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Single-Crystal-to-Single-Crystal Structural Transformation in a Flexible Porous Gadolinium-Organic Framework with Selective and Controlled Sorption Properties

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ABSTRACT: A novel pillared-bilayer gadolinium-organic framework, $\{[\text{Gd}_2(\text{dhbdc})(\text{dhbdcH}_2)(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}\}_n$ (**1**), ($\text{dhbdcH}_4 = 2,5\text{-dihydroxyterephthalic acid}$), has been synthesized using hydrothermal technique and structurally characterized. 2D pillared-bilayer networks are interdigitated and H-bonded, forming a 3D supramolecular framework with two different channels along the *c*-axis. Framework exhibits stepwise release of the guest and coordinated water molecules and reversible single-crystal-to-single-crystal structural transformation upon removal and reintroduction of the guest water molecules. Partially dehydrated frameworks, $\{[\text{Gd}_2(\text{dhbdc})(\text{dhbdcH}_2)(\text{H}_2\text{O})_5]\}_n$ (**1'**) and $\{[\text{Gd}_2(\text{dhbdc})(\text{dhbdcH}_2)(\text{H}_2\text{O})_4]\}_n$ (**1''**) show different sorption capacity of N_2 realized by structural contraction in **1''**. Framework **1''** reveals strong hydrophilic character compare to **1'** and both the frameworks **1'** and **1''** do not uptake other organic vapors like MeOH, CH_3CN , and EtOH, suggesting size dependence in sorption properties.

The study of porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) materials in recent years has developed into a significant area of research because of its feasible applications in gas storage (like H_2 , CH_4 , and CO_2),¹ separations,² catalysis,³ sensing,⁴ and ion exchange⁵ processes. Such frameworks with different transition metal ions are well-documented in the literature. In this context, MOFs containing lanthanide (Ln) ions are attractive because of their versatile coordination geometry (with the coordination number ranging from the 7 to 12),⁶ unique luminescence⁷ and magnetic properties,⁸ and possible high framework stability.⁹ Also, lanthanides are known for their stronger coordination with oxygen donor ligands and frequently contains solvent molecules for the gratification of higher coordination number.⁶ However, often, collapse of the framework occurs when such ancillary solvents are removed from the coordination sites. But stable desolvated frameworks with unsaturated Lewis acidic Ln^{III} centers show catalytic activity¹⁰ and interesting porous functionalities.¹¹ However, to date, a few lanthanide-organic frameworks with porous functionalities have been reported.¹² Among the different organic linkers, 2,5-dihydroxyterephthalic acid (dhbdcH_4), is exciting because of the two hydroxyl groups at 2,5-positions along with the two carboxylic groups at 1,4 positions, which has been recently used for the construction of porous MOFs with transition metal ions.¹³ Such a multifunctional linker that has constitutional stiffness with four pH dependent abstractable protons can be useful for generating the different kinds of rigid and stable higher dimensional lanthanide-organic frameworks. With the aim to synthesize porous Ln-organic frameworks, we exploited the versatile binding ability of dhbdcH_4 and the flexible coordination geometry of the Ln^{III} ions. Here, we report the synthesis, structural characterization, and sorption properties of a flexible Gd^{III} -organic framework, $\{[\text{Gd}_2(\text{dhbdc})(\text{dhbdcH}_2)(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}\}_n$ (**1**). The 2D pillared-bilayer framework of **1** shows bidirectional water-filled channels and undergoes interdigitation and H-bonding interactions toward a 3D supramolecular framework. Framework **1** also exhibits interesting thermal behavior, including

reversible single-crystal-to-single-crystal dehydration and rehydration of the guest water molecules. Most interestingly partially dehydrated porous frameworks, $\{[\text{Gd}_2(\text{dhbdc})(\text{dhbdcH}_2)(\text{H}_2\text{O})_5]\}_n$ (**1'**) and $\{[\text{Gd}_2(\text{dhbdc})(\text{dhbdcH}_2)(\text{H}_2\text{O})_4]\}_n$ (**1''**) show different sorption affinity for N_2 and H_2O , but both exclude other organic solvents like MeOH, CH_3CN , and EtOH.

The greenish-yellow single crystals of **1** were synthesized under hydrothermal conditions using $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and dhbdcH_4 in the presence of KOH (see the Supporting Information). IR spectrum of **1** (see Figure S1 in the Supporting Information) shows strong absorptions at 1552 and 1347 cm^{-1} , corresponding to $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ of the carboxylate groups, respectively, indicating that all the COOH groups of dhbdcH_4 are involved in coordination to Gd^{III} centers.¹⁴ A broad and strong peak at 3390 cm^{-1} corresponds to the O–H stretching frequency, suggesting the presence of water molecule in the framework. The structure of **1** was determined by X-ray crystallography^{15a} and found **1** crystallizes in monoclinic $P2_1/c$ space group. There are two crystallographically independent Gd^{III} atoms (Gd1 and Gd2) in the asymmetric unit connected by two different dhbdcH_4 linkers (Figure 1a). Each nine coordinated Gd1 atom is chelated to two different dhbdc linkers through carboxylate oxygen atoms (O3 , O4 , and O3_c , O4_c , $c = -x, y, 1/2 - z$) and attached to two other oxygen atoms (O8 , O8_c) from two different dhbdcH_2 linkers. The rest of the coordination sites around Gd1 are occupied by the three water molecules (O1 , O1_c , and O2). Gd2 is octacoordinated and surrounded by two chelated dhbdc through carboxylate and hydroxyl oxygen atoms (O4 , O5 and O4_b , O5_b ; $b = -1 - x, y, 1/2 - z$), another two oxygen atoms (O7 , O7_b) from two dhbdcH_2 linkers and rest of the coordination sites are filled by two water molecules (O6 , O6_b). Therefore, each tetraanionic dhbdc chelated to two Gd1 and two Gd2 centers, whereas dianionic dhbdcH_2 linker connected two Gd1 and Gd2 centers through syn–syn carboxylate bridges (Figure 1a). $\text{Gd1}-\text{O}$ and $\text{Gd2}-\text{O}$ bond distances are in the range of $2.362(3)$ – $2.645(3)\text{ \AA}$ and $2.242(3)$ – $2.486(3)\text{ \AA}$, respectively (see Table S1 in the Supporting Information). Each Gd1 is connected to two nearest neighbors Gd2 through $\mu_2\text{-O4}$, forming a 1D $\text{Gd}-\text{O4}-\text{Gd}$ chain and further connection of the chains by dhbdc resulting a 2D corrugated sheet lying in the crystallographic *ac* plane (see Figure S3 in the Supporting Information). The 2D sheet further pillared by the dhbdcH_2 through syn–syn bridges between Gd1 and Gd2 forming a novel 2D pillared-bilayer network with

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2D water filled channels along crystallographic c and a -axis (Figure 1b and Figure S3a in the Supporting Information). The pillar dhhbdcH₂ linkers are alternating positioned in parallel to the direction of the side channels and the thickness of the bilayer galleries is 17.17 Å (Figure 1b). Each 2D pillared-bilayer networks further interdigitated with the coordinated water (O2) molecules through H-bonding interactions (see Table S2 in the Supporting Information) forming a 3D supramolecular network with 1D supramolecular channels along the crystallographic c -axis (Figure 2a and Figure S3b in the Supporting Information). The dimensions of the rectangular and supramolecular oval-shaped channels along the crystallographic c -axis are 4.43×3.32 Å² and 4.43×1.94 Å², respectively.¹⁶ The dimension of the triangular channels along the crystallographic a -axis is about 4.48×1.40 Å². The calculations using PLATON suggest 3.2 and 13.8% void space of **1** to the total crystal volume after removal of guest and coordinated water molecules, respectively.¹⁷ The Gd1...Gd2 separation along the Gd–O–Gd chain is 4.771 Å and Gd1...Gd1 and Gd1...Gd2 separation are 8.503 Å and 9.317 Å, respectively, in the 2D sheet lying in the ac plane. The separation of the Gd1...Gd2 in the bilayer is 10.870 Å.

To examine the framework stability of **1**, we carried out thermal gravimetric (TG) analysis (see Figure S4 in the Supporting Information) and X-ray powder diffraction (XRPD) measurements (Figure 3) at different temperature. TGA of **1** indicates that the release of the guest water molecules occurs at ~65 °C to give the form $\{[\text{Gd}_2(\text{H}_2\text{dhhbdc})_2(\text{H}_2\text{O})_5]\}_n$ (**1'**) (weight loss observed, 3.9%; calculated, 4.34%), which is stable up to ~175 °C. Upon further heating, one coordinated water molecule is released at ~210 °C, resulting in the form of $\{[\text{Gd}_2(\text{H}_2\text{dhhbdc})_2(\text{H}_2\text{O})_4]\}_n$ (**1''**), which is stable up to 320 °C (weight loss observed, 5.48%;

calculated, 6.51%). Another four coordinated water molecules are released in the temperature range of ~320–480 °C making the form of $\{[\text{Gd}_2(\text{H}_2\text{dhhbdc})_2]\}_n$ (**2**) and then consecutively decomposes to the unidentified products. Figure 3 shows PXRD patterns of simulated from X-ray single-crystal data of **1**, as-synthesized of **1**, dehydrated **1'** and **1''**, and the rehydrated form. The PXRD pattern of **1'**, which is unchanged from **1**, corroborates that the porous framework is maintained even without guest water molecules. However, in the case of **1''**, there is a significant shifting of the (010) peak to the higher-angle (5.67–6.76°) region, suggesting the decrease in separation between 2D pillared bilayer framework. This structural contraction can be realized by the release of the O2 water molecules coordinated to Gd1, which are located in the (010) plane in between 2D pillared bilayer networks (see Figure S5 in the Supporting Information). High-temperature release of the other four water molecules (O1, O1_c, O6, O6_b) can be correlated to the involvement of multiple H-bonding interactions compare to the O2.

Stepwise release of the guest and coordinated water molecules and high thermal stability of the framework **1**, inspired us to determine the corresponding crystal structures after removing guest as well as coordinated water molecules by controlled heating. The as-synthesized crystals were heated at 110 °C for 3 hours under a N₂ atmosphere to remove the guest water molecule. The change in color and morphology of the crystals were monitored by a microscope, which suggests a greenish yellow color of the crystals remain unchanged during the heating process (see Figure S6 in the Supporting Information). The crystal (**1'**) shows similar crystal system and space group as of compound **1**.^{15b} Structural determination of **1'** reveals the formulation $\{[\text{Gd}_2(\text{dhhbdc})(\text{H}_2\text{O})_5]\}_n$, suggesting complete removal of the guest

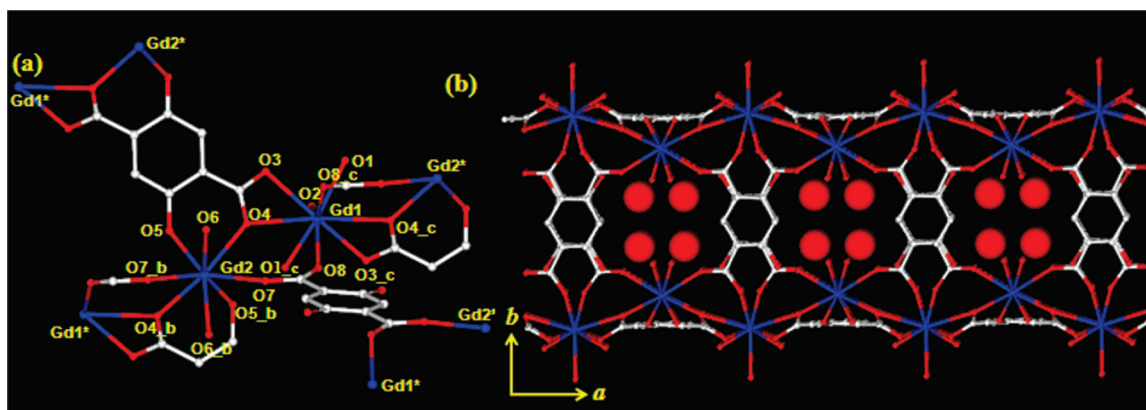


Figure 1. (a) View of the coordination environments of two Gd^{III} centers in **1**; (b) view of the 2D pillared-bilayer framework of **1** showing water-filled channels along the crystallographic c -axis.

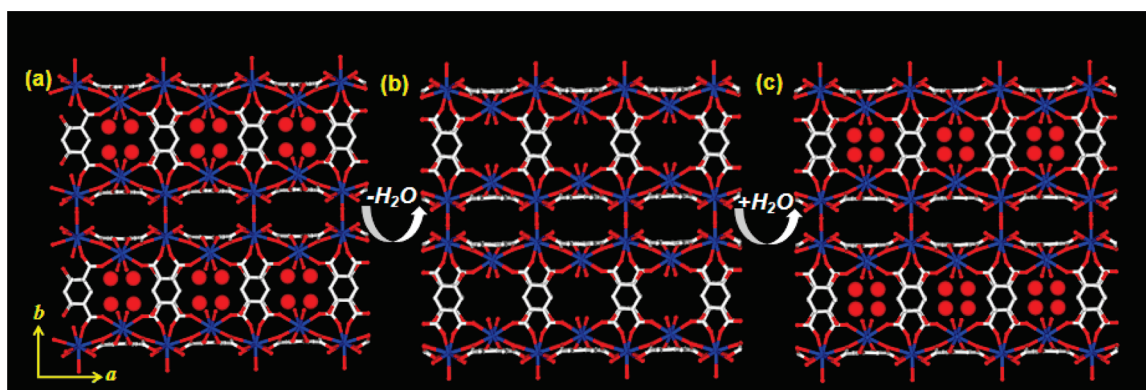


Figure 2. (a) View of the interdigitated 3D supramolecular framework of **1** formed by the 2D pillared-bilayer framework showing two different channels along the c -axis; (b) view of the 3D framework of **1'**; (c) view of the 3D rehydrated framework of **1a** showing structural reversibility.

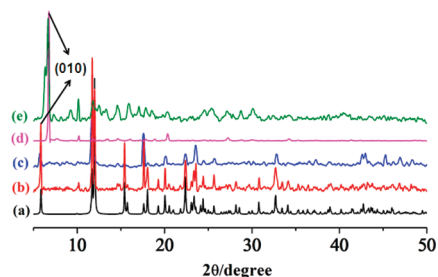


Figure 3. PXRD pattern of **1** in different state: (a) simulated from X-ray single crystal data; (b) as-synthesized **1**; (c) as-synthesized compound **1** heated at 120 °C (i.e., compound **1'**); (d) as-synthesized compound heated at 220 °C (i.e., compound **1''**); (e) water-exposed (for 7 days) compound of **1''**.

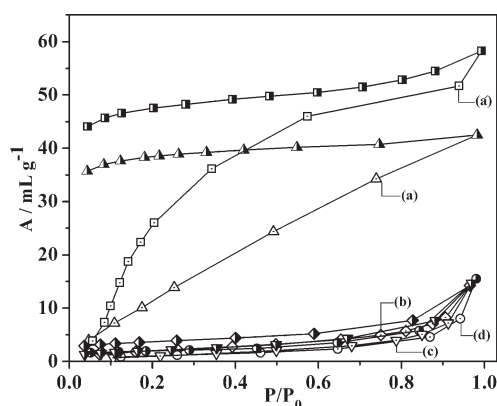


Figure 4. Sorption isotherm for **1'**: (a) H₂O; (b) MeOH; (c) CH₃CN; and (d) EtOH. Sorption profile (a') showing H₂O for **1''**. P_0 is the saturated vapor pressure of the respective adsorbate at corresponding temperature. (Curves with half shade symbol correspond to the desorption profile of the respective adsorbates).

water molecule (Figure 2b) and 2D pillared-bilayer network is retained without significant change in cell parameters, exhibiting the rigidity of the framework **1** (Figure 2b). There are not significant changes in the channel sizes after removal of the guest water molecules (Figure 2b). In **1'**, the Gd–O bond distances are comparable to **1** and small changes were observed in the corresponding bond angles (see Table S3 in the Supporting Information). It is worth mentioning that the single crystal breaks into the several pieces with loss of single crystallinity upon heating to high temperature (~220 °C) for removing the coordinated water molecules. The dehydrated crystal **1'** exposed to the water vapor for 3 days (see Figure S6 in the Supporting Information) and structure determination of **1a** reveals that **1'** returned to the virgin as-synthesized compound **1** with the formulation of $\{[\text{Gd}_2(\text{dhbdc})(\text{dhbdcH}_2)(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}\}_n$ (**1**), (Figure 2c). Cell parameters of the rehydrated compound **1a** are almost similar to that of **1**, suggesting complete reversibility of the structure.^{15c} The bond lengths and angles are also comparable to that of compound **1** (see Table S4 in the Supporting Information). It is worth mentioning that complete dehydrated form of both **1'** and **1a** exhibits the same void volume (13.8%) as the as-synthesized framework **1**. Such single-crystal-to-single-crystal structural transformation in flexible porous Ln-organic frameworks is scant in the literature compared to transition metal-organic frameworks.¹⁸

The dehydrated phase **1'** contains regular bidirectional channels along *a* and *c*-axis, which inspired us to gas as well as different solvent sorption studies. N₂ (kinetic diameter = 3.6 Å) sorption for **1'** at 77 K exhibits a small steep uptake at the low-pressure region and then monotonous increases with increasing pressure and ended with the value of 78 mL/g at $P/P_0 = 1$ (see Figure S7a in

the Supporting Information). Such type of N₂ sorption curve was recently reported by Chen et al. in Cu(I) flexible coordination framework with small pore window.²¹ They have also confirmed N₂ accommodation in the pores by X-ray single crystal structure determination. Moreover, we have also studied N₂ sorption isotherm for **1''** at 77 K shows almost linear increase with increasing pressure and final sorption amount is 48 mL/g at $P/P_0 = 1$ without saturation (Figure S7b). The sorption amount in **1''** is quite smaller than the corresponding value of **1'**, which is due to the structural contraction after removal of the coordinated water molecules (O₂) from the GdI center. The structural contraction was realized in PXRD pattern upon shifting of the (010) peak. The channels ($4.43 \times 1.94 \text{ Å}^2$) between two pillared layer frameworks containing (010) plane significantly reduced in **1''**, which cannot accommodate the N₂ molecules (see Figure S5 in the Supporting Information).

We have also studied the adsorption properties for **1'** and **1''** with the different solvent molecules (H₂O, MeOH, CH₃CN, and EtOH) to study the effect of the channel size and coordinatively unsaturated Gd^{III} sites in **1''** (Figure 4 and S8). H₂O (kinetic diameter = 2.68 Å)^{19,20} sorption study with **1'** shows that with increasing pressure the amount of sorption increases, and the final amount is 45 mL/g at $P/P_0 = 1$, agreeing with two guest water molecules occupying the channels in the as-synthesized framework (Figure 4a). This curve is characteristic for H₂O sorption in a porous solid, where the adsorbate–adsorbate interaction is also plays an important role along with the adsorbate–adsorbent interactions. Hysteresis adsorption can be correlated to the H-bonding interactions of the H₂O molecules with the pore surfaces. We have also performed H₂O sorption with the dehydrated phase **1''**, which shows a steep uptake of H₂O molecules at low-pressure regions, suggesting a strong affinity of H₂O molecules to the pore surfaces of **1''** in comparison to **1'** (Figure 4a'). The amount of sorption suggests about 2.8 molecules of H₂O adsorbed in **1''**, which correlates to the two guest and one coordinated H₂O molecules. Both the H₂O sorption profiles were analyzed by the Dubinin–Radushkevich (DR) equation²² and the corresponding βE_0 values, which reflect the adsorbate–adsorbent affinity, are 3.40 and 4.26 kJ/mol, for **1'** and **1''**, respectively, indicating the stronger affinity of the H₂O molecules to **1''**. The strong affinity of H₂O molecules compare to **1'** is due to the coordinatively unsaturated GdI sites in **1''**, which provide strong interaction to the H₂O molecules. However, both the frameworks **1'** and **1''** do not adsorb other organic solvents, like MeOH (kinetic diameter 4.0 Å), CH₃CN (4.2 Å), and EtOH (5.2 Å) (Figure 4 and Figure S8 in the Supporting Information), which may be due to larger size compared to the pore size of **1'** and **1''**; they also have a weak coordinating ability compared to the H₂O.

In conclusion, we have successfully synthesized a new porous 2D pillared-bilayer coordination framework of Gd^{III} using H₄dhbdc as a multifunctional organic linker. The guest water molecules were selectively removed and reintroduced in the framework in single-crystal-to-single-crystal manner without affecting the overall framework topology and porosity. However, upon further heating of the framework **1'**, $\{[\text{Gd}_2(\text{dhbdc})(\text{dhbdcH}_2)(\text{H}_2\text{O})_3]\}_n$ transforms to $\{[\text{Gd}_2(\text{dhbdc})(\text{dhbdcH}_2)(\text{H}_2\text{O})_4]\}_n$ (**1''**) with significant structural contraction along the (010) plane, which was also realized by the N₂ sorption studies. Most interestingly, framework **1''** shows a strong hydrophilicity compare to **1'** correlated by the large sorption affinity (βE_0), and both the framework **1'** and **1''** completely exclude other organic solvent molecules, like MeOH, CH₃CN, and EtOH molecules. Therefore, this type of guest-induced structural contraction and expansion in a 2D pillared-bilayer framework of Gd^{III} is one of the novel examples of framework flexibility and dynamicity and may find application in sensor and separation H₂O molecules from a mixture of small organic and water molecules.

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Supporting Information Available: Detailed experimental procedure and Figures S1–S8 (PDF); X-ray crystallographic files in CIF format for **1**, **1'**, and **1a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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