

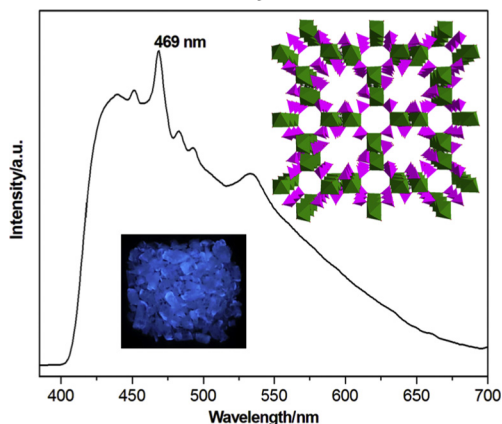
Short communication

Solvent-free synthesis of metal phosphate-oxalates with layered and zeolitic structures

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GRAPHICAL ABSTRACT

Three open-framework metal phosphate-oxalates were prepared under solvent-free conditions. They have 4-connected nets with sql and zeolitic crb topologies. The zeolitic framework containing disordered amines can emit blue luminescence under excitation of 365 nm UV light.



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ABSTRACT

Three new metal phosphate-oxalates, namely, $(\text{H}_2\text{dmp})_{0.5}\text{Mn}(\text{H}_2\text{PO}_4)(\text{C}_2\text{O}_4)$ (**1**), and $\text{H}_2\text{R-In}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_2(\text{C}_2\text{O}_4)\cdot\text{H}_2\text{O}$ ($\text{R} = \text{dmp}$ (**2**) and dmapa (**3**)) were prepared under solvent-free conditions, where $\text{dmp} = 1,4$ -dimethylpiperazine and $\text{dmapa} = 3$ -(dimethylamino)-1-propylamine. Compound **1** has a layered structure with an sql net. Compounds **2** and **3** are isostructural and have large 16-ring channels with a zeolitic crb net. The temperature dependence of the magnetic susceptibility of compound **1** and the photoluminescent property of compound **3** were investigated.

Open-framework organo-metallophosphates have attracted considerable attention because of their appealing properties such as magnetism and photoluminescence [1–4]. These inorganic-organic hybrid solids display diverse topologies by combining the structural features of zeolitic metal phosphates and metal-organic frameworks. Notable examples include the zinc phosphate-terephthalate NTHU-2 with bimodal

porosity and the gallium phosphate-oxalate NTHU-6 showing yellow luminescence with high quantum efficiency [5,6]. Crystalline organo-metallophosphates are usually prepared under hydrothermal and solvothermal conditions in sealed autoclaves [7–13]. Recent developments show that solvent-free crystallization may offer a new approach for the formation of open-framework structures by removing the competition

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between template-framework and solvent-framework interactions [14–18]. For example, Xiao and co-workers have demonstrated that the solvent-free reaction intermediate for zeolite ZSM-5 is different from those obtained under hydrothermal conditions [19]. In our previous studies, several open-framework metal phosphate/sulfate-oxalates with new framework topologies were prepared by a solvent-free approach using different amines as the structure-directing agents [20–24]. It is worth noting that some of them that are sensitive to hydrolysis are normally not accessible under hydrothermal and solvothermal conditions. As part of our continuous work in this system, here we report the solvent-free synthesis of three new metal phosphate-oxalates, namely, $(\text{H}_2\text{dmp})_{0.5}\text{Mn}(\text{H}_2\text{PO}_4)(\text{C}_2\text{O}_4)$ (**1**), and $\text{H}_2\text{R}\cdot\text{In}_2(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_2(\text{C}_2\text{O}_4)\cdot\text{H}_2\text{O}$ (R = dmp (**2**) and dmapa (**3**)), where dmp = 1,4-dimethylpiperazine and dmapa = 3-(dimethylamino)-1-propylamine. Compound **1** has a layered structure with an sql net, while compounds **2** and **3** have three-dimensional structures with a zeolitic crb net [25]. As far as we know, the zeolitic crb topology was observed for the first time in metal phosphate-oxalates. Notably, compound **3** could emit a blue luminescence upon excitation at 365 nm.

In a typical synthesis, a mixture of MnO (0.142 g), H_3PO_4 (85%, 135 μL), $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (0.504 g), and 1,4-dimethylpiperazine (135 μL) was sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 150 °C for 7 days. The autoclave was subsequently allowed to cool to room temperature. Yellow crystals of compound **1** were manually separated from the resulting product under an optical microscope (52% yield based on manganese). Compounds **2** and **3** were prepared under similar synthetic conditions. The phase purity of the three hybrid-framework solids was confirmed by powder X-ray diffraction.

Compound **1** crystallizes in the triclinic space group *P*-1 (no. 2). The asymmetric unit contains one manganese atom, one H_2PO_4 unit, two halves of oxalate ligands, and one half of an H_2dmp cation. The manganese atom is octahedrally coordinated by six oxygen atoms with the Mn–O bond length varying from 2.058(1) to 2.241(1) Å. The oxalate ligands adopt two different coordination modes: a chelating bis-bidentate coordination mode and a chelating/bridging bis-bidentate coordination mode. The linkages between manganese atoms and oxalates ligands produce layered structures parallel to the *ab* plane. The H_2PO_4 units attach to the manganese oxalate layers and protrude into the interlayer region (Fig. 1a). By regarding Mn_2O_{10} dimers as 4-connected

nodes, the layered structure of **1** can be represented as an sql net [26]. The O–H...O hydrogen bonds between the H_2PO_4 units extend the hybrid layers into a three-dimensional supramolecular structure. The H_2dmp cations are ordered within the free void and interact with the host framework through extensive hydrogen bonds.

The layered structure of **1** is reminiscent of the three-dimensional manganese phosphate-oxalate $\text{H}_2\text{dap}\cdot\text{Mn}_2(\text{HPO}_4)(\text{ox})_2$ with a pcu topology [20]. Both compounds contain the same sql-type manganese oxalate layers with Mn_2O_{10} dimers as the 4-connected nodes. In the case of compound **1**, the presence of dangling H_2PO_4 units on the surface of the layers prevents the formation of a three-dimensional structure. If the manganese oxalate layers are further connected by HPO_4 unit, the three-dimensional manganese phosphate-oxalate with a pcu net will be created (Fig. 1b). It is worth noting that the manganese oxalate layers can be also cut into low-dimensional metal oxalate motifs, such as chain, ladder, and nanobelt fragments. These metal oxalate motifs could serve as useful structural building units for the formation of various open-framework structures. In our previous work, several metal phosphate-oxalates with 3-, 4-, 6-, (3,4)-, and (4,6)-connected nets were successfully assembled by the low-dimensional metal oxalate motifs and phosphate units [20–22].

Compound **2** crystallizes in the triclinic space group *P*-1 (no. 2). The asymmetric unit consists of two indium atoms, two HPO_4 units, two H_2PO_4 units, two halves of oxalate ligands, one water molecule, and two halves of H_2dmp cations. Each indium atom is octahedrally coordinated by six oxygen atoms with the In–O bond length varying from 2.075(2) to 2.204(2) Å. Each phosphate unit serves as a bridge between two adjacent indium atoms. The strict alternation of InO_6 octahedra and P-centered tetrahedra gives rise to inorganic layers parallel to the *bc* plane. The indium phosphate layers have 8-, and 16-ring windows. Their pore sizes are $6.5 \times 7.4 \text{ \AA}^2$ and $5.6 \times 7.4 \text{ \AA}^2$, respectively (calculated from the distance between two oxygen atoms across the window). The indium phosphate layers are further connected by oxalate ligands to form a three-dimensional structure (Fig. 2a). H_2dmp cations and water molecules are ordered within the channels, which occupy 36.8% of the unit cell volume.

Compound **3** has the same framework structure as compound **2**. However, the organic cations within its free void are highly disordered. The framework structures of the two compounds can be represented as

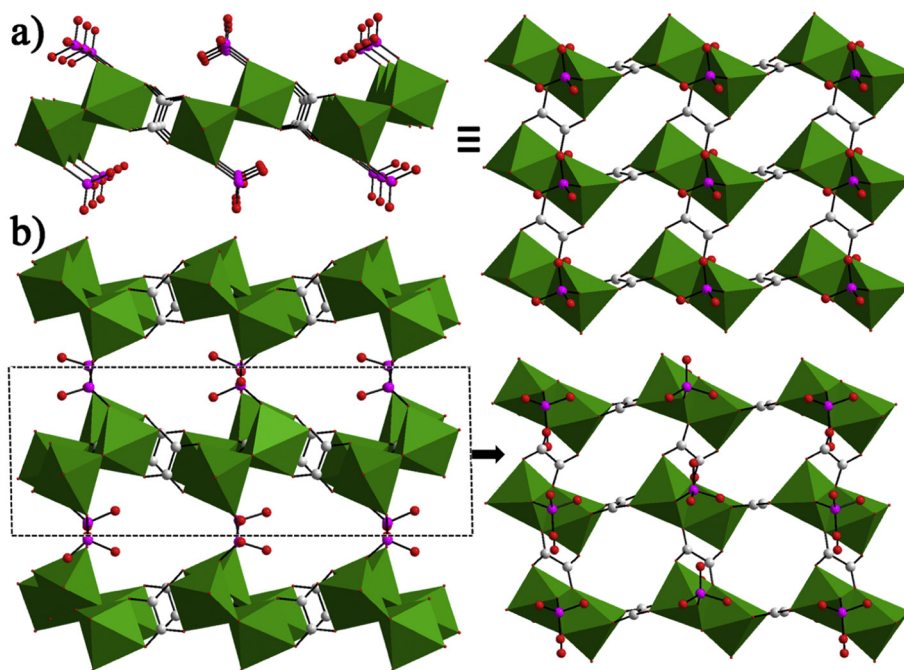


Fig. 1. Comparison of the manganese oxalate layers in (a) the layered structure of compound **1** and (b) the three-dimensional structure of $\text{H}_2\text{dap}\cdot\text{Mn}_2(\text{HPO}_4)(\text{ox})_2$.

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