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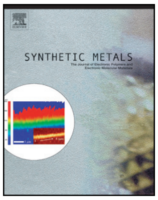

Self-ordering of organic-metal hybrid microstructures based on tetrathiafulvalene derivatives

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ABSTRACT

Two divalent transition metal complexes of EDT-TTF-4-py (EDT-TTF-4-py = 4-ethylenedithiotetrathiafulvalenyl-pyridine) have been prepared and characterized in micro and bulk crystal forms. These hybrid microstructures were synthesized by coordinative self-assemble through a solution process. The isostructural $Cu(hfac)_2$ and $Mn(hfac)_2$ (hfac = hexafluoroacetylacetonate) complexes crystallize in the monoclinic space group $P2_1/c$. Two pyridyl N atoms from two different molecules of EDT-TTF-4-py are coordinated in the trans configuration to the metal ion of $M(hfac)_2$ to form an octahedral complexes. The results of the elemental analysis, FT-IR, SEM-EDX and PXRD, show the chemical composition of the microstructures which are same as that of bulk crystals. Moreover, these two microstructure compounds are precursor for both conducting and magnetic materials. These investigations show the intriguing potentials of the coordinative bond in the development of multifunctional hybrid microstructures.

1. Introduction

The development of one-dimensional (1D) micro- and nanostructures has received considerable interest in recent years for their uses as tunable electronic and optical properties [1,2]. In the molecular conductor research field, mostly molecular conductors are usually prepared and studied in single crystals. Because the single-crystalline samples are brittle for practical applications, the micro- and nanostructures scale size molecular conductors are needed. Control over self-assembling nanostructures constitutes a major challenge in contemporary research [3–5]. Many synthetic methods have been reported to accomplish 1D growth of nanostructures of molecular conductors, such as by using electrocrystallization with templates such as porous aluminum oxide and phospholipid multilamella as the electrode [6–8], and more, creation of temple-free and facile approaches are still required for future practical application [9–11].

As famous donor molecules, TTF is a π-conjugated system that has been exploited thoroughly as a conductive material [12,13]. Many attempts have been made to derivatize TTF with functional groups which capable of binding to transition-metal ions. In particular, pyridyl derivatives have been widely used for their chelating ability toward various transition metals. These properties make them attractive building blocks for multifunctional hybrid materials. Consequently, hybrid TTF-py (py = pyridyl) with paramagnetic transition metal has formed an important category of bifunctional materials [14–23].

Coordinative interaction based on metal ions coordinated with organic ligands has been fashioned into micro- or nanometer-size materials [24–26]. Wu et al. reported that donor molecule which TTF motif and pyridyl group are linked by π-conjugated bridge would form semiconducting neutral polymers microstructure by coordinative self-assemble [27]. However, there are only a few reports of metal-induced solution phase self assembly of electronically active molecules and more efforts to realize self assembly of π-donor systems to metal ions are required.

Our strategy involves the TTF derivatives EDT-TTF-4-py, (as shown Scheme S1 in the Supporting information), which have a pyridine group (metal-ion binding group) directly attached at the periphery without a space. Such a donor molecule could have the strong tendency to assemble among a specific direction by strong coordination interaction. Recently, Shao et al. demonstrated that donor molecule with strong tendency to assemble along a specific direction could form micro/nanocrystals of magnetic molecular conductor by electrocrystallization without template [10]. Among them, EDT-TTF-4-py with a pyridine ring seems to have the strong

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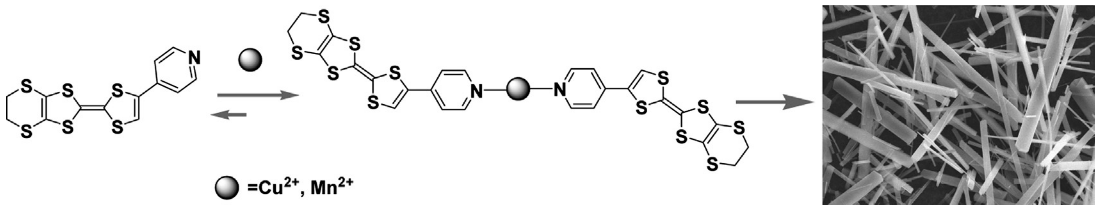

Scheme 1. The schematic formation of the organic-metal hybrid microstructures of EDT-TTF-4-py.

tendency to assemble along a specific direction by directional coordination-bond interaction.

In the present work, we report a new type of TTF-based microstructures that is formed by the coordinative method. Taking advantage of the ability of the pyridine-based organic ligands to coordinate transition metals, we prepared two new coordination complexes formulated as (EDT-TTF-4-py)$_2$M(hfac)$_2$ (M = Cu^{2+} **1**, Mn^{2+} **2**) (Scheme 1). One-dimension (1D) micro and bulk crystal have been prepared when M(hfac)$_2$ (M = Cu^{2+}, Mn^{2+}) ions were added with EDT-TTF-4-py at different reaction conditions. Moreover, we got the crystal structures of the bulk crystals, and elemental analysis, FT-IR, SEM-EDX and powder XRD results show that the chemical composition of the microstructures is the same as that of bulk crystal.

2. Experiment

2.1. Materials and methods

All reagents were of analytical grade and used as received. The TTF compound EDT-TTF-4-py (a) and the reference compound EDT-TTF-4-ph (b) (Scheme S1 in the Supporting information) were synthesized according to the procedures we have previously reported [28]. FT-IR spectra were recorded on a Bruker IFS 66. The SEM images and EDX results were obtained on a Hitachi S-4300. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C analyzer. The powder XRD results were performed by using a Brucker D8 X-ray diffractometer with graphite-monochromator Cu Kα radiation (λ = 0.15418 nm).

2.2. Synthesis and characterization

2.2.1. Preparation of microcrystal

In a typical experiment, M(hfac)$_2$ (0.05 mmol) in hexane (5 mL) was layered over a solution of precursor a EDT-TTF-4-py (0.05 mmol) in dichloromethane (5 mL). The mixed solution was stirred for 30 min at 35 °C, a purple precipitate was found.

(EDT-TTF-4-py)$_2$Cu(hfac)$_2$: (M = Cu) microcrystal **1**
Yield: 31.1; mg, 50.8%.

Elemental analysis calcd (%) for $C_{36}H_{20}CuF_{12}N_2O_4S_{12}$: C 35.42, H 1.64, N 2.29; Found: C 35.45, H 1.68, N 2.32.

(EDT-TTF-4-py)$_2$Mn(hfac)$_2$: (M = Mn) microcrystal **2**
Yield: 34.2; mg 56.5%.

Elemental analysis calcd (%) for $C_{36}H_{20}MnF_{12}N_2O_4S_{12}$: C 35.67, H 1.65, N 2.31; Found: C 35.71, H 1.68, N 2.33.

2.2.2. Preparation of bulk single crystal

Single crystals of complexes (EDT-TTF-4-py)$_2$M(hfac)$_2$ (M = Cu and Mn) suitable for X-ray diffraction analysis were obtained by slow diffusion. M(hfac)$_2$ (0.01 mmol) in hexane (5 mL) was layered over a solution of precursor a EDT-TTF-4-py (0.02 mmol) in dichloromethane (5 mL) at 10 °C. The reaction mixture was left to stand undisturbed for 2 weeks. Shiny purple crystals were isolated by filtration, washed with hexane, and air-dried at room temperature.

(EDT-TTF-4-py)$_2$Cu(hfac)$_2$: (M = Cu) bulk crystal **1** Yield: 2.4 mg, 19.6%.
(EDT-TTF-4-py)$_2$Mn(hfac)$_2$: (M = Mn) bulk crystal **2** Yield: 1.8 mg, 14.9%.

2.3. *Single-crystal structure determination for bulk crystal of (EDT-TTF-4-py)$_2$M(hfac)$_2$ (M = Cu and Mn) [M = Cu^{2+} **1**, Mn^{2+} **2**]*

X-ray diffraction data were collected at room temperature on a Rigaku AFC-7 Mercury CCD diffractometer with a graphite monochromated Mo Kα radiation (λ = 0.71070 Å). Lorentz and polarization corrections were applied. The structures of these compounds were solved by a direct method (SIR92) [29], expanded by DIRDIF94 [30], and refined on *F* with a full-matrix least squares analysis. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model [d(C—H) = 0.95 Å]. All the calculations were performed using the Crystal Structure crystallographic software package of the Molecular Structure Corporation [31]. Crystal data and structure refinement parameters are given in Table 1. All data (except structure factors) have been deposited with the Cambridge Crystal-

Table 1
Crystal data and structure refinement for complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{36}H_{20}F_{12}CuN_2O_4S_{12}$	$C_{36}H_{20}F_{12}MnN_2O_4S_{12}$
Formula weight	1220.82	1212.20
T (K)	293.1	293.1
Wavelength (Å)	0.71075	0.71075
Crystal system	Monoclinic	Monoclinic
Space group	$P21/c$	$P21/c$
a (Å)	18.763(5)	19.182(4)
b (Å)	6.8501(17)	6.7631(12)
c (Å)	19.935(6)	20.171(4)
β (°)	116.206(3)	116.2907(19)
V (Å^3)	2298.9(11)	2346.1(8)
Z	4	4
Dc (g cm^{-3})	1.764	1.716
Abs. coeff. (mm^{-1})	1.111	9.047
F(0 0 0)	1222.00	1214.00
Crystal size (mm^3)	0.60 × 0.10 × 0.05	0.70 × 0.30 × 0.25
Limiting indices	$-18 \le h \le 25, -6 \le k \le 9, -26 \le l \le 26$	$-25 \le h \le 19, -6 \le k \le 9, -25 \le l \le 26$
Reflections collected	18,001	20,074
Independent reflections	3813[R(int) = 0.0581]	4528[R(int) = 0.0581]
Abs. correction	None	None
Refinement method	Full-matrix least-squares on F	Full-matrix least-squares on F
Data/restraints/parameter	3813/0/314	4528/0/314
GOF on F^2	1.076	1.066
R indices (all data)	$R_1 = 0.0433$, $wR_2 = 0.0540$	$R_1 = 0.0467$, $wR_2 = 0.0595$
Largest differences in peak and hole (e Å^{-3})	0.70 and −0.48	0.59 and −0.47