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Short communication

Dual-ligand approach for the solvent-free synthesis of indium-based coordination polymers

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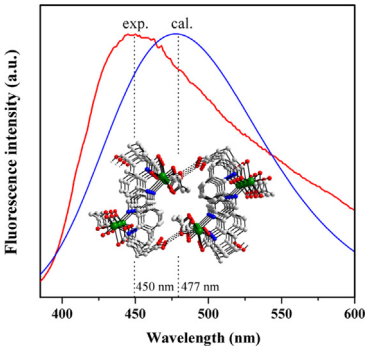
GRAPHICAL ABSTRACT

Three indium-based coordination polymers were prepared under solvent-free conditions. These compounds feature ribbonlike, chainlike, and layered structures. The experimental and theoretical studies of the luminescence of the chainlike compound were also presented.



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ABSTRACT

Three indium-based coordination polymers, formulated as $In_2(glu)_3(2,2'\text{-bpy})_2$ (**1**), In(glu)(Hglu)(phen) (**2**), and In(glu)(Hglu)(4,4′-bpy) (**3**), were prepared under solvent-free conditions, where H_2glu = glutaric acid, 2,2′-bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, and 4,4′-bpy = 4,4′-bipyridine. Structural analyses reveal that these compounds have ribbonlike, chainlike, and layered architectures, respectively. The fluorescent property of compound **2** was also investigated.

Coordination polymers or metal-organic frameworks are of great importance because of their appealing properties and many potential applications [1–3]. These crystalline materials have precise structures constructed from organic ligands and metal ions [4–6]. A well-known example is the zinc benzenedicarboxylate MOF-5 with a high surface area of 3800 $m^2 g^{-1}$ [7]. It has been demonstrated that the structures of coordination polymers are primarily dependent on the connection modes of organic ligands and the coordination geometries of metal centers [8–11]. The effect of different reaction media (e. g., water, organic solvents, ionic liquids, and surfactants) on the framework structures have also been investigated [12–16]. Recently, solvent-free synthesis has attracted considerable attention because it possesses several advantages over conventional solution-mediated methods [17–21]. For example, the safety concerns associated with high reaction pressure under hydrothermal and solvothermal conditions will be eliminated by solvent-free approach. In addition, this synthetic approach may offer new opportunities to find novel functional materials by removing the effect of solvent on the framework structure. In our previous studies, a number of metal oxalates and oxalate-based hybrid frameworks were prepared at elevated temperature without the

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addition of water and other organic solvents [22–26]. A key factor for these solvent-free syntheses is the use of low-melting-point reactants such as oxalic acid. Given the low melting point of glutaric acid (about 98 °C), we expect that metal glutarates may be readily prepared under similar solven-free conditions. Furthermore, the addition of ancillary ligands into the reaction systems will further enrich the structural chemistry of metal glutarates. During the courses of such investigations, three new indium-based coordination polymers, formulated as $In_2(glu)_3(2,2'\text{-bpy})_2$ (**1**), In(glu)(Hglu)(phen) (**2**), and In(glu)(Hglu)(4,4′-bpy) (**3**) in which H_2glu = glutaric acid, 2,2′-bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, and 4,4′-bpy = 4,4′-bipyridine, were prepared by a dual-ligand approach under solvent-free conditions. Structural analyses reveal that these compounds have ribbonlike, chainlike, and layered architectures, respectively [27]. Notably, compound **2** could emit a blue luminescence upon excitation at 368 nm.

Colorless block-like crystals of compound **1** were obtained by heating a mixture of $In(OH)_3$, glutaric acid, and 2,2′-bipyridine in a 25 mL Teflon-lined stainless steel autoclave at 150 °C for 7 days. This compound crystallizes in the monoclinic space group $P2_1/c$ (No. 14). There are two indium atoms, two 2,2′-bpy molecules, and three glu ligands in its asymmetric unit. Each indium atom is coordinated by six oxygen atoms from three glu ligands and two nitrogen atoms from one 2,2′-bpy molecule. The 2,2′-bpy molecule attaches to the indium atom as a terminal ligand. Each glu ligand locates between two indium atoms and acts as a cross-linker. It has been demonstrated that glu ligand may adopt three likely conformations: *anti-anti*, *anti-gauche*, and *gauche-gauche* [28]. In the structure of compound **1**, only *anti-gauche* and *gauche-gauche* conformations have been observed. The linkages between indium atoms and glu ligands generate a ribbonlike structure running along the [010] direction (Fig. 1). The width of the ribbon is about 20.5 Å.

Coloreless prism-like crystals of compound **2** were obtained by heating a mixture of $In(OH)_3$, glutaric acid, and 1,10-phenanthroline in a 25 mL Teflon-lined stainless steel autoclave at 150 °C for 7 days. This compound crystallizes in the triclinic space group *P*-1 (No. 2). The asymmetric unit contains one indium atom, one phen molecule, one glu ligand, and one Hglu ligand. The indium atom is coordinated by six oxygen atoms from two glu ligands and one Hglu ligand, and two nitrogen atoms from one phen molecule. The glu ligand adopts *anti-gauche* conformation, while the Hglu ligand adopts *gauche-gauche* conformation. The phen molecule and Hglu ligand serve as terminal ligands, while the glu ligand acts as a cross-linker. The linkages between indium atoms and glu ligands result in the formation of zigzag chains running along the [100] direction (Fig. 2a). There are hydrogen bond interations and π···π interations between adjacent indium glutarate chains (Fig. 2b). The closest O(8)···O(2) distance is 2.699(5) Å. The average distance between the least-squares planes of two adjacent phen molecules is about 3.60 Å, and the centroid-to-centroid distance between two parallel phen molecules is about 3.87 Å.

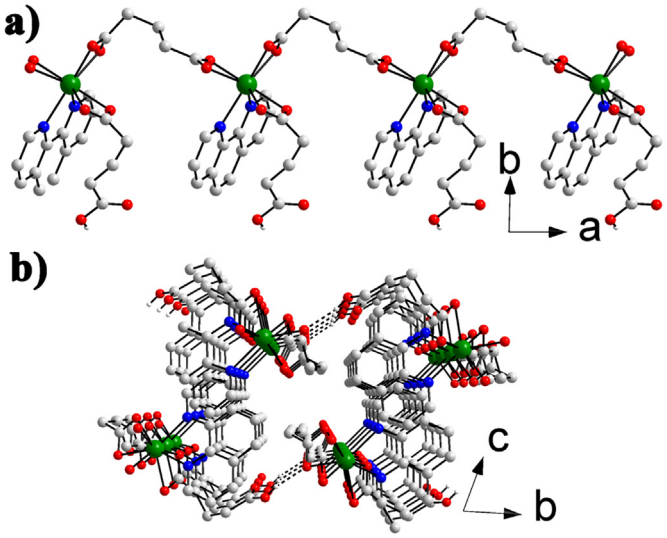

Fig. 2. (a) View of the chainlike structure of compound **2**. (b) Packing diagram of compound **2**.

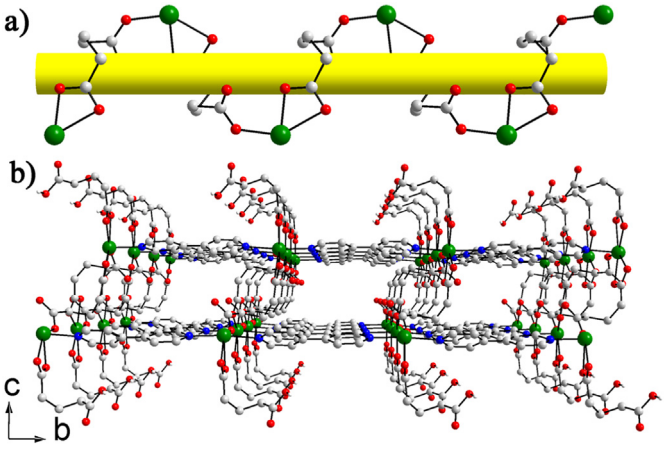

Fig. 3. (a) View of the indium glutarate helical chain with a pitch of 10.57 Å. (b) View of the layered structure of compound **3** along the [100] direction.

Coloreless block-like crystals of compound **3** were obtained by heating a mixture of $In(OH)_3$, glutaric acid, and 4,4′-bipyridine in a

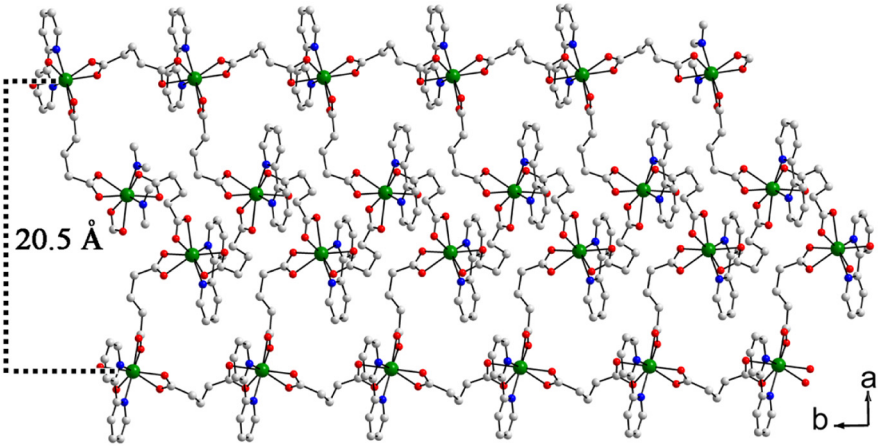

Fig. 1. View of the ribbonlike structure of compound **1** with the width of ca. 20.5 Å.