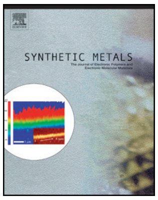
Synthetic Metals 203 (2015) 255–260

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Synthesis, structure, and properties of coordination complexes based on zinc halides and TTF-pyridyl ligand

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ARTICLE INFO

Article history:
Received 25 December 2014
Received in revised form 12 February 2015
Accepted 17 February 2015
Available online 10 March 2015

Keyword:
TTF derivative
Pyridine substitution
Coordination complexes
Microstructures
Self-assembly

ABSTRACT

Two Zn^{II} coordination complexes of EDT-TTF-4-py, (EDT-TTF-4-py = 4-ethylenedithiotetrathiafulvalenyl-pyridine) have been synthesized and characterized in micro and bulk crystal forms. These two complexes were synthesized by coordinative self-assemble through a solution process. At room temperature, the complex **2**, $(\text{EDT-TTF-4-py})_2{\cdot}ZnBr_2{\cdot}CH_2Cl_2$ shows high conductivity without external manipulation, whereas the complex **1**, $(\text{EDT-TTF-4-py})_2{\cdot}ZnCl_2$ is an insulator. These investigations show that the size of the halide and the difference of the molecular packing motif could result different conductive properties in these two complexes.

1. Introduction

Coordinative interaction based on metal ions coordinated with organic ligands has been fashioned into micro- or nanometer-size materials, and more, coordinative self-assembly method has attracted much attention as it is an easy procedure to implement, under very mild conditions, to afford micro- or nanometer-sized materials [1]. And the development of electrically active low-dimensional micro- and nano-materials, such as metallic or semiconducting particles, wires, and tubes, have attracted considerable interest due to their uses as tunable electronic and optical properties [2,3]. In particular, the assemblies of π-conjugated molecules have attracted special interest because of their great potential for the directional transportation of electrons and energy along with their molecular stacks. As a famous donor molecule, tetrahiafulvalene (TTF) is a π-conjugated system that has been exploited thoroughly as electrically conducting materials [4,5]. Significantly, high electrical conductivity has also been got by neutral metal complex such as $Ni(tmdt)_2$ with electroactive TTF ligands [6]. Furthermore, Wu et al. reported that the donor molecule which the TTF motif and one pyridyl group are linked by a π-conjugated bridge would form semiconducting neutral polymer microstructure by the coordinative self-assembly method [1,13–16].

Recently, several TTF-py(py = pyridine) compounds have been reported, which the pyridyl group is directly attached to the TTF core without any spacer part, which could increase the electronic coupling between the TTF moiety and the pyridine group [7–12]. And our group also reported a TTF-py donor molecule, EDT-TTF-4-py, **L1** (Scheme 1) could form microstructures by the coordinative self-assembly method [13]. However, there are only a few reports of the metal-induced self-assembly of electrically active molecules and more efforts to realize self-assembly of π-donor systems with metal ions are required.

In our previous work, we reported that the molecule which a pyridyl group is directly attached to the TTF core without any spacer showed remarkable sensing and coordinating properties only toward Zn^{2+} ion in solution [17]. Here, when we used the ligands as ZnX_2 (X=Br, Cl) and **L1**, we obtained two coordination complexes formulated as $(\mathbf{L1})_2{\cdot}ZnX_2$ (X=Br, Cl) due to the remarkable coordinating properties of the ligand **L1** to the Zn^{2+} ion. One-dimensional (1D) micro and bulk crystals had been prepared when ZnX_2 (X=Br, Cl) were added with **L1** at the different reaction conditions. Moreover, we determined the molecular structures of the bulk crystals. And more, elemental analysis, FT-IR and SEM-EDX results showed that the chemical composition of the microstructures were the same as that of the bulk crystal except for

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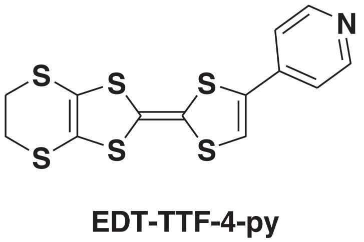
http://dx.doi.org/10.1016/j.synthmet.2015.02.022
0379-6779/



Scheme 1. Molecular structures of EDT-TTF-4-py.

solvent molecules. Unexpectedly, the neutral hybrid $(\mathbf{L1})_2{\cdot}ZnBr_2{\cdot}CH_2Cl_2$ showed a high conductivity at room temperature whereas the $(\mathbf{L1})_2{\cdot}ZnCl_2$ is an insulator at the same condition.

2. Experiment

2.1. Materials and methods

All reagents were of analytical grade and used as received, the TTF compound EDT-TTF-4-py (**L1**) was synthesized according to the procedures we had previously reported [13]. 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 PerkinElmer 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 of $(\mathbf{L1})_2{\cdot}ZnX_2$ [X=Cl **1**, Br **2**]

ZnX_2 (0.05 mmol) in hexane (5 mL) was layered over a solution of EDT-TTF-4-py (0.1 mmol) in dichloromethane (5 mL). After the mixed solution was stirred for 30 min at room temperature, black or red precipitates were formed.

$(\mathbf{L1})_2{\cdot}ZnCl_2$ (X=Cl) red microcrystal **1**: Yield: 52.8%; 23.2 mg.

Elemental analysis calcd (%) for $C_{26}H_{18}Cl_2N_2S_{12}Zn$: C 35.51, H 2.06, N 3.19; Found: C 35.58, H 2.14, N 3.22.

$(\mathbf{L1})_2{\cdot}ZnBr_2$ (X=Br) black microcrystal **2**: Yield: 65.4%; 34.5 mg.

Elemental analysis calcd (%) for $C_{26}H_{18}Br_2N_2S_{12}Zn$: C 32.25, H 1.87, N 2.89; Found: C 32.31, H 1.91, N 2.91.

2.2.2. Preparation of bulk single crystal of $(\mathbf{L1})_2{\cdot}ZnX_2$ [X=Cl **1**, Br **2**]

Single crystals of complexes $(\mathbf{L1})_2{\cdot}ZnX_2$ (X=Cl and Br) suitable for X-ray diffraction analysis were obtained by a slow diffusion method. ZnX_2 (0.01 mmol) in hexane (5 mL) was layered over a solution of **L1** (0.02 mmol) in dichloromethane (5 mL) at room temperature. The reaction mixture was left to stand undisturbed for 2 weeks. Shiny black or red crystals were isolated by filtration, washed with hexane, and air-dried at room temperature.

$(\mathbf{L1})_2{\cdot}ZnCl_2$: bulk crystal **1** Yield: 1.8 mg, 21.2%.

$(\mathbf{L1})_2{\cdot}ZnBr_2{\cdot}CH_2Cl_2$: bulk crystal **2** Yield: 3.2 mg, 30.4%.

2.3. Single-crystal structure determination for bulk crystal of $(\mathbf{L1})_2{\cdot}ZnX_2$ [X=Cl **1**, Br **2**]

X-Ray diffraction data were collected on a Rigaku AFC-7 Mercury CCD or Bruker APEX-II CCD diffractometer with a graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystal structures were solved by direct methods within SHELXS-97 [18], and refined by full matrix least-squares methods on F^2 by means of SHELXL-97 [18]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced at calculated positions. Details of crystal data, data collections, and structure refinement are summarized in Table 1. All data (except structure factors) had been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 975324 and 978567 for **1** and **2** in this paper. Copies of the data can be obtained free of charge by application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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

	1	**2**
Emperical formula	$C_{26}H_{18}Cl_2N_2S_{12}Zn$	$C_{27}H_{20}Br_2Cl_2N_2S_{12}Zn$
Formula (wt)	879.41	1053.26
T(K)	153(2)	153(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pmna*	*Pbcn*
a(Å)	7.5697(3)	13.0824(4)
b(Å)	31.9824(13)	9.9000(3
c(Å)	13.8214(6)	28.6178(10)
$V(Å^3)$	3346.1(2)	3706.5(2)
Z	4	4
Dc ($g\,cm^{-3}$)	1.746	1.887
Abs coeff. ($m\,m^{-1}$)	1.668	3.665
F(000)	1776	2088
Limiting indices	$-9 \le h \le 9$	$-16 \le h \le 16$
	$-39 \le k \le 39$	$-12 \le k \le 11$
	$-17 \le l \le 14$	$-35 \le l \le 35$
Reflns collected	38571	51384
Indep reflns	3010	3319
Abs correction	multi-scan	multi-scan
Data/restraints/param	3490/63/199	3797/61/217
GOF on F^2	1.056	1.031
R indices (all data)	$R1 = 0.033$, $wR2 = 0.0579$	$R1 = 0.0293$, $wR2 = 0.0532$

2.4. Electrical conductivity measurement for bulk crystal of $(\mathbf{L1})_2{\cdot}ZnX_2$ [X=Cl **1**, Br **2**]

Electrical conductivity of bulk crystal of **2**, $(\mathbf{L1})_2{\cdot}ZnBr_2{\cdot}CH_2Cl_2$ was measured on a single crystal in the temperature region of 150–298 K. Four gold electrodes (15 μØ) were contacted with a gold paste in parallel with the largest plane of the needle crystals. Electrical conductivity of **1**, $(\mathbf{L1})_2{\cdot}ZnCl_2$ was measured on the single crystals using a Solartron Schlumlerger 7081 digital voltmeter. The Keithley 4200-SCS semiconductor characterization system was used to measure I–V characteristics of the micro crystal **2**, $(\mathbf{L1})_2{\cdot}ZnBr_2$ based on SiC and the data were recorded using a computer controlled by a Lab view program.

3. Results and discussion

3.1. Preparation of micro and bulk crystals of complexes $(\mathbf{L1})_2{\cdot}ZnX_2$ [X=Cl **1**, Br **2**]

The solvent diffusion method was used to form the coordination microstructure. In a typical experiment, ZnX_2 (X=Cl, Br) solution in hexane (5 mL) was added to the donor molecule **L1** solution in dichloromethane (5 mL) at room temperature, then the precipitates were formed. Note that a slow diffusion method afforded bulk crystals of $(\mathbf{L1})_2{\cdot}ZnX_2$ with typical sizes of 0.38 mm × 0.15 mm × 0.13 mm for **1** and 0.4 mm × 0.34 mm × 0.12 mm for **2**, respectively. Crystalline phase purities of the compounds **1** and **2** were investigated by comparing the experimental XRPD and the simulated pattern obtained from the single-crystal data using the Mercury 1.4 program (Fig. S1 in the Supporting information). The major peaks in these cases do match well with the corresponding