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Bidimensional cadmium metal-organic frameworks based on 1,3-bis(4-pyridyl)propane displaying long lifetime photoluminescence emission

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ABSTRACT

Bidimensional novel cadmium metal-organic frameworks (MOFs) based on the 1,3-bis(4-pyridyl)propane linker and flexible dicarboxylate ligands derived from glutarate (2-methylglutarate, 2-dimethylglutarate and 3-methylglutarate) have been synthesized by conventional routes. These MOFs show fascinating structural features and they display long lifetime photoluminescence emission in the solid state, at room temperature.

1. Introduction

The evolution of metal-organic framework materials is an area of intense current interest, not only because of their potential technological applications [1], which range from hydrogen storage [2] to gas separation [3], from enantio-selective catalysis [4] to proton conduction [5], from drug delivery [6] to contrast agents [7], but for the plethora of topologies they can display [8], and their connection to the intended purpose as well [9]. These materials are commonly prepared through a bottom-up approach [10], using conventional routes, connecting ions with the appropriate bridging ligands [11].

Amongst ligands, multidentate N or O-donor building-blocks have drawn extensive attention in the construction of these novel systems [12]. Special attention has been devoted to the synthesis of unusual coordination polymers based on carboxylate and/or pyridine-based ligands [13], as we have recently highlighted with the design and synthesis of a new flexible MOF with Cu_2 paddle-wheels connected to glutarate (glu) and 1,3-bis(4-pyridyl)propane (bpp) ligands, which led to a high capacity MOF with outstanding CO_2 selectivity [14]. We believe that the conformational freedom of the glutarate and 1,3-bis(4-pyridyl)propane ligands could promote the self-assembly of MOFs with novel and unexpected topologies [15], that could also present greater breathing capabilities [16].

Many six- or seven-coordinated and some five- or eight-coordinated Cd(II) coordination polymers have recently received attention because of their excellent photoluminescence properties, well beyond the interest raised by their new structural features [17]. The Cd^{2+} metal ion is particularly suited for the construction of coordination polymers due to its spherical d^{10} configuration, that associated with a flexible coordination environment, can generate a great variety of topological types of MOFs [18].

In this context, we present here the synthesis, structural aspects studies and luminescence properties of three novel metal-organic-frameworks, $\{[Cd(bpp)(2Me_2\text{-}Glu)]\}_n$ (**1**), $\{[Cd(bpp)(2Me\text{-}Glu)(OH_2)]\cdot 2H_2O\}_n$ (**2**) and $\{[Cd(bpp)(3Me\text{-}Glu)(OH_2)]\}_n$ (**3**) based on 1,3-bis(4-pyridyl)propane (bpp), 2-dimethylglutarate ($2Me_2$-Glu), 2-methylglutarate (2Me-Glu) and 3-methylglutarate (3Me-Glu), respectively. To the best of our knowledge, there are very few studies on luminescence properties of 1,3-bis(4-pyridyl)-propane ligand, however, these materials display long lifetime

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photoluminescence emission in the solid state, at room temperature.

2. Experimental section

2.1. General

All analytical reagents were purchased from commercial sources and used without further purification.

2.2. Preparation of $\{[Cd(bpp)(2Me_2\text{-}Glu)]\}_n$ (**1**)

An aqueous solution (4 ml) containing 2,2′-dimethylglutaric acid (1 mmol, 160 mg) and cadmium(II) nitrate tetrahydrate (1 mmol, 308 mg) was placed at the bottom of a test tube. Then a DMSO solution (4 ml) of bpp (1 mmol, 198 mg) was dropped slowly. The tube was covered with parafilm and left at room temperature. X-ray quality crystals were grown after a few days. Yield ca. 71% (based on Cd). *Anal.* Calc. for $C_{20}H_24N_2O_4Cd$ (1): C, 51.24; H,

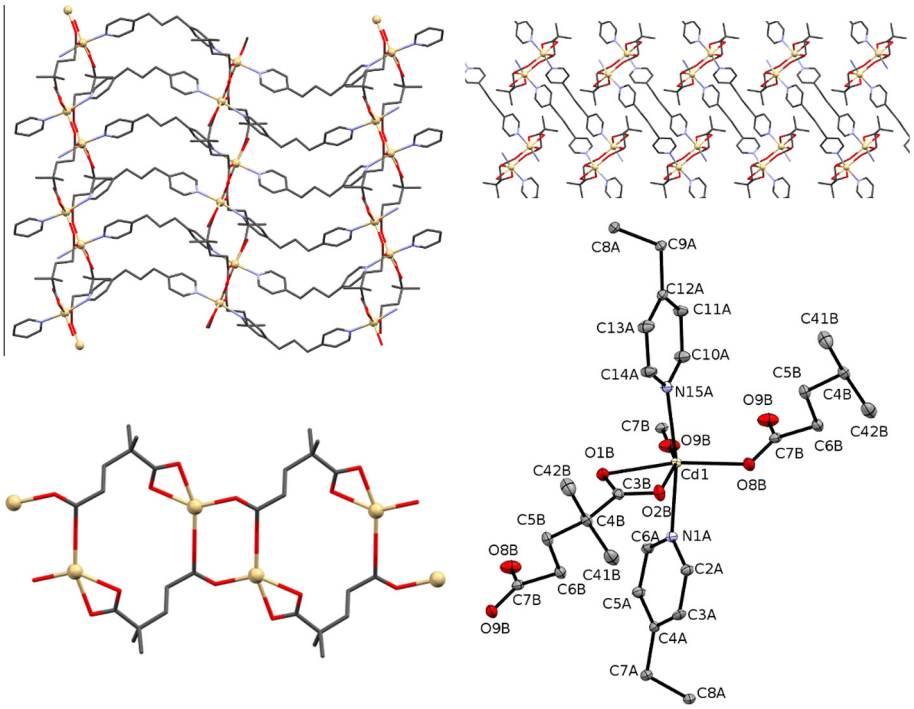

Fig. 1. Top-left, view of layers in compound **1**. Bottom-left, neutral chains made of glutarate and cadmium ions. Top-right, 3D packing of sheets of **1**. Bottom-right, numbering scheme of the asymmetric unit of **1**, A refers to bipyridine atoms and B to glutarate atoms, ellipsoids drawn to the 50% of probability. Hydrogen atoms have been omitted for clarity.

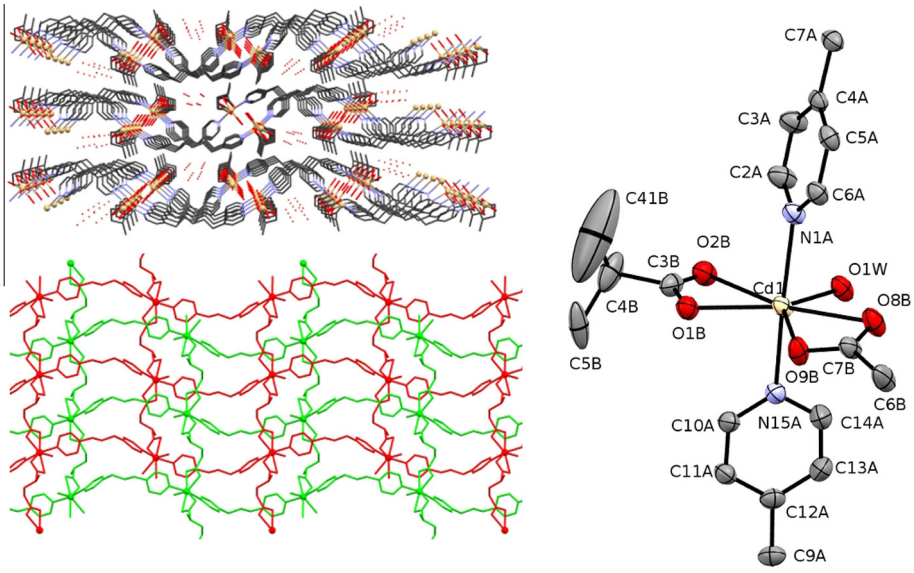

Fig. 2. Top-left, perspective down the *ab* plane of network in compound **2**. Bottom-left, view of the two interpenetrated corrugated layers. Right, numbering scheme of the asymmetric unit of **2**, A refers to bipyridine atoms and B to glutarate atoms, ellipsoids drawn to the 50% of probability. Hydrogen atoms have been omitted for clarity.