

A STUDY ON APPLICATION OF METAL-ORGANIC FRAMEWORKS

Setti Rajani

Research Scholar

Dept of Chemistry, Kalinga University, Raipur, Chhatisgarh

Dr. Anil Sharma

Professor

Dept of Chemistry, Kalinga University, Raipur, Chhatisgarh

ABSTRACT

In recent years, there has been a lot of interest in the expanding domains of metal organic frameworks (MOFs) focused at solving the riddles of self-assembly and creating new useful materials. Targeted applications include the creation of new porous crystalline materials with the goal of replicating and even outperforming crucial zeolite features like storage, separation, and catalysis that occur naturally. The separation and purification of gases or vapors among other industrial applications calls for particular materials exhibiting some highly guest-selective adsorption characteristics. This need can be solved by synthesizing suitable porous metal-organic coordination polymers that have the ability to differentiate or particularly recognize guest molecules. Porous metal-organic frameworks have attracted the attention of numerous research projects all over the world thanks to the groundbreaking work, primarily of Yaghi and Kitagawa. The process of assembling a coordination polymeric MOF with solvent molecules trapped in its lattice and then releasing the solvent without damaging the host framework is the one used the most frequently to create porosity crystals. However, it is amazing if the guest removal and exchange procedure has no negative effects on single crystals suitable for single crystal X-ray diffraction investigation. Greater flexibility in the design of pore form and other properties is possible in metal-organic frameworks synthesized using two different types of stiff linkers than in those based on only one.

KEY WORDS: *Metal Organic Frameworks (MOFs), Flexibility, Carbon Dioxide (CO₂).*

INTRODUCTION

Because of their simple synthetic process, which enables the formation of a variety of materials with relevant properties like high surface area, adjustable pore dimensions, and the opportunity for functionalization post

synthetic modification (PSM) of their internal pore walls have enabled applications in various fields, metal-organic frameworks (MOFs) have drawn an increasing amount of attention in recent years. Conceptually speaking, solid-state chemistry and coordination chemistry principles are intertwined in this field of study. According to the official definition, MOFs are coordination polymers having a distinct open framework that may contain voids or pores. The first man-made coordination polymer, often known as Prussian blue, was the precursor to coordination chemistry in the beginning of the eighteenth century. Then it began to draw a lot of attention and became a hot spot for the discovery of materials with potential uses in the following fields: magnetism, electrical, separations, heterogeneous catalysis, gas adsorption and storage, and so on. As a new class of porous materials created by coordinate bonding through self-assembly processes, MOFs have recently emerged as one of the fastest-growing study areas at the nexus of materials science and molecular coordination chemistry. Luminescent MOFs have emerged as very promising functional materials for use in sensing, detection, medical diagnostics, and cell biology. They are among the successful production of functional MOFs reported to date and combine luminescence capabilities with a porous nature. However, the widespread release of carbon dioxide (CO₂) as a result of human activity is a significant environmental problem, which has increased the need for effective CO₂ adsorbents made from flue-gas and other sources. However, a planned design or careful selection of the organic ligand integrating with a proper geometry oriented metal ions must practically depend on a successful building of the target MOFs (commonly d10 or lanthanides metal ions). The azolate-carboxylate bifunctional ligands have garnered a lot of interest as another class of helpful ligands in the creation of MOFs, as is well known. However, the bifunctional ligands with guest-dependent luminescence characteristics have received little attention. To make luminous MOFs, however, substantial π -conjugated bridging ligands are also necessary. For instance, imidazole and its derivatives are combined with tetrahedral coordinated metals to create MOFs having zeolitic or zeolite-like structures. In addition, HIBA MOFs (imidazole-containing benzoic acid) have been reported. However, the MOFs based on triazole derivate of 4-(1H triazol-1-yl) benzoic acid (HTBA) and divalent six coordinated metals have been reported¹⁴ with interpenetrated framework structure to produce unique MOFs possessing the 4-connected zeolitic structures. The bifunctional ligand of HTBA, however, shares structural similarities with HIBA and is easily made using DEF as a solvent. According to what we now know, HTBA has not yet been used to create a coordination polymer. With one carbon replaced by a nitrogen atom, HTBA differs little structurally from the ligand of HIBA. This is advantageous for selective gas sorption, and it may produce exciting luminescence features following various guest inclusions, such as various nitro aromatics and some metal ions. The solvent molecules were successfully placed in the framework's voids and formulated as [Cd(tba)₂]•1DEF in our recent work, which resulted in the production of unique 3D coordination polymers (4). X-ray single crystal analysis,

elemental analysis, IR spectroscopy, powder X-ray diffraction (PXRD), thermo gravimetric analysis (TGA), and applications like gas adsorption as well as sensing research are used to characterize the generated crystalline products.

Recently, methods have been reported that link well-defined two-dimensional metal-carboxylate layers using appropriate N, N'-donor bidentate pillars, allowing for easy control of the pore size and chemical functionality of the resulting open frameworks. Such networks can occasionally trigger interpenetration, in which two or more distinct frameworks self-assemble within one another as a result of lengthening the organic linkers. However, it has been hypothesized that interpenetration can boost the stability and effectiveness of porous metal-organic frameworks towards gas adsorption because the smaller pores bring gas molecules with more aromatic rings closer together and strengthen guest binding. We describe the solvothermal synthesis of a novel interpenetrated pillared-layer framework, $[\text{Cd}_2(\text{TBA})_2(\text{bpy})] \cdot \text{DMF}$, using 4-(1H-triazole-1-yl)benzoate (TBA) and 4,4'-bipyridine (bpy) as organic linkers (6). The possibility for the creation of self-penetrating networks is increased by the TBA ligand's incorporation of triazole and aromatic carboxylate groups linked by a rotatable C–N bond that compels it to be tilted when coordinates to a metal center. Thermogravimetric analysis (TGA) and variable temperature X-ray diffraction (VTPXRD) tests have shown that Framework 6 has thermal stability. Through sorption experiments using several gas molecules (N_2 , CO_2 , and H_2) and the desolvated framework (6), we further demonstrate its dynamic character.

RESEARCH METHODOLOGY

Each chemical that was acquired was of the analytical grade and was used directly. N, N'-Diethylformamide (DEF) and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ of reagent grade, both from Sigma-Aldrich. All of the solvents were purchased from S. D. Fine Chemicals in India, including DMF, CH_3CN , MeOH, and IPA. All of the nitro aromatics utilized in this work, including the 1, 2, 4-triazole, 4-fluoroethyl benzoate, and others, were acquired from TCI chemicals.

The commercially available, analytical-grade chemicals that were employed for synthesis were all used without further purification. S. D. Fine Chemicals in India provided reagent quality $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and solvents such N, N'-dimethylformamide (DMF), CHCl_3 , meOH, and IPA. The PANalytical Empyrean (PIXcel 3D detector) system with Cu K ($\lambda = 1.54$) radiation in the 2θ range $5-50^\circ$ at a scan speed of 0.1°sec^{-1} was used to record the powder X-ray diffraction (PXRD) data. To get PXRD data, a small quantity (20–30 mg) of softly and finely milled sample was placed on a flat sample holder. Using a TGA 209 F1-Libra (Netzsch, Germany) thermal

analyser, thermal stabilities of the as-synthesised framework (5 mg) were investigated at a heating rate of 10 °C/minute in a nitrogen atmosphere. The percentage mass change (m) is plotted as a function of temperature as the temperature is increased from room temperature to 800 °C. The Perkin Elmer GX-FTIR spectrometer was used to record the FTIR spectra using KBr pellets in the wave range of 4000-400 cm⁻¹. To ensure identical circumstances and the comparability of the spectra, each powder sample was milled and held at air conditions for 30 min. The spectra were captured up to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. Shimadzu UV-3101 PC spectrometer was used to record the UV-Vis spectra, and a Fluorolog Horiba Jobin Yvon spectrophotometer was used to capture the luminescence at room temperature. Using an elemental vario MICRO CUBE analyzer, the substances underwent elemental tests. Using the ASAP 2020 surface area and poresize analyser, measurements of gas adsorption on the dehydrated samples were made (Micromeritics Inc. USA). Dichloromethane (DCM) was used to replace all of the lattice solvent molecules in the as-synthesized compounds for three days at room temperature prior to adsorption studies. To create guest free sample 4, the solvent-exchanged frameworks were next heated to 120 °C for 4 hours while under vacuum.

CHARACTERISATION

The spectroscopic information below was gathered. Using the KBr pellet technique, the samples' infrared spectra (IR) were captured in the 400–4000 cm⁻¹ range using a Perkin-Elmer GX FTIR spectrometer. Under an optical microscope, single crystals with the right diameters were selected and put on a glass fiber to capture structural data. Utilizing graphite-monochromated Mo K (=0.71073) radiation and a Bruker SMART APEX diffractometer with a CCD area detector at 100K, intensity measurements for crystals were gathered. From worldwide X-ray crystallography tables, the linear absorption coefficients, atom-specific scattering factors, and anomalous dispersion corrections were extracted. The SAINT software program from Bruker was used in a conventional approach for data reduction. Utilizing SADABS, empirical corrections were made. Direct approaches were used to solve the structure using SHELXS-97, and full-matrix least-squares methods based on F2 were then refined using SHELXL-9714 and the graphical interface application X-Seed. The molecular graphics images were created using the applications X-Seed and POV-Ray. Anisotropic refinement was performed on all non-hydrogen atoms. Using riding models, the hydrogen atoms were positioned in their calculated locations. Large regions of disordered solvent molecules are present in the unit cell, making it impossible to describe them as discrete atomic sites. The "SQUEEZE" protocol from the PLATON package, which created a collection of solvent free diffraction intensities, was used to explain the disordered electron densities connected to these solvent molecules. Using the new data set and the SQUEEZE algorithm, final cycles of least-squares refinements considerably increased both

the R values and goodness of fit after removing the contribution from the disordered solvent molecules. Table contains the crystal and refinement information for the number. PANalytical Empyrean (PIXcel 3D detector) system with Cu K ($\lambda=1.5418$, 45 kV, and 40 Ma) radiation operating in Bragg-Brentano geometry was used to place the samples on a flat aluminum sample holder and collect data for powder X-ray diffraction (PXRD) and variable temperature powder X-ray diffraction (VTPXRD) studies. The diffractograms were measured between 5° and 50° in the range. Using an elemental vario MICRO CUBE analyzer, the chemicals were microanalyzed. Using a Mettler Toledo Star SW 8.10 system, thermogravimetric analyses (TGA) (heating rate of $5^\circ\text{C}/\text{min}$ in nitrogen atmosphere) were carried out.

RESULTS AND DISCUSSION

FRAMEWORK ACTIVATION

To create framework 6 for gas adsorption investigations, the as-synthesised framework 6 underwent solvent exchange with CHCl_3 for 4 days. Following that, it was degassed under vacuum for 5 hours at 120°C .

CRYSTAL STRUCTURE DESCRIPTION OF FRAMEWORK 4 AND 5

The solvothermal approach was used to synthesize the two frameworks using DEF and DMF. These two frameworks, which share the same structural type, were produced by the interaction of Cd(II) with the ligand of HTBA in the presence of solvents DEF and DMF. Divalent six-coordinated transition metal cations were used as the metal ions in the synthesis in the hopes that they would combine with the ligands of HTBA and HIBA to create neutral six-connected frameworks. However, their X-ray single-crystal data allowed for the determination of their crystal structures and the experimentally acquired X-ray powder diffraction patterns of the bulk materials, which were in agreement with those simulated patterns. Framework is a monoclinic crystal system with a $C2/c$ space group, according to the results of the X-ray single crystal diffraction investigation. The Cd(II) ion, one TBA ligand, one DEF molecule, and each of the Cd(II) metal centers are six coordinated by two nitrogen atoms from two different triazole moiety of TBA ligands in the trans-position and four carboxylate oxygen from another four different completely deprotonated TBA ligands. Each TBA ligand bridges three Cd(II) ions using the syn-anti coordination mode and exhibits a dihedral angle of 29.6° between the triazole and benzoyl rings. Because of the coordination arrangement, the Cd(II) ions in this structure display distorted octahedral geometry around the Cd(II) core. It is entirely different from the Cd(II) framework's octahedral coordination geometry that was discovered by a solvothermal reaction. The octahedral geometry of this framework is also revealed by all of its metal nodes,

with nitrogen atoms occupying the apical positions and carboxylate oxygen donors occupying the equatorial positions. The asymmetric unit with solvent molecule (DEF), Cd(II) coordination environment, and framework 4's Cd(II) ion's octahedral shape (yellow-cadmium, blue- nitrogen, red- oxygen, gray- carbon, white- hydrogen) Additionally, the triazole ring and benzene moieties of the ligand are not coplanar with one another but rather are somewhat twisted (dihedral angles of 34.98° and 42.75° , respectively). Bond distances between Cd and N and Cd and O are discovered to be comparable to those of the previously reported Cd(II)-based octahedral coordination polymer²³. The equatorial Cd-O distances range from 2.29 to 2.33, while the two apical Cd-N distances are identical (2.34), revealing a relatively regular octahedron. The N-Cd-O angles slightly vary (91.13° - 101.67°) from 90° . The stacking interaction between the triazole ring and benzene ring hydrogens stabilizes the lattice of DEF molecules in this crystal structure. The interaction between the metal ion and ligands of framework 4 is further examined in order to comprehend the full framework structure as follows: The Cd(II) chains in this structure are connected by carboxylate groups of TBA along the [001] direction (b-axis) at a CdCd distance of 4.61.

The pore aperture, on the other hand, is determined by taking the atom-to-atom distance, which is the separation between the nearest atoms apart from the hydrogen atom. Van der Waals radii are taken into account, opening the pore aperture along the c-axis in every 1D channel of 8.70 16.67 windows with no discernible pore channel along the a- or b-axis. 8.70 and 16.67 are the closest distances between two imidazole rings, respectively. The entire framework is interconnected with these uni-direction channels, resulting in a 3D porous structure with a 1D channel. The entire cage-like configuration exhibits non-interpenetration in parallel mode, and the channel size is determined by taking the Van der Waals radii of the constituent atoms into account. Triazole moiety nitrogen atoms are used to adorn the pore walls of the channels, therefore a framework containing basic nitrogen should promote CO₂ interactions during gas adsorption. The guest solvent molecules, such as DEF, are accommodated inside the pore channels according to the PLATON squeeze data, and the framework 4's potential solvent accessible void volume is determined to be 639.2 Å³, which is roughly 28.6% of the unit cell volume (2235.9 Å³). In addition to being stabilized by weak hydrogen bonding C-H-O interactions between 1, 2, 4-triazole and DEF molecules, this void volume may have an effect on the adsorption of gases.

**TABLE- 1 CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT OF FRAMEWORK
4(DEF) AND 5(DMF)**

Empirical formula	4 C₁₈H₁₂CdN₆O₄·DEF	5 C₁₈H₁₂CdN₆O₄·DMF
Formula weight	488.74	488.74
Temperature (K)	100 K	100 K
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
a[Å]	15.371(3)	15.446(5)
b[Å]	16.195(3)	15.902(5)
c[Å]	9.2296(16)	9.210(3)
α [°]	90.00	90.00
β [°]	103.300(2)	104.656(3)
γ [°]	90.00	90.00
Volume[Å ³]	2235.93	2188.58
Z	8	4
Density (calculated)[Mg/m ³]	1.452	1.884
Absorption coefficient [μ]	1.009	1.063
<i>F</i> (000)	968	1232
Refl. used [$I > 2\sigma(I)$]	1844	1689
Independent reflections	2406	1868
<i>R</i> int	0.0579	0.0474
GooF	1.805	1.065
Final <i>R</i>	0.1220	0.1239

indices [$I > 2\sigma(I)$]		
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According to the results of the X-ray analysis, Framework 5 crystallizes in a monoclinic crystal system with the same space group ($C2/c$), asymmetric unit, and distorted octahedral geometry around the Cd(II) center as Framework 4. The bonding nature is also created using a similar coordination arrangement. DMF molecules are present in the crystal lattice as expected. The 3D channel of framework 4 pores with an occupied DMF molecule in the lattice (on the left) and the same structure with empty voids (on the right), both after the DMF molecules had been eliminated by the PLATON Squeeze software. The triazole ring and benzene moieties, for example, are not coplanar with respect to one another but instead have dihedral angles of 34.98° and 42.75° , respectively. The equatorial Cd-O distances range from 2.28 to 2.35, while the two apical Cd-N distances are similar (2.34), indicating a relatively regular octahedron.

The N-Cd-O angles slightly vary (91.13° - 101.67°) from 90° . The stacking interaction between the triazole ring and the hydrogens of the benzene ring stabilizes the lattice of DEF molecules in this crystal structure. The Cd(II) chains in this crystal structure are connected by carboxylate groups of TBA along the [001] direction (b-axis), with a Cd distance of 4.60. The pore aperture, on the other hand, is determined by taking the atom-to-atom distance, which is the separation between the nearest atoms apart from the hydrogen atom. Van der Waals radii are taken into account, opening the pore aperture along the c-axis in every 1D channel of 8.40 Å windows with no discernible pore channel along the a- or b-axis. The distance between two imidazole rings is 8.40 Å, whereas the carboxylate oxygen of benzene is 15.44 Å apart. The entire framework is interconnected with these unidirectional channels, resulting in a 3D porous structure with a 1D channel. A single cage has a small amount of empty space, which prevents structural interpenetration and causes the development of non-interpenetrated 3-D MOF channels with a cross section that extends down the c-axis. The guest solvent molecules, such as DMF, are accommodated inside the pore channels according to the PLATON squeeze data, and the framework 4's potential solvent accessible void volume is determined to be 639.2 Å³, which is roughly 28.6% of the unit cell volume (2235.9 Å³). In addition to being maintained by weak hydrogen bonding C-H-O interactions between 1, 2, 4-triazole and DMF molecules, this void volume may have an effect on the adsorption of gases.

PXRD OF THE FRAMEWORK

By analyzing the powder X-ray diffraction (PXRD) pattern of 4 and 5, it was possible to independently establish

the integrity and phase purity of the bulk sample of porous framework. The majority of the experimental and simulated peak positions are in good agreement with one another, and the variations in intensity may be caused by the preferred orientation of powder samples. The crystalline solid phase remained virtually same following solvent exchange at room temperature, according to a comparison of PXRD patterns recorded from the as-synthesised and solvent exchanged (activated) framework 4 with simulated ones from the single-crystal studies.

This shows that during the guest exchange, the porous framework maintained the integrity of the crystals. In the meantime, measurements using the variable temperature powder X-ray diffraction (VT-PXRD) technique were made to determine how the porous framework would be preserved when heated to breakdown. The VT-PXRD pattern of 4 was effectively maintained up to 300 °C. After gas adsorption and after absorbing different organic solvent molecules, activated framework 4 maintains its rigidity and stability even after these post-treatments were utilized to screen the crystallinity using PXRD measurements. No significant loss of crystallinity was seen in this instance. Indicating that framework can maintain its framework integrity even in the absence of guest species or after gas adsorption analysis, which further emphasizes its framework robustness, the PXRD patterns under various conditions maintain similar diffraction peaks to those of the as-synthesized sample. The organic solvent guest-absorbed samples (b) 3A.4.3 Complexes' capacity to withstand heat. As-synthesised frameworks 4 and 5 show a steady initial weight loss of around 12.47% in the RT to 150 oC according to the thermogravimetric analysis. The DEF and DMF solvent molecules, both of which have boiling points around 150 oC, are probably to blame for the first weight loss for framework 4 about 140 oC. After then, a plateau is maintained between 140 and 260 oC, and the structure collapses. DCM was swapped with frameworks 4 and 5 for 4 days before being heated to 100 °C for 4 hours or left at room temperature overnight under vacuum, which allowed all of the solvent molecules to be totally evacuated. At around 300 °C, the de-solvated framework 4's TGA curves stop showing any weight loss, and then there is an abrupt weight drop, which suggests structural disintegration. The experiment reveals unequivocally the temperature resistance and stability of the host structures up to 300°C.

A PILLARED-LAYER CD II POROUS FRAMEWORK CONSTRUCTED FROM MIXED LIGANDS

By using the solvothermal reaction of 4-(1H-triazole-1-yl) benzoate and 4,4'-bipyridine with Cd(NO₃)₂•4H₂O in DMF, the title chemical was created as colorless rectangular crystals. Single crystal X-ray diffraction analysis of the synthesized crystals revealed that 6 crystallizes in the monoclinic space group C2/c and that the asymmetric unit is made up of two crystallographically independent Cd(II) ions, two TBA- ligands, one bpy spacer, two lattice DMF, and three water molecules. Four oxygens [CdO = 2.301 2.382] from three carboxylates of TBA- ligand and

two pyridyl nitrogens [Cd-N = 2.265] of bpy provide Cd(1) its distorted octahedral coordination geometry. A dinuclear subunit with a Cd...Cd separation of 3.955(2) is formed by two equivalent Cd(1) ions being bridged by two carboxylate groups of various TBA- ligands in a syn-anti manner. Cd(2coordination)'s environment differs greatly from Cd's in many ways (1). Here, four triazole nitrogen atoms [Cd-N = 2.304 (5) 2.364 (7)] are octahedrally coordinated to the metal Cd(2), which is situated in a particular position.

The desolvated framework (6) has undergone gas adsorption tests toward CO₂ and H₂ to ascertain its potential utility for gas separation and storage. The 6 exhibited relatively little N₂ uptake despite the robust framework and appropriate effective pore size along the c-axis. At 77 K, the N₂ (3.64) adsorption isotherms indicate 18 m²/g of BET surface area). Due to the absence of pore openings across the framework axes a and b and the presence of 2-fold interpenetration, there is reduced surface area, which is solely suggestive of surface adsorption. However, the isotherm displays type-IV isotherm with relatively weak interactions between the adsorbed adsorbent and the hysteresis. However, after the evacuation of framework 6, along the c-axis, a pore opening gives an appreciable amount of CO₂ (3.3) and H₂ (2.89) at ambient temperature which depicts a type-1 isotherm at RT up to 35 bar gives 59.1 cm³/g (11.6 wt%), displays the CO₂ adsorption isotherms for desolvated framework (6) at room temperature. The existence of an absorption plateau means that even at increasing pressure, the ability for more gas uptake cannot be assumed. Hydrogen gas sorption investigation depicts the steep rise in the adsorption isotherm and the capacity of the guest free framework (6) to adsorb 14.8 cm³/g (0.13 wt%) H₂ at 298 K and up to 30 pressures. These uptakes are on par with or better than those noted for layered coordinating frameworks under related circumstances. The fact that both CO₂ and N₂ adsorption exhibit strong hysteresis upon desorption at all points along the sorption isotherm suggests contact with the framework's surface.

CONCLUSION

Isostructural frameworks that are thermally stable, [Cd(TBA)₂] Cd(TBA)₂ and 1DEF (4) •1DMF (5) has been effectively synthesized under solvothermal conditions employing a triazolate-carboxylate bifunctional ligand such as 4-(1H-1,2,4-triazol-1-yl) benzoic acid (HTBA) with Cd²⁺ ions. However, employing alternative solvent molecules like DEF and DMF, two distinct solvent accessible void volumes of frameworks 4 and 5 are created. These volumes are then crystallized in a monoclinic crystal system with a C₂/c space group and a non-interpenetrated network via 1-D channels. Additionally, ligand coordination mechanisms in frameworks 4 and 5 are comparable. The aforementioned synthesized frameworks, however, exhibit selective CO₂ adsorption over N₂ and CH₄ with significant CO₂ adsorption enthalpy (Q_{st}). In conclusion, a new dynamic porous coordination polymer 3D pillared layer framework called [Cd₂(TBA)₂(bpy)]•1DMF_n, (6) (TBA = 4-(1H-triazole-1-

yl)benzoate, bpy = 4,4'-bipyridine, and DMF = N,N-dimethylformamide) has been synthesized and structurally characterized using hydrothermal methods. Triazole and carboxylate groups of TBA-ligands bind the metal ions to create 2D layers, which are then pillared by the secondary metal linker (bpy) to create a 3D architecture with doubly interpenetrated layers. Solvent molecules fill the big holes in the framework, which can be cleaned out with heat treatment. The porous, desolvated structure can accommodate a variety of gas molecules. As a result, despite the desolvated material's ability to adsorb gas, its crystal structure is still unknown. The ability to study the structural characteristics of a gas sorption substrate at the atomic scale in the hope of eventually understanding the underlying principles that govern gas-solid interactions and the dynamic nature of the framework makes the formation of porous materials by means of single-crystal transformations extremely valuable. Finally, two different types of pores that are occupied by solvent molecules are provided by the interpenetrated framework. Through sorption experiments using several gases, it has been demonstrated that the solvent-free framework (6) is porous (N₂, CO₂ and H₂).

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