



Article

From 1D to 2D Cd(II) and Zn(II) Coordination Networks by Replacing Monocarboxylate with Dicarboxylates in Partnership with Azine Ligands: Synthesis, Crystal Structures, Inclusion, and Emission Properties

Victor Ch. Kravtsov ¹, Vasile Lozovan ^{2,3}, Nikita Siminel ¹, Eduard B. Coropceanu ^{2,3},
Olga V. Kulikova ¹, Natalia V. Costriucova ¹ and Marina S. Fonari ^{1,*}

¹ Institute of Applied Physics, Academiei 5, MD2028 Chisinau, Moldova; kravtsov@phys.asm.md (V.C.K.); siminel.n@gmail.com (N.S.); olga.kulikova@phys.asm.md (O.V.K.); constriucova@phys.asm.md (N.V.C.)

² Institute of Chemistry, Academiei 3, MD2028 Chisinau, Moldova; lozovanvasile90@gmail.com (V.L.); coropceanu.eduard@ust.md (E.B.C.)

³ Chemistry Department, Tiraspol State University, Iablocikin 5, MD2069 Chisinau, Moldova

* Correspondence: fonari.xray@phys.asm.md

Academic Editor: Uwe Monkowius

Received: 3 November 2020; Accepted: 25 November 2020; Published: 29 November 2020



Abstract: Eight mixed-ligand coordination networks, $[\text{Cd}(2\text{-aba})(\text{NO}_3)(4\text{-bphz})_{3/2}]_n \cdot n(\text{dmf})$ (1), $[\text{Cd}(2\text{-aba})_2(4\text{-bphz})]_n \cdot 0.75n(\text{dmf})$ (2), $[\text{Cd}(\text{seb})(4\text{-bphz})]_n \cdot n(\text{H}_2\text{O})$ (3), $[\text{Cd}(\text{seb})(4\text{-bpmhz})]_n \cdot n(\text{H}_2\text{O})$ (4), $[\text{Cd}(\text{hpa})(3\text{-bphz})]_n$ (5), $[\text{Zn}(1,3\text{-bdc})(3\text{-bpmhz})]_n \cdot n(\text{MeOH})$ (6), $[\text{Cd}(1,3\text{-bdc})(3\text{-bpmhz})]_n \cdot 0.5n(\text{H}_2\text{O}) \cdot 0.5n(\text{EtOH})$ (7), and $[\text{Cd}(\text{NO}_3)_2(3\text{-bphz})(\text{bpe})]_n \cdot n(3\text{-bphz})$ (8) were obtained by interplay of cadmium nitrate tetrahydrate or zinc nitrate hexahydrate with 2-aminobenzenecarboxylic acid (H(2-aba)), three dicarboxylic acids, sebacic (decanedioic acid, H₂seb), homophthalic (2-(carboxymethyl)benzoic acid, H₂hpa), isophthalic (1,3-benzenedicarboxylic acid, H₂(1,3-bdc)) acids, bis(4-pyridyl)ethane (bpe) and with four azine ligands, 1,2-bis(pyridin-4-ylmethylene)hydrazine (4-bphz), 1,2-bis(1-(pyridin-4-yl)ethylidene)hydrazine (4-bpmhz), 1,2-bis(pyridin-3-ylmethylene)hydrazine (3-bphz), and 1,2-bis(1-(pyridin-3-yl)ethylidene)hydrazine (3-bpmhz). Compounds 1 and 2 are 1D coordination polymers, while compounds 3–8 are 2D coordination polymers. All compounds were characterized by spectroscopic and X-ray diffraction methods of analysis. The solvent uptakes and stabilities to the guest evacuation were studied and compared for 1D and 2D coordination networks. The de-solvated forms revealed a significant increase of emission in comparison with the as-synthesized crystals.

Keywords: carboxylate ligands; azine ligands; coordination polymers; crystal structure; spectroscopic studies; solvent exchange; emission properties

1. Introduction

Having been launched as intriguing adsorption materials with the possibility to be applied in gas storage due to the exceptional low density, large surface area, pore function regulation, and structural flexibility [1,2], currently, the coordination polymers (CP) demonstrate their significance as materials for luminescence [3], catalysis [4], magnetism [5], optics [6], electric conductivity [7], and so on. The pore regulation by design can be considered as an advantage of CPs compared to the traditional porous materials such as zeolites and activated carbons. The guest species like solvents, ions, or confined organic molecules accommodated in the pores can act as templates and determine the shapes and sizes of pores [8,9]. Alongside the rigid 3D Metal-Organic Frameworks (MOFs), impressive

adsorption properties accompanied by the guest selectivity were reported for 1D and 2D coordination networks [10–12].

The carboxylates are among the most demanded ligands in the synthesis of homo-ligand and hetero-ligand CPs with either rigid or flexible coordination backbones [13]. The rational choice of the metal provides the ability of the carboxylic group to coordinate to the metal in different ways and ensures the formation of coordination networks with different dimensionality and complexity [14–16]. The carboxylate ligands afford an access to the neutral metal-organic carcasses due to the direct cation-anion coordination bonds, compared to the cationic networks with the neutral ligands, where the anions occupy the voids in the polymeric network. The increase in the number of ligand donor atoms accompanied by the increase in the number of chelate rings usually leads to greater stability of the complexes [17,18].

Schiff-bases that possess a spectrum of useful properties [19] are widely used as carboxylates' co-ligands in coordination polymers [20]. Several groups showed how manipulating by rigidity of both dicarboxylates and N, N'-donor ligands provided an access to different Zn(II) and Cd(II) 2D and 3D coordination networks. The 2D interdigitated structures revealed a change not only the void volume in the framework, but also the flexibility of structures, the chemical affinity, and effective pore shape and selectivity in guest sorption [21–25].

Recently, we reported a series of 1D Zn(II)/Cd(II) CPs comprising monocarboxylic 2-thiophenecarboxylic acid and different N, N'-azine ligands where the criss-cross packing mode of rigid coordination chains facilitated an access to the significant amount of space in the crystal structures predisposed to the guest accommodation and exchange [26].

Herein, we report our study on the influence of synthetic conditions on the resulting structure topology and dimensionality of eight Cd/Zn CPs comprising different azine and carboxylate ligands and their solvent exchange and emission properties. We have demonstrated that replacement of monocarboxylate by dicarboxylate anions allowed extending the dimensionality of coordination polymers from 1D to 2D, keeping invariable the coordination polymeric chains originating from azine ligands.

2. Results and Discussion

2.1. Generals

The reported CPs 1–8 (Scheme 1) were obtained by slow evaporation of the solvent or slow diffusion method, either in the glass beaker or in the test tube, starting from the solution Zn(II) or Cd(II) nitrate salts, mono-/dicarboxylic acid, and one of four azomethine ligands or by using two bipyridine-type ligands in the case of 8. The crystal images for 1–8 are shown in Figure 1. Crystal colors vary from yellow to orange-red.

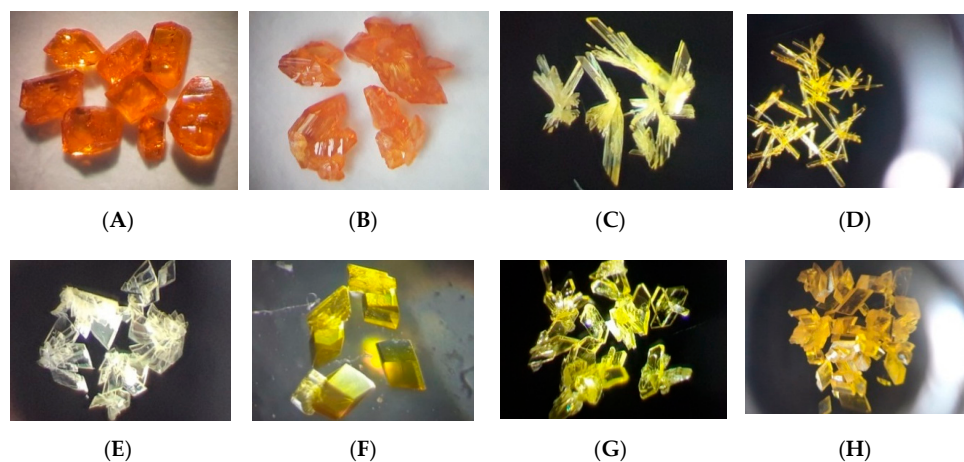


Figure 1. Crystal images for compounds 1–8 (A–H).