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Two Zn^{II} Metal-Organic Frameworks with Coordinatively Unsaturated Metal Sites: Structures, Adsorption, and Catalysis

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Abstract: Assembly of $Zn(NO_3)_2$ with the tripodal ligand H_3TCPB (1,3,5tri(4-carboxyphenoxy)benzene) affords two porous isoreticular metal-organic frameworks, $[Zn_3(TCPB)_2 \cdot 2DEF]$ · 3DEF (1) and $[Zn_3(TCPB)_2 \cdot 2H_2O]$ · 2H₂O·4DMF (2). Single-crystal X-ray diffraction analyses reveal that 1 crystallizes in the monoclinic space group $P2_1/c$ and possesses a 2D network containing 1D microporous opening channels with an effective size of $3.0 \times$ $2.9 Å^2$, whereas 2 crystallizes in the trigonal space group $P\bar{3}c1$ and also possesses a 2D network containing 1D channels, with an effective aperture of 4.0×4.0 Å². TOPOS analysis reveals that both **1** and **2** have a (3,6)-connected network topology with the Schläfli symbol of $(4^{3}\cdot6^{12})$ $(4^{3})_{2}$. According to the variable-temperature powder X-ray

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diffraction patterns, the solid phase of **1** can be converted into that of **2** during a temperature-induced dynamic structural transformation, thus indicating that the framework of **2** represents the most thermally stable polymorph. Desolvated **2** exhibits highly selective adsorption behaviors toward H_2/N_2 , CO_2/N_2 , and CO_2/CH_4 ; furthermore, it displays size-selective catalytic activity towards carbonyl cyanosilylation and Henry (nitroaldol) reactions.

Introduction

As one type of metal-organic materials, metal-organic frameworks (MOFs) have gained current attention mainly because of their potential applications in gas adsorption and heterogeneous catalysis.^[1] MOFs adsorb gas principally by physisorption, and two strategies can be envisioned to reach stronger physisorption energy: 1) smaller pore sizes, being slightly larger than the kinetic diameter of gas molecules, so that the gas molecules can simultaneously interact with more pore walls; and 2) incorporation of coordinatively unsaturated metal sites that can bind gas molecules, so that the gas molecules interact with the framework strongly; moreover, these sites could selectively adsorb certain compontents from gas mixtures based on their different polarizability and/or quadrupole moment.^[2]

On the other hand, MOFs can work as catalysts through: 1) the metallic components, which either provide the coordinatively unsaturated nodes or form the active metal complexes incorporated into the linker ligand; and 2) ligands that are functionalized with organic groups. In the former case, MOFs can act as Lewis acid catalysts because of the Lewis acidity of metal cations, whereas in the latter case MOFs can behave as Lewis base catalysts due to the Lewis basicity of the functional groups such as pyridine, amide, and amine. As crystalline MOFs are generally poorly soluble in common solvents, they can be used as heterogeneous

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catalysts.^[3,4] Moreover, metals and ligands are strongly bound within the framework to prevent its decomposition in solution.

One of our goals is to design and synthesize robust MOFs containing coordinatively unsaturated metal sites that can display selective adsorption and catalytic abilities.^[5] Herein we select a semi-rigid tripodal ligand of H₃TCPB (1,3,5tri(4-carboxyphenoxy)benzene; Scheme 1) due to the following considerations: 1) the multifunctional carboxylate groups have good prospects for the construction of well-defined porous MOFs; and 2) the incorporation of flexible ether groups to the rigid benzene spacers could generate subtle structural diversifications owing to the conformational freedom in the assembly process. Two porous isoreticular Zn-MOFs, $[Zn_3(TCPB)_2:2DEF]:3DEF$ (1; DEF = N,N'-diethylformamide and $[Zn_3(TCPB)_2 \cdot 2H_2O] \cdot 2H_2O \cdot 4DMF$ (2), have been constructed, of which phase 1 can be converted into phase 2 upon heating. Desolvated 2 exhibits a highly selective adsorption behavior toward H₂/N₂, CO₂/N₂, and CO₂/ CH₄;^[6,7] moreover, it displays size-selective catalytic activity towards carbonyl cyanosilylation^[8] and Henry (nitroaldol) reactions^[9].



Scheme 1. 1,3,5-Tri(4-carboxyphenoxy)benzene (H₃TCPB).

Results and Discussion

Syntheses and Crystal Structures

A solvothermal reaction of Zn(NO₃)₂·6H₂O and H₃TCPB in DEF at 85°C afforded colorless block-shaped crystals of

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 $[Zn_3(TCPB)_2 \cdot 2DEF] \cdot 3DEF$ (1). Single-crystal X-ray diffraction studies reveal that 1 crystallizes in the monoclinic space group $P2_1/c$ (Table 1), and the asymmetric unit contains two TCPB³⁻ ligands, three Zn²⁺ ions, two coordinated DEF, and

Table 1. Crystallographic data for 1 and 2.

| MOF | 1 | 2 |
|--|----------------|--------------------------|
| Empirical formula | C79H85N5O23Zn3 | $C_{54}H_{34}O_{20}Zn_3$ |
| Formula weight | 1668.63 | 1198.97 |
| Crystal system | monoclinic | trigonal |
| Space group | $P2_{1}/c$ | $P\bar{3}c1$ |
| a [Å] | 16.5826(3) | 16.7057(4) |
| <i>b</i> [Å] | 28.3958(6) | 16.7057(4) |
| <i>c</i> [Å] | 17.8352(3) | 14.3418(5) |
| α [°] | 90 | 90 |
| β[°] | 108.980(2) | 90 |
| γ [°] | 90 | 120 |
| V [Å ³] | 7941.6(3) | 3466.28(17) |
| Ζ | 4 | 2 |
| $\rho_{cald} [g cm^{-3}]$ | 1.396 | 1.145 |
| F(000) | 3472 | 1456 |
| $\mu [{ m mm}^{-1}]$ | 1.707 | 1.721 |
| Reflections collected | 28163 | 11970 |
| GOF | 1.081 | 1.037 |
| R_1, wR_2 indices [I > 2 σ (I)] | 0.0830, 0.1972 | 0.0376, 0.1137 |
| R_1 , wR_2 indices (all data) | 0.1080, 0.2109 | 0.0423, 0.1172 |

three lattice DEF molecules (Figure 1 a). The Zn(1) atom links Zn(2) and Zn(3) atoms through six ligands, forming a trinuclear cluster of Zn₃(O₂C)₆ with the Zn(1)…Zn(2) distance of 3.639 Å, the Zn(1)…Zn(3) distance of 3.629 Å, and the \gtrsim Zn(2)-Zn(1)-Zn(3) angle of 177.6°. Each Zn₃(O₂CR)₆ cluster is linked with six other Zn₃(O₂CR)₆ clusters by six 3connecting TCPB³⁻ ligands, thus leading to a 2D (3,6)-connected net with a mesh size of 12.9×13.8 Å² (atom-to-atom separation, Figure 1b). To the best of our knowledge, such doubly connecting 2D network represents a rare net topolo-



Figure 1. Crystal structures of 1 (a–c) and 2 (d–f). a,d) The coordination environment of the Zn²⁺ ions. b,e) Polyhedral view of the 2D network along the *c*-axis. c,f) A space-filling view of the porous network along the *c*-axis, showing the 1D channels. Solvent molecules are omitted for clarity.

gy of the MoS₂-H structure with the Schläfli symbol of $(4^3 \cdot 6^{12})$ $(4^3)_2$ (Scheme 2).^[10] As seen from Figure 1 b, two TCPB³⁻ ligands doubly connect three Zn₃(O₂CR)₆ clusters with an eclipsed arrangement, which generates a $\pi \cdots \pi$ stacking interaction with the distance of 3.6 Å between the two



Scheme 2. View of the schematic 2D network with the net topology comprising the Schläfli symbol of $(4^{3}.6^{12})$ $(4^{3})_{2}$.

central phenyl rings (Figure S1 a,b in the Supporting Information). Thus, the formed 2D networks are stacked in an offset fashion, with the distance of 5.8 Å between two central phenyl rings from two adjacent layers (Figure S1 c,d in the Supporting Information). Although the $-(AB)_n$ - stacking modes between the 2D layers significantly reduce the crossing window size, 1D channels are still formed along the *c*axis with an effective size of 3.0×2.9 Å² (after considering the van der Waals radii), in which the void space is filled with DEF molecules (Figure 1 c). Removal of the guest molecules reveals that the effective free volume of **1** is 49% of the crystal volume (3889.1 Å³ of the 7941.6 Å³ unit cell volume), as calculated by PLATON analysis.

Interestingly, the solvothermal reaction of Zn- $(NO_3)_2$ ·6H₂O and H₃TCPB at 85 °C in DMF instead of DEF generates $[Zn_3(TCPB)_2·2H_2O]·2H_2O·4DMF$ (2). The structural determination of 2 shows that the crystal system and space group are obviously different from those of 1, with 2 crystallizing in the higher symmetric trigonal space group

 $P\bar{3}c1$. The Zn(1) atom, being located at an inversion center, is surrounded by six oxygen atoms from six equivalent TCPB³⁻ ligands, whereas the Zn(2) atom is fourfold coordinated, with a coordination geometry similar to that in 1, with the coordinating DEF replaced by H_2O (Figure 1 d). The 2D network of 2 has a similar (3,6)-connected net topology $(14.0 \times 14.0 \text{ Å}^2, \text{ Figure 1 e}).$ The distance between the central phenyl rings is 3.3 Å within the same layer, while the interplanar distance between two adjacent layers is 3.9 Å, which is obviously shorter than 5.8 Å in 1, thus indicating a stronger interplanar

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packing in **2** (Figure S1e,g in the Supporting Information). The offset packing of the 2D networks also affords 1D microchannels along the *c*-axis. The effective aperture is $4.0 \times 4.0 \text{ Å}^2$ (Figure 1 f) and thus obviously larger than that of **1**. Removal of the guest molecules reveals that the effective free volume of **2** is 40% of the crystal volume (1396.5 Å³ of the 3466.3 Å³ unit cell volume), as calculated by PLATON analysis.

Based on the above description of the syntheses and crystal structures of 1 and 2, we could conclude that the solvents play an important role in influencing the crystallization of MOFs, whereas the semi-rigidity of TCPB³⁻ ligand has strong ability to affect the connectivity and topology of the coordination networks. MOFs 1 and 2 feature the same (3,6)-connected 2D net topology but display different molecular and lattice symmetry. The latter has a higher point and lattice symmetry, resulting in a highly regular net arrangement and lattice packing, and therefore results in larger network meshes and 1D lattice channels. Neglecting the coordinating solvent molecules, 2 can be regarded as the high symmetric polymorph of 1 attained by rearrangement and sliding of the 2D networks of 1 in the crystal lattice to achieve high symmetry (see below). This can be seen from the twisting angles of the 4-carboxyphenoxy groups versus the central benzene ring (see Table S2 in the Supporting Information), which vary from 76.9 to 89.6° in 1, but are constant with a value of 68.9° in 2.

From the viewpoint of potential applications, as long as the coordination frameworks of 1 and 2 are retained upon the removal of solvent molecules, they could be used in selective adsorption and Lewis acid catalysis, on the basis of the following arguments: 1) they have a large effective free volume (1, 49%; 2, 40%) so that the cavities could accommodate guest molecules; 2) they have micropores $(1, 3.0 \times$ 2.9; 2, $4.0 \times 4.0 \text{ Å}^2$) so that they could selectively adsorb gases of small kinetic diameters (e.g., H₂, 2.89; CO₂, 3.30 Å) through a size-exclusion effect; 3) they contain the trinuclear cluster $Zn_3(O_2CR)_6(solvent)_2$, which could generate coordinatively unsaturated metal sites (CUMs) upon removal of the coordinating solvent molecules, so that they could selectively adsorb specific molecules through adsorbate-adsorbent interactions between CUMs and the gas molecules; and 4) the CUMs of Zn²⁺ could function as Lewis acid catalysts.^[8d, 9c, 11]

Thermal Stability and Dynamic Framework Transformation

To examine the thermal stability, thermal gravimetric (TG) curves of 1 and 2 were recorded. As shown in Figure 2, the TG curves of 1 and 2 in the range of 30-250 °C show a total loss of 29.9 and 23.1%, respectively, which corresponds to the loss of all solvent molecules (calcd. 30.3 and 23.9%, respectively). Above 400 °C, an abrupt weight loss appears, which is indicative of the decomposition of the frameworks.

To determine whether the frameworks could be retained upon heating, variable-temperature powder X-ray diffraction (VT-PXRD) measurements were carried out in the



Figure 2. The TG curves of 1, 2, and desolvated 2.

range of 30–180 °C. As shown in Figure 3, the patterns of 1 remain unchanged below 60 °C; however, another set of patterns gradually appears upon further increase in the temperature. At about 80 °C, a new well-resolved pattern is



Figure 3. Variable-temperature PXRD patterns of 1 (top) and 2 (bottom). Inset: Comparison of PXRD patterns of heated 1 with 2.

formed, thereby indicating the formation of a new phase. This new phase is stable up to $180 \,^{\circ}$ C. In comparison, the main diffraction peaks of 2 remain unchanged at $30-180 \,^{\circ}$ C, thus indicating that its framework is stable in this temperature range. A noticeable observation is that the new pattern of 1 above $80 \,^{\circ}$ C is identical to that of 2. This means that the framework of 1 has turned into 2 through a temperature-induced dynamic structural transformation process.^[12] Therefore, 2 should represent the most thermally stable phase of the 2D (3, 6)-connected network packing, while 1 is the metastable polymorph. Heating could cause rearrangement and sliding of the 2D layers in the solid state to reach the high symmetric and stable polymorphic phase.

Sorption Properties

Based on the above discussion, **2** constitutes the most thermally stable framework and the solvent molecules can be completely evacuated to leave a robust porosity; hence, we selected **2** to study the gas/vapor adsorption property. The bulk sample of desolvated **2** can be obtained by soaking asprepared **2** in methanol for three days and heating at $130 \,^{\circ}$ C for 10 hours under vacuum. As verified by TG analysis (Figure 2), no weight loss occurs below 400°C, indicating that both coordinating and free solvent molecules have been completely removed. Desolvated **2** remains crystalline with PXRD patterns resembling the diffraction patterns of the single crystal, only showing a slight broadening of some diffraction peaks (Figure S2 in the Supporting Information), suggesting that the framework is robust upon removal of coordinating water molecules.

To evaluate the storage capability of desolvated **2**, different gas sorption studies were conducted. Gas adsorption–desorption isotherms for desolvated **2** are shown in Figure 4 and in Figure S4 in the Supporting Information. In the case of N₂ (77 K) or CH₄ (273 K), only a small loading occurs. For H₂, the sorption isotherm reveals a storage capacity of up to 0.80 wt % (90.0 cm³g⁻¹, STP) at 77 K, and it displays a significant hysteresis loop. The H₂ adsorption value is comparable to that of Zn₄O(tmbdc)₃ (IRMOF-18, 0.89 wt %) but less than those of other Zn₄O-based MOFs such as Zn₄O(bdc)₃ (MOF-5, 1.32 wt %) and Zn₄O(btb)₂ (MOF-177, 1.25 wt %) under similar conditions.^[2a,13] The CO₂ uptake capacities at 1 atm are 21.7 wt % (141.2 cm³g⁻¹,



Figure 4. Gas adsorption/desorption isotherms of CO₂, H_2 , and N_2 at low temperatures (a), of CO₂ and CH₄ at 273 K (b), of methanol, ethanol and 1propanol vapor at 298 K (c), and of water vapor at 298 K (d). Solid symbols, adsorption; open symbols, desorption.

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STP), 11.4 wt % (65.0 cm³g⁻¹, STP), and 4.8 wt % (25.4 cm³g⁻¹, STP) at 195 K, 273 K, and 298 K, respectively. These values are better than those of MOF-5 (6.2 wt%, 273 K; 3.2 wt %, 298 K) and MOF-177 (3.6 wt %, 298 K) at 1 atm.^[13] Based on the CO₂ adsorption isotherm at 195 K, the Brunauer-Emmett-Teller surface area of 2 is calculated to be about $573 \text{ m}^2\text{g}^{-1}$, a value much smaller than those of MOF-5 $(3320 \text{ m}^2 \text{g}^{-1})$ and MOF-177 $(4508 \text{ m}^2 \text{g}^{-1})$.^[13] As demonstrated above, the framework displays preferential adsorption of H₂ and CO₂ over N₂ at low temperatures. In addition, desolvated 2 exhibits selective adsorption of CO_2 over CH₄ at 273 K. In light of the selective adsorption of H₂ over N₂ as well as CO₂ over CH₄, 2 may be applied in hydrogen enrichment of the H₂/N₂ exhaust in ammonia synthesis, natural gas purification, and landfill gas separation, respectively.

The principal mechanisms underlying selective gas adsorption in rigid MOFs are based on a size-exclusion effect and/or adsorbate-adsorbent interactions. According to the Horvath-Kawazoe (HK) pore distribution plot of desolvated 2, the pore diameter of the sample is approximately 4.3 Å (Figure S5 in the Supporting Information). This value is consistent with the single-crystal analysis and slightly larger than the kinetic diameter of N₂ (3.64 Å), H₂ (2.89 Å), CO_2 (3.30 Å), and CH_4 (3.76 Å). In our case, the preferential adsorption of H₂ over N₂ might be due to the size-exclusion effect, whereas the selective sorption of CO₂ over N₂ and CH₄ might be attributed to a combined effect of size and of host-guest interactions between CO2 molecules of a significant quadrupole moment $(13.4 \times 10^{-40} \text{ Cm}^2)$ and the coordinatively unsaturated Zn²⁺ sites on the host framework.

Desolvated 2 was also subjected to vapor sorption of alcohols and water. The sorption isotherms of alcohols present typical type-I curves with apparent hysteresis loops (Figure 4c). Approximately 6.2 MeOH, 3.9 EtOH, or 1.8 PrOH molecules can be absorbed per formula unit at 0.95 atm. It is clear that the adsorption of alcohol molecules is size-dependent. The vapor-loaded sample powders still display the characteristic PXRD patterns, thus indicating that the framework remains stable after alcohol adsorption (Figure S3d in the Supporting Information). The sorption isotherms of water vapor show a hysteretic adsorption behavior, with an uptake of 10.66 wt% (133 cm³g⁻¹, STP) at P/ $P_0 = 0.95$ (Figure 4d). The water uptake increases abruptly between 0.08 and 0.13 atm, with an uptake of 6.9 and 48.3 cm³g⁻¹, respectively. It is noted that dehydated **2** takes up 2.1 water molecules per $[Zn_3(TCPB)_2]$ unit between these two pressures, thereby indicating coordination of the water molecules to the Zn ions, which matches well with the single-crystal X-ray structure.

Size-Selective Catalysis

As illustrated in Scheme 3, there are two kinds of Zn^{II} CUMs that could act as catalytically active sites: one is ex-



Scheme 3. Illustration of the exterior and interior catalytic sites in desolvated **2**.

posed on the external surface of the framework (blue arrows) and the other is located on the second layers adjacent to the external surface (off-white arrows). Single-crystal structural analysis shows that the mesh size of 2 is $14.0 \times$ 14.0 $Å^2$ (Figure 1 e). Therefore, as long as the substrates are smaller in size than the meshes, they could access both the exterior and the interior ZnII CUMs. Nevertheless, smallersized substrates could enter the meshes more easily and have more chances to access the interior Zn^{II} CUMs. As a result, 2 might display size-selective catalysis. To characterize the possible acid-type catalytic behaviors of the coordinatively unsaturated Zn-MOF of 2, carbonyl cyanosilylation in the presence of desolvated 2 was performed. The addition of CN⁻ to a carbonyl compound to form a cyanohydrin is one of the fundamental C-C bond formation reactions in organic chemistry.^[8]

Since 2 is insoluble in most organic solvents (e.g., nhexane, dichloromethane, tetrahydrofurane, ethyl acetate, acetonitrile, and ethanol), we used a 1:2 molar ratio of benzaldehyde and cyanotrimethylsilane in n-hexane at room temperature to explore the heterogeneous catalysis of desolvated 2. We found that a loading of 2.5 mol% of desolvated **2** leads to 100% conversion of benzaldehyde after a reaction time of 13 hours. By contrast, the removal of 2 by filtration after 2 hours stopped the reaction, resulting in only 7% additional conversion upon stirring for another 12 hours (Figure S6 in the Supporting Information). The leached Zn content in the filtrate was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and only a trace amount of Zn (0.1%) was found in the filtrate. In addition, the reaction in the presence of a mixture of 5 mol % H₃TCPB and 7.5 mol % Zn(NO₃)₂·6H₂O only gives a conversion of benzaldehyde of 8% under similar conditions. These results evidently demonstrate that 2 acts as an effective heterogeneous catalyst. The solids of 2 can be easily isolated from the reaction suspension by simple filtration and can be reused at least four times with only a slight decrease in the reactivity (Figure 5). Judging from the PXRD pattern, the framework of 2 is intact after the fourth run (Figure S3 in the Supporting Information). According to our results presented here, the activity of 2 is much higher than that of Cu₃(btc)₂ (HKUST-1) but lower than that of $Cr_3O(H_2O)_2F(BDC)_3$ (MIL-101), which is so far the most powerful Lewis acid catalyst of a MOF. A small amount of



Figure 5. Recycling tests for carbonyl cyanosilylation catalyzed by desolvated **2**.

MIL-101 (0.5 mol%) could promote the reaction with 100% conversion in 3 hours,^[8c] whereas only a moderate yield of 50% was obtained after 48 h in the presence of 5 mol% HKUST-1.^[8b]

To probe whether the interior coordinatively unsaturated Zn^{II} sites (Scheme 3) contribute to the catalysis, substrates of increasing dimension were tested. As can be seen in Table 2, the reaction with benzaldehyde $(8.9 \times 6.7 \text{ Å}^2)$ was

Table 2. Results for carbonyl cyanosilylation catalyzed by desolvated $\mathbf{2}^{[14]}$



[a] Catalyzed by a mixture of $5\,mol\,\%$ H_3TCPB and $7.5\,mol\,\%$ Zn-(NO_3)_2-6 H_2O.

accomplished with 100% conversion after 13 hours. By contrast, the conversions for 1-naphthaldehyde $(9.6 \times 8.6 \text{ Å}^2)$ and 4-phenylbenzaldehyde $(13.1 \times 6.7 \text{ Å}^2)$ are reduced to 85% and 65% under the same reaction conditions, respectively. These size-selective behaviors support the assumption that catalysis is promoted by the interior catalytic sites and not only by the exterior ones.

To examine the versatility of the heterogeneous Zn-MOF **2** catalytic system, the Henry (nitroaldol) reaction was also investigated. Although this reaction is known as one of the most powerful reactions forming a new C–C bond, few reports on MOF-catalyzed Henry reactions exist.^[9] As shown in Table S3 in the Supporting Information, the conversion of substrate systematically depends on the molecular size of

the nitroalkanes, which again verifies that the interior Zn^{II} sites could advance the reaction and endow size-selectivity to this catalytic reaction.

Conclusions

In summary, we have presented the syntheses and crystal structures of two new Zn-MOFs containing 1D channels, [Zn₃(TCPB)₂·2DEF]·3DEF (1) and $[Zn_3]$ (TCPB)₂·2H₂O]·2H₂O·4DMF (2). Upon heating above 80 °C, the framework of 1 converts into that of 2. Fortunately, the framework of 2 is robust enough to maintain after removal of solvent molecules, and exhibits a highly selective adsorption behavior toward H₂/N₂, CO₂/N₂, and CO₂/CH₄. Moreover, the coordinatively unsaturated Zn^{II} sites in the framework can serve as Lewis acid catalytic centers for carbonyl cyanosilylation and the Henry reaction. Both catalytic systems are dependent on the size of the substrates. The Zn-MOF catalyst can be recovered and maintains its activity in subsequent runs. Further study of the applications of this robust porous Zn-MOF is in progress.

Experimental Section

General Information

All reagents and solvents were commercially available and used as received. 1,3,5-Tri(4-carboxyphenoxy)benzene (H₃TCPB) was prepared as described.^[15] Infrared spectra were collected from KBr pellets in the region of 4000–400 cm⁻¹ on a Nicolet/Nexus-670 FT-IR spectrometer. ¹H NMR spectra were recorded with a Varian Mercury Plus 300 MHz spectrometer. X-ray powder diffraction patterns were measured on a Bruker D8 Advance diffractometer at 40 kV and 40 mA with a Cu target tube and a graphite monochromator. Thermogravimetric analyses (TGA) were performed on a Netzsch Thermo Microbalance TG 209 F3 Tarsus from room temperature to 900°C with a heating rate of 10°Cmin⁻¹ under flowing nitrogen. The elemental analyses were obtained with a Perkin–Elmer 240 elemental analyzer. The sorption isotherms were measured with a Quantachrome Autosorb-iQ-MP gas sorption analyzer.

Synthesis of [Zn₃(TCPB)₂·2DEF]·3DEF (1)

A mixture of Zn(NO₃)₂·6H₂O (60 mg, 0.2 mmol) and H₃TCPB (50 mg, 0.1 mmol) in 3 mL DEF was sealed in a Teflon-lined autoclave and heated under autogenous pressure at 85 °C for three days. After cooling to room temperature, colorless block-shaped crystals of **1** were obtained and washed twice with DEF. Yield: 60 mg (75 % based on the ligand); IR (KBr): $\tilde{\nu} = 3419$ (br), 2976(m), 1652(s), 1593(s), 1501(m), 1390(w), 1264(s), 1219(s), 1159(m), 1117(m), 1007(m), 853(w), 782(m), 707(m), 646(m), 453 cm⁻¹ (w); elemental analysis calcd (%) for C₇₉H₈₅N₅O₂₃Zn₃: C 56.86, H 5.13, N 4.20; found: C 56.78; H 5.21; N 4.25.

Synthesis of $[Zn_3(TCPB)_2 \cdot 2H_2O] \cdot 2H_2O \cdot 4DMF$ (2)

A mixture of Zn(NO₃)₂·6H₂O (30 mg, 0.1 mmol) and H₃TCPB (25 mg, 0.05 mmol) in 4 mL DMF was sealed in a Teflon-lined autoclave and heated under autogenous pressure at 85 °C for three days. After cooling to room temperature, colorless block-shaped crystals of **2** were obtained and washed with DMF. Yield: 30 mg (76% based on the ligand); IR (KBr): $\tilde{\nu}$ =3393(br), 1661(m), 1595(s), 1402(m), 1392(s), 1224(s), 1160(m), 1121(m), 1009(m), 855(w), 815(w), 783(w), 707(w), 650(m), 457 cm⁻¹ (w); elemental analysis calcd (%) for C₆₆H₆₆N₄O₂₆Zn₃: C 51.90, H 4.36, N 3.67; found: C 52.42, H 4.32, N 3.65.

X-Ray Structure Determination

Single-crystal X-ray data for 1 and 2 were collected on an Oxford Gemini S Ultra diffractometer equipped with Cu_{Ka} radiation ($\lambda =$ 1.54178 Å) at 150 K by using ϕ and ω scan.^[16] The reflections have been corrected by empirical absorption corrections. The structures were solved by the direct method and refined by full-matrix least-squares on F^2 using SHELXL programs.^[17] All non-hydrogen atoms were refined anisotropically. The H atoms of the solvated water molecules in 1 were added. Due to the fact that all guest solvent molecules of complex 1 are located in the voids of the coordiantion frameworks, they display typical large thermal displacements; therefore, constrained refinements were applied by using DELU/SIMU to approximate to isotropic behaviors. In complex 2, free solvent molecules were disordered: therefore, the diffused electron densities resulting from these residual solvent molecules were removed from the data set using the SQUEEZE routing of PLATON and refined further using the data generated.^[18] A summary of the crystal structure refinement data are shown in Table 1, and selected bond angles and distances are listed in Table S1 in the Supporting Information. The contents of the solvent region in 2 are not represented in the unit cell contents in the crystal data. CCDC 879380 (1) and CCDC 879381 (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.

Gas Sorption Measurements

Prior to the sorption examination, the sample was activated by the following procedure: the as-prepared sample was soaked in methanol for three days, during which methanol was refreshed five times, and then the sample was placed under vacuum at 130°C for 10 h. Gas sorption isotherm measurements were performed on a Quanta chrome Autosorb-iQ-MP sorption analyzer. The temperature was maintained at 77 K with liquid nitrogen, at 87 K with liquid argon, or at 195 K with acetone/dry ice slush.

Typical Procedure for Carbonyl Cyanosilylation

Before the reaction, the as-made samples were activated and treated in the same way as described for the sorption measurements. Desolvated **2** (7.3 mg, 2.5 mol%) was added to a mixture of benzaldehyde (26.5 mg, 0.25 mmol) and cyanotrimethylsilane (49.6 mg, 0.5 mmol), and then the resulting reaction mixture was stirred at room temperature for 13 h. The conversions were determined by 1H NMR analysis.

Typical Procedure for Henry (Nitroaldol) Reaction

In the presence of desolvated **2** (15 mg, 5 mol%), a mixture of 4-nitrobenzaldehyde (37.7 mg, 0.25 mmol) and nitroalkanes (3 mL) was heated at 70 °C with stirring for 3 d. The conversions were determined by ¹H NMR analysis.

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