



Synthesis, structure and properties of crystalline and nanocrystalline MnPS₃-poly(phenylene vinylene) intercalates



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ABSTRACT

The preparation of luminescent semiconducting nanocomposites of crystalline and amorphous manganese phosphorus trisulfide (MnPS₃), containing intercalated poly(phenylene vinylene) [PPV] is reported. The materials were characterized by thermogravimetric analysis, infrared and Raman spectroscopy and X-ray diffractometry. Scanning electron microscopy was used to monitor the crystallinity and morphology of the host materials.

An average increase of 5.05 Å in the interlayer distance of MnPS₃ was observed by XRD, as a result of the intercalation of PPV. The resulting composite materials presented more stable photoluminescent properties than unintercalated PPV, and with slightly blue-shifted emission; they exhibited significantly higher electronic conductivities than MnPS₃ or the polymer alone. The effects of the intercalation host on the optical and electronic properties of the PPV guest are discussed.

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1. Introduction

Poly(*p*-phenylene vinylene) (PPV) is one of the most-studied electroluminescent conjugated polymers. It exhibits bright yellow-green fluorescence with an emission maximum at 551 nm (2.25 eV), and that property made it a prototype polymer for light-emitting diodes. Its electrical conductivity is enhanced upon oxidation (or reduction), which creates mobile radical ions and makes it a *p*-type (or *n*-type) semiconductor. However, like all opto-electronic polymers, it can degrade in the presence of oxygen and moisture; this results in the formation of crosslinks between the polymer chains, loss of delocalization and decreased electronic conductivity [1–3].

A possible solution to such problems is to synthesize composites containing the emissive polymer inside a lamellar-structured inorganic host that can accommodate organic molecules between its layers. The geometrical restrictions imposed by the inorganic host could result in better-organized polymer chains that would facilitate charge injection and transfer between the conducting units. Several research groups have reported the formation of composites of PPV and inorganic two-dimensional insulators [4–7]; however, intercalates of PPV between the layers of transparent semiconducting divalent metal

thiohypophosphates (M^{II}PS₃ or M^{II}₂P₂S₆) and their luminescent properties have not been explored. In this paper, we report the synthesis and characterization of luminescent organic-inorganic composites containing PPV-intercalated MnPS₃.

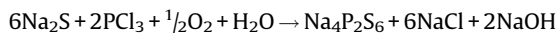
The divalent metal thiohypophosphates are layer-structured compounds that have been studied by several research groups, mostly due to their ability to intercalate guest molecules, forming organic-inorganic materials with interesting magnetic and electronic properties [8–11]. In addition to their versatile intercalation chemistry, M^{II}PS₃ materials are often quite transparent in the visible region, which makes them ideal hosts for luminescent polymers with optoelectronic applications [12].

MPS₃ compounds are usually prepared as macroscopic crystals by high-temperature techniques [8–11]; however, they can also be produced as colloidal nanoparticles in aqueous solution at room temperature. This was first done by Foot et al. [13] by mixing a source of thiohypophosphate (P₂S₆)⁴⁻ anions and a solution of M²⁺ cations. The process results in the production of large quantities of amorphous or nanocrystalline MPS₃ with analogous properties to those made by the inconvenient solid-state synthesis at high temperatures. Moreover, the crystallinity can be readily increased by annealing the products at about 300 °C for 2–4 h [13]. This method permits the production of thin-film coatings suitable for photovoltaic or photo-electrochemical applications.

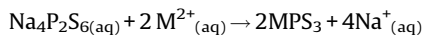
One of the sources of (P₂S₆)⁴⁻ used in the low-temperature route was the soluble sodium salt Na₄P₂S₆, first prepared by Falius [14]. The stoichiometric equation for the synthetic reaction is:

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Colloidal MPS_3 compounds or amorphous precipitates are subsequently formed by reacting solutions of $\text{Na}_4\text{P}_2\text{S}_6$ with solutions of the metal in the M^{2+} state, and the overall reaction can be written as follows:



The main aim of the present work was to synthesize and study manganese (II) thiohypophosphate (MnPS_3 or $\text{Mn}_2\text{P}_2\text{S}_6$) as a host material for the preparation of conjugated polymer/inorganic composites. Much previous investigation has been carried out on other MPS_3 intercalates of simple molecules, but this work has focused on the intercalation of the luminescent semiconductor PPV into MnPS_3 .

As well as synthesizing single crystals and polycrystalline samples of MnPS_3 by the conventional high temperature method, we have used the alternative low-temperature route to produce them from colloidal suspensions, and have studied the physical and spectroscopic properties of the resulting nanocomposite materials with PPV.

2. Experimental

The overall synthetic strategy is outlined in [Scheme 1](#).

2.1. Synthesis of intercalated composites

Intercalation of MnPS_3 (obtained by high-temperature synthesis)

All chemicals were purchased from Sigma Aldrich Ltd., UK, and used without further purification.

2.1.1. Synthesis of *p*-xylylene-bis(tetrahydrothiophenium chloride) (monomer) and poly(*p*-xylylene-bis(tetrahydrothiophenium chloride)) (PPV precursor polymer)

Both of the above salts were synthesized by following the route described by Wessling and Zimmerman [15].

2.1.2. Synthesis of MnPS_3

Stoichiometric amounts of sulfur (99.9%) (2.12 g; 0.06 mol), red phosphorus (99.9%) (1.02 g; 0.03 mol) and manganese (II) sulfide (99.9%) (1.81 g, 0.02 mol) were sealed in 20 cm long evacuated quartz tubes. The tubes were then heated at 720 °C with a linear temperature gradient to form crystalline products by sublimation at 680 °C, in a 3-zone tube furnace for 4 weeks, according to established methods [8,11].

Green polycrystalline material and thin platelet crystals were obtained from the crystal growth ampoule. The single crystals were typically about $1.4 \times 1.2 \times 0.03 \text{ mm}^3$. ICP analysis of a sample (single crystal) after dissolution in aqua regia led to the approximate formula $\text{Mn}_{0.93}\text{P}_{1.0}\text{S}_{3.3}$, but powder x-ray diffractometry (see below) only gave peaks in accordance with those for the stoichiometric compound, $\text{Mn}_2\text{P}_2\text{S}_6$ (JCPDS file #33-0903). Yield obtained: 4.38 g (73%).

2.1.3. Potassium ion intercalation

Single crystals of MnPS_3 (0.04 g; 2.14×10^{-4} mol) were added to an aqueous solution of KCl (5.0 mL; 2 M). The mixture was stirred for 2 h at ambient temperature. The solid was filtered off, washed with distilled water and dried under vacuum for 24 h at 80 °C. The product obtained (designated K_MnPS_3) was $\text{K}_{0.5}\text{Mn}_{0.75}\text{PS}_3$. Yield: 0.020 g (44%).

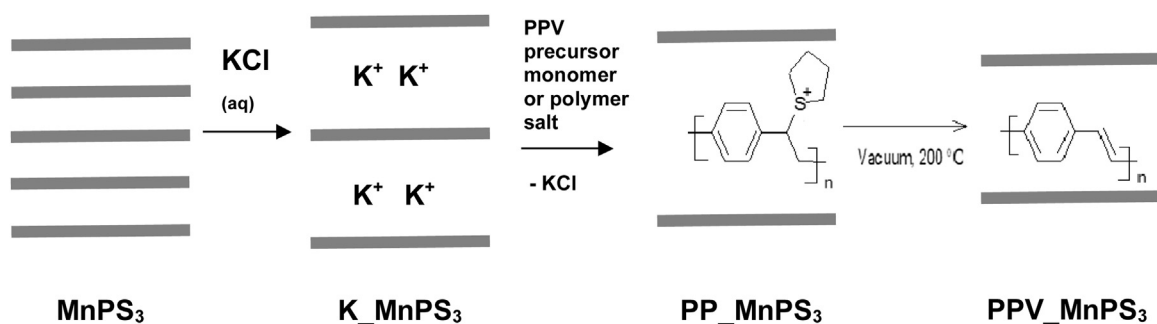
2.1.4. PPV intercalation

K_MnPS_3 crystals (0.06 g; 2.73×10^{-4} mol) were added to a methanolic solution of the precursor monomer *p*-xylylene-bis(tetrahydrothiophenium chloride) (11 mL; 0.2 M). The mixture was left stirring for 24 h under nitrogen; then it was cooled to 0 °C and NaOH (11 mL; 0.2 M; 0 °C) was added, after which it was stirred for a further hour. HCl (1 M) was then added to neutralize it, and stirring was continued for two more hours, keeping the mixture at 0 °C throughout the reaction. A green-yellow suspension was formed, containing the intercalated crystals, and it was dialyzed against water ($3 \times 2 \text{ L}$) for 3 days to remove K^+ , Mn^{2+} , Na^+ and Cl^- ions. After this, the intercalated crystals containing poly(*p*-xylylene-bis(tetrahydrothiophenium chloride)) (PPV precursor polymer) were filtered off, washed with methanol several times and then dried. Finally, they were placed under a stream of nitrogen and heated to 230 °C for 30 min to convert the precursor to PPV.

2.2. Intercalation of MnPS_3 (obtained by ambient-temperature solution route)

$\text{Na}_4\text{P}_2\text{S}_6 \cdot 6\text{H}_2\text{O}$ was synthesized according to the literature method of Falius [14].

Two micellar solutions were prepared separately, using a similar approach to one in the literature [16,17]. One of them contained Brij-97 surfactant (3.2 g) in cyclohexane (40 mL), aqueous $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.02 g in 1.5 mL H_2O) and precursor polymer solution (5 mL, 0.2 M). The other solution contained Brij-97 (4.0 g) in cyclohexane (50 mL) and $\text{Na}_4\text{P}_2\text{S}_6 \cdot 6\text{H}_2\text{O}$ (0.03 g in 3 mL H_2O). The two solutions were mixed and left stirring for 48 h, and ethanol



Scheme 1. Synthetic pathway for PPV intercalation in MnPS_3 .

Abbreviations: MnPS_3 , MnPS_3 synthesized by a solid-state reaction at high temperature; $\text{MnPS}_3\text{-LT}$, MnPS_3 synthesized by solution chemistry at room temperature.; K_MnPS_3 , K^+ -intercalated MnPS_3 ; PP_MnPS_3 , PPV precursor polymer-intercalated MnPS_3 ; PPV_MnPS_3 , PPV-intercalated MnPS_3 ; $\text{PPV_MnPS}_3\text{-LT}$, PPV-intercalated $\text{MnPS}_3\text{-LT}$.

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