Decametallic Co\textsuperscript{II}-Cluster-Based Microporous Magnetic Framework with a Semirigid Multicoordinating Ligand

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Abstract: We have synthesized a microporous magnetic framework that contained supertetrahedral decametallic cobalt clusters as nodes and 4-(tris(hydroxymethyl)methyl)pyridine ligands as linkers in a NaCl-like network. This complex shows canted antiferromagnetism with spin-glass behavior. After the removal of the guest molecules, the spin-canting and spin-glass behaviors are maintained. The permanent porosity was evaluated by N\textsubscript{2}-adsorption measurements. This complex mainly shows a hydrophobic nature, as validated by MeOH- and water-adsorption measurements, which is consistent with the grand canonical Monte Carlo (GCMC) theoretical simulation.

Introduction

The construction of multifunctional materials has received considerable attention on account of their intriguing properties and potential applications in sorption,\textsuperscript{[1]} heterogeneous catalysis,\textsuperscript{[2]} molecular recognition,\textsuperscript{[3]} and other technologies.\textsuperscript{[4]} Microporous magnetic materials are currently at the forefront of such multifunctional materials, which can be achieved by the judicious design of polynuclear metal clusters as joints that are connected by suitable spacer ligands.\textsuperscript{[5]} It is well-known that high-nuclearity magnetic clusters can not only circumvent interpenetration to increase porosity in the self-assembly process, but are also beneficial for obtaining fascinating magnetic properties.\textsuperscript{[6]} In this regard, polynuclear Co\textsuperscript{II} clusters are very attractive, owing to their exceptional magnetochemistry. Recently, Chen and co-workers have assembled a dynamic porous magnet by employing an isophthalic acid ligand, which represents a NaCl-like topology net that is based on [Co\textsubscript{10}] clusters as nodes with peculiar magnetic properties.\textsuperscript{[7]} Notably, most of the previously reported cluster-based microporous magnetic materials were obtained by employing ligating groups, such as carboxylate, pyridyl, and/or phosphonate ligands.\textsuperscript{[8,9]} Therefore, a new target in the exploration of other ligating ligands to assemble microporous magnetic materials is needed that is expected to obtain fascinating structures and properties.

Herein, we report a microporous magnetic framework that is based on a tripodal alcohol derivative with a pyridyl group, 4-(tris(hydroxymethyl)methyl)pyridine (4-thmpyH\textsubscript{3}). This complex shows a NaCl-like topology net with the formula unit $[\text{Co}_{10}\text{(4-thmpy)}_3\text{(CH}_3\text{COO)}_3\text{(H}_2\text{O})_6\text{(CH}_3\text{O})_3\text{]}\cdot 8\text{MeOH}$, which is denoted as TAF-1 (TAF is the abbreviation for tripodal alcohol framework). Our result indicates that such a ligand is a promising candidate for the preparation of microporous magnetic materials for several reasons.\textsuperscript{[10]} First, the triol group of the 4-thmpyH\textsubscript{3} ligand shows a tripodal\textsuperscript{1} level (4-thmpyH\textsubscript{3}) of deprotonation, which combines other bridging and/or terminal co-ligands (CH\textsubscript{3}COO\textsuperscript{-}, CH\textsubscript{3}O\textsuperscript{-}, H\textsubscript{2}O), thus forming [Co\textsubscript{10}] clusters as nodes. Second, the rigid pyridyl groups act as struts to link the [Co\textsubscript{10}] metal clusters, thus forming an inner pore. To the best of our knowledge, this is the first porous coordination polymer based on the tripodal alcohol 4-thmpyH\textsubscript{3} ligand. In addition, the unimodal [Co\textsubscript{10}] cluster is the highest-nuclearity porous coordination network cluster with cobalt atoms as nodes reported to date.\textsuperscript{[6c,7a,8,11]} MeOH- and water-adsorption measurements indicate that the complex mainly has a hydrophobic nature, which is validated by the grand canonical Monte Carlo (GCMC) theoretical simulations. Furthermore, TAF-1 shows characteristics of canted antiferromagnetism with spin-glass behavior, according to the magnetic measurements. When the guest molecules within TAF-1 are removed

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to obtain the activated TAF-1a, the spin canting and spin-glass behaviors are maintained.

Results and Discussion

Synthesis and X-ray crystal structure: Ligand 4-thmpyH₃ was synthesized by the reaction of 4-methyl-pyridine with formaldehyde according to a literature procedure.[13] The solvothermal reaction of Co(Ac)₂·4H₂O with the above crude product in a 1:1 molar ratio in MeOH at 393 K for 72 h yielded TAF-1 as red quadrate block single-crystals.

Single-crystal X-ray analysis revealed that TAF-1 crystalized in the cubic space group Pa₃. The asymmetric unit is shown in the Supporting Information, Figure S1. Four crystallographically distinct Co atoms are all located in an octahedral coordination environment. The coordination geometry of Co(1) is completed by four oxygen atoms from two different 4-thmpy ligands, one oxygen atom from a CH₃O group, and one central µ₆-O(1) atom. Four coordinated sites of Co(2) are surrounded by oxygen atoms from two different 4-thmpy ligands. The other two sites are coordinated to one central µ₆-O(1) atom and one oxygen atom from an acetate ligand. Co(3) is surrounded by three oxygen atoms from three different 4-thmpy ligands, one nitrogen atom from one 4-thmpy ligand, one oxygen atom from an acetate ligand, and one coordinated water molecule. The acetate ligand in TAF-1 forms syn−syn η¹⁻η¹⁻µ₂ coordination to link two Co sites, that is, Co(2) and Co(3). Co(4) lies at a site with threefold symmetry, which is coordinated to three oxygen atoms from three different 4-thmpy ligands and three water molecules. The central µ₆-O(1) atom is located on the threefold symmetry axis to link together six Co ions. Notably, the roles of two independent 4-thmpy groups are different, that is, the linker for the type-I ligand exhibits the µ₆-η¹⁻η¹⁻η¹⁻µ¹ coordination mode and the terminal group for the type-II ligand exhibits the µ₆-η¹⁻η¹⁻η¹⁻µ¹ coordination mode (see the Supporting Information, Figure S2). In this complex, the oxygen-rich ligands form a supertetrahedral core that contains ten Co ions (Figure 1a,b and the Supporting Information, S4). Here, the topology of the open framework. The large yellow sphere represents the largest van der Waals sphere that would fit inside the cavity without touching the framework. Only one orientation of the disordered atoms is shown for clarity. Color scheme: C (gray), N (blue), O (red), Co (aqua), polyhedron (aqua). Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] for complex TAF-1[14]

<table>
<thead>
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<th>Bond</th>
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<tr>
<td>Co(1)−O(1)</td>
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<tr>
<td>Co(1)−O(4)</td>
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<tr>
<td>Co(2)−O(5)</td>
<td>2.061(5)</td>
</tr>
<tr>
<td>Co(3)−O(3)</td>
<td>2.037(5)</td>
</tr>
<tr>
<td>Co(1)−O(9A)</td>
<td>2.010(5)</td>
</tr>
<tr>
<td>Co(1)−O(4)#1</td>
<td>2.043(5)</td>
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<td>Co(2)−O(6)</td>
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<td>2.111(5)</td>
</tr>
<tr>
<td>Co(2)−O(5)#2</td>
<td>2.076(5)</td>
</tr>
</tbody>
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[a] Symmetry transformations used to generate equivalent atoms: #1: z, x, y; #2: y, z, x; #3: y, −z+1/2, x+1/2.

Table 2. BVS calculations for TAF-1.

<table>
<thead>
<tr>
<th>Atom label</th>
<th>Calcd for Co⁷</th>
<th>Calcd for Co¹⁰</th>
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<tr>
<td>Co(1)</td>
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<td>2.39</td>
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<td>Co(2)</td>
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<td>Co(3)</td>
<td>2.05</td>
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</tr>
<tr>
<td>Co(4)</td>
<td>2.40</td>
<td>2.45</td>
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</table>

From a topological point of view, TAF-1 has a 3D uninodal six-connected framework (Figure 1c and the Supporting Information, S4). Here, the topology of the pore system is described as a NaCl-like network in which the vertices are [Co₆] clusters and the edges are type-I 4-thmpy struts (see the Supporting Information, Figure S2). Such connectivity is repeated, thus periodically forming an extended 3D frame-work (Figure 2). The solvent-accessible volume of TAF-1, as estimated by the PLATON program,[15] is 40.4% of the total crystal volume.
Thermal properties and powder X-ray diffraction: Elemental analysis of the as-synthesized crystals reveals that the pore accommodates eight MeOH molecules per formula unit, as confirmed by TGA (see the Supporting Information, Figure S5). TAF-1 loses all of the guest MeOH molecules below 100°C under a nitrogen atmosphere, with a total weight loss of 13.83% (calcd 13.07%). In the range of 100–526°C, consecutive decompositions suggest the total destruction of the framework. A plateau region is observed from 526–800°C, and a residue of CoO (obs 38.15%, calcd 38.22%) remained. The phase purity of the as-synthesized TAF-1 is corroborated by the similarities between the simulated and experimental powder X-ray diffraction (PXRD) patterns (see the Supporting Information, Figure S6). Samples of TAF-1 were evacuated under vacuum at 90°C for 24 h to remove the guest molecules and, hence, to form guest-free phase TAF-1a. Our attempts to obtain the structure of the de-solvated sample by using single-crystal X-ray diffraction have so far been unsuccessful, owing to poor single crystallinity. However, the crystalline nature of TAF-1a can be validated by PXRD analysis, despite the slight weakening or absence of some peaks, which results from the release of the guest solvent (see the Supporting Information, Figure S6).

Sorption behavior and theoretical simulations: Permanent porosity is evaluated by nitrogen-adsorption measurements on activated TAF-1a at 77 K. As shown in Figure 3a, the isotherm exhibits a typical type-I curve, according to IUPAC classification,[16] which is consistent with the microporous nature of the structure. The HK-plot model estimates an effective pore size of about 4.6 Å (see the Supporting Information, Figure S7), which is consistent with the X-ray analysis. Moreover, the adsorption data also gives a BET surface area of 268.5 m²g⁻¹ and a Langmuir surface area of 356.9 m²g⁻¹. We investigated the behavior of carbon-dioxide uptake at 298 K and 273 K, respectively (see the Supporting Information, Figure S8), which showed a moderate degree of uptake compared with previously reported results.[17]

Inspired by the channel that is decorated with pyridine rings, alkyl groups, and oxygen-rich groups, water- and MeOH-sorption isotherms were performed at 298 K to analyze the different effects of small molecules on the basis of their size and polarity. As shown in Figure 3b, activated TAF-1a takes up different amounts of saturated MeOH and water molecules (3.75 and 0.71 mmolg⁻¹, respectively), which suggests the mainly hydrophobic nature of TAF-1a. The desorption profile does not trace the adsorption profile and shows larger hysteresis for MeOH than for water, which indicates stronger interactions between MeOH molecules and the channel surface, owing to the present of the pyridine rings.

Theoretical GCMC simulations were performed for the N₂- and MeOH-adsorption isotherms.[18] The curve of a simulated N₂-adsorption isotherm for TAF-1a at 77 K (Figure 3a) is in good agreement with the experimental data, thus implying that the sample is completely de-solvated. Furthermore, a simulated MeOH-adsorption isotherm at 298 K can reproduce the results of experimental data extremely well (see the Supporting Information, Figure S9). MeOH-binding sites were also obtained from the simulation.
We observed that the MeOH molecule was located inside the hole and formed short contacts with the pyridine ring (C−H···π 2.879 Å). This result further confirms a strong bonding interaction, which perhaps results in the high MeOH-adsorption ability of TAF-1a. Magnetic properties: The temperature-dependent magnetic susceptibility of TAF-1 was determined from 300 to 2 K in an applied magnetic field of 1000 Oe (Figure 4a). The $\chi_m$ versus $T$ value at room temperature is 26.14 cm$^3$ mol$^{-1}$ K, which is markedly larger than the spin-only value of 18.75 cm$^3$ mol$^{-1}$ K for ten isolated Co$^{II}$ ions ($g = 2, S = 3/2$), owing to the spin-orbit coupling of Co$^{II}$ ions. Upon cooling, the $\chi_m$ value first drops gradually to a minimum value of 13.87 cm$^3$ mol$^{-1}$ K at 20 K. A fitting of the data above 50 K to the Curie–Weiss law gives $C = 29.66$ cm$^3$ mol$^{-1}$ K and $\theta = -39.78$ K. The negative Weiss temperature and the decrease in $\chi_m$ both indicate a dominated antiferromagnetic interaction between the Co$^{II}$ ions within the [Co$_{10}$] cluster above 20 K. Upon further cooling, the $\chi_m$ value increases to a maximum of 14.75 cm$^3$ mol$^{-1}$ K at 12 K, thus suggesting the onset of ferromagnetic behavior. This result may suggest that the magnetic behavior at low temperatures ($T < 20$ K) may be attributed to canted antiferromagnetism and/or zero-field splitting of the anisotropic high-spin Co$^{II}$ ions. Secondly, below 12 K, the $\chi_m$ value decreases to 8.83 cm$^3$ mol$^{-1}$ K at 2 K, which may arise from the magnetic field saturation effect and/or antiferromagnetic interactions between the [Co$_{10}$] clusters. To elucidate their actual nature, more-detailed measurements for TAF-1 were performed. In fact, the maximum of the $\chi_m$ value for TAF-1 shows a more noticeable change in lower magnetic fields (10 and 100 Oe) than in higher field (1000 Oe), which suggests the spin-canting phenomenon (Figure 5a). A similar magnetic behavior has been observed in the reported isolated [Co$_{10}$] molecule. The field dependence of magnetization within the range 0–7 T for TAF-1 was measured at 2 K. As shown in the Supporting Information, Figure S11, the M value increases quickly at low fields and then more slowly at high fields, but without saturation. The magnetization at the highest field (7 T) is 10.55 N$\beta$ per [Co$_{10}$] unit, which is far below the expected saturation value of 30 N$\beta$ for ten Co$^{II}$ ions. Thus, this lack of saturation at high field further confirms the canted antiferromagnetic behavior of TAF-1 at $T < 20$ K. Such a phenomenon is common in Co$^{II}$-containing compounds. In addition, as shown in the Supporting Information, Figure S12, a hysteresis loop for TAF-1 is observed, which denotes a coercive field of 100 Oe and a remnant magnetization of 0.058 N$\beta$. Moreover, the zero-field-cooled (ZFC) and field-cooled (FC) data for TAF-1 show a bifurcation in the low-tempera-
ture region (below 12 K), which possibly reveals a long-range-ordered, spin-glass, or superparamagnetic state (Figure 6a).\[23\] The frequency dependence of the magnetic susceptibility of TAF-1 in alternating current (AC) was determined to further investigate the underlying magnetic nature; the in-phase ($\chi_m$') and out-of-phase magnetic susceptibility ($\chi_m$") both exhibit slight frequency dependence at around 8 K (Figure 7a) and the shift parameter, $\phi=(\Delta T_{p}/T_{p})/\Delta(\log\omega)$ (\(\omega\) applied frequency), of $\chi_m$' peak is at approximately 0.02, which falls within the usual range (10\(^{-2}\)–10\(^{-3}\)) of spin-glass behavior.\[24\] According to the above observations, the TAF-1 system demonstrates a frequency-dependent in-phase signal compared with the reported single molecular [Co\(_{10}\)] system,\[11\] thus suggesting improved magnetic properties by using the tripodal alcohol ligand 4-thmpyH.

To investigate whether the spin-glass and spin-canting behaviors are maintained after removal of the guest molecules, magnetic measurements of TAF-1a were also performed. The plots of $\chi_m'T$ and $\chi_m^{-1}$ versus $T$ of TAF-1a are shown in Figure 4b. The $\chi_m'T$ profile for TAF-1a is similar to that of TAF-1, which further indicates that the framework is maintained after removal of the guest. The maximum $\chi_m'T$ value is 13.84 cm\(^3\) mol\(^{-1}\) K at 9.8 K. The susceptibility data between 50 and 300 K follows the Curie-Weiss law, which gives $C=29.66$ cm\(^3\) mol\(^{-1}\) K and $\theta=-47.15$ K. The $\chi_m'T$ value at low temperature increases as the applied field drops, which is characteristic of spin-canting (Figure 5b). The magnetization is 8.44 N$\beta$ in the highest measured field (5 T), which is far from the saturation value, thus confirming the canted antiferromagnetism of TAF-1a (see the Supporting Information, Figure S13). A coercive field of 160 Oe and a remnant magnetization of 0.09 N$\beta$ were obtained from the isothermal hysteresis loop (M–H) at 2 K (see the Supporting Information, Figure S14). A bifurcation of the ZFC and FC curves at low temperatures is also observed below 14 K (Figure 6b); in the same way as for TAF-1, both the $\chi_m'$ and $\chi_m''$ of TAF-1a display a frequency-dependent peak at around 10.7 K (Figure 7b). The shift parameter ($\phi$) of the $\chi_m$" peak is approximately 0.002, which is still within the characteristic range of spin-glass.

The $\chi_m'T$, magnetization, and spin-glass shift parameter of TAF-1a are slightly different from those of TAF-1. The larger absolute value of the $\phi$ constant for TAF-1a suggests a stronger antiferromagnetic interaction. The $\chi_m'T$ value jumps more pronouncedly in low fields for TAF-1a than that of TAF-1. In addition, the larger remnant magnetization for TAF-1a indicates a larger canting angle than that of TAF-1 (the equation\[23\] $\sin(\alpha)=M_d/M_s$ gives a canting angle of $\alpha=0.17$ for TAF-1a and $\alpha=0.11$ for TAF-1). The temperature of the bifurcation of the ZFC and FC, as well as the temperature of the peaks of $\chi_m'$ and $\chi_m''$, for TAF-1a are both shifted to higher temperature. However, the spin-glass shift parameter for TAF-1a is one order of magnitude lower than that of TAF-1a. We have tentatively attributed such differences to the hydrogen-bonding interactions between the guest MeOH molecules and the framework of TAF-1. The removal of guest molecules may lead to the
slight change in the structure of TAF-1a, which benefits the spontaneous magnetization at higher temperature. Nevertheless, the spin-canting and spin-glass behaviors are maintained after the removal of the guest molecules. Our result indicated that the title complex may be a good candidate for magnetic-separation media.

Conclusion

In summary, a new 3D microporous magnetic network, TAF-1, has been successfully prepared by employing the semirigid ligand 4-thmpyH3. This complex consists of a deca-metallic CuII core, which exhibits permanent porosity. Magnetic measurements revealed that both TAF-I and TAF-1a show canted antiferromagnetism with spin-glass behavior. These results suggest that this strategy could be effective for the construction of bifunctional materials by using such a semirigid tripodal alcohol ligand. This ligand possesses two types of coordinating sites, thus forming the high-nuclearity clusters through its “rigid part”, which may provide a procedure for the assembly of magnetic porous materials. Future work will focus on tuning of the rigid part of the linker to design new magnetic porous materials with various pore sizes.

Experimental Section

Materials: Ligand 4-thmpyH3 was synthesized from the reaction between 4-methyl-pyridine and formaldehyde according to a literature procedure.[23]

Synthesis of TAF-1: A solution of the crude 4-thmpyH, product (0.092 g, 0.5 mmol) in MeOH (15 mL) was added to a stirring solution of Co(acac)2·4H2O (0.125 g, 0.5 mmol) in MeOH (2 mL). Then, the resulting solution was heated to 393 K in a Teflon-lined steel autoclave (20 mL) over 72 h and then cooled to RT over 25 h. The resulting x-ray-quality, red quadrat block-shaped single crystals of TAF-1 were obtained in about 60% yield (relative to Co). IR (KBr; see the Supporting Information, Figure S15 for the spectrum): ν = 3374 (m), 2921 (m), 2865 (m), 1565 (s), 1413 (s), 1342 (m), 1234 (w), 1094 cm⁻¹ (s); elemental analysis calcld (%) for Co6Cu10O63N12H42 (TAF-1): Co 34.67, C 28.67, H 5.32, N 2.76; found: Co 34.62, C 28.8, H 5.26, N 2.8. X-ray crystallography: Single-crystal X-ray diffraction data for TAF-1 were obtained on a Bruker SMART APEX CCD area-detector diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 298 K. The structure was solved by using direct methods with SHELXS-97 and refined on F² by using full-matrix least-squares with the SHELXL-97 program.[29] The positional disorder of the C(18), C(19), and O(10) atoms was resolved with equal occupancies for each position. The C atoms on the pyridine ring of the 4-thmpy ligand, that is C(13), C(14), C(15), C(16), were highly disordered over three positions, each with 1/3 occupancy, and the possible places are shown in the Supporting Information, Figure S2b. The hydrogen atoms on all of the C atoms except for C(19A)/C(19B) were highly disordered over three positions, each with 1/3 occupancy, and the possible places are shown in the Supporting Information, Figure S2b. The hydrogen atoms on all of the C atoms except for C(19A)/C(19B) were subsequently located from a theoretical model. The hydrogen atoms on the coordinated water molecules, except for O(10A)/O(10B), were also located. However, the hydrogen atoms on the MeOH molecules, that is C(19A)/C(19B), and on the water molecules, that is O(10A)/O(10B), that are coordinated to the Cu(4) ion were not located. According to charge balance and crystallographic parameters, the coordinated MeOH molecule was deprotonated. Moreover, the pore cavities in the TAF-1 complex were located by highly disordered solvent molecules, which made the refinements difficult to converge. Thus, we used the SQUEEZE subroutine in the PLATON[30] software suite to eliminate disordered guest molecules. X-ray crystallographic data in the CIF format is given in the Supporting Information, Table S1. CCDC-886640 (TAF-1) 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.

Physical techniques: IR spectroscopy was performed within the range 4000–400 cm⁻¹ by using KBr pellets on an Alpha Centaur FTIR spectrophotometer. Co elemental analysis was determined on a Leeman inductively coupled plasma (ICP) spectrometer. C, H, and N elemental analysis was performed on a Perkin-Elmer Model 240C elemental analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer at a heating rate of 10°C min⁻¹ from RT to 800°C under a flowing nitrogen atmosphere. Powder X-ray diffraction (PXRD) measurements were recorded under radiation ranging from 5 to 60° at room temperature on a Siemens D5005 diffractometer with CuKα radiation (λ = 1.5418 Å) at a scan speed of 5°·min⁻¹ and a step size of 2θ = 0.1°. The as-synthesized compound was heated for 24 h under vacuum at 90°C to remove the guest molecules. Magnetic measurements: Magnetic-susceptibility measurements for TAF-1 and TAF-1a were performed on a Quantum Design SQUID MPMS XL-7 instrument within the temperature range 300–2 K under an applied magnetic field of 1000 Oe or 100 Oe. Field-dependent magnetization was measured at 2 K within the field range 0–7 T for TAF-1 and 0–5 T for TAF-1a. The hysteresis loop was recorded between −7 and +7 T for TAF-1 and between −5 and +5 T for TAF-1a at 2 K on a microcrystal line sample. The field-cooled (FC) and zero-field-cooled (ZFC) data for TAF-1 and TAF-1a were assessed under a direct current (DC) field of strength 10 Oe. The alternating-current (AC) susceptibility measurements of TAF-1 and TAF-1a were performed under a field strength of HAC = 0, HP = 3 Oe (under the 3.5 Oe alternating current field at the operating limits of our SQUID) in the temperature range 20–30 K.

Sorption measurements: CO₂ and N₂ sorption isotherms, BET surface area, and Langmuir surface area were measured on a micrometrics ASAP 2020 Surface Area and Porosity Analyzer. Before the measurements, the sample was degassed under a dynamic vacuum at 90°C for 24 h. The differential pore volume distribution was estimated according to the Horvath–Kawazoe (HK) model. A RUBOTERM magnetic-suspension balance (Ankersmid B.V., Netherlands) was used to measure water and MeOH sorption. To obtain the de-solvated sample (TAF-1a), the as-synthesized crystal of TAF-1 was directly degassed at 90°C for 24 h under vacuum. Before the measurements, the sample was situated on the vapors of water and MeOH for 24 h, respectively.

Computational details: Grand canonical Monte Carlo (GCMC) simulations were performed for the adsorption of N₂ and MeOH in TAF-1a. The MUSCI[31] code was used, including a 5 × 10⁶ step equilibration period, followed by a 5 × 10⁶ step production run. The van der Waals interaction was described by using the Lennard–Jones (LJ) potentials with a cutoff distance of 10.0 Å, according to Equation (1), where r and j are atoms of the gases and TAF-1a, r is the distance between two atoms, and ε and σ are the LJ well-depth and diameter, respectively.

\[
V_q = 4 \epsilon \left( \frac{\sigma^6}{r^6} - \frac{2 \sigma^3}{r^3} \right) \quad (1)
\]

Lorentz–Berthelot mixing rules were used to calculate the ε and σ values between different atomic species. For N₂, three different types of Monte Carlo trials were used in the simulations, that is, insertion, removal, and translation. For the models of MeOH, an additional Monte Carlo trial rotation was used. For the MeOH adsorption, besides van der Waals interactions, coulombic interactions were considered by using the Ewald sum.

The partial charges for atoms of TAF-1a were derived by using the QEq method.[29] The LJ parameters for TAF-1a[29] and the gases are listed, together with the partial charges, in the Supporting Information, Table S2.
Acknowledgements

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