

# Synthesis, crystal structures and optical properties of two coordination polymers from 4-(1H-tetrazol-5-yl) benzoic acid

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## Abstract

The coordination polymers  $[\text{Mn}(4\text{-TZBA}^{2-})(\text{H}_2\text{O})_2]$  (**1**) and  $[\text{Mn}_4(4\text{-TZBA}^{2-})_4(\mu_2\text{-H}_2\text{O})_2(\text{H}_2\text{O})(\text{py})]$  (**2**) (py = pyridine) were prepared by the treatment of  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  with 4-(1H-tetrazol-5-yl) benzoic acid ( $\text{H}_2(4\text{-TZBA})$ ) under hydrothermal conditions. Compound **2** has nanosize triangular channels with a dimension of  $11.924 \times 11.686 \times 14.835 \text{ \AA}$ , in which guest water molecules are encapsulated. Compound **1** and **2** show strong fluorescence at room temperature in the solid state and compound **2** exhibits a second-order coefficient about 0.3 time that of KDP.

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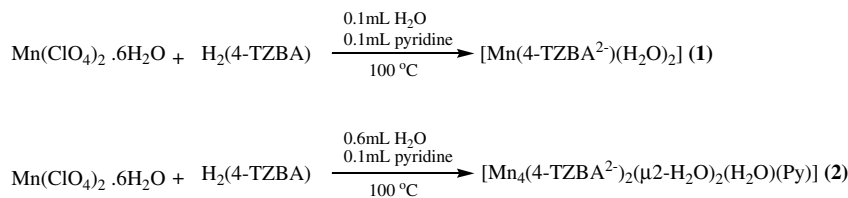
The rational design of metal–organic frameworks (MOFs) has attracted considerable attention in supramolecular and material chemistry due to their enormous variety of interesting structural topologies [1], and wide potential applications in catalysis, molecular adsorption, magnetism, non-linear optics (NLO), luminescence, and molecular sensing [2,3]. It is well-known that organic ligands play crucial roles in the design and construction of desirable frameworks because changes in the flexibility, length, and symmetry of the organic ligands can result in a remarkable class of coordination polymers bearing diverse architectures and functions [4]. Because of the aromaticity and multiple N-donor atoms of tetrazol group, ligands containing tetrazole groups could serve as excellent multidentate or bridging building blocks for the construction of polymeric structures [5]. In the past several years, the preparation of 5-substituted tetrazolate ligands has now become a safe and convenient procedure [6]. Recently, a number of metal–organic frameworks based on a variety of 5-substituted tetrazoles have been reported [7–9]. These

complexes show diverse structural features and topological networks, and these tetrazole ligands demonstrate various coordination modes.

Our previous work had shown that the 5-substituted tetrazolate ligands could be used to construct novel coordination polymers [10]. Herein, we turn our attention to a novel 5-substituted tetrazolate ligand, 4-(1H-tetrazol-5-yl) benzoic acid ( $\text{H}_2(4\text{-TZBA})$ ). To our knowledge, only rare example of metal-tetrazole coordination polymer built by 5-(carboxylatophenyl)-tetrazole has been reported [11]. In this paper, we report the synthesis, crystal structures and luminescent properties of two 3D metal-tetrazolato coordination polymers,  $[\text{Mn}(4\text{-TZBA})(\text{H}_2\text{O})_2]$  (**1**) and  $[\text{Mn}_2(4\text{-TZBA})_2(\mu_2\text{-H}_2\text{O})(\text{H}_2\text{O})]$  (**2**) ( $\text{H}_2(4\text{-TZBA})$  is 4-(1H-tetrazol-5-yl) benzoic acid). Additionally, the non-linear optical (NLO) property of compound **2** is described.

Compound **1** was readily obtained by treating  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_2(4\text{-TZBA})$  in a mixture of pyridine and  $\text{H}_2\text{O}$  (pyridine: $\text{H}_2\text{O}$  = 6:1) at 100 °C for 12 h [12]. When the ratio of pyridine: $\text{H}_2\text{O}$  was decreased to 1:1, compound **2** was obtained under the same condition (Scheme 1). Their formulations are supported by IR, microanalysis and thermogravimetric analysis (TGA) results.

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Scheme 1.

The single crystal X-ray diffraction analysis [13] reveals that compound **1** crystallizes in the centric space group  $P2_1/c$ . The asymmetric unit of compound **1** contains one Mn atom, one 4-TZBA<sup>2-</sup> ligand and one water molecule. The coordination geometry of each Mn(II) ion is a slightly distorted octahedron, in which the Mn(II) ion is coordinated by two water oxygen atoms (O(5) and O(6)), two carboxylate oxygen atoms (O(1) and O(2<sup>B</sup>)), and two nitrogen atoms (N(3<sup>A</sup>) and N(4<sup>B</sup>)) from three TZBA<sup>2-</sup> ligands (Fig. 1). The four Mn–O bond lengths range from 2.1633(8) to 2.2027(9) Å, and the Mn–N bond lengths are 2.2413(9) and 2.2892(9) Å, respectively.

In compound **1**, each 4-TZBA<sup>2-</sup> ligand adopts coordination mode II (Scheme 2). Two oxygen atoms of the carboxylate group bridge two metal centres while the tetrazolate group bridges two metal centres through its 2- and 3- nitrogen atoms. Two 4-TZBA<sup>2-</sup> ligands bridge adjacent two Mn atoms to form a dimer through the 2- and 3- nitrogen atoms of tetrazolate groups with a

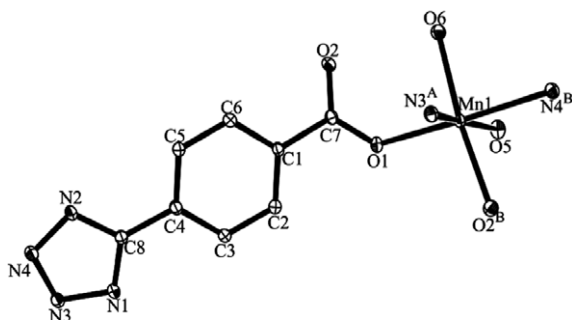
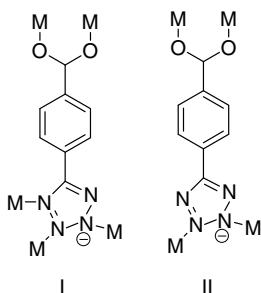


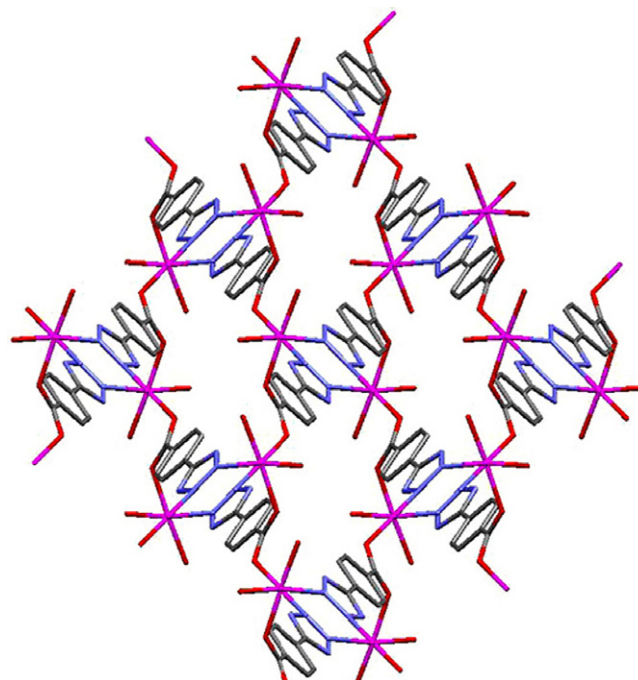
Fig. 1. ORTEP drawing at the 50% probability level showing the Mn(II) coordination environment and 4-TZBA<sup>2-</sup> ligand in **1**. Hydrogen atoms are omitted for clarity. Symmetry code: A:  $-x, y + 1/2, -z + 1/2$ ; B:  $x, -y - 1/2, z - 1/2$ .



Scheme 2.

Mn–Mn distance of 4.383 Å and a N–Mn–N angle of 92.60(3)°. The torsion angles between the Mn1–N4–N3 plane and the N4–N3–N1 plane, and between the Mn1–N3–N4 plane and the N3–N4–N2 plane are  $-161.09$  and  $157.60^\circ$ , respectively. In *bc* plane, each dimer is connected with four dimers through the carboxylate oxygen atoms (O(1)) from the 4-TZBA<sup>2-</sup> ligands to form a 2D sheet (Fig. 2). Then along the direction quasi-perpendicular to the dimer plane, each dimer is connected with two dimers from adjacent sheets through the remaining carboxylate atoms (O(2)). Thus each dimer is connected with six dimers. In this way, a 3D supramolecular architecture is formed.

Compound **2** crystallizes in an acentric space group  $C222_1$ . The asymmetric unit comprises four distinct Mn atoms, four 4-TZBA<sup>2-</sup> ligands, one pyridine molecule, two  $\mu_2$ -H<sub>2</sub>O molecules and one terminal water molecule. Mn(1) has a distorted octahedral coordination geometry in which three tetrazolate nitrogen atoms (N(6<sup>D</sup>), N(11<sup>A</sup>) and N(16)) and one carboxylate oxygen atoms (O(7)) from three 4-TZBA<sup>2-</sup> ligands form an equatorial plane. The  $\mu_2$ -H<sub>2</sub>O molecule (O(10)) and one carboxylate oxygen atom (O(6<sup>E</sup>)) occupy the axial position (Fig. 3). The bond angles

Fig. 2. The 2D sheet of **1** in *bc* plane.

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