

Short communication

Constructing two new crystalline metal–organic frameworks based on a mixed-donor ligand



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ABSTRACT

The self-assembly of a prominent ligand, 5-(4-(1H-tetrazolyl)phenyl)isophthalic acid (H_3TZPI), with Zn^{2+}/Cu^{2+} centres generates two new MOFs, $[Zn_2(TZPI)(\mu_3-OH)(H_2O)_2] \cdot 2H_2O$ (**JUC-161**) and $[Cu(HTZPI)(\mu_2-H_2O)_{0.5}(H_2O)_{1.5}] \cdot 5(H_2O)$ (**JUC-162**). **JUC-161** exhibits fascinating three-dimensional structures containing rectangular channels with dimensions of $6.5 \times 3.0 \text{ \AA}^2$, and **JUC-162** displays 3D supramolecular structures with $12.5 \times 14.6 \text{ \AA}^2$ hexagonal channels. The observed structural diversity in these frameworks is due to the two distinct coordinating moieties of the H_3TZPI ligand. The photoluminescence of **JUC-161** and the magnetic properties of **JUC-162** are also measured at room temperature. Photoluminescence investigations reveal that **JUC-161** displays a strong main emission spectrum peak at 388 nm. **JUC-162** is found to exhibit an antiferromagnetic interaction between Cu^{2+} ions.

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Metal–organic frameworks (MOFs), which are built from multi-dentate organic ligands and metal ions or in situ generated metal ion clusters with coordinate bonds, have attracted much attention over the last two decades [1–5], due to their intriguing variety of molecular architectural structures and numerous potential applications, such as gas storage and separation [6,7], catalysis [8], drug delivery [9,10], chemical sensing and luminescence [11] and magnetism [12]. Many factors are known to affect the self-assembly of coordination structures [13,14]. However, the construction of MOFs is determined primarily by metal centres and organic ligands. Organic ligands acting as bridging linkers between metal centres play a key role in tuning the structural topology and functionality of MOFs when the coordination number and geometry of the metal centres are relatively fixed. Most organic ligands are multicarboxylic O-donor ligands, which have been proven to be useful in the preparation of MOFs. For example, *m*-benzenedicarboxylate aromatic ligands have been used to construct porous MOFs for the assembly of a paddlewheel secondary building unit to obtain a porous metal–organic polyhedron. Chen and Schröder et al. found that the porous MOFs in the first series exhibited not only the same topology but also a systematically tunable porosity due to their *m*-benzenedicarboxylate subunits, making them highly suitable for gas storage [15]. Researchers have also investigated N-donor ligands such as imidazole, triazole and tetrazole and their derivatives. Tetrazole and its derivatives, five-membered N-heterocyclic azoles, have received particular attention for their multi-connectivity and high structural stability [16,17]. Tetrazole can also be used to form similar metal clusters and robust carboxylate MOFs, leading to increased interest in the use

of tetrazole for crystal engineering [18,19]. Therefore, ligands containing both *m*-benzenedicarboxylate and tetrazole subunits have extraordinary potential to create useful materials. Coordination in different modes between donors and metal centres leads to unforeseen structural patterns and packing frameworks, offering the opportunity to construct more complex and more functional new structures. To the best of our knowledge, however, few researchers to date have explored the synthesis of MOFs from bifunctional ligands with both *m*-benzenedicarboxylate acid and tetrazole groups [20–23].

To fill this gap in the research, we focused on the bifunctional ligand 5-(4-(1H-tetrazolyl)phenyl)isophthalic acid (H_3TZPI), which integrates *m*-benzenedicarboxylate acid and tetrazole subunits. We synthesised two new MOFs: $[Zn_2(TZPI)(\mu_3-OH)(H_2O)_2] \cdot 2H_2O$, named **JUC-161**, (JUC = Jilin University China), and $[Cu(HTZPI)(\mu_2-H_2O)_{0.5}(H_2O)_{1.5}] \cdot 5(H_2O)$, named **JUC-162**. Notably, although H_3TZPI is a rigid linker, the rotation of motifs in the ligand brings about a variety of configurations. The ligand has a remarkable capacity to create different architectural structures by adopting arbitrary torsion angles. In this study, H_3TZPI was found to link Zn^{2+} centres to give the 3D framework of **JUC-161**, and to coordinate Cu^{2+} ions to give 3D supramolecular frameworks. We also investigated the fluorescence properties of **JUC-161** and the magnetic properties of **JUC-162**.

Single crystal X-ray diffraction revealed that **JUC-161** crystallises in the orthorhombic space group *Cmcm* [24]. Half of the asymmetric unit comprised Zn^{2+} cations; a quarter was made up of $TZPI^{3-}$ anions; another quarter of μ_3-OH ; and the final half comprised terminal coordinated water molecules (Fig. S1). The ligand linked six Zn^{2+} centres in the coordination mode $\mu_6-\eta^1: \eta^0: \eta^0: \eta^1: \eta^1: \eta^1$ (Fig. 1a). The dihedral angle between the *m*-benzenedicarboxylate subunit and the tetrazolyl ring was 90.0° . Interestingly, the *m*-benzenedicarboxylate subunit was

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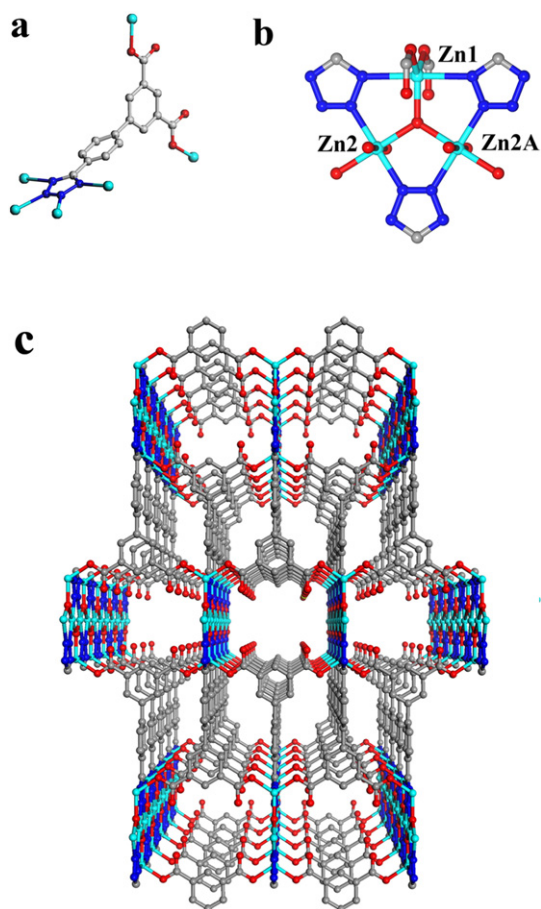


Fig. 1. (a) Coordination mode of TZPI³⁻ in **JUC-161**. (b) Zn²⁺ centres connected by μ₃-OH. (c) 3D networks of **JUC-161**. Colour code: Zn, cyan; O, red; N, blue; C, grey.

perpendicular to the phenyl ring, while the tetrazolyl ring was coplanar with the phenyl ring. The structure contained two kinds of zinc centre (Zn1 and Zn2) (Fig. 1b). The Zn1 atom was five-coordinated by three oxygen atoms (two carboxylate oxygen atoms from two TZPI³⁻ anions, respectively, and one bridging oxygen atom from a μ₃-OH ligand in the equatorial plane), and two nitrogen atoms from two TZPI³⁻ ligands distributed in the axial position, forming a triangular biconical ZnN₂O₃ coordination geometry. The Zn2 atom was six-coordinated by two nitrogen atoms from two TZPI³⁻ ligands, respectively; one oxygen atom each from two μ₃-OH ligands; and two coordinated water molecules. This formed an octahedral geometry. Zn–O bond distance ranged from 1.996(10) to 2.194(19) Å, and Zn–N bond distance ranged from 2.119(8) to 2.367(10) Å (Table S1). The Zn²⁺ centres were connected by μ₃-OH (Fig. 1b), forming ribbons along the *c* axis and giving the interactions described above between the metal sites and the ligands (Fig. S2). Adjacent ribbons were linked by whirling *m*-benzenedicarboxylate groups to form a 3D framework with one-dimensional rectangular channels along the *c* axis. The dimensions of the channels were calculated as 6.5 × 3.0 Å² (Fig. 1c).

Single crystal X-ray diffraction revealed that **JUC-162** crystallises in the orthorhombic space group *Fmmm* [24]. The asymmetric unit contained a half of Cu²⁺ cation, a half of HTZPI²⁻ ligand, 0.25 μ₂-H₂O and 0.75 terminal coordinated water molecule (Fig. S3). The coordination mode of the HTZPI²⁻ ligand in **JUC-162** was μ₃-η¹: η⁰: η⁰: η⁰: η¹: η¹: η⁰ (Fig. 2a), linking three Cu²⁺ centres. The dihedral angle between the *m*-benzenedicarboxylate subunit and the tetrazolyl ring was 90.0°, and the *m*-benzenedicarboxylate subunit was coplanar with the phenyl ring. In contrast with **JUC-161**, however, the tetrazolyl ring was perpendicular to the phenyl ring, as required for the ligand to form the unique structure of **JUC-162**. The coordination environments of Cu1 and Cu2 were distinct (Fig. 2b). The Cu1 atom was five-coordinated by two carboxylate oxygen atoms from two HTZPI²⁻ ligands in the equatorial position, respectively, and three coordinated water molecules in the axial position, forming a tetragonal pyramid coordination geometry. The Cu2 centre was six-coordinated by four ligands linked by nitrogen atoms and two oxygen atoms from μ₂-H₂O. Cu–O bond distance ranged from 1.940(4) to 2.652(3) Å, and the Cu–N

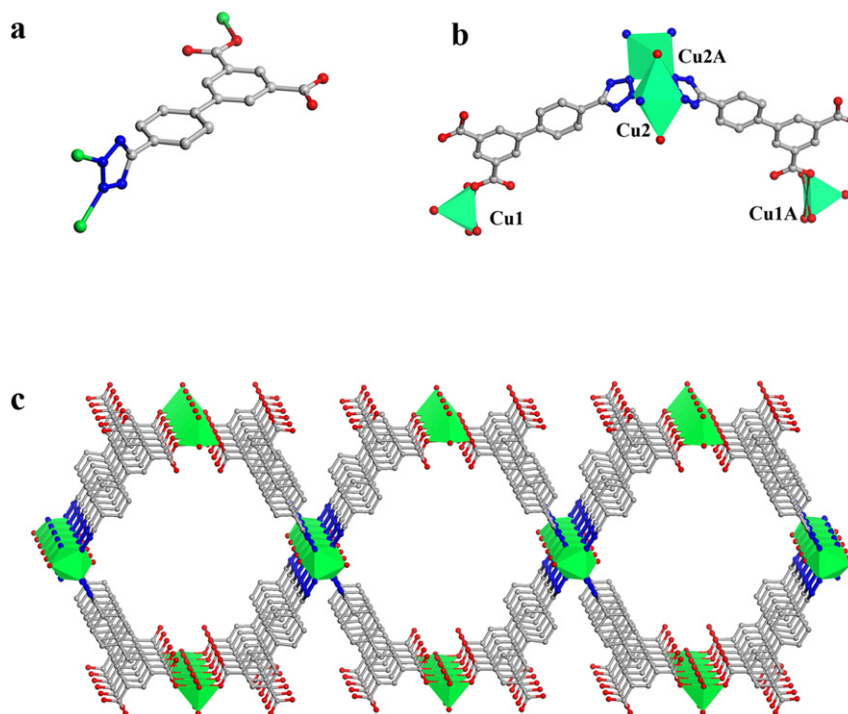


Fig. 2. (a) Coordination mode of HTZPI²⁻ in **JUC-162**. (b) Coordination environment of Cu²⁺ centres. (c) 2-fold networks of **JUC-162**. Colour code: Cu, green; O, red; N, blue; C, grey.

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