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Introducing a longer versus shorter acylhydrazone linker to a metal-organic framework: parallel mechanochemical approach, non-isoreticular structures and diverse properties

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Abstract

A 20-Å-long diacylhydrazone linker was used for the first time as a building block for the construction of a metal-organic framework (MOF). The terephthalaldehyde diisonicotinoylhydrazone (*tdih*) is considerably longer than its 11-Å-long mono-acylhydrazone counterpart, 4-pyridinecarboxaldehyde isonicotinoylhydrazone (pcih), used so far as a MOF linker. By utilizing the two ditopic hydrazone linkers providing linear connectivity, two nonisoreticular cadmium-organic frameworks, $\{[Cd_2(oba)_2(hydrazone)_2]\}_n$ (with oba = 4,4'oxybis(benzenedicarboxylate) co-linker) were obtained by solution and mechanochemical methods. In spite of the same secondary building units, the frameworks differ in dimensionality as well as exhibit various stability and adsorption behavior, that are compared and discussed. The insights into structure-property relationships are provided by single-crystal X-ray diffraction (SC-XRD), temperature-dependent powder XRD, thermogravimetric analysis, CO₂ (at 195 K), N₂ (at 77 K) and H₂O (at 298 K) gas adsorption measurements, as well as quasi-equilibrated temperature-programmed desorption and adsorption (QE-TPDA). The work opens possibilities to synthesize new functional materials based on the longer linker.

Introduction

The considerable interest of academia and industry in the chemistry of metal-organic frameworks (MOFs)¹⁻³ is driven to a large extent by their well-ordered porosity connected with structural flexibility and modularity.^{4,5} These features allow for tunability of MOF properties beyond conventional solid-state materials, to address plethora of challenging applications in the fields of drug delivery^{6,7}, electronic devices,⁸⁻¹⁰ catalysis,^{11,12} photocatalysis,¹³ gas adsorption,^{14–17} water purification¹⁸ and others. Tuning of MOF functionalities can be carried out through a careful selection of appropriate linker precursors used for the assembly of extended networks. In particular, the first example of a systematic change of pore size and polarity was demonstrated for an isoreticular series of MOFs based on Zn₄O nodes linked by linear dicarboxylates.¹⁹ This series included the prototypal MOF-5 with terephthalate linkers and comprised other frameworks of the same primitive cubic topology differing in linker lengths and side groups. This elegant isoreticular approach allowed to identify the best candidate for methane storage and became a more common strategy successfully realized in other MOF families. Naturally, the implementation of a given synthetic strategy may vary in details but the preferable approaches reduce the use of energy and solvents. In this regard, solvent-free mechanochemistry, relying on grinding of solid substrates, has recently emerged as a powerful tool for the synthesis of MOFs.²⁰

Following the synthetic challenge to build functional MOFs, we have recently been exploring the chemistry of metal-organic frameworks based on mixed carboxylate and acylhydrazone linkers, the latter bearing both hydrogen-bond donor and acceptor groups as well as showing coordination versatility towards a diverse range of metals.^{21–24} In 2016 we reported the first mixed-linker MOFs based on an acylhydrazone and a dicarboxylate.²⁵ Since then several articles describing new frameworks from this family and their properties, have been published. In particular, the carboxylate-acylhydrazone MOFs have been reported to exhibit numerous interesting behaviors, such as flexibility,²⁶ high mechanical and hydrothermal stability,^{27,28} gas adsorption selectivity,^{25,26,28,29} structural diversity,²⁹ multifunctional catalytic activity³⁰ and sensing potential.³¹ However, all of the aforementioned frameworks have been based on the same relatively short (~11 Å) 4-pyridinecarboxaldehyde isonicotinoylhydrazone (*pcih*) linkers and different dicarboxylate co-linkers. Therefore, this work was undertaken with the following motivation: (i) to construct the first MOF with a longer acylhydrazone linker than *pcih* used so far, possibly by a solvent-free method; (ii) to determine and compare its crystal structure and properties with the analogous *pcih*-based material; (iii) to verify hypothesis of isoreticular expansion based on acylhydrazone linkers.

Herein, we present two new cadmium metal-organic frameworks based on acylhydrazone linkers providing linear connectivity: a shorter *pcih* or a longer terephthalaldehyde di-isonicotinoylhydrazone (tdih), each with the same additional dicarboxylate co-linker. In spite of the same secondary building units, the frameworks have non-isoreticular structures with different dimensionalities. We present and compare various alternative methods of synthesis of the two materials including deposition from solutions and optimized grinding of solid reactants. Both Cd-MOFs exhibit adsorption behaviors that are untypical of the so far known mixed-linker carboxylate-acylhydrazone MOFs, with CO_2/N_2 non-selectivity being the major difference. The adsorption properties towards CO₂ (at 195 K) and N_2 (at 77 K) gases are discussed along with structural features of the frameworks. Furthermore, by using of single-crystal X-ray diffraction (SC-XRD), temperature-dependent powder XRD, thermogravimetric analysis and quasi-equilibrated temperature-programmed desorption and adsorption (QE-TPDA) method, versatile types of the frameworks' stability are also investigated and discussed. Our study is the first example of utilization of terephthalaldehyde di-isonicotinoylhydrazone molecule as a MOF linker. This opens new synthetic possibilities with other metals and/or co-linkers which may provide interesting materials for a variety of applications.

Results and Discussion

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Parallel solvent-based and solvent-free syntheses

Two mixed-linker cadmium(II) metal-organic frameworks of various dimensionalities: 2D ${[Cd_2(oba)_2(pcih)_2] \cdot 3DMF}_n(1)$ and ${3D} {[Cd_2(oba)_2(tdih)_2] \cdot 7H_2O \cdot 6DMF}_n(2)$, based on 4,4'-(oba²⁻) oxybis(benzenedicarboxylate) and either 4-pyridinecarboxaldehyde isonicotinovlhydrazone (pcih) or terephthalaldehyde di-isonicotinovlhydrazone (tdih) (Figure 1), were synthesized by parallel solvent-based and solvent-free methods. In the solvent-based case, relatively high amounts of both organic solvent and energy (heating at 70 °C for approx. 4 days) were consumed to yield single crystals of compounds 1 and 2 suitable for X-ray diffraction measurements. Alternatively, the two materials were prepared by the solvent-free mechanochemical method, where solid reagents were ground together in a ball-mill in either a one-pot or a two-step variant (Figure 1 and Figures S1-S4, Supplementary Information). The latter approach meets the expectations of green chemistry, i.e. a reaction is fast and no organic solvent is used. The purity of products 1 and 2 obtained by the two methods was confirmed by elemental analysis, IR spectroscopy and powder X-ray diffraction (Table S1; Figures S2-S4, Supplementary Information).



Figure 1. (a) Linkers/linker precursors used for syntheses of compounds 1 and 2. H_2 oba: 4,4²-oxybis(benzenedicarboxylic) acid; *pcih*: 4-pyridinecarboxaldehyde isonicotinoylhydrazone (in 1); *tdih*: terephthalaldehyde di-isonicotinoylhydrazone (in 2). (b) Various synthetic approaches to compounds 1 and 2; LAG: liquid-assisted grinding.

In the mechanochemical one-pot approach, CdO or Cd(OH)₂, H₂oba and *pcih* or *tdih* were ground together in the 1:1:1 molar ratio with the addition of a small amount of DMF (150 μ L), and in case of the CdO substrate, with the addition of a catalytic amount of NH₄NO₃ (4 wt%). In contrast, the two-step reaction which proceeds via an intermediate coordination polymer of [Cd(μ -H₂O)(oba)(H₂O)]_n (CCDC1476612),³² does not require addition of the catalyst. Both products **1** and **2** are obtainable in the two-step variant from a pre-assembled intermediate which is built of Cd²⁺ ions that are linked by the oba²⁻ dicarboxylates and aqua bridges into a 3D framework, wherein each metal centre has a labile terminal aqua ligand. Analogous behavior was shown for example for archetypical UiO-66 and its NH₂ analogue which were easily obtained in a gram-scale milling by utilization of pre-assembled benzoate or methacrylate precursors.³³

In our experiments, cadmium hydroxide was found as the preferable metal substrate. Firstly, when it was used as the substrate for grinding then independently on the variant used in the mechanochemical approach, no catalyst was required for the formation of **1** and **2** (see Figure S2-S3, Supplementary Information and Materials and Method section). Secondly, in case of the materials obtained from CdO, larger discrepancies were found in their elemental analyses (Table S1, Supplementary Information), which may indicate the presence of unreacted CdO as an impurity. The main factor responsible for reactivity is the chemical character of $Cd(OH)_2$ which is a stronger base than CdO and thus favours deprotonation of H-20ba. Additionally, in order to get an insight into homogeneity as well as size and morphology of crystals, scanning electron microscopy (SEM) analysis has been carried out for the samples obtained in a ball mill from Cd(OH)₂ (Figure S5, Supplementary Information). SEM images of **1** and **2** confirm the homogeneity of the mechanochemically obtained materials which form plate-shaped crystals of similar size and uniform morphology.

Crystal structures

Single crystals of compounds $\{[Cd_2(oba)_2(pcih)_2]\cdot 3DMF\}_n$ (1) and $\{[Cd_2(oba)_2(tdih)_2]\cdot 7H_2O\cdot 6DMF\}_n$ (2) used for X-ray diffraction (XRD) were grown in a DMF/H₂O mixture (see Materials and Methods section). Despite using the same type of building blocks for the construction of the two materials, i.e. the H₂oba linker precursor and a pyridyl-functionalized acylhydrazone building block of a linear connectivity (*pcih* or *tdih*)

differing in length), resulting products 1 and 2 do not form an isoreticular series. The MOFs crystallize in monoclinic and triclinic crystal systems with the space groups $P\overline{1}$ and C2/c, respectively. As revealed by XRD experiments, the Cd²⁺ ions in both frameworks have disordered pentagonal bipyramidal geometry where central ion is coordinated equatorially by five oxygen atoms from three different dicarboxylate acids (oba²⁻) (Figure S6, Supplementary Information). The coordination sphere is completed by axial N-pyridyl atoms from two neutral N,N-donor linkers; terephthalaldehyde di-isonicotinoylhydrazone (tdih) and 4pyridinecarboxaldehyde isonicotinoylhydrazone (*pcih*), respectively for 1 and 2 (Figure 2, Figure S6, Supplementary Information). In both materials the oba²⁻ ligands and Cd²⁺ ions form the $[Cd_2(COO)_2]$ secondary building units (SBUs) with Cd-Cd distances of 3.836 Å (1) and 3.868 Å (2) in each cluster. The oba²⁻ carboxylates act as $\mu_3 - \kappa^2 \kappa^2 \kappa^1$ angular ligands connecting SBU units into the $[Cd_2(oba)_2]_n$ double chains (1) and layers (2). The double chains in 1 are further connected by the *pcih* ligands into the 2D framework of *sql* topology (determined by ToposPro software).³⁴ The adjacent layers in **1** interact via strong N-H···O hydrogen bonds between NH group of the pcih acylhydrazone and carboxylate oxygen atom $[d(N9-H(N9)\cdots O47) = 2.85 \text{ Å}, angle = 171^{\circ}]$ forming a two-dimensional pore structure (Figure 2; Figure S7, Supplementary Information). In contrast, the layers of $[Cd_2(oba)_2]_n$ in the framework 2 are further linked by the *tdih* ligand to form a three-dimensional noninterpenetrated pillar-layered structure. Solvent-accessible voids in the structure, occupied by DMF and H₂O molecules in the as-synthesized material, consist of two intersecting 1D channels that form a 2D channel system propagating along the (001) plane. Two types of hydrogen bonds can be distinguished in the as-synthesized compound 2: intraframework and between the framework and guest molecules. The former includes carboxylate oxygen atoms interacting with NH groups of the *tdih* ligands $(d(N20-H(N20)\cdots O57)) = 2.89$ Å, angle = 170°), whereas the latter involves NH group of the *tdih* ligands and oxygen atoms of DMF molecules $d((N9-H(N9)\cdots O64)) = 2.84 \text{ \AA}$, angle = 164°). The formation of hydrogen bonds in both MOFs is corroborated by their IR spectra. The spectra show the presence of the v(NH)amide bands that are shifted as compared to pure ligands [3218 (1) as compared to 3190 cm^{-1} (*pcih*); 3235 (2) as compared to 3249 cm⁻¹(*tdih*)]

In spite of identical acylhydrazone linker topology, the use of linear acylhydrazone linkers of various length leads to non-isoreticular cadmium-organic frameworks **1** and **2**. Replacing shorter *pcih* with longer *tdih* linker strongly affects conformation of the oba²⁻ co-linker that is capable of twisting about the C-O and the C-C single bonds. As a result, dihedral angles between the CdOOC planes of the oba²⁻ co-linker are significantly different in the two compounds (20.0° and 78.3° for **1** and **2**, respectively), and the Cd···Cd distance (via the oba²⁻ linker) is shorter for **2** (15.09 Å) than for **1** (15.20 Å) [Figure S8, Supplementary Information]. The main consequence, however, is significantly different angles between axial axes of neighboring coordination centres, i.e. parallel versus nearly perpendicular arrangement, for **1** and **2**, respectively. This considerable difference leads to different network dimensionalities and topologies: three-dimensional 3,5-c network of unknown topology for **2** as opposed to two-dimensional *sql* topology for **1** (according to ToposPro).



Figure 2. X-ray crystal structures of MOFs 1 (top) and 2 (bottom): (a) cluster coordination spheres of $[Cd_2(oba)_2(pcih)_2]$ (in 1) and $[Cd_2(oba)_2(tdih)_2]$ (in 2), (b) $[Cd_2(oba)_2]_n$ fragments (1D double chains in 1 and 2D layers in 2), (c) interlayer (in 1) and intraframework (in 2) hydrogen bonds, (d) contact surface (calculated with Mercury software by using a probe molecule with a radius of 1.2 Å. In a), b), d) hydrogens atoms are omitted for clarity.

Thermal stability and adsorption properties

In order to assess thermal stability as well as to determine activation conditions for porous coordination polymers 1-2, both thermogravimetric (TG) and *in situ* temperature-dependent powder X-ray diffraction analyses (TD-PXRD) have been utilized (Figure 3). The TG curves indicate that the materials are thermally stable approx. up to 300 °C with derivative thermogravimetric (DTG) curves minima of 362 °C (1) and 342 °C (2), wherein upon heating to 280 °C weight losses of 15.7% and 29.1% are observed, respectively. These weight losses observed for both compounds are associated with removal of guests molecules from channels of the frameworks, and are in agreement with theoretical values (calculated for 3DMF: 15.6 % (1); for 7H₂O and 6DMF: 27.6 % (2)).



Figure 3. Thermal stability of the as-synthesized (in solution) compounds 1 and 2. TG and DTG curves (left), and TD-PXRD patterns (right).

Temperature-dependent powder X-ray diffraction patterns confirm thermal stability of compound 1 determined by thermogravimetric analysis. When the sample is conditioned for 10 min at 330 °C, first clear changes in the XRD pattern, including the decrease of the distinguished peak at $2\Theta = 6.5^{\circ}$, are observed (Figure 3). In contrast, variable temperature PXRD patterns recorded for compound 2, indicate that the framework undergoes two phase transitions in the range of 80-160 °C. The phase at higher temperatures and below 310 °C is characterized by two broad reflections which indicates loss of long-range ordering within the MOF and its predominant amorphous character above 160 °C.

In order to avoid potential decompositions/phase transitions of the frameworks 1-2 indicated by TD-PXRD analysis (Figure 3), further confirmed by adsorption measurement upon thermal activation of 1 at 180 °C (Figure S9, Supplementary Information), gentle activation procedures have been adopted for both compounds before adsorption measurements. The samples were soaked for a few days in dichloromethane (DCM), with several replacement of the supernatant by fresh portions of DCM (such samples are referred to as 1.DCM and 2.DCM, respectively), followed by room-temperature activation for approx. 16 hours under vacuum (Figure S10, Supplementary Information). The adsorption experiments reveal that the two MOFs 1 and 2, regardless of the method of their synthesis, are porous towards both N₂ at 77 K and CO₂ at 195 K (Figure 4 and Figure S11, Supplementary Information). This observation is in contrast with previous adsorption behavior in the family of mixed-linker acylhydrazone/carboxylate metal-organic frameworks $\{[M_2(dca)_2(pcih)_2] \cdot guest\}_n (M = Zn^{2+}, Cd^{2+}; dca^{2-} - dicarboxylate),^{25-29} where the adsorption$ selectivity towards CO₂ versus N₂ was explained by the sieving effect and the presence of Lewis basic NH groups from acylhydrazone moieties that decorated pores walls.²⁷ However, unlike compounds 1-2, the representatives of this family so far possess only one-dimensional channels or zero-dimensional voids. Even three-dimensional highly robust MOF $[Cd_2(sba)_2(pcih)_2]_n$ (sda²⁻ - 4,4'-sulfonyldibenzoic carboxylate), which has bigger window size (4.4 Å) than kinetic diameter of nitrogen (3.64 Å), demonstrates selective adsorption of CO₂.²⁷ Contrary to the previously reported mixed-linker acylhydrazone/carboxylate metal-

organic frameworks, the as-synthesized materials **1-2** have two-dimensional voids (Figure 2) constructed by two intersecting channels: i) a bigger one, decorated by polar acylhydrazone - C(O)=N-NH- groups of the *pcih* or *tdih* linkers, and ii) a smaller one, propagating in close proximity of the oba²⁻ linkers. The latter, more nonpolar channels, provide extra diffusion pathways for N₂ into the frameworks **1-2**. The following discussion refers to the data obtained for the materials synthesized in solution and the corresponding data for the samples synthesized mechanochemically are shown in Figure S11, Supplementary Information.



Figure 4. Physisorption isotherms of N₂ (77 K) and CO₂ (195 K) for materials 1 and 2 synthesized in solution.

The CO₂ (195 K) and N₂ (77 K) physisorption isotherms for framework 1 after activation show maximum loading of 128 cm³·g⁻¹ at $p/p_0 = 0.99$ and 148 cm³·g⁻¹ at $p/p_0 = 0.98$, respectively. These values, according to the Gurvich rule³⁵ (for both gases) correspond to a total pore volume of 0.23 cm³·g⁻¹ (Table 1).

Table 1. Porosity parameters for 1-2 calculated by Zeo^{++} software and obtained from CO_2 (195 K) adsorption isotherms.

MOF	$p_{ws}[A]^*$	m_{pd} [Å] *	$V_{pt} [cm^3 \cdot g^{-1}]^*$	$V_{pe} [cm^3 \cdot g^{-1}]^*$
1	6.01	4.05	0.23	0.23#
2	6.94	9.07	0.32	0.32##

*probe radius = 1.6 Å, p_{ws} -pore window size, m_{pd} - maximum pore diameter, V_{pt} -theoretical pore volume, V_{pe} - experimental pore volume (based on limiting loading in adsorption isotherms for CO₂)

 $p/p_0 \sim 1.0$, uptake 128 cm³·g⁻¹

 $^{\#}p/p_{o} \sim 1.0$, uptake 181 cm³·g⁻¹

This is in agreement with the theoretical pore volume of $0.23 \text{ cm}^3 \cdot \text{g}^{-1}$ calculated for the $[\text{Cd}_2(\text{oba})_2(\text{pcih})_2]$ framework by the Zeo⁺⁺ software³⁶ using the probe with a radius of 1.6 Å (corresponding to carbon dioxide diameter of 3.30 Å). The slight hysteresis for CO₂ between adsorption and desorption branches is caused by weak interactions of the adsorptive with polar acylhydrazone -C(O)=N-NH- groups of the *pcih* linkers. The framework 1 belongs to a rare family of interdigitated 2D coordination polymers of general formula $[M_2(\text{adc})_2(\text{lig})_2]_n$ (adc – angular dicarboxylate, lig – neutral N-donor ligand), whose members show selective CO₂ (195K) adsorption over N₂ (77 K). The utilization of the longer bent dicarboxylate, as compared e.g. to isophthalates, is responsible for the second highest CO₂ uptake as well as for the loss of CO₂ over N₂ selectivity in this family (Table 2). In spite of the highest void volume of 1 in this group, the CO₂ uptake is lower than for $[\text{Zn}_2(\text{iso})_2(\text{dptztz})_2]_n$. This is caused by a

> structural transformation of $[Zn_2(iso)_2(dptztz)_2]_n$ that led to creation of additional free space and enhanced adsorption. In general, the lack of straightforward correlation between theoretical pore volumes and CO₂ uptakes for compounds without groups known for strong interactions with CO₂, indicates the occurrence of structural changes upon adsorption.

In order to verify reversibility of adsorption, the second run of N₂ (77 K) has been carried out on the sample evacuated at room temperature after the first run (Figure S12, Supplementary Information). The total uptake of N₂ is almost unchanged in the second run (147 cm³·g⁻¹) as compared to the first (148 cm³·g⁻¹), however in the first stage of the adsorption branch, at $p/p_o \sim 0.05$, the capacity drops from 141 to 130 cm³·g⁻¹. These phenomena can be explained by increasing disorder of interdigitated layers of **1** upon subsequent activation process, which as a result causes more steric hindrances and limits gas diffusion into pores. This explanation is additionally supported by PXRD patterns recorded for samples that were soaked in DCM, thermally activated, and after N₂ adsorption (Figure S10, Supplementary Information)²⁹ The latter confirms that the structure of **1** remains unchanged after N₂ adsorption.

MOF	CO_2 uptake at 195 K $[cm^3 \cdot g^{-1}]$	Theoretical pore volume* [cm ³ ·g ⁻¹]	Ref.
$Cd_2(oba)_2(pcih)_2$	128	0.23	this work
$Cd_2(iso)_2(pcih)_2$	88	0.08	29
Cd ₂ (tBu-iso) ₂ (pcih) ₂	66	0.14	29
$Zn_2(iso)_2(pcih)_2$	91	0.09	26
Zn ₂ (OH-iso) ₂ (pcih) ₂	94	0.09	28
Zn ₂ (CH ₃ -iso) ₂ (pcih) ₂	96	0.15	28
$Zn_2(iso)_2(dptztz)_2$	138	0.19	37
Zn ₂ (iso) ₂ (bpy) ₂ CID-1	58	0.08	38
$Zn_2(azdc)_2(bpy)_2$ CID-13	77	0.17	39
Zn ₂ (iso) ₂ (bpb) ₂ CID-21	44	0.18	40
Zn ₂ (iso) ₂ (bpt) ₂ CID-22	33	0.18	40
Zn ₂ (iso) ₂ (bpa) ₂ CID-23	89	0.18	40
$Zn_2(ndc)_2(bpy)_2 CID-3$	77	0.17	41
Zn ₂ (NO ₂ -iso) ₂ (bpy) ₂ CID-5	57	0	14
Zn ₂ (CH ₃ O-iso) ₂ (bpy) ₂ CID-6	58	0.11	14

Table 2. Examples of mixed-linker (dicarboxylate/N,N-donor) Image: state of the state of	
coordination polymers with layered interdigitated structures.	

Xiso² = 5-substituted isophthalate (X = H, CH₃, OCH₃, OH, NH₂, NO₂, tBu)

bpy = 4,4'-bipyridyl

bpndc²⁻ = benzophenone-4,4' -dicarboxylate bpb = 1,4- bis(4-pyridyl)benzene bpt = 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine bpa = 1,4-bis(4-pyridyl)acetylene) dptztz = 2,5-di(4-pyridyl)thiazolo[5,4-d]thiazole azdc²⁻ = 1,6-azulenedicarboxylate ndc²⁻ = 2,6-naphthalenedicarboxylate *calculated from X-ray crystal structures

Replacement of the *pcih* linker with the longer *tdih* diacylhydrazone ligand, utilized as a linker in MOFs for the first time, leads to 3D acylhydrazone-carboxylate framework **2** which has the highest theoretical pore volume of 0.32 cm³·g⁻¹, the highest CO₂ (195 K) uptake of 181 cm³·g⁻¹ as well as the highest maximum pore diameter (9.1 Å) and window size (6.94 Å) of all mixed-linker acylhydrazone-carboxylate frameworks reported to date. However, this is still far from the values found in the literature for MOFs that show excellent CO₂ storage capacities (e.g. at 293K and 40 bar: MOF-5, 495 cm³/g; MOF-177, 759 cm³/g; IRMOF-6, 443 cm³/g).⁴² The experimental pore volume calculated from the CO₂ adsorption branch at $p/p_0 = 0.99$ equals to 0.32 cm³·g⁻¹ (V_{pe})_{CO2} and is in a agreement with the value calculated at $p/p_0 = 0.99$ (320 cm³·g⁻¹) from the N₂ (77 K) adsorption isotherm, surpasses (V_{pe})_{CO2} by nearly 50%. To verify whether it is not an experimental error, a few adsorption-desorption cycles were performed as well as different batches of compounds were verified (Figure S13, Supplementary Information). The result is repeatable and the discrepancy between calculated V_{pe} values for various adsorbates will be subject of further more detailed investigations.

In order to get a fuller insight into adsorption processes, water vapor adsorption isotherms and isobars have been measured for activated MOFs 1 and 2 (Figures 5 and Figure S14). The isotherms recorded at 298 K for both MOFs have shown their instability towards this small adsorptive demonstrating by large untypical hysteresis, long time of measurement (even 5 days) as well as the highest H₂O uptake for lower p/p_0 (105 cm³·g⁻¹ at $p/p_0 = 0.94$ for 1; and 225 cm³·g⁻¹ at $p/p_0 = 0.94$ for 2) than for maximal partial pressure (103 cm³·g⁻¹ for 1; and 199 cm³·g⁻¹ for 2). To investigate the stability in liquid H₂O, frameworks 1-2 have been immersed in water at ambient temperature for 1-6 days, and after this treatment, the waterloaded MOFs were soaked in DMF or DMF/H₂O (9:1 v/v) solution, to study their guest exchange reversibility. The framework 1 undergoes fully reversible phase transition (Figure S15, Supplementary Information), which according to our previous study of interdigitated frameworks, is caused by a reversible change of relative arrangement of adjacent layers, induced by exchange of guest molecules.²⁸ However, this MOF is not stable during repeatable cycles of water adsorption-desorption, which is demonstrated by loss of porosity (Figure S16, Supplementary Information). In contrast, material 2 after soaking in water, has undergone irreversible transformation to a highly water stable phase ${[Cd_2(oba)_2(tdih)_2] \cdot 13H_2O_n}$ $(2 \cdot H_2 O)$ that shows characteristic narrow band at ~ 3500 cm⁻¹ in IR spectrum, ascribed to the presence of highly ordered water molecules engaged in strong hydrogen bonds with acylhydrazone groups (Figure S17, Supplementary Information). Analogous hydrogen bonds involving an acylhydrazone group and water guest molecules have been observed in the structure of $[Cd_2(sba)_2(pcih)_2]_n$.²⁷



Figure 5. The as-synthesized (in solution) MOF **2**: QE-TPDA profiles of water vapor desorption-adsorption cycles at 2250 Pa (left), desorption-adsorption isobars (middle) and stability of porosity upon repeated water vapor desorption-adsorption cycle (right).

The stability of the $[Cd_2(oba)_2(tdih)_2]$ phase obtained via thermal activation of $\{[Cd_2(oba)_2(tdih)_2]\cdot 13H_2O\}_n$ (**2**·**H**₂**O**) as well as its porosity towards H₂O have been elucidated by QE-TPDA (quasi-equilibrated temperature-programmed desorption and adsorption), which clearly demonstrated that H₂O loading of the $[Cd_2(oba)_2(tdih)_2]$ framework does not change after 22 cycles (Figure 5). The maximal amount of water adsorbed in isobaric conditions (~150 cm³·g⁻¹; 12.1% by mass) is in agreement with the data obtained from thermogravimetric and elemental analyses for the water-loaded material **2** (Figure S18, Supplementary Information and Experimental section).

Conclusion

By utilizing two ditopic acylhydrazone linkers providing linear connectivity: shorter 4pyridinecarboxaldehyde isonicotinoylhydrazone or longer terephthalaldehyde diisonicotinoylhydrazone, two non-isoreticular cadmium-organic frameworks have been obtained. The frameworks possess the same secondary building units including Cd₂ cluster but differ in dimensionality. The Cd-MOFs exhibit sorption behavior untypical of the so far known mixed-linker carboxylate-acylhydrazone MOFs, without CO₂/N₂ selectivity, commonly observed in this framework family. This phenomenon is explained by the coexistence of two types of channels in their structures, not observed for previous MOFs, that provide extra diffusion pathways for adsorptives. The frameworks immersed in water undergo either reversible or irreversible phase transitions, for shorter- or longer-linker MOF respectively; whereas the latter gives the longer-linker framework ability to reversibly absorb water vapor. The first use of a diacylhydrazone building block for the construction of metalorganic frameworks opens new synthetic possibilities e.g. with other metals and co-linkers and this work is currently in progress.

Experimental

Materials and Methods

4-pyridinecarbaldehyde isonicotinoylhydrazone (*pcih*) was prepared according to the published method.²⁵ All other reagents and solvents were of analytical grade (Sigma Aldrich, POCH, Polmos) and were used without further purification.

Carbon, hydrogen and nitrogen were determined by conventional microanalysis with the use of an Elementar Vario MICRO Cube elemental analyzer.

IR spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrophotometer equipped with an iD7 diamond ATR attachment.

 Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo TGA/SDTA 851^e instrument at a heating rate of 10 °C min⁻¹ in a temperature range of 25 – 600 °C (approx. sample weight of 8-14 mg). The measurement was performed at atmospheric pressure under argon flow.

Powder X-ray diffraction (PXRD) patterns were recorded at room temperature (295 K) on a Rigaku Miniflex 600 diffractometer with Cu-K α radiation ($\lambda = 1.5418$ Å) in a 2 θ range from 3° to 45° with a 0.02° step at a scan speed of 2.5° min⁻¹. Temperature-dependent powder X-ray diffraction experiments were performed using Anton Paar BTS 500 heating stage from 30 to 350 °C. At each temperature samples were conditioned for 10 minutes prior to the measurement.

Nitrogen and carbon dioxide adsorption/desorption studies were performed on a BELSORP-max adsorption apparatus (MicrotracBEL Corp.); 77 K was achieved by liquid nitrogen bath and 195 K was achieved by dry ice/isopropanol bath. Water vapor isotherms were recorded on Hydrosorb (Quantachrome). Prior to the sorption measurements the samples 1 and 2 (synthesized either in solution or by mechanochemical methods from Cd(OH)₂) were soaked with DCM for 5 - 7 days. After that the samples were evacuated at 80 °C (1) or RT (2) for 16 h. For some experiments, indicated in the manuscript, sample 1 was evacuated at 180 °C for 20 h.

The ¹H NMR spectrum was recorded with a Bruker Avance III 600 at 300 K. The chemical shifts (δ) are reported in parts per million (ppm) on a scale downfield from tetramethylsilane. The ¹H NMR spectra were referenced internally to the residual proton resonance in DMSO-d⁶ (δ 2.49 ppm).

Scanning electron microscope (SEM) analysis was performed on the SU8020 scanning electron microscope (HITACHI, Japan) with an accelerating voltage of 1-2 kV. The samples of 1 and 2 (mechanosynthesized from $Cd(OH)_2$) were sputtered with gold prior to measurements.

In order to determine stability of porosity of 1 and 2 upon adsorption of water molecules we used a quasi-equilibrated temperature-programmed desorption and adsorption (QE-TPDA) technique.^{43,44} Prior to the experiment a sample of 6.1 mg (1·DCM) and 5.9 mg $(2 \cdot H_2 O)$ were activated by heating in a flow (6.75 cm³/min) of pure helium (purity 5.0, Air Products) to 120 °C (1·DCM) and 200 °C (2·H₂O) at 5 °C/min and then cooled down. After activation the flow was switched to helium containing steam saturated at 25 °C and room temperature sorption began. After stabilization of the TCD signal, 9 (1) and 21 (2) desorptionadsorption cycles were measured with linear temperature program (5 °C /min rate). Maximum temperature was equal to 120 °C (1) and 200 °C (2) for each cycle. To make sure that adsorption process fully ended, 90 minutes of RT isothermal sorption was applied after each finished desorption-adsorption cycle. The maxima obtained in experiment correspond to desorption and the minima to adsorption, while together they form the QE-TPDA profiles (Figure 5 and Figure S16, Supplementary Information). Sorption capacities were determined by integrating desorption maxima over the range from 25 °C to 120 °C and recalculating the obtained areas by adequate calibration constant.⁴⁵ Desorption and adsorption isobars were calculated from the first desorption/adsorption cycle (Figure 5 and Figure S16, Supplementary Information).⁴⁶

Syntheses

Synthesis of $\{[Cd_2(oba)_2(pcih)_2] \cdot 3DMF\}_n(1)$ in solution:

4-Pyridinecarboxaldehyde isonicotinoylhydrazone (*pcih*) (67.9 mg, 0.300 mmol), Cd(NO₃)₂·4H₂O (92.5 mg, 0.295 mmol) and 4,4'-oxybis(benzenedicarboxylic) acid (H₂oba) (77.4 mg, 0.300 mmol) were dissolved in DMF (16 mL) and H₂O (1.8 mL) by sonification (60 s) and heated at 70 °C for 4 days. Colorless crystals of **1** were filtered off, washed with

DMF and dried in oven at 60 °C for 0.5 hour. Yield: 159.9 mg (73.7 %). *Anal.* Calc. for $C_{61}H_{57}N_{11}O_{15}Cd_2$: C 51.92, H 4.21, N 10.92. Found: C 51.49, H 03.90, N 10.72. FTIR (ATR, cm⁻¹): v(COO)_{as} 1402s, v(COO)_s 1559m/1532s, v(C=O)_{DMF} 1675s, v(C=N)_{pcih} 1594s, v(CH)_{pcih} 3071w, v(NH) 3218m. Synthesis of single crystals suitable for SC-XRD measurement: *Pcih* (22.6 mg, 0.100 mmol), Cd(NO₃)₂·4H₂O (31.3mg, 0.100 mmol) and H₂oba (25.8 mg, 0.1 mmol) were dissolved in DMF (9.0 mL) by sonification (60 s), next H₂O (9.0 mL) was added and the mixture was heated at 70 °C for 4 days.

Synthesis of $\{[Cd_2(oba)_2(pcih)_2] \cdot 3H_2O\}_n$ (1·H₂O): $\{[Cd_2(oba)_2(pcih)_2] \cdot 3DMF\}_n$ (1) (100 mg) was immersed in 15 mL water for 2 days at room temperature. Cream-colored powder was filtered off, washed with H₂O and dried in air at ambient conditions for 0.5 hour. *Anal.* Calc. For $\{[Cd_2(oba)_2(pcih)_2] \cdot 3H_2O\}_n$:C 50.22, H 3.40, N 9.01. Found: C 50.31, H 3.11, N 8.95%.

Synthesis of terephthalaldehyde di-isonicotinoylhydrazone (tdih)

Isonicotinic acid hydrazide (1.37 g, 10.0 mmol) was added to ethanol (20 mL), and the mixture was heated to boiling. Terephthalaldehyde (0.67 g, 5.0 mmol) suspended in ethanol (20 mL) was added. The reaction mixture was refluxed for 1.5 hours, then allowed to cool and stand overnight, producing a white crystalline solid, which was filtered off, washed with 10 mL of ethanol and dried in air. Yield: 1.26 g (94.6 %). *Anal.* Calc. for $C_{20}H_{16}N_{6}O_{2}$: C 64.51, H 4.33, N 22.57 %. Found: C 64.16, H 4.37, N 22.11%. v(C=N) 1544m, v(C=O) 1653s, v(CH) 3070w, v(NH) 3249m. ¹H-NMR and IR spectra are attached in the SI file (Figures S15-S16, Supplementary Information).

Synthesis of $\{ [Cd_2(oba)_2(tdih)_2] \cdot 7H_2O \cdot 6DMF \}_n$ (2) in solution

Tdih (55.9 mg, 0.150 mmol), Cd(NO₃)₂·4H₂O (46.3 mg, 0.150 mmol) and H₂oba (38.6 mg, 0.150 mmol) were dissolved in DMF (16.2 mL) and H₂O (1.8 mL) by sonification (60 s) and heated at 70 °C for 96 hours. Yellow crystals of **2** were filtered off, washed with DMF and dried in oven at 60°C and 500 mbar for 0.5 hour. Yield: 127.8 mg (85.5 %). *Anal.* Calc. for $C_{86}H_{104}N_{18}O_{27}Cd_2$: C 50.47, H 5.12, N 12.32 %. Found: C 51.51, H 4.77, N 12.71 %. FTIR (ATR, cm⁻¹): v(COO)_s 1395_{sh}m, 1407m; v(COO)_{as} 1534m, 1558m; v(C=O)_{tdih} 1658s; v(C=O)_{DMF} 1674s, v(CH)_{tdih} 3070w, v(NH) 3235w.

Synthesis of $\{[Cd_2(oba)_2(tdih)_2] \cdot 13H_2O\}_n$ (2·H₂O): $\{[Cd_2(oba)_2(tdih)_2]7 \cdot H_2O \cdot 6DMF\}_n$ (2) (200 mg) was immersed in 18 mL water for 1-3 days at room temperature. Cream-colored powder was filtered off, washed with H₂O and dried in air at ambient conditions for 0.5 hour. *Anal.* Calc. For $\{[Cd_2(oba)_2(tdih)_2] \cdot 13H_2O\}_n$: C 47.59, H 4.35, N 9.79, Found: C 47.76, H 4.24, N 9.76%.

One-pot mechanosynthesis of $\{[Cd_2(oba)_2(pcih)_2] \cdot 3DMF\}_n$ (1) and $\{[Cd_2(oba)_2(tdih)_2] \cdot 7H_2O \cdot 6DMF\}_n$ (2)

Pcih (67.8 mg, 0.300 mmol) or *tdih* (111.7 mg, 0.300 mmol), CdO (38.5 mg, 0.300 mmol), H₂oba (77.5 mg, 0.300 mmol) and NH₄NO₃ (7.4 mg, 0.093 mol, 4 wt% for 1 and 9.1 mg, 114 mol, 4 wt% for 2) were ground together with an addition of DMF (120 μ L, $\eta = 0.65 \mu$ L·mg⁻¹ for 1; 150 μ L, $\eta = 0.66 \mu$ L·mg⁻¹ for 2) in an agate milling ball (40 min, 15 Hz). After that the product was washed several times with DMF. The same approach was used to synthesize 1 and 2 from Cd(OH)₂, but reaction was carried out without NH₄NO₃ and Cd(OH)₂ (43.9 mg , 0.300 mmol) was used instead of CdO.

Stepwise mechanosynthesis of $\{[Cd_2(oba)_2(pcih)_2]\cdot 3DMF\}_n$ (1) and $\{[Cd_2(oba)_2(tdih)_2]\cdot 7H_2O\cdot 6DMF\}_n$ (2)

CdO (38.5 mg, 0.300 mmol) and H₂oba (77.5 mg, 0.300 mmol) were ground together with an addition of 150 μ L H₂O (η = 1.30 μ l·mg⁻¹) an agate milling ball (40 min, 15 Hz). After that *pcih* (67.8 mg, 0.300 mmol) (1) or *tdih* (111.7 mg, 0.300 mmol) (2) and 156 μ L DMF (η = 0.85 μ L·mg⁻¹) for 1; 190 μ L DMF (η = 0.83 μ L·mg⁻¹) for 2 were added to the intermediate products and grinding was carried out for 40 min (15 Hz). The same approach was used to synthesize 1 and 2 from Cd(OH)₂, but Cd(OH)₂ (43.9 mg, 0.300 mmol) was used instead of CdO.

Crystallographic data collection and structure refinement

Diffraction intensity data for single crystals of compounds 1 and 2 were collected at 100 K on a KappaCCD (Nonius) diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å). Cell refinement and data reduction were performed using firmware.^{47,48} Positions of all of non-hydrogen atoms were determined by direct methods using SIR-97.49 All nonhydrogen atoms were refined anisotropically using weighted full-matrix least-squares on F^2 . Refinement and further calculations were carried out using SHELXL 2014/7.50,51 All hydrogen atoms joined to carbon atoms were positioned with an idealized geometries and refined using a riding model with $U_{iso}(H)$ fixed at 1.5 U_{eq} of C for methyl groups and 1.2 U_{eq} of C for other groups. The hydrogen atoms of the water (O66) molecule in 2 are indeterminate, H atoms attached to the N atoms were found in the difference-Fourier map and refined with an isotropic thermal parameter. Additionally, the crystal structure data shows that one DMF solvent molecule is heavily disordered and was removed using the SQUEEZE procedure implemented in the PLATON package.⁵⁰ In case of other two DMF solvent molecules atoms were refined using DFIX and DANG instructions.^{51,52} The SQUEZZE procedure was also applied for 1 due to the presence of disordered guest molecules. The figures were made using CCDC1852965 (1) and CCDC1581727 (2) cif files that contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Compound	1	2
Empirical formula	$CdC_{26}H_{18}N_4O_6$	CdC ₄₃ H ₄₅ N ₉ O ₁₁
Formula weight	594.84	976.28
Crystal size (mm)	$0.400\times0.300\times0.200$	0.300 x 0.200 x 0.030
Crystal system	Triclinic	Monoclinic
Space group	P1	C2/c
Unit cell dimensions		
a (Å)	9.6614(2)	40.7755(7)
<i>b</i> (Å)	12.2246(3)	8.8797(2)
<i>c</i> (Å)	15.1946(3)	29.8769(5)
α (°)	110.712(2)	90
β (°)	102.063(2)	109.734(1)
γ (°)	93.664(2)	90
Volume (Å ³)	1622.79(7)	10182.3(3)
Temperature (K)	100(2)	100(2)
Z	2	8
Density (calculated) (g/cm ³)	1.217	1.274
Absorption coefficient (mm ⁻¹)	0.710	0.490
F(000)	596	4016

Table 3. Crystal data and structure refinement parameters for ${[Cd_2(oba)_2(pcih)_2] \cdot 3DMF}_n$ (1) and ${[Cd_2(oba)_2(tdih)_2] \cdot 7H_2O \cdot 6DMF}_n$ (2).

Theta range for data collection (°)	2.947 to 29.431	2.354 to 27.485
Index ranges	-13≤h≤13, -16≤k≤17, -21≤l≤21	-52≤h≤52, -11≤k≤11, - 38≤l≤38
Reflection measured	78072	20787
Reflections unique	9086 [R(int) = 0.0484]	11632 [<i>R</i> (int) = 0.0351]
Reflections observed $[I > 2$ sigma $(I)]$	7659	8927
Completeness	94.7% to theta = 29.431°	99.5% to theta = 27.485°
Absorption correction	MULTI-SCAN	none
Max. and min. transmission	1.000, 0.788	0.985, 0.889
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	9086 / 1 / 338	11632 / 3 / 543
Goodness-of-fit on F^2	1.076	1.061
Final <i>R</i> indices [I>2sigma(I)]	$R_1 = 0.0293, wR_2 = 0.0622$	$R_1 = 0.0673, wR_2 = 0.1726$
<i>R</i> indices (all data)	$R_1 = 0.0416$, $wR_2 = 0.0680$	$R_1 = 0.0887, wR_2 = 0.1838$

Associated Contents

The Supporting Information is available free of charge on the RSC Publication website at DOI:... IR spectra, PXRD patterns, N₂ adsorption isotherms, TG curves additional structure drawings and X-ray crystal data (CCDC 1852965, 1581727 and 1476612) for **1**, **2** and [Cd(μ -H₂O)(oba)(H₂O)]_n respectively.

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Introducing a longer versus shorter acylhydrazone linker to a metal-organic framework: parallel mechanochemical approach, non-isoreticular structures and diverse properties

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SYNPOSIS:

Two varied length ditopic hydrazone linkers providing linear connectivity have been used with a dicarboxylate co-linker to prepare metal-organic frameworks of different dimensionality, stability and gas adsorption adsorption.

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sorption capacity / cm³ STP·g⁻¹ cycle 1 – 3 cycle 4-6 loading / cm3 STP-g⁻¹ desorption cycle 7 – 9 ***.*.** ssr / µmol·g⁻¹·s⁻¹ 5 °C/min cycle 10 – 12 cycle 13 – 15 cycle 16 – 18 cycle 19 – 21 -2 adsorption background level -4 max temperature – 200 °C 5 °C/min -6 temperature / °C temperature / K ACS Paragon Plus Environment cycle

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