

# Synthesis, structures and luminescence properties of three manganese coordination polymers with bis(1,2,4-triazol-1-ylmethyl)benzene

Haiyan Ge<sup>a</sup>, Kui Liu<sup>a</sup>, Yuan Yang<sup>a</sup>, Baolong Li<sup>a,b,\*</sup>, Yong Zhang<sup>a</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, Key Laboratory of Organic Synthesis of Jiangsu Province, Suzhou University, Hengyi Lu No. 80, Industry Park of Suzhou, Suzhou, Jiangsu 215123, PR China

<sup>b</sup> State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, PR China

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## Abstract

One-dimensional chain manganese coordination polymers  $[\text{Mn}(\text{mbtz})_2(\text{dca})_2(\text{H}_2\text{O})]_n$  (**1**),  $[\text{Mn}(\text{mbtz})_2\text{Cl}_2]_n$  (**2**) and  $[\text{Mn}(\text{mbtz})_2(\text{NCS})_2]_n$  (**3**) (mbtz = 1,3-bis(1,2,4-triazol-1-ylmethyl)benzene, dca = dicyanamide) have been synthesized and characterized. X-ray crystal structure shows that there are two kinds of mbtz ligands in **1**. One acts as the bridging (bidentate) coordination mode and shows the *anti*-conformation. The other shows the terminal (monodentate) coordination mode and exhibits the *syn*-conformation. The bridging mbtz ligands link the Mn(II) atoms to form the one-dimensional helical chain in **1**, **2** and **3** are similar one-dimensional chain containing the double bridges of mbtz ligands. **1**, **2** and **3** exhibit blue luminescent emissions maximum at 385, 405 and 414 nm, respectively, in the solid state at room temperature.

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**Keywords:** One-dimensional chain; Helical; Coordination polymer; Manganese complex; Bis(1,2,4-triazol-1-ylmethyl)benzene; Luminescence

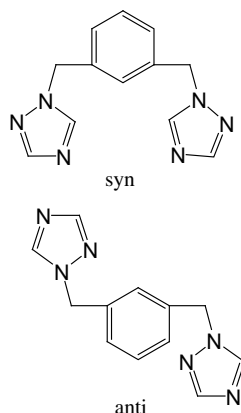
The design and construction of coordination polymers has attracted great attention in recent years for their potential application as well as the variety of architectures and topologies [1]. The selection of proper ligands as “building blocks” is undoubtedly the key point in manipulating the network structures of the coordination polymers. When rigid bifunctional ligands are used as spacers to connect metal centers, the topology of the network is usually determined by the coordination geometry of the central metal preference. Contrary to rigid ligands, the bifunctional flexible ligands with conformational flexibility can induce variety of structures and may lead to the formation of the

supramolecular isomers [2]. The ligands 1,2,4-triazole and its derivatives have received a great attention because of their intriguing structures and unique properties [3–5].

Although many coordination polymers with helical structures have been synthesized [6,7], the self-assembly of helical structures is still a great challenging project due to the difficulty of the selection of optimal components. Our interest is to study the coordination chemistry of 1,2,4-triazole and its derivatives together with their potential application in material science. Recently, we reported the crystal structures of a series of transition metal coordination polymers with the flexible bis(triazole) ligands such as 1,2-bis(1,2,4-triazol-1-yl)ethane [8] and 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene [9] due to their different conformations [10,11]. 1,3-Bis(1,2,4-triazol-1-ylmethyl)benzene (mbtz) (Scheme 1), a position isomer of 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene, should have the different coordination properties [12]. In order to study the coordination

\* Corresponding author. Address: College of Chemistry and Chemical Engineering, Key Laboratory of Organic Synthesis of Jiangsu Province, Suzhou University, Hengyi Lu No. 80, Industry Park of Suzhou, Suzhou, Jiangsu 215123, PR China. Tel.: +86 512 62523062; fax: +86 512 65880089.

E-mail address: [libaolong@suda.edu.cn](mailto:libaolong@suda.edu.cn) (B. Li).

Scheme 1. The *syn*- and the *anti*-conformations of the mbtz.

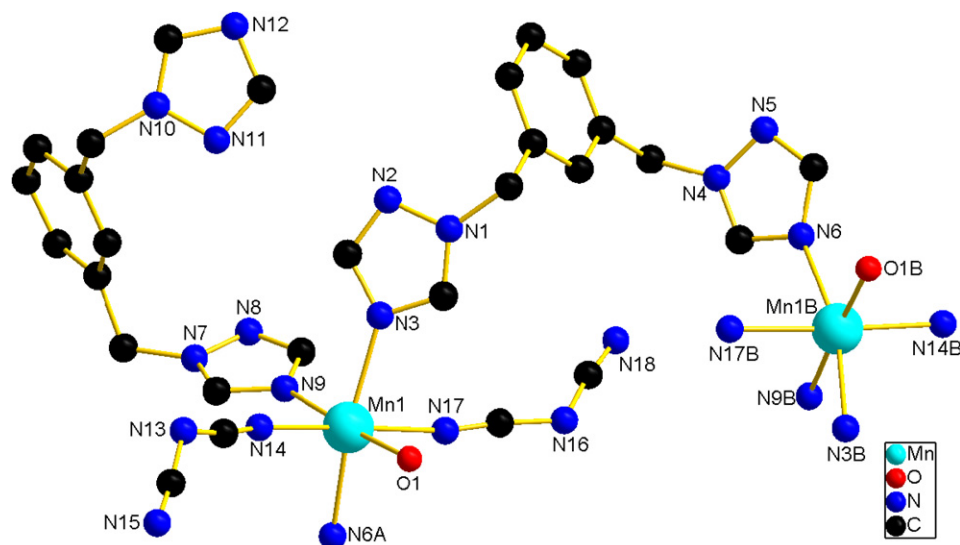
properties of mbtz and construct novel coordination polymers, in this paper, we have synthesized three manganese coordination polymers  $[\text{Mn}(\text{mbtz})_2(\text{dca})_2(\text{H}_2\text{O})]_n$  (**1**),  $[\text{Mn}(\text{mbtz})_2\text{Cl}_2]_n$  (**2**) and  $[\text{Mn}(\text{mbtz})_2(\text{NCS})_2]_n$  (**3**) by combining mbtz and anion co-ligands dicyanamide (dca),  $\text{Cl}^-$ ,  $\text{NCS}^-$ . The crystal structures and luminescence properties of three coordination polymers **1**, **2**, and **3** were reported.

Coordination polymer **1** [13] was synthesized by the slow diffusion method in  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  medium with a “H-shaped” tube. The crystal structure of **1** [14] shows that each Mn(II) atom displays a distorted octahedral coordination geometry, coordinated by four nitrogen atoms from two dicyanamide ( $\text{Mn}(1)\text{--N}(14)$  2.162(3) Å;  $\text{Mn}(1)\text{--N}(17)$  2.254(2) Å) and two mbtz ligands ( $\text{Mn}(1)\text{--N}(3)$  2.279(2) Å;  $\text{Mn}(1)\text{--N}(6A)$  2.264(3) Å) in the equatorial plane, and one nitrogen atom from one mbtz ( $\text{Mn}(1)\text{--N}(9)$  2.245(2) Å) and one oxygen atom ( $\text{Mn}(1)\text{--O}(1)$  2.164(2) Å) from the coordination water in the axial positions (Fig. 1) [15]. Two dicyanamide molecules exhibit

monodentate coordination mode. There are two kinds of mbtz ligands. One acts as the bridging (bisdentate) coordination mode. The other shows the terminal (monodentate) coordination mode. The bridging mbtz molecule shows the *anti*-conformation and the dihedral angles between two triazole ring planes, between the triazole ring plane and benzene ring planes are 168.0°, 68.8° and 101.3°, respectively. However the terminal mbtz molecule exhibits the *syn*-conformation and the dihedral angles between two triazole ring planes, between the triazole ring plane and benzene ring planes are 53.4, 82.2 and 114.5°, respectively.

The bridging mbtz ligands link the Mn(II) atoms to form the one-dimensional helical chain (Fig. 2 and Fig. S1) along the *b*-axis in which the Mn(II) atoms are translated by  $2_1$ -screw axis. The helical repeat distance is equal to the *b*-axis translation. Similarly, some examples of one-dimensional helical coordination polymers have been reported [6].

The Mn···Mn distance separation *via* the mbtz bridge is 9.729(3) Å. The *anti*-conformation mbtz ligands play important roles both in forming the helix and in helix chain assembly. There are intra- and inter-chain hydrogen bonding interaction between the coordination water and the nitrogen atoms of dca ( $\text{O}(1)\cdots\text{N}(18)$  ( $-x, y - 1/2, -z + 1/2$ ) 2.845 Å) and terminal mbtz ( $\text{O}(1)\cdots\text{N}(12)$  ( $x, -y + 1/2, z + 1/2$ ) 2.749 Å). There is no intra-chain  $\pi$ – $\pi$  stacking interactions between the benzene rings and triazole rings due to long distance separation. There are inter-chains  $\pi$ – $\pi$  stacking interactions between the benzene rings C(1)–C(6) of the bridging mbtz molecules (Fig. S2). The center-to-center and perpendicular distances of the benzene rings C(1)–C(6) with the symmetry benzene rings ( $-x, 1 - y, -z$ ) and ( $-x, -y, -z$ ) are 4.011 and 3.605, 4.230 and 4.011 Å, respectively. Complex **1** forms the two-dimensional network *via* these inter-chains  $\pi$ – $\pi$  stacking and hydrogen bonding interactions.

Fig. 1. The coordination environment around the Mn(II) atom of **1**.

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