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ARTICLE

Adsorption and Luminescence Properties of First 2D-Cadmium MOF and Gismondine-Like Zinc Coordination Network Based on N-(2-tetrazolethyl)-4'-Glycine Linker

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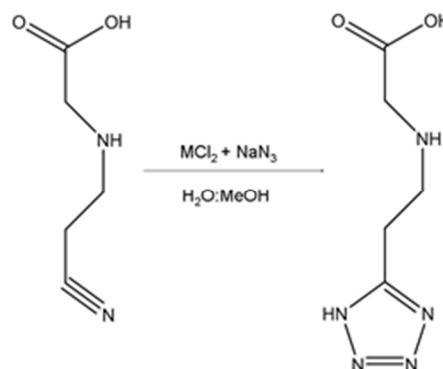
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We designed and synthesized two new metal-organic-frameworks (MOFs) using the novel N-(2-tetrazolethyl)-4'-glycine spacer (TeGly)²⁻. We report the in situ formation of cadmium- and zinc-based MOFs using hydrothermal routes. The cadmium-based MOF shows a bi-dimensional network with luminescence emission while the zinc-based MOF exhibits a three-dimensional structure with gismondine topology and intense blue-greenish photoluminescence emission at room temperature in the solid state. In addition, the porosity of the Zn-based MOF has been fully characterized using a combination of computational methods and experimental techniques.

Introduction

Metal-organic frameworks (MOFs) are a relatively new class of materials that have received great interest due to their structural and topological diversity as well as the properties that arise from their structural features.^[1] In particular, the study of Cd- and Zn-based MOFs has evolved enormously^[2] in areas such as luminescence,^[3] gas adsorption,^[4] sensing, and optical storage.^[5] MOFs are generally prepared using solvothermal methods, by connecting metal ions with the appropriate bridging organic ligands. Still, there is a great interest in the design of new ligands for the preparation of novel MOFs. In the last years, we have designed and synthesized novel Cd- and Zn-based MOFs with different tetrazolate derivated ligands with luminescent properties.^[6] These ligands have been obtained in situ during the MOFs synthesis by Demko-Sharpley [2+3] cycloaddition reactions of organonitriles and sodium azide.^[7] Following these works, we report here the design and synthesis, using hydrothermal routes, of a new multidentate bridging dianionic ligand derivated from N-(2-cyanoethyl)-4'-glycine which contains one carboxylate group and one tetrazolate ring with a nitrogen atom in the middle of the spacer. Further, complexes containing polynuclear d¹⁰ metals have attracted extensive interest in recent years due to their abilities of exhibiting appealing structures^[8]. The Cd²⁺ ion is particularly suited for the construction of coordination polymers since the spherical d¹⁰ configuration is associated with a flexible coordination environment and, therefore, the variety of geometries achievable by these complexes can be finely tuned, easily

generating multiple types of MOFs with various topologies. Thanks to its extended aromaticity and to the presence of polyheterosubstituted penta-atomic ring, N-(2-tetrazolethyl)-4'-glycine spacer (TeGly)²⁻ (Scheme 1) is a good candidate to show enhanced emissive properties, which are in principle tunable by coordination to different metals with different chemical environments. In addition to the organic ligand, we report the synthesis, structure, luminescence and adsorption properties of the 2D-MOF [Cd(TeGly)(H₂O)]_n (1) and the 3D-MOF [Zn(TeGly)]_n (2), demonstrating the potential of this new linker to construct novel MOFs.



Scheme 1. In situ preparation of the anionic (TeGly)²⁻ ligand by hydrothermal routes

Results and Discussion

The hydrothermal reaction of the appropriate metal chloride (1 mmol) with the N-(2-cyanoethyl)glycine (1 mmol) and sodium azide (3 mmol) in water (10 ml) at 150 °C for 12 h followed by cooling at room temperature over 3 h produced pris-matic colourless crystals of **1** and **2** in 65% and 43% yields, respectively. Their crystal structures were determined using single crystal X-ray crystallography.

Description of the structures.

Compound **1** crystallizes in the monoclinic space group $C2/c$. The 2D-MOF structure is composed of ditetrazolate double-bridged Cd(II) dimers connected by oxygen atoms pertaining to the carboxylate group of the (TeGly)⁻² ligand (Figure S1). The distortion of the CdII coordination polyhedron is induced mainly by the angle (111.61°) generated by the tetrazolate groups in the dimeric ring (CdN1N2CdN1N2). The Cd atom is coordinated to three nitrogen atoms pertaining to two different (TeGly)⁻² ligands (N1, N2 and N4), two oxygen atoms (O11 and O12) belonging to one carboxylate group from (TeGly)⁻² ligand and one water molecule. Cd-N distances are in the range of 2.288(2)-2.324(2) Å, whereas Cd-O distances have values of 2.299(2), 2.373(2) and 2.426(2) Å, for O11, O12 and O1W, respectively. *Cis* and *trans* angles of metal environment are in the range of 72.81(8)-114.19(7)° and 153.48(7)-158.66(8)°, respectively, highlighting the N8A-Cd-O12A angle with a large value of 114.19(7).

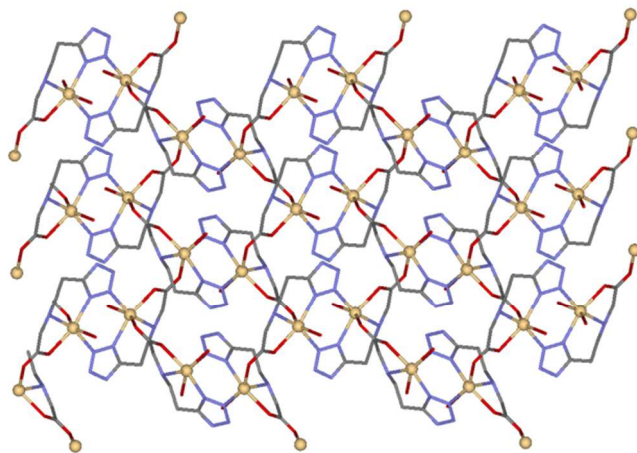


Figure 1. View down the *bc* plane of layers in compound **1**. Hydrogen atoms have been omitted for clarity. Color code N = blue, O = red, C = grey and Cd = yellow.

Cd^{II}...Cd^{II} distance through the tetrazolate ligand is 3.924 Å, while Cd^{II}...Cd^{II} distance across (TeGly)⁻² ligand has a value of 5.214 Å. The coordinated water molecule (O1W) is strongly hydrogen bonded to the N4A and O12A atoms (H bond: O1W...N4 = 2.824 Å, O1W...O12A = 2.825 Å). The dimers are formed by two cadmium atoms bridged through nitrogen atoms N1 and N2 from tetrazolate group, and are linked to others dimers through O12 atom of the same ligand. The dimers form a dihedral angle of 57.16° and generate honeycomb (*hcb*) layers with the Cd atoms at the nodes (Figure

1). Within the dinuclear Cd₂ units, each cadmium atom adopts a strongly distorted octahedral coordination geometry in which the CdN₃O₃ environment adopts a *mer* disposition.

Compound **2** crystallizes in the tetragonal space group $I41/a$. The asymmetric unit consists of one zinc ion and one (TeGly)⁻² ligand. Zn ion exhibits distorted trigonal bipyramidal ZnN₃O₂ geometry in which the apical positions are occupied by N1A and O11A atoms pertaining to the same (TeGly)⁻² ligand. N4A, N8A and O12A atoms from three different (TeGly)⁻² ligands are located in the equatorial positions (Figure 2).

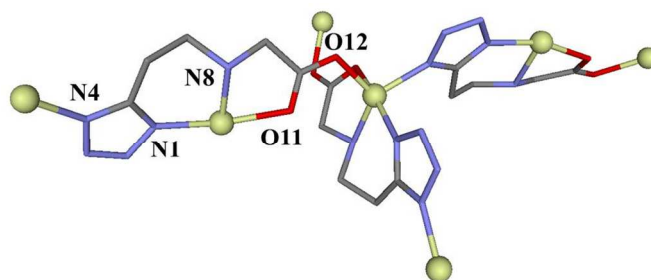


Figure 2. View of the metal environment and coordination mode of the (TeGly)⁻² ligand for **2**.

In this case, the linker connects with three zinc ions, resulting in the formation of a 3D-MOF (Figure 3) with a gismondine (*gis*) topology (ESI), in which each tetrazolate moiety coordinates in a bidentate fashion (N1N4) to zinc atoms. Zn-N distances are in the range of 2.039(2)-2.099(2) Å, whereas Zn-O distances have values of 1.980(2) and 2.185(2) Å, for O11A and O12A, respectively. *Cis* bond angles of metal environment are in the range of 76.37(8)-105.47(9)° and Zn^{II}...Zn^{II} distances through carboxylate and tetrazolate groups are 5.062 and 6.121 Å, respectively.

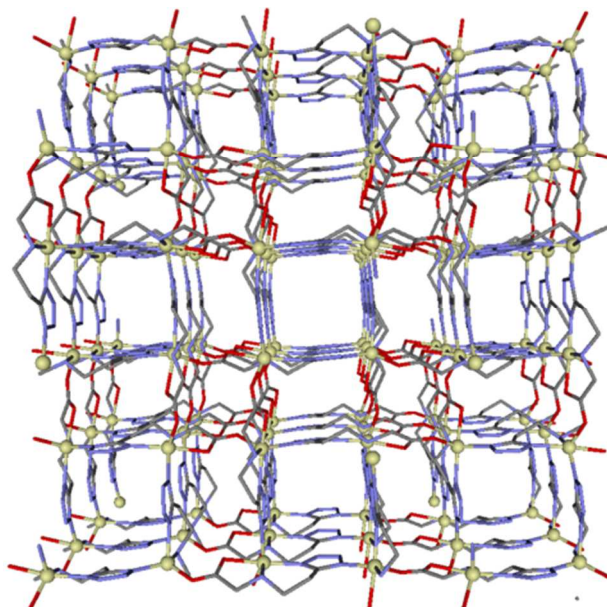


Figure 3. Bottom, view down the *c* axis of the structure in the three-dimensional network. Hydrogen atoms have been omitted for clarity. Color code N = blue, O = red, C = grey and Zn = yellow.

In **2**, we can observe two types of square-shaped channels formed by carboxylates, with 3 Å of diameter as calculated with PLATON,^[9] and tetrazolate groups, with 2.2 Å of diameter (Figure S2). Remarkably, the channels formed by the tetrazolates are not closed, thus generating the mentioned *gis* topology.

Luminescence Properties.

The extended aromaticity of the (TeGly)⁻² ligand coordinated with the Cd and Zn centers suggests the existence of enhanced emissive properties in **1** and **2**. In this regard, it is known that d¹⁰ metal complexes can show excellent luminescent properties, and therefore have received great attention for chemical sensing, photochemistry and electroluminescence applications.^[10] Figure 4 shows the emission spectra of compounds **1** and **2** in solid state at room temperature upon excitation at 310 nm. **1** exhibits a broad intense emission band centered at 540 nm, while compound **2** shows an intense emission band at 465 nm.

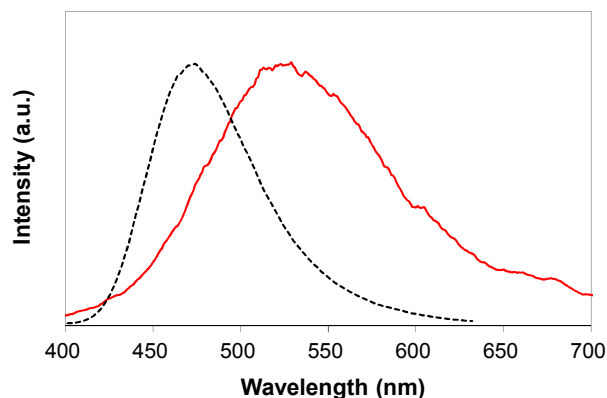


Figure 4. Emission spectra of compound **1** (red solid line) and **2** (black dotted line) at room temperature in the solid state.

The emission in compound **1** can be tentatively assigned to a metal to ligand charge transfer (MLCT) and/or to a ligand to ligand charge transfer (LLCT). Emissions in compound **2** arise from ligand-centered π - π^* transitions, as it has been reported for analogous compounds.^[11] The emission of **1** is significantly red-shifted compared to **2**. This bathochromism may be due to Cd having higher d* energy levels, which is consistent with similar bathochromic shifts that have been observed in other compounds.^[12] The luminescence decays curves of the compounds were obtained at room temperature (Figure S4). We try to fit the data to a mono exponential function: $I = I_0 + A \exp(-t/\tau)$, where I and I_0 are the luminescent intensities at time t and 0, τ is defined as the luminescent lifetime. For this function, the best fit of the experimental luminescence intensities to the above equation led to the lifetimes of 0.8±0.2 ms and 2.0±0.5 ms for **1** and **2** complexes respectively, thus indicating phosphorescence. The parameter for

complexes **1** and **2** are $A_1 = 736 \pm 93$, $I_0 = 123 \pm 27$, $A_2 = 189 \pm 12$, $I_0 = 20 \pm 5$, respectively..

Adsorption Properties.

The adsorption properties of **2** were studied using grand canonical Monte Carlo (GCMC) simulations^[13] to predict the N₂ (77 K), H₂ (77 K) and CO₂ (273 K) adsorption isotherms. GCMC simulation using a rigid MOF structure predicted no adsorption. In addition, it revealed an extremely low void fraction, obtained with He (rigid sphere size, $\sigma = 2.64$ Å) of 3.36 %. When moving to experimental measurements, N₂ adsorption at 77 K revealed no gas uptake. On the other hand, H₂ adsorption at 77 K revealed an uptake of 1.8 wt.% at 1 bar, whereas the CO₂ adsorption isotherm at 273 K showed a first step with a loading ca. 3.5 wt.% at 10 bar, followed by another increment up to 6 wt.% uptake at 27 bar (Figure 5). This stepwise filling is associated to the filling of the microporosity followed by the filling of interstitial mesoporous cavities between particles. The fact that simulations were not able to predict the gas uptake of **2** correctly, is probable related to the existence of small structural changes during the adsorption phenomenon, something that has been observed before in MOFs such as ZIF-8.^[14] These flexible effects were not taken into account during our GCMC studies, since our models were assumed to be rigid. The successful experimental adsorption of H₂ and CO₂ at 77 and 273 K, respectively, is attributed to the narrow porosity (ca. 3 Å) of the carboxylate channels. While experimental N₂ (77 K) adsorption is impeded due to the low temperature and the existence of kinetic barriers, a small molecule such as H₂ (77 K) can diffuse through the narrow porosity, as well as CO₂ (273 K) due to the higher temperature.^[15]

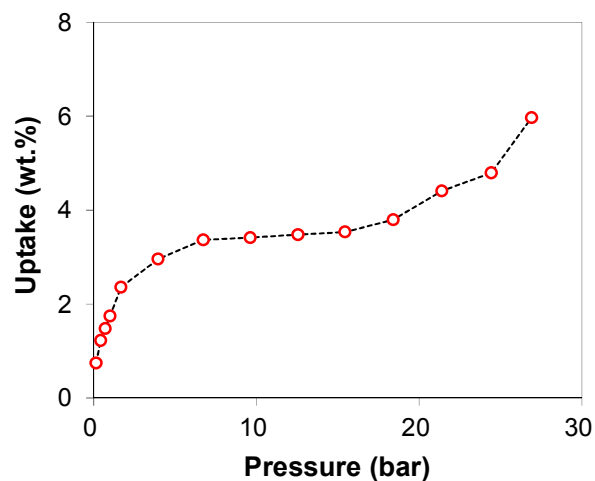


Figure 5. Experimental CO₂ adsorption isotherms at 273 K on **2**.

Conclusions

In this work, we have been successful in the synthesis of the two first Metal Organic Frameworks with the novel N-(2-tetrazolethyl)-4'-glycine spacer, with strong luminescence emissions. While the cadmium-based polymer shows a bi-dimensional network, the Zn-compound has a three-

dimensional structure with gismondine topology. The latter material shows a non-porous behavior according to the H₂ and CO₂ adsorption isotherms though the porosity of the Zn-based compound has been fully characterized using a combination of computational methods and experimental techniques, revealing an extremely low void fraction obtained with He of 3.36 %. Work along this line using other paramagnetic/lanthanides metals and XR Diffraction measures with high pressure are in progress in our lab.

Experimental Section

General Procedures: Unless otherwise stated, all reactions were conducted by hydrothermal conditions, with the reagents purchased commercially and used without further purification.

Preparation of complexes.

N-(2-cyanoethyl)-4'-glycine: This compound was obtained by Cyanoethylation of Alpha Amino Acids reaction. See J. Am. Chem. Soc., 1950, 72 (6), pp 2599–2603.

[Cd(TeGly)·(H₂O)]_n(1): A mixture of CdCl₂ (183.3 mg, 1 mmol), N-(2-cyanoethyl)-4'-glycine (128.1 mg, 1 mmol), sodium azide (195 mg, 3 mmol) and water (14 mL) was sealed in a Teflon-lined acid digestion autoclave and heated at 135°C under autogenous pressure. After 12 h of heating, the reaction vessel was cooled down at room temperature during a period of 2 h. Prismatic colorless crystals of **1** were obtained. Yield: 65% based on Cd. Anal. Calcd for (Cd₂C₅N₅O₃H₉): C 25.45, H 2.49, N 14.85. Experimental: C 25.35, H 2.41, N 14.97. FT-IR (KBr pellet): 3388 (s), 1622 (m), 1575 (s), 1450 (m), 1392 (s), 1244 (m), 1105 (w), 759 (m), 729 (m) cm⁻¹.

[Zn(TeGly)]_n(2): Compound **2** was prepared similar to that of compound **1**, but the ZnCl₂ (136.3 mg, 1 mmol) was used instead of CdCl₂. Prismatic colourless crystals of **2** were obtained. Yield: 43% based on Zn. Anal. Calcd for (ZnC₅N₅O₂H₇): C 33.89, H 2.73, N 8.24. Experimental: C 33.99, H 2.76, N 8.21. FT-IR (KBr pellet): 3416 (m), 3128 (s), 1626 (m), 1544 (s), 1400 (s), 1219 (w), 1020 (m), 747 (m), 714 (m) cm⁻¹.

Physical measurements.

Elemental analyses were carried out at the “Centro de Instrumentación Científica” (University of Granada) on a Fisons Carlo Erba analyser model EA 1108. IR spectra on powdered samples were recorded with a ThermoNicolet IR200FTIR using KBr pellets.

Single-Crystal Structure Determination.

Suitable crystals of **1** and **2** were mounted on a glass fibre and used for data collection on a Bruker AXS APEX CCD area detector

equipped with graphite monochromated Mo K α radiation (λ = 0.71073 Å) by applying the ω -scan method. Lorentz-polarization and empirical absorption corrections were applied. The structures were solved by direct methods and refined with full-matrix least-squares calculations on F^2 using the program SHELXS97.^[16] Anisotropic temperature factors were assigned to all atoms except for hydrogen atoms, which are riding their parent atoms with an isotropic temperature factor arbitrarily chosen as 1.2 times that of the respective parent.

Selected bond lengths and angles are given in Tables S1 and S2 (ESI). CCDC reference numbers for the structures of **1** and **2** were 981722 and 981723. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223 336-033; e-mail, deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic Data and Structural Refinement Details for **1** and **2**

compound	1	2
Chemical Formula	C ₅ H ₉ N ₅ O ₃ Cd	C ₅ H ₇ N ₅ O ₂ Zn
CCDC	981722	981723
M (g·mol ⁻¹)	299.57	234.53
T (K)	273(2)	273(2)
λ /Å	0.71073	0.71073
Cryst Syst	Monoclinic	Tetragonal
Space Group	C2/c	I41/a
a/Å	18.628(3)	21.710(3)
b/Å	7.5600(12)	21.710(3)
c/Å	14.269(2)	6.8793(11)
α /deg	90.00	90.00
β /deg	119.874(2)	90.00
γ /deg	90.00	90.00
V/Å ³	1742.4(5)	3242.3(9)
Z	8	16
ρ (g cm ⁻³)	2.284	1.922
μ (mm ⁻¹)	2.497	3.003
Unique reflections	4393	17580
R(int)	0.0191	0.0435
GOF on F ²	1.075	1.069
R1 [I > 2 σ (I)]	0.0204	0.0381
wR2 [I > 2 σ (I)]	0.0487	0.1001
^a R(F) = $\sum F_o - F_c / \sum F_o $, wR(F ²) = $[\sum w(F_o^2 - F_c^2)^2 / \sum wF^4]^{1/2}$		

Luminescence measurements.

A Varian Cary-Eclipse Fluorescence Spectrofluorimeter was used to record the fluorescence spectra. The spectrofluorimeter was equipped with a xenon discharge lamp (peak power equivalent to 75 kW), Czerny-Turner monochromators, R-928 photomultiplier tube which is red sensitive (even 900 nm) with manual or automatic voltage controlled using the Cary Eclipse software for Windows 95/98/NT system. The photomultiplier detector voltage was 700 V

and the instrument excitation and emission slits were set at 5 and 5 nm, respectively.

Computational Details.

The material was characterized geometrically, starting from the crystallographic coordinates. The pore size distributions were calculated using the method of Gelb and Gubbins, where the largest sphere that can fit in a random point within a structure without overlapping the Van der Waals surface of the framework is recorded for a large number of random points.^[17]

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Crystal Data, Coordination Environments of Metal Ions, Gas Adsorption Simulations and Computational Structural Characterization, Gas Adsorption Measurements and Luminescence Properties]. See DOI: 10.1039/b000000x/. CCDC reference numbers are 981722-981723

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