Metal–Organic Frameworks

Flexible and Rigid Amine-Functionalized Microporous Frameworks Based on Different Secondary Building Units: Supramolecular Isomerism, Selective CO₂ Capture, and Catalysis

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Abstract: We report the synthesis, structural characterization, and porous properties of two isomeric supramolecular complexes of ([Cd(NH₂-bdc)(bphz)_{0.5}]·DMF·H₂O}, (NH₂-bdc = 2-aminobenzenedicarboxylic acid, bphz=1,2-bis(4-pyridylmethylene)hydrazine) composed of a mixed-ligand system. The first isomer, with a paddle-wheel-type Cd₂(COO)₄ secondary building unit (SBU), is flexible in nature, whereas the other isomer has a rigid framework based on a µ-oxobridged Cd₂(µ-OCO)₂ SBU. Both frameworks are two-fold interpenetrated and the pore surface is decorated with pendant $-NH_2$ and =N-N= functional groups. Both the frameworks are nonporous to N₂, revealed by the type II adsorption profiles. However, at 195 K, the first isomer shows an unusual double-step hysteretic CO₂ adsorption profile, whereas the second isomer shows a typical type I CO₂ profile. Moreover, at 195 K, both frameworks show excellent se-

lectivity for CO₂ among other gases (N₂, O₂, H₂, and Ar), which has been correlated to the specific interaction of CO₂ with the $-NH_2$ and =N-N= functionalized pore surface. DFT calculations for the oxo-bridged isomer unveiled that the $-NH_2$ group is the primary binding site for CO₂. The high heat of CO₂ adsorption ($\Delta H_{ads} = 37.7 \text{ kJ mol}^{-1}$) in the oxo-bridged isomer is realized by NH₂···CO₂/aromatic π ···CO₂ and cooperative CO₂···CO₂ interactions. Further, postsynthetic modification of the $-NH_2$ group into $-NHCOCH_3$ in the second isomer leads to a reduced CO₂ uptake with lower binding energy, which establishes the critical role of the $-NH_2$ group for CO₂ capture. The presence of basic $-NH_2$ sites in the oxo-bridged isomer was further exploited for efficient catalytic activity in a Knoevenagel condensation reaction.

Introduction

Inorganic–organic hybrid porous solids represent a new class of crystalline porous material, commonly known as metal–organic frameworks (MOFs) or porous coordination polymers (PCPs).^[1] These materials possess the merits of both organic and inorganic building units, and surmount all the limitations that other contemporary materials, such as zeolites^[2] or activated carbon compounds,^[3] could not. A hefty catalogue of metal ions and organic linkers makes it feasible to synthesize hybrid materials for versatile applications in gas storage and separa-

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rials.^[7] A proper combination of metal ion and organic linker(s) initiates the self-assembly process and by simply tuning the reaction conditions (temperature, pH, solvent) for the self-assembly process, a variety of structures with different network topologies and dimensionalities can be obtained. Use of the same set of metal ions and linkers may yield compounds of identical stoichiometry but with different network superstructures; they are known as structural supramolecular isomers.^[8] Such supramolecular isomers are expected to exhibit different porous properties based on their different network superstructures, which are yet to be properly explored.^[9] Furthermore, to the best of our knowledge, the synthesis of catenated supramolecular isomers based on two different secondary building units (SBUs), and their porous properties as a result of structural flexibility and rigidity in each isomer, are yet to be reported. In theory, the use of long linkers can enhance the surface

tion,^[4] catalysis,^[5] ion exchange,^[6] and as opto-electronic mate-

area of the MOF; in reality, this tactic often results in framework interpenetration, which significantly reduces the porosity of the MOF. However, recent results suggest that interpenetrated frameworks show better interactions with small molecules, such as H_2 and CO_2 , through an entrapment mechanism, in which the molecules are in close proximity with several aromatic rings from different interpenetrating nets.^[10] Further-



more, selective capture of CO₂ from flue gases or natural gas purification is of paramount importance in energy and environmental contexts. The current amine-based technology of CO2 capture from flue gas has the major drawback of a high energy cost for regeneration. Other related issues are the corrosive nature, volatility, and occasional decomposition of amines. An alternative approach is to functionalize the pore surface of a solid adsorbent with less basic amines, for example, aryl amines, which would provide strong physiosorption $(30-50 \text{ kJmol}^{-1})$ with CO₂ rather than chemisorption. An amine (-NH₂) tethered/decorated MOF could give easy-on/easy-off reversible CO₂ uptake balanced with selectivity.^[11] However, such functionalization is not straightforward in practice because these groups can easily interfere with the coordination chemistry associated with the assembly of nodes. To date, there are only few reports of -NH2-containing MOFs achieved by direct synthesis, among more than 10000 MOFs reported.^[12] In addition to the incorporation of functionality, a stimulating extension of such work is to increase the binding strength of CO₂ by modification of the pore surface. Extensive reports of postsynthetic modification of MOFs by Cohen et al. are good motivation to approach such challenges.^[13] Inclusion of -NH₂ functionality on the pore surface also opens up the prospect of base catalysis.^[14] Knoevenagel condensation, a base-catalyzed reaction, can be studied with the help of such materials and a literature survey reveals very few reports of this kind.^[14] Moreover, a multifunctional material apposite for storage as well as catalysis would be one of the rare examples of its class.^[15] To design materials with all the above-mentioned measures is a stupendous task and a critical choice is important. We envisioned that a framework that contained linkers 2aminobenzenedicarboxylic acid (NH₂-bdc) or 1,2-bis-(4-pyridylmethylene)hydrazine (bphz) could generate MOFs with a backbone decorated with basic functional groups (-NH₂ and =N-N=), which will afford interaction sites for CO₂ and also create a platform for base catalysis. In this work, we have assembled NH₂-bdc and bphz ligands with Cd^{II} under two different set of reaction conditions to yield two catenane supramolecular isomers, {[Cd(NH₂-bdc)(bphz)_{0.5}]·DMF·H₂O}_n (1 and 2). Both the frameworks are two-fold interpenetrated and show SBU-modulated structural flexibility and rigidity (Scheme 1). Compound 1 shows a double-step hysteretic CO₂ adsorption profile, whereas 2 exhibits a type I profile at 195 K. Both the frameworks exhibit excellent selectivity for CO₂ among other gases (H₂, N₂, O₂, and Ar). The high isosteric heat of adsorption $(\Delta H_{ads} = 37.7 \text{ kJ mol}^{-1})$ in **2** is supported by DFT calculations, which suggest that the $-NH_2$ group is the primary binding site for CO₂ and also demonstrate a cooperative interaction between the CO₂ molecules. Further, 2 was exploited as a base catalyst in a Knoevenagel condensation reaction and very good efficiency and size selectivity were realized with different substrates.

Results and Discussion

Single-crystal X-ray diffraction analysis illustrates that **1** and **2** both crystallize in an orthorhombic crystal system with space





Scheme 1. Schematic representation of the synthesis of structural (catenane) supramolecular isomers 1 and 2 based on different SBUs.

Table 1. Crystal data and structure refinement parameters for 1 and 2.			
Parameters	1	2	
empirical formula	C ₁₇ H ₁₉ CdN ₄ O ₆	C ₁₇ H ₁₉ CdN₄O ₆	
<i>M</i> _r	487.767	487.767	
crystal system	orthorhombic	orthorhombic	
space group	Стст	Стса	
a [Å]	15.5918(15)	15.939(5)	
b [Å]	15.3726(14)	20.857(5)	
c [Å]	18.2802(16)	14.374(5)	
V [ų]	4381.5(7)	4779(3)	
Ζ	8	8	
<i>T</i> [K]	293	293	
λ (Mo _{κα})	0.71073	0.71073	
$ ho_{calcd}$ [g cm ⁻³]	1.287	1.183	
μ [mm ⁻¹]	1.022	0.937	
$ heta_{max}$ [°]	24	25.8	
total refins	18132	20830	
unique reflns	1732	2084	
R _{int}	0.139	0.092	
data $[l > 2\sigma(l)]$	1201	1081	
R ^[a]	0.0781	0.0883	
R _w ^[b]	0.1987	0.2349	
GOF	1.272	1.76	
[a] $R = \Sigma F_0 - F_c /\Sigma F_0 $, [b] $R_w = [\Sigma \{w(F_0^2 - F_c^2)^2 / \Sigma \{w(F_0^2)^2 \}]^{1/2}$.			

groups *Cmcm* and *Cmca*, respectively (Table 1). Compound 1, synthesized at 90 °C, has one Cd^{II} metal center, half a bphz and one NH₂—bdc linker, along with one DMF and one H₂O molecule in the asymmetric unit (Figure 1 a). A paddle-wheel Cd₂(COO)₄ SBU is the key component of the framework and this is further connected by NH₂—bdc in the *ab* plane to furnish a 2D square sheet-like structure (Figure 1 b). The 2D sheets are pillared by bphz linkers to extend the network in three dimensions and provide a 3D α -polonium-type pillared-layer porous framework (Figure 1 c). The octahedral Cd^{II} center deviates slightly from a perfect octahedral geometry and this is reflected in the *cisoid* and *transoid* angles (see Table S1 in the Supporting Information). The Cd^{II}—O bond length is 1.995 Å and Cd^{II}—N bond lengths are in the range of 2.022–2.036 Å. The pore size of the single net along the *c* axis is 8.4×8.4 Å², which





Figure 1. a) Coordination environment of Cd^{II} in 1 with a paddle-wheel SBU, b) 2D sheet of the $\{Cd_2(NH_2-bdc)_2\}_n$ unit in the crystallographic *ab* plane, c) 3D framework of 1 with an α -polonium-type network topology. The two $-NH_2$ groups in the NH_2 -bdc linker are due to its positional disorder.

reduces to 4×4 Å² due to a twointerpenetration fold (see Figure S1 in the Supporting Information).^[16] These channels are occupied by two different quest molecules, H₂O and DMF. The presence of these guests was confirmed by elemental analysis, TGA, IR, and ¹H NMR spectroscopy (see Figures S2-S4 in the Supporting Information). Removal of the guest molecules creates a void volume of 2129 ${\rm \AA^3}$ (49 %of the unit cell volume).^[17] Along with high void space, the pore surfaces are decorated with pendant $-NH_2$ groups.

Unlike **1**, **2** is made of a different SBU, $Cd_2(\mu$ -OCO)_2, in which two Cd^{\parallel} centers are μ -oxobridged. The NH₂—bdc linkers connect the SBUs along the *bc* plane to furnish 2D sheets of $\{Cd_2(NH_2-bdc)_2\}_n$ (Figure 2 a and b). These 2D sheets are pillared by bphz to generate a 3D bipillared framework, in which the $-NH_2$ group remains pendant,



Figure 2. a) Coordination environment of Cd^{II} in 2 with a μ -oxo bridge SBU, b) 2D sheet of the {Cd₂(NH₂-bdc)₂}, unit in the crystallographic *bc* plane, c) 3D bipillared layer framework **2**.

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similar to framework **1** (Figure 2 c and Scheme 1). The Cd^{\parallel} metal center is seven coordinate; the Cd^{II}–O bond lengths are in the range 2.282–2.658 Å and the $Cd^{II}\!-\!N$ bond length is 2.468 Å (see Table S2 in the Supporting Information). A twofold interpenetration creates rectangular channels along the c axis with a dimension of $3 \times 5 \text{ Å}^2$ and one H₂O and one DMF molecule occupy the free space, as found for 1 (Scheme 1). The presence of solvent molecules was confirmed by elemental analysis, TGA, IR, and ¹H NMR spectroscopy (see Figures S5–S7 in the Supporting Information). The calculated solvent-accessible volume was found to be about 28%, which is less than for 1. A striking similarity between both structures was the presence of pendant -NH₂ groups along the pore surfaces. Both the compounds have an identical molecular formula but have different network superstructures comprised from different SBUs, hence, they are structural supramolecular isomers (Scheme 1). They are two-fold catenated and can also be termed as catenane supramolecular isomers.

TGA of **1** (see Figure S3 in the Supporting Information) shows a mass loss in the temperature range 150-200°C, which indicates the loss of DMF and water. The desolvated framework { $[Cd(NH_2-bdc)(bphz)_{0.5}]$ } (1') is stable up to 250 °C without further loss of mass. Upon further heating, a rapid mass loss indicates decomposition of the compound. In the case of 2, the guest molecules are released at 200 °C (see Figure S5 in the Supporting Information) and the desolvated structure (2')is stable up to 280 °C. Upon desolvation at 200 °C under vacuum, 1 undergoes structural transformation, which is evident from the differences between the PXRD patterns of 1' and 1 (Figure 3a). First, two peaks that correspond to reflections (110) and (111) are almost absent in the desolvated state 1', which suggests contraction in the framework. When the pores were refilled exclusively with DMF further change was noted in the PXRD pattern but it does return to its as-synthesized phase (Figure 3a). However, the PXRD pattern of desolvated framework 2' does not show any change and also re-

tains its structural integrity upon exposure to solvent vapors (MeOH, EtOH, CHCl₃, and CH₃CN) [Figure 3b; Figure S8 in the Supporting Information]. The structural change associated with framework 1 upon desolvation and the rigid nature of 2 can be explained on the basis of the different SBUs and their orientations in the interpenetrated nets. In 1, the axis that passes through the metal centers of the paddlewheel SBU is parallel to the bphz pillars and NH₂bdc plane. This orientation leaves space along the c axis (Figure 4a and b), hence, there is a possibility of net movement upon desolvation, which results in structural transformation of 1. In the case of 2 this sliding is not possible due to perfect fitting of the nets along the *a* axis; the axis that passes through the metal centers in the µ-oxo bridged SBU is perpendicular to the pillars and, in addition, the bipillar nature leaves no space along the a axis (Figure 4c and d). Furthermore, in **2** the pendant $-NH_2$ (donor) of one net and =N-N= (acceptor) of a second net are connected by hydrogen bonding interactions



Figure 3. PXRD patterns of a) 1 and b) 2.

(N3-H.N1=3.253 Å). Two other weak hydrogen bonds operate between the -CH=N- hydrogen atom of one net and a carboxylate oxygen atom of a second net (C14-H.O1=3.216 Å, C14-H.O1=3.402 Å). Due to these interactions, the two 3D nets are stabilized and do not move upon desolvation. But in the case of **1**, no such interactions exist between the nets and



Figure 4. View of 1 along the *c* axis: a) single net, b) interpenetrated net. View of 2 along the *a* axis: c) single net, d) interpenetrated net.



space for sliding of the nets is available. Hence, the structural flexibility in **1** and rigidity in **2** are realized.

Large void spaces and the amine-functionalized pore in both 1 and 2 led us to perform different gas adsorption measurements. Prior to measurement, 1 was activated to 1' by removal of the guest molecules at 190 °C. At 77 K, 1' shows a typical type II N₂ isotherm (see Figure S9 in the Supporting Information), which indicates surface-adsorption phenomenon. The calculated BET surface area is $82 \text{ m}^2 \text{ g}^{-1}$. To our surprise, at 195 K 1' shows a two-step commensurate uptake profile for CO₂ and the saturated uptake amount is approximately 118 mL g⁻¹, which corresponds to 23 wt% (2×CO₂ molecules/ formula; Figure 5). MOF 1' also shows unique hysteresis in the



Figure 5. Adsorption isotherms for 1' at 195 K: CO_2 adsorbtion (half-filled diamonds), CO_2 desorption (open diamonds), N_2 (stars), H_2 (circles), Ar (triangles), O_2 (squares); Inset: CO_2 adsorption profile at 195 K (log scale).

adsorption-desorption isotherm, withholding about 9 wt% of CO₂ in the framework. With a flexible framework this kind of unusual adsorption behavior is not uncommon.^[18] The first step of the uptake (until pressure $P/P_0 \approx 0.5$) equates to one molecule of CO_2 per formula and in the next step another CO_2 molecule is adsorbed. Initial steep uptake (type I) is probably due to interaction with the pendent -NH₂ groups present at the pore surface and is reflected in the heat of adsorption $(q_{st\Phi})$ value of approximately 28.5 kJ mol⁻¹, calculated by using the Dubinin–Radushkevich (DR) equation.^[19] The second step is probably due to sliding of the 3D nets, which opens up more void space for CO₂ molecules to diffuse in. From the CO₂ uptake profile (until the first step, $P/P_0 \approx 0.5$) the calculated BET surface area is 185 m²g⁻¹. Interestingly, **1** showed negligible uptake for other gases [kinetic diameter: H₂ (2.83 Å),^[20] Ar (3.5 Å), O₂ (3.46 Å), N₂ (3.64 Å)] at 195 K and, thus, is very selective for CO_2 gas. Compound **2**, like **1**, shows no uptake of N_2 at 77 K (see Figure S10 in the Supporting Information), but at 195 K, it shows a type I adsorption profile for CO₂ and the final uptake amount is 101 mLg⁻¹, which corresponds to approximately 19 wt % of CO₂ (1.8 molecules/formula) [Figure 6a]. The BET surface area, calculated from the CO₂ adsorption profile,



Figure 6. a) Adsorption isotherm for **2**' at 195 K: CO₂ adsorption (half-filled diamonds), CO₂ desorption (open diamonds), N₂ (stars), H₂ (filled diamonds), Ar (squares), O₂ (squares). b) CO₂ adsorption profile at 273 and 293 K. Inset: plot of heat of adsoption (ΔH_{ads}) versus CO₂ loading.

was found to be approximately 298 m²g⁻¹. The enthalpy of adsorption of CO₂ was obtained by measuring two isotherms at T=273 and 293 K, followed by a fit of the data to virial equation.^[21] At zero loading, $\Delta H_{ads} = 37.7$ kJ mol⁻¹, which clearly indicates moderate interaction between framework **2** and CO₂. Remarkably, at maximum loading, $\Delta H_{ads} = 39.6$ kJ mol⁻¹. After initial loading, ΔH_{ads} falls slowly and rises again to a value that is higher than that at zero loading (Figure 6b and Figure S11 in the Supporting Information). This is likely due to a cooperative interaction between the adsorbed CO₂ molecules. Similar to compound **1**, **2** is also found to be selective for CO₂ at 195 K among other gases (H₂, Ar, O₂, and N₂).

After removal of the guest molecules, **1** undergoes structural transformation. We do not have any structural information for the desolvated phase **1**', therefore DFT calculations would not provide accurate insight into the CO₂ adsorption phenomena. Rather, we chose the rigid framework **2**, to carry out DFT calculations to find favorable binding sites. To find these sites, gas molecules were initially placed randomly inside **2**', the desolvated framework of **2**. Geometry optimization of the gasloaded framework was carried out. Two favorable locations for the CO₂ molecules, CO₂-I and CO₂-II, were obtained. The former is near the $-NH_2$ group and its molecular axis passes through the bisector of the amine at a distance of 3.10 Å (Figure 7). The backbone angle of CO₂-I marginally deviates from linearity

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Figure 7. a) Cooperativity between two adsorbed CO₂ molecules within MOF **2**'. Carbon atom of CO₂-I interacts with the nitrogen lone pair of the amino group and CO₂-II interacts with the π cloud of the benzene ring. C (cyan), H (gray), N (blue), O (red); b) View of the CO₂ molecules inside one pore of **2**'.

(177.7°), which suggests a specific interaction between $-NH_2$ and CO₂-I. Electron-density-difference maps (i.e., the difference in electron density between the MOF with the guest gas molecule and that of the individual components minus pure MOF and isolated gas molecule) over the nitrogen atom of $-NH_2$ and the carbon atom of CO₂-I indicates a moderate interaction of the quadrupole moment of CO₂-I with the lone pair of the -NH₂ group (Figure 8a). A positive-difference map over one of the two oxygen atoms of CO₂ indicates a weak hydrogen bond formed with hydrogen atoms of the bphz ligand. The distances between O and H are 2.59, 2.79, 2.89, and 3.49 Å. The second CO₂ molecule (CO₂-II) is found to be present on top of bphz with its center at the midpoint between the aromatic ring and amino group, which suggests aromatic π interaction with CO₂ (Figure 7). The distance between this midpoint and the carbon atom of CO₂-II is 3.63 Å. CO₂-II also interacts electrostatically with the hydrogen atoms of the aromatic ring of bphz. The distances between the oxygen atom of CO₂-II and the hydrogen atoms are 2.64, 2.89, and 3.13 Å. The electron-density-difference map for this molecule (Figure 8b) reveals two types of interaction: 1) Lewis acid-base interaction, in which the elec-



Figure 8. Electron-density-difference maps for a) CO_2 -I and b) CO_2 -II interacting with MOF **2**', presented at isosurface values of 0.005 and 0.004 a.u., respectively. Only a portion of the MOF is shown for clarity. CO_2 molecules form weak hydrogen bonds with the MOF. Electron-rich and -deficient regions are shown in green and pink, respectively. C (cyan), H (gray), N (blue), O (red).

tron-deficient carbon atom of CO₂-II loses some electronic charge to the aromatic ring, and 2) weak hydrogen bonding between the hydrogen atoms of the aromatic ring and oxygen atoms of CO₂-II. Recently, such aromatic π ···CO₂ interactions in MOFs have been established by single-crystal X-ray diffraction studies.^[22]

The two CO₂ molecules are also stabilized by a cooperative effect, evident from the short distance (3.76 Å) between the oxygen atom of CO₂-I and carbon atom of CO₂-II. This distance is comparable to that observed between two neighboring CO₂ molecules in supercritical CO2.[23] The angle between the backbone vectors of the two CO_2 molecules in the MOF is 59.5°, whereas it is 70° in crystalline $\text{CO}_2\text{.}$ This observation suggests that the dimer inside the MOF is in a distorted T-shaped configuration, similar to that found in the crystalline phase and supercritical CO₂.^[23] The interaction energy of the CO₂ molecules with 2' was compared to the experimental heat of adsorption values. The CO₂-I and CO₂-II molecules interact with the framework individually and give binding energies of 36.03 and 30.03 kJ mol⁻¹, respectively. When both these two molecules are present in 2', the mean binding energy per molecule is calculated to be 33.94 kJ mol⁻¹. At low pressures, from the Boltzmann ratio, the most preferable binding site is the one that provides a strong affinity for CO₂. As a result CO₂ binds preferentially near an amino group (CO₂-I; $E = 36.03 \text{ kJmol}^{-1}$), which is comparable to that calculated from adsorption isotherms by using the virial equation ($E = 37.7 \text{ kJmol}^{-1}$). Notably, although there is evident proof of NH_2 ...CO₂ interaction and a moderate ΔH_{ads} value, we do not observe any distinct hysteresis in the adsorption isotherm. As it is a case of mere physiosorption, hysteresis is unlikely to occur^[11b,d,e] unless there is any structural transformation (rearrangement), which can act as barrier for gas molecules to diffuse out of the pores. In this case, 2 is rigid in nature and the observations found here align with the literature reports.[11b,d,e]

We could visualize the role of the $-NH_2$ functional group from the DFT calculations; therefore, we also carried out an indirect experiment to establish its immense importance. We modified the -NH₂ group to a -NHCOCH₃ group in a postsynthetic method and as a result the polarity of the pore surface was altered. We obtained about 90% conversion of 2 to ${[Cd(NH_2-bdc)_{0.1}(NHCOCH_3-bdc)_{0.9}(bphz)_{0.5}] \cdot CHCI_3)}_n$ (2 a), confirmed by ¹H NMR spectroscopy (see Figure S12 in the Supporting Information). PXRD patterns of 2a showed no distinct change relative to the parent compound 2, which suggests that the structure remains intact (Figure 9a). The CO₂ adsorption isotherm at 195 K showed interesting changes relative to the parent compound 2 (Figure 9b). The adsorption curve clearly indicates that up to a relative pressure (P/P_0) of approximately 0.1 the uptake is not as sharp as for 2, but in the high pressure range CO₂ molecules enter the pores and the uptake reaches a saturation of about 9 wt%. Heat of adsorption calculations from the DR equation show $q_{\mathrm{st},\Phi}$ is approximately 28 kJ mol⁻¹ and the BET surface area is 98 m²g⁻¹; both values are lesser than for 2. Evidently absence of the strong Lewis base $-NH_2$ and less available space accounted for the low heat of adsorption and smaller uptake.

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Figure 9. a) PXRD patterns of compounds 2 and 2a, b) CO₂ adsorption-desorption isotherm of postsynthetically modified 2 (2a) at 195 K.

The presence of pendent -NH₂ groups, structural rigidity, and high thermal stability of 2 encouraged us to carry out a base-catalyzed Knoevenagel condensation reaction. Prior to the catalytic reaction, we activated the catalyst by removal of the guest DMF and water molecules from the pore, then carried out the condensation of 4-nitro- and 4-chloro-benzaldehyde derivatives with malononitrile and a range of solvents at 60 °C (Table 2; see Figures S13 and S14 in the Supporting Information). When malononitrile and 4-nitrobenzaldehyde were used, we observed about 99% conversion within 6 h in acetonitrile (Table 2, entry 1) but only 85% conversion was observed after 6 h in methanol (Table 2, entry 2). A change from aprotic to protic solvent hampered the reaction rate. The reaction kinetics of malononitrile and 4-nitrobenzaldehyde show very fast conversion within 2 h and about 99% conversion was reached in 6 h (Figure 10). A decrease in the reaction temperature to $40\,^{\circ}C$ decreased the conversion rate (Table 2, entry 3). We also observed excellent size selectivity by the catalyst; when the larger substituent methyl cyanoacetate was present, the conversion was only 41 or 52% after 6 and 12 h, respectively (Table 2, entry 4; see Figure S15 in the Supporting Information). We have performed six catalytic cycles to check the efficiency of the catalyst and we observed no change in the conversion rate. Similar catalytic reactions with (-CONH-)-functionalized MOFs have been reported by Kitagawa et al.^[14a] and Zhou et al.^[14c] These reactions show much slower conversion time $(\approx 12 \text{ h})$ than our results. This is due to better diffusion of the reactants into the pores but this higher diffusion of reactants also decreases the size selectivity in the present case compared with the report by Kitagawa et al. The PXRD pattern of the catalyst after six catalytic cycles was found to remain the same as that of the as-synthesized catalyst, which suggests high thermal and chemical stability of the framework (Figure 10, inset). Notably, a reaction performed in the presence of NH₂-bdc resulted in a negligible yield. When malono-



was used. [b] Calculated by GCMS. [c] No catalyst was used.



Figure 10. Conversion [%] versus time [min] for Knoevenagel condensation reaction of 4-nitrobenzaldehyde and malononitrile at 60 $^{\circ}$ C in acetonitrile. Inset: PXRD patterns of **2** a) before and b) after six catalytic cycles.

nitrile and 4-nitrobenzaldehyde were mixed without any catalyst at 60 °C in acetonitrile no product was formed (Table 2, entry 6).

Conclusion

We have synthesized two isomeric catenane supramolecular complexes of Cd^{II} with 3D porous structures. Compound 1 contains a paddle-wheel SBU and shows structural flexibility upon guest removal. Compound 2 is rigid in nature with a μ -oxo bridged SBU. The origin of rigidity and flexibility arises from the orientation of the two interpenetrated nets in the framework, controlled by the different SBUs. Both frameworks show selective CO₂ uptake. Compound 1 shows a two-step uptake profile with large hysteresis, which emphasizes the flexible nature of the framework. In contrast, 2 shows a type I uptake profile with moderate heat of adsorption (ΔH_{abs} =



37.7 kJ mol⁻¹). DFT calculations further describe the $-NH_2$ ···CO₂ and CO₂···CO₂ cooperative interactions in the framework. The importance of the $-NH_2$ group towards CO₂ capture was further realized through a postsynthetic modification of $-NH_2$ to $-NHCOCH_3$. This modification drastically reduces the uptake of CO₂ and also the binding energy. Compound **2** also acts as a very efficient base catalyst for a Knoevenagel condensation reaction and shows size selectivity. The present study is significant because it displays an elegant example of structural supramolecular isomerism with multifunctional properties, such as selective CO₂ uptake and catalysis.

Experimental Section

Materials

All the reagents employed were commercially available and used as provided without further purification. $[Cd(NO_3)_2 \cdot 6H_2O]$ was obtained from Spectrochem. 2-Aminobenzenedicarboxylic acid, acetic anhydride, malononitrile, methyl cyanoacetate, *p*-nitro- and *p*-chloro-benzaldehyde were obtained from Sigma Aldrich. 1,2-Bis-(4-pyridylmethylene)hydrazine was synthesized by a literature method.^[24]

Physical measurements

Elemental analysis was carried out with a Thermo Fischer Flash 2000 Elemental Analyzer. IR spectra were recorded as KBr pellets with a Bruker IFS 66v/S spectrophotometer in the region $\tilde{v} = 4000-400 \text{ cm}^{-1}$. TGA was carried with on a Metler Toledo instrument under a nitrogen atmosphere (flow rate = 50 mL min⁻¹) in the temperature range 30–500 °C (heating rate = 3 °C min⁻¹). PXRD patterns of 1 and 2 were recorded with a Bruker D8 Discover instrument (40 kV, 30 mA) by using Cu_{kα} radiation. ¹H NMR spectra were measured on a Bruker AV-400 spectrometer with chemical shifts reported as ppm (in DCI/[D₆]DMSO or CDCl₃/CD₃CN; TMS as internal standard).

Synthesis of 1 and 2

 $[Cd(NO_3)_2 \cdot 6H_2O]$ (0.2 mmol, 0.049 g) was added to a solution of NH_2 —bdc (0.2 mmol, 0.035 g) and bphz (0.2 mmol, 0.042 g) in DMF (14 mL) and the mixture was sonicated for 10–15 min. This solution was then equally divided into two glass vials; one was kept at 90 °C and one at 120 °C, for 24 h. After cooling to rt, rectangular block-shaped yellow crystals were found at the walls of the vials. We obtained 1 from the reaction at 90 °C and 2 from the reaction at 120 °C. Crystals were separated from the solution and then thoroughly washed with DMF. Crystals of both compounds were found to be weakly diffracting and, hence, for further characterization we used ¹H NMR spectroscopy, elemental analysis, and TGA.

Compound 1: Yield: 67 %, relative to Cd. FTIR (KBr pellet): $\tilde{\nu} = 3490$ (br), 3234 (w), 3072 (w), 2326 (s), 2238 (m), 2128 (m), 1614 (s), 1562 (s), 1502 (s), 1428 (s), 1310 (w), 1228 (s), 1068 (s), 1020 (s), 912 (w), 874 (w), 820 cm⁻¹ (s); elemental analysis calcd (%) for C₁₇H₁₉CdN₄O₆: C 41.86, H 3.92, N 11.48; found: C 41.21, H 4.41, N 10.97.

Compound 2: Yield: 58%, relative to Cd. FTIR (KBr pellet): $\tilde{v} = 3490$ (br), 3234 (w), 3072 (w), 2326 (s), 2238 (m), 2128 (m), 1614 (s), 1562 (s), 1502 (s), 1428 (s), 1310 (w), 1228 (s), 1068 (s), 1020 (s), 912 (w), 874 (w), 820 cm⁻¹ (s); elemental analysis calcd (%) for

 $C_{17}H_{19}CdN_4O_6;\ C$ 41.86, H 3.92, N 11.48; found: C 42.11, H 4.17, N 11.01.

Synthesis of 2a

Activated (desolvated) **2** (**2**'; \approx 50 mg) was stirred with a solution of acetic anhydride (5 mL) in chloroform (0.5 mmol) for 6–7 d at rt. Compound **2a** was filtered and washed several times with CHCl₃, then dried in air. Compound **2a** was characterized by PXRD and ¹H NMR spectroscopy (Figure 9b; Figure S12 in the Supporting Information). FTIR (KBr pellet): $\bar{\nu} = 3498$ (br), 3240 (w), 3091 (w), 2329 (s), 2241 (m), 2133 (m), 1615 (s), 1569 (s), 1507 (s), 1425 (s), 1311 (w), 1232 (s), 1069 (s), 1021 (s), 915 (w), 877 (w), 831 cm⁻¹ (s); elemental analysis calcd (%) for C_{16.8}H_{12.8}CdN₄O_{4.9}: C 36.41, H 2.31, N 10.11; found: C 37.51, H 3.01, N 10.51.

X-ray crystallography

X-ray single-crystal structural data of 1 and 2 were collected with a Bruker Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed-tube X-ray source with graphite monochromated Mo_{ka} radiation ($\lambda = 0.71073$ Å), operating at 50 kV and 30 mA. The program $\mathsf{SAINT}^{\scriptscriptstyle[25]}$ was used for integration of diffraction profiles and absorption correction was made with the SADABS^[26] program. All the structures were solved by SIR 92^[27] and refined by the fullmatrix least-squares method by using SHELXL-97.^[28] All the hydrogen atoms were fixed by HFIX and placed in ideal positions. Due to the weakly diffracting nature of the single crystals we could not locate the guest molecules and carried out ¹H NMR and IR spectroscopy and TGA and elemental analysis to confirm the presence of guest molecules. Potential solvent-accessible areas or void space was calculated by using the PLATON multipurpose crystallographic software.^[17] All crystallographic and structure-refinement data for 1 and 2 are summarized in Table 1. Selected bond lengths and angles for 1 and 2 are given in Tables S1 and S2 (see the Supporting Information), respectively. All calculations were carried out by using PLATON and the WinGX system, Ver 1.70.01.^[29] CCDC-941967 (1) and 941968 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Adsorption study

The adsorption isotherms of CO₂, H₂, N₂, Ar, and O₂ (T=195 K) measured from the dehydrated samples of **1** (**1**'), **2** (**2**'), and **2a** were measured with a QUANTACHROME QUADRASORB-*SI* analyzer. The adsorbent sample (100–150 mg), which had been prepared at 453 K under a 1×10^{-1} Pa vacuum for about 6 h prior to measurement of the isotherms, was placed in the sample tube. Helium gas (99.999% purity) at a known pressure was introduced into the gas chamber and allowed to diffuse into the sample chamber by opening the valve. The amount of gas adsorbed was calculated readily from the pressure difference ($P_{cal}-P_{e}$); P_{cal} is the calculated pressure with no gas adsorption, P_{e} is the observed equilibrium pressure. All operations were computer controlled and automatic.

Computational details

All periodic calculations were carried out by DFT as implemented in the QUICKSTEP module in CP2K.^[30] A mixed basis set was used, in which Kohn–Sham orbitals were expanded in an atom-centered Gaussian basis set and electronic charge density was described by using an auxiliary-plane wave basis set. Initial coordinates were

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taken from the experimental structure and then the cell parameters and geometry were optimized iteratively until the lowestenergy structure was found. A super cell of size 1×1×1 was used. Goedecker-Teter-Hutter-type norm-conserving pseudo potentials were used to represent the combined effect of the core electrons and nucleus. $^{\scriptscriptstyle [31]}$ Exchange and correlation interactions were accounted for by using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE).^[32] Long-range interactions were taken into account by using Grimme's dispersion corrections for this functional.^[33] Double-zeta single-polarized molecularly optimized basis sets (DZVP) were used to describe the valence electrons. Because this basis set is not available for cadmium, the shorter-range version of the same type was used. Structural relaxation was carried out until forces on all atoms were less than 10^{-4} a.u. Binding energy (ΔE) of CO₂ with the MOF was calculated by using the formula given in [Eq (1)],

$$\Delta E = E(MOF + CO_2) - E(MOF) - E(CO_2)$$
(1)

in which, $E(MOF+CO_2)$, E(MOF), and $E(CO_2)$ represent the energy of the MOF with CO_2 , the MOF, and CO_2 , respectively. All structures were visualized by using visual molecular dynamics (VMD).^[34]

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