  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  (0.20 g) with  $(\text{BEDT-TTF})_2\text{I}_x$  (0.40 g) in the dry acetonitrile (20 ml) for two months at  $60$  °C, followed by filtration and washing several times with dichloromethane and acetonitrile, respectively. Elemental analyses led to the stoichiometry of the intercalate to be  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  (Found: Fe, 12.02; C, 16.37; H, 1.05; P, 8.79 (%). Calculated: Fe, 11.98; C, 16.28; H, 1.09; P, 8.74 (%)). TGA of the intercalate powder shows a single step weight loss from about  $240$  to  $600$  °C, where the total weight loss is 55.52%. This result is in agreement with the molecular formula as  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  that gives the calculated total weight loss of 52.12% if only the organic species are completely decomposed.

## Results and discussion

### Synthesis

In the synthesis of  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$ , it was found that the UV-vis spectrum of the filtrate for preparation of intercalate  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  combines the spectra of  $[\text{Fe}(\text{phen})_3]\text{I}_2$  and  $(\text{BEDT-TTF})_2\text{I}_x$

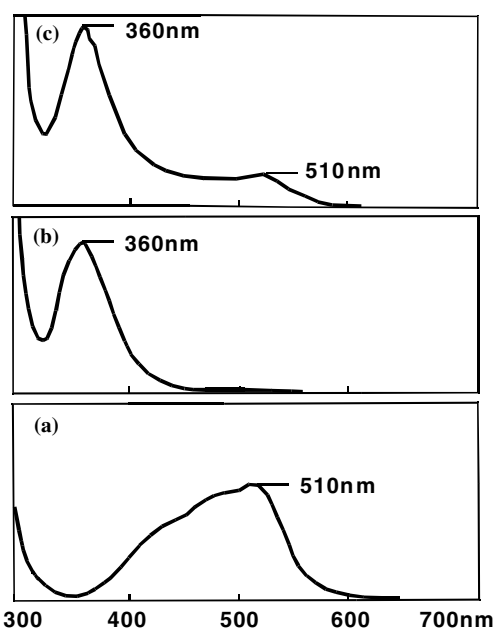


Figure 1. The UV-vis spectra of  $[\text{Fe}(\text{phen})_3]\text{I}_2$  in acetonitrile (a),  $(\text{BEDT-TTF})_2\text{I}_x$  in acetonitrile (b) and the filtrate of  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  (c).

$(\text{BEDT-TTF})_2\text{I}_x$  in acetonitrile, which shows two characteristic  $\lambda_{\text{max}}$  at around 360 and 510 nm (Figure 1). The absorption at 510 nm is the characteristic absorption band of  $\text{Fe}(\text{phen})_3^{2+}$  indicating the occurrence of  $\text{Fe}(\text{phen})_3^{2+}$  in the filtrate [28]. It is clear that 1,10-phenanthroline acting as a complex agent which removes extra intralamellar  $\text{Fe}^{2+}$  ions into the solution during the intercalation. Thus, there exist more  $\text{Fe}^{2+}$  ion vacancies in the intralayer sites of  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  than that of pre-intercalate  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$ .

### Powder X-ray diffraction

The occurrence of the intercalation is ascertained by the XRD of the final product (Figure 2). The reflections of pre-intercalate  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  are fully absent in the XRD patterns of the intercalate. Instead, a new series of reflection peaks appeared, which is also different from those of pristine  $\text{FePS}_3$  (Figure 2). The lamellar distance of the intercalate is 10.4 Å, expanding by 4.0 Å with respect to the pristine  $\text{FePS}_3$  indicating the orientation of BEDT-TTF molecular plane is parallel to layer of the host similar to that of pyridine molecule inserted into  $\text{FePS}_3$  [25] (Figure 3). This expansion is much different from that of BEDT-TTF intercalated in  $\text{FeOCl}$ , where the increasing space is around  $14.0 \sim 15.0$  Å, indicating that the long  $\text{C}_2$  axial of BEDT-TTF molecule is arranged in a canted angle from the perpendicular with respect to  $\text{FeOCl}$  layers [23]. From the XRD patterns it is obviously found that the reflection patterns of  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  is not sharper than those of pure  $\text{FePS}_3$  and pre-intercalate  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$ . This clearly shows that the crystallinity of this intercalate is

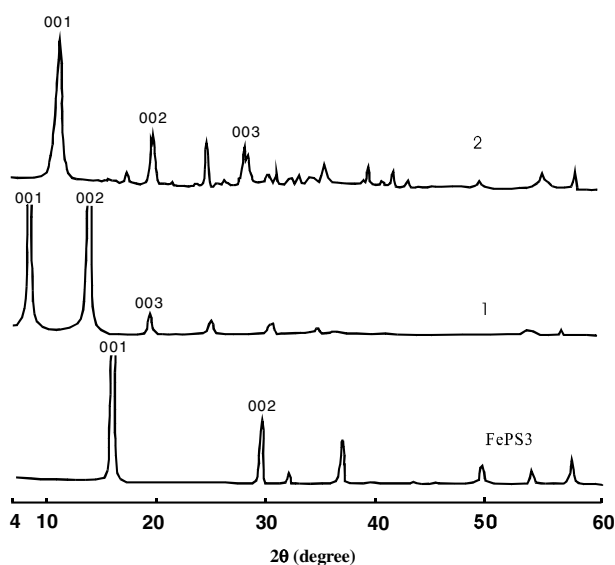


Figure 2. The XRD patterns of pure  $\text{FePS}_3$ , pre-intercalate  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  (1) and Intercalate  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  (2).

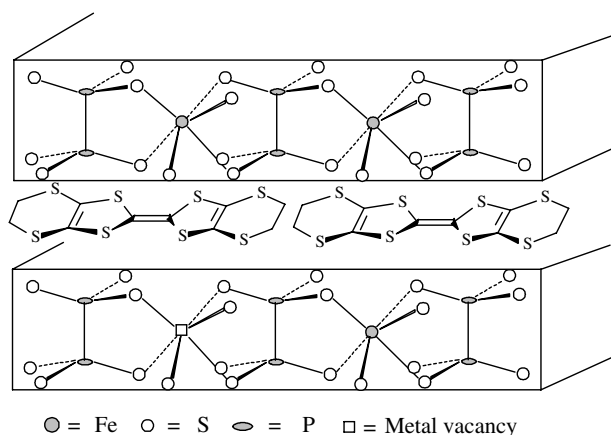


Figure 3. The possible orientation of BEDT-TTF molecule between the interlayer region of  $\text{FePS}_3$ .

not as good as that of pure  $\text{FePS}_3$  and pre-intercalate  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$ .

#### Infrared spectra

Figure 4 shows the IR spectra of pre-intercalate  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$ , intercalate  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$ , BEDT-TTF for comparison.

In general, the intercalation compounds based on  $\text{MPS}_3$  ( $M = \text{Mn, Fe, Cd}$  etc) have two or three sharp absorptions in the range of  $550 \sim 610 \text{ cm}^{-1}$ , which are assigned to the  $(\text{PS}_3)$  asymmetric stretching band coming from the splitting of  $570 \text{ cm}^{-1}$  in pure  $\text{MPS}_3$  owing to departure of a fraction of ions into the solution during the intercalation. The occurrence of the intralaminar  $\text{M}^{2+}$  vacancies makes the P-S bonds in the group of  $\text{PS}_3$  unequivalent because some of  $\text{PS}_3$  groups are surrounding the  $\text{M}^{2+}$  vacancies and others are also coordinated to the  $\text{M}^{2+}$  ions [25]. Therefore, the infrared absorptions at  $610, 590$  and  $556 \text{ cm}^{-1}$  in the  $\text{Fe}_{0.76}$

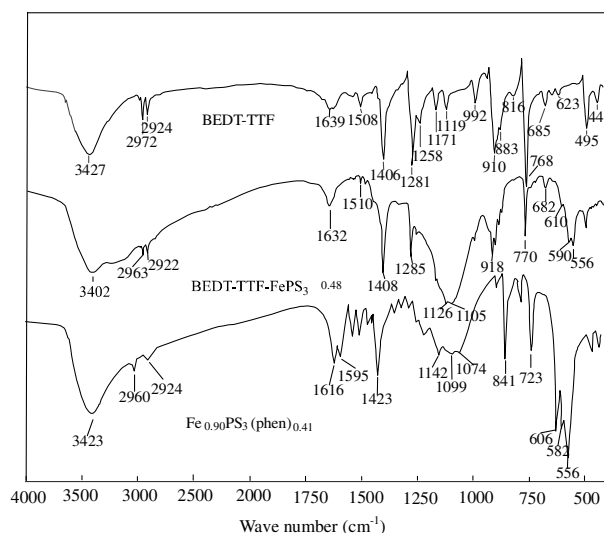


Figure 4. The comparison of IR spectra of pre-intercalate  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$ , intercalate  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  and BEDT-TTF.

$\text{PS}_3(\text{BEDT-TTF})_{0.48}$ , which is similar to those of TTF inserted into  $\text{MPS}_3$  ( $M = \text{Mn, Fe}$ ) [29], are assigned to  $\nu(\text{PS}_3)$  asymmetric stretching vibration of the host. This comes from the splitting of  $570 \text{ cm}^{-1}$  in pure  $\text{FePS}_3$ , reflecting the presence of intralayer  $\text{Fe}^{2+}$  ion vacancies. In the range of  $650 \sim 1700 \text{ cm}^{-1}$ , the infrared spectrum of  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  shows the similar characteristic absorption bands (at around  $1408, 1285, 918$  and  $770 \text{ cm}^{-1}$ ) to those of BEDT-TTF molecule [30]. It also proves that the existence of BEDT-TTF as a guest inserted into the interlayer region between the host layers.

#### Electrical conductivity and magnetic properties

The conductivity of  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  (as the compressed pellet) at room temperature measured with two-probe method is about  $10^{-7} \text{ s cm}^{-1}$ , which is at the same order of magnitude to the pristine  $\text{FePS}_3$  ( $\sim 10^{-7} \text{ s cm}^{-1}$ ). From the XRD result, it was found that the orientation of BEDT-TTF molecule ring plane is arranged parallel to layer of the host. Apparently, the BEDT-TTF molecules cannot arranged in the column stacking in the interlayer region, so the conductivity of interaction compound is due to the host layer.

The magnetic properties of  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  were studied with a SQUID magnetometer. The antiferromagnetic transition at around  $120 \text{ K}$  in pure  $\text{FePS}_3$  no longer exists. Figure 5 displays the molar susceptibility versus temperature and Figure 6 shows the plot of  $\chi T$  versus  $T$  of  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$ .

Figure 5 clearly shows the antiferromagnetic phase transition at around  $100 \text{ K}$ . The  $\chi T$  value slightly decreases from  $300$  to  $130 \text{ K}$  shown by the plot of  $\chi T$  vs.  $T$  (in Figure 6), which indicates that the coupling interaction between the  $\text{Fe}^{2+}$  ions is a weak antiferromagnetic one in the paramagnetic range. This behavior is confirmed by the inverse of the paramagnetic susceptibility of  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  displayed as a function of temperature (Figure 5). Above  $140 \text{ K}$ , the

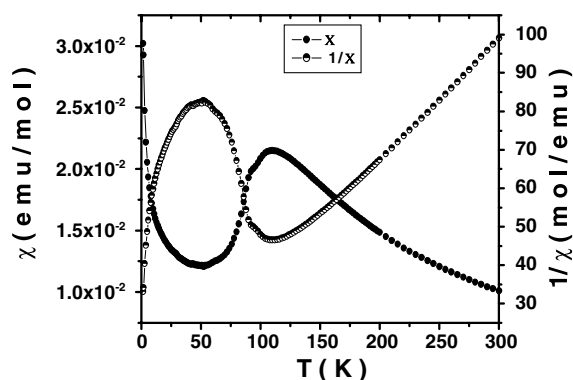


Figure 5. The temperature dependence of magnetic susceptibility and inverse of magnetic susceptibility of  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$ .

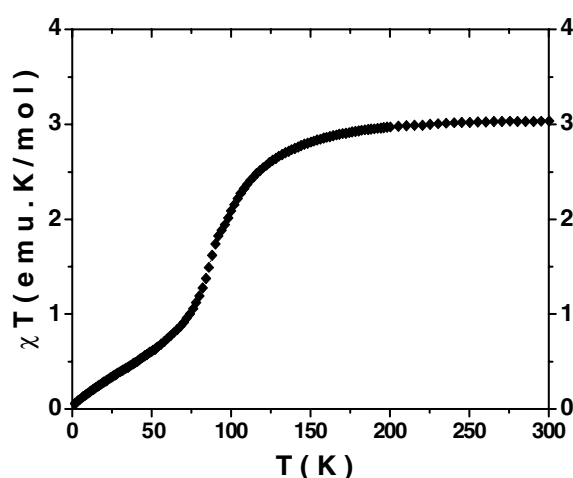


Figure 6. The plot of  $\chi T$  vs.  $T$  of  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$ .

inverse of the paramagnetic susceptibility fits to Curie-Weiss Law very well. The Curie constant is  $3.03 \text{ emu K mol}^{-1}$  and the effective magnetic moment per  $\text{Fe}^{2+}$  ion is evaluated as  $4.92 \text{ BM}$ , which is closed to that of the spin-only value of high spin  $\text{Fe}^{2+}$  ion ( $4.94 \text{ BM}$ ) [31]. This suggests that the  $\text{Fe}^{2+}$  ion is still in the  $+2$  oxidation state in  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  after intercalation. The Curie-Weiss temperature ( $\theta$ ) is only  $-24.69 \text{ K}$  that also reflects the weak localized antiferromagnetic coupling interaction between the  $\text{Fe}^{2+}$  ions due to the strong dilution of the more intralamellar  $\text{Fe}^{2+}$  ion vacancies of the host in the high temperature range. Below  $120 \text{ K}$ , the  $\chi T$  value decreases rapidly, which supports the occurrence of strong antiferromagnetic phase transition too.

## Conclusion

The intercalate,  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$ , is synthesized though the ion exchange of the pre-intercalate  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  with  $(\text{ET})_2\text{I}_x$ . The structural characterization is ascertained with XRD and IR spectra as well as the elemental analysis, in which XRD result indicates that the BEDT-TTF molecules is adap-

ted in parallel orientation to the layer of the host. For the compressed pellet of  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$ , the room-temperature electrical conductivity of  $\sim 10^{-7} \text{ S/cm}$  is about the same order of magnitude to that of pure  $\text{FePS}_3$ . The magnetic measurements indicate that  $\text{Fe}_{0.76}\text{PS}_3(\text{BEDT-TTF})_{0.48}$  exhibits an antiferromagnetic transition at  $T_N$  of  $100 \text{ K}$  and the curve of the inverse of the molar susceptibility versus temperature obeys the Curie-Weiss Law above  $140 \text{ K}$ .

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