INTRODUCTION

The structural uncertainty of metal-organic coordination polymers increases the construction challenge of crystal engineering due to many factors such as metal coordination polyhedron, organic ligands, counter anions, solvent, and experimental conditions [1–3]. Supramolecular isomerism is a common phenomenon in the construction of coordination polymers, and it can be divided into two situations: (a) the metal centre ions are different but the structure is similar; (b) the base chemical compositions are the same but the networks are different [4–7]. Lots of supramolecular isomerism have been researched and reported not only for their structural diversity, but for the differences of their potential properties [8–11]. The induced reasons for the formation of supramolecular isomerism are complex and the mechanism is still vague, in which the guest-induced, solvent-induced and reaction temperature-induced supra-molecular isomerisms are general [12–14], however, the additive-induced ones are several examples [15].

In this paper, we selected imidazo-[4,5-f]-1,10-phenanthroline (IDP) with the big conjugated system as an organic ligand to construct coordination polymers with Mn(II) salts in solvothermal conditions, and obtained a pair of supramolecular isomerisms with different structures – [Mn(IDP)SO₄ · 2H₂O]ₙ (I) and [{Mn(IDP)SO₄ ⋅ H₂O} ⋅ H₂O]ₙ (II). Experiment analysis discovered that it was induced by an additive carboxyl organic ligand. Their crystal structures, IR, UV and FS spectrum have been determined and discussed.

EXPERIMENTAL

Materials and methods. All chemicals were commercially available and used as received without further purification. Elemental analyses (CHN) were performed using a Vario EL elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm⁻¹ on a Nicolet Avatar 360 FT-IR spectrometer. UV-Vis absorption experiments were performed on a SHIMADZU UV 2500PC spectrometer equipped with an integrating sphere for diffuse-reflectance spectroscopy, and the spectra were collected in the 200–800 nm range at room temperature. Fluorescence measurements were carried out with a F-4500 spectrofluorophotometer.

Recrystallization of IDP. The ligand was purchased commercially and recrystallized in water by hydrothermal method at 180 °C for 72 h. The yellow prism-like crystals of IDP were collected by filtration, washed with ethanol and dried in air.

For C₁₃H₈N₄
anal. calcd., %: C, 70.90; H, 3.66; N, 25.44.
Found, %: C, 71.12; H, 3.78; N, 25.62.

1 The article is published in the original.
IR data for IDP (KBr; ν, cm⁻¹): 3447 m, 3103 w, 2363 m, 2344 m, 1606 m, 1566 m, 1409 w, 1064 m, 932 m, 802 m, 738 m.

**Synthesis of I.** A mixture of MnSO₄·H₂O (0.018 g, 0.1 mmol) and IDP (0.032 g, 0.1 mmol) in the mixed solvent of 1 mL H₂O and 1 mL isopropanol was stirred for 15 min, then added Na₂Hstp (0.013 g, 0.1 mmol), and placed in a 23-mL Teflon-lined autoclave and heated at 140°C for 96 h. The autoclave was cooled over a period of 10 h by natural cooling. The straw yellow lath-like crystals of I were collected by filtration, washed with ethanol, and dried in air (the yield was 10 mg, ~21% based on Mn).

IR data for I (KBr; ν, cm⁻¹): 3445 m, 3103 w, 2365 m, 2337 m, 1607 m, 1559 m, 1419 w, 1117 m, 1067 m, 971 w, 940 m, 803 m, 731 m.

**Synthesis of II.** A mixture of MnSO₄·H₂O (0.018 g, 0.1 mmol) and IDP (0.032 g, 0.1 mmol) in the mixed solvent of 1 mL H₂O and 1 mL ethanol was stirred for 15 min, then placed in a 23-mL Teflon-lined autoclave and heated at 140°C for 96 h. The autoclave was cooled over a period of 10 h by natural cooling. The straw yellow lath-like crystals of II were collected by filtration, washed with ethanol, and dried in air (the yield was 10 mg, ~21% based on Mn).

IR data for II (KBr; ν, cm⁻¹): 3442 m, 3103 w, 2364 m, 2343 m, 1608 m, 1559 m, 1421 w, 1130 m, 1084 m, 1069 m, 988 w, 971 w, 941 m, 809 m, 734 m.

**X-ray structure determination.** Single crystal X-ray diffraction analysis of compounds IDP, I, II were carried out on a Bruker SMART APEX CCD diffractometer equipped with a graphite monochromated MoKα radiation (λ = 0.71073 Å). Raw data were integrated with the SAINT program [16]. The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares on F² using SHELXS-97 [17]. An empirical absorption correction was applied with the program SADABS [18]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined by a riding mode. The crystallographic details of compounds IDP, I, II are provided in Table 1, and the selected bond distances and angles are listed in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 988128 (IDP), 988129 (I), and 988130 (II); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

**RESULTS AND DISCUSSION**

In IDP ligand, the hydrogen bonds of N–H···N join the IDP molecules into one-dimension chains along x axis as shown in Fig. 1 (in N(3)–H(3A)···N(1), N···N 3.007 Å). The dihedral angel between two adjacent IDP molecules is 49.41°, which results the 1D chain into an undulating chain. Such 1D chains come into being 2D layer-structure in xy plane by π–π packing interactions (the distance of two adjacent IDP molecules is 3.578 Å) between IDP molecules with the big π-conjugated system (Fig. 2). Furthermore, these 2D layers stack into 3D supramolecular structure in ···ABAB··· order along z axis.

Single-crystal X-ray diffraction analysis indicates that compound I exhibits a one-dimensional double-helical chain-like structure. As shown in Fig. 3a, the Mn(1) ion is hexa-coordinated by two nitrogen atoms (N(1) and N(2)) from IDP ligand, two oxygen atoms (O(3) and O(4A)) from two SO₄²⁻ anions, and two oxygen atoms (O(1) and O(2)) from two coordinated water molecules. The center metal Mn(1) ion lies in a distorted slightly octahedral geometry, for which O(1) and O(4A) atoms are two vertexes and N(1), N(2), O(2), and O(3) consist of the equatorial plane of octahedron as shown in Fig. 3a. The Mn–N bond lengths are 2.253(1) and 2.277(1) Å, and Mn–O bonds range from 2.143(1) to 2.202(1) Å. The adjacent metal ions bridged by μ₂-fashion SO₄²⁻ anions into 1D chain-like structure and the IDP ligands hang vertically on the sides of the chain (Fig. 4). These chains are left- and...