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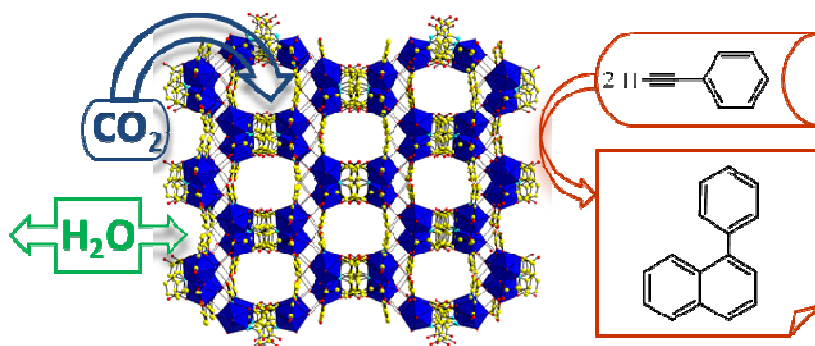
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A graphical contents entry:



A novel molecular porous zirconium-organic material, CAUMOF-12, reveals a differential gas adsorption, high thermal stability, a reversible dehydration/rehydration phenomenon, facile ligand exchange reactions, and dimerization reactions of phenylacetylene.

# A molecular porous zirconium-organic material exhibiting highly selective CO<sub>2</sub> adsorption, high thermal stability, reversible hydration, facile ligand exchanges, and exclusive dimerization of phenylacetylene

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A new molecular porous zirconium-organic material, Zr{[NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>](OH<sub>2</sub>)<sub>2</sub>}·1.3H<sub>2</sub>O (CAUMOF-12) has been synthesized by a hydrothermal reaction using Zr(NO<sub>3</sub>)<sub>4</sub>, 2,6-NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>H)<sub>2</sub>, HNO<sub>3</sub>, and water at 180 °C. Single-crystal X-ray diffraction was used to determine the crystal structure of the reported material. Although the material can be classified as a molecular compound, CAUMOF-12 exhibits a pseudo-three-dimensional open-framework structure with void space obtained by intermolecular hydrogen bonds. CAUMOF-12 reveals a differential gas adsorption characteristics and high thermal stability. Reversible hydrations, facile ligand exchange reactions, and an exclusive dimerization of phenylacetylene for CAUMOF-12 are presented, as are electronic structure calculations.

## Introduction

Porous materials have been drawing great attention attributable to their momentous applications in adsorption, molecular sensing, ion-exchange, isolation, gas separation, catalysis, carbon capture, and gas storage.<sup>1</sup> Porous materials such as inorganic zeolites and porous coordination polymers (PCPs) generally exhibit open-framework structures with large channels or pores. Especially, a controlled construction of PCPs containing desired geometries, morphologies, and functionalities are possible, if proper metal cations and organic linkers are judiciously introduced.<sup>2</sup> In general, most porous PCPs reveal extended structures with 2D or 3D networks. However, a class of 0D coordination compounds with porosity, namely, a molecular porous material (MPM) exists and has been of great interest attributed to the reversible gas adsorption properties.<sup>3</sup> Several reported examples of MPMs are metal-organic polyhedra (MOPs),<sup>4</sup> metal-organic squares (MOSSs),<sup>5</sup> metal-organic cubes (MOCs),<sup>6</sup> metal-organic macrocycles,<sup>7</sup> organic cage compounds,<sup>8</sup> cucurbit[*n*]urils,<sup>9</sup> and *tert*-butylcalix[4]arene.<sup>10</sup> In fact, most of the above mentioned MPMs contain intrinsic pores within the molecules. One very important force that can maintain fine-tunable networks of MPMs is a hydrogen-bonding. In fact, a robust MPM constructed by the hydrogen-bonding with high CO<sub>2</sub> selectivity and uptake has been recently reported.<sup>11</sup> Regardless of how the porosity is created, once the PCPs or MPMs are applied for practical purposes, however, the open-framework materials often reveal detrimental drawbacks such as low thermal, mechanical, and chemical stabilities. Recently, several materials exhibiting exceptional thermal stabilities in air and most chemical solvents have been reported from zirconium based PCPs.<sup>12</sup> We also have been very interested in discovering novel zirconium-organic coordination compounds for a variety of versatile

applications. Herein we report a new molecular porous zirconium-organic material, Zr{[NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>](OH<sub>2</sub>)<sub>2</sub>}·1.3H<sub>2</sub>O (CAUMOF-12) containing channels generated by intermolecular interactions such as hydrogen-bondings and  $\pi$ - $\pi$  interactions. In this paper, differential gas adsorptions, reversible hydrations, facile ligand exchanges, and a selective dimerization of phenylacetylene are also presented, as are electronic structure calculations.

## Experimental

### Synthesis

Zr(NO<sub>3</sub>)<sub>4</sub> (Acros, 99%), 2,6-NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>H) (Alfa Aesar, 98%), and HNO<sub>3</sub> (Daejung, 60%) were used as received. CAUMOF-12 was synthesized by combining Zr(NO<sub>3</sub>)<sub>4</sub> (0.339 g, 1.00 × 10<sup>-3</sup> mol), 2,6-NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>H)<sub>2</sub> (0.334 g, 2.00 × 10<sup>-3</sup> mol), HNO<sub>3</sub> (0.5 mL), and 8 mL of deionized water. The reaction mixture was transferred to a Teflon-lined stainless steel autoclave. The autoclave was subsequently sealed and heated to 180 °C for 3 days, before being cooled to room temperature at a rate of 6 °C h<sup>-1</sup>. The autoclave was opened and the product was recovered by filtration and washed with water. Colorless crystals were recovered for CAUMOF-12 in 93% yield based on Zr(NO<sub>3</sub>)<sub>4</sub>. Powder X-ray diffraction data on the bulk sample revealed that the synthesized material was pure and in good agreement with the generated pattern from the single-crystal data (see the ESI).

### Single-crystal X-ray diffraction

The structure of CAUMOF-12 was determined by a standard crystallographic method. A colorless block crystal of dimension 0.014 × 0.027 × 0.075 mm<sup>3</sup> for CAUMOF-12 was used for structural determination. Diffraction data were

collected at 173 K using a Bruker SMART BREEZE diffractometer equipped with a 1K CCD area detector using graphite monochromated Mo K $\alpha$  radiation. A narrow-frame method was used with an exposure time of 10 s/frame, and scan widths of 0.30° in omega to collect a hemisphere of data. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability. The maximum correction applied to the intensities was < 1%. The data were integrated using the SAINT program,<sup>13</sup> with the intensities corrected for polarization, Lorentz factor, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. The data were solved with SHELXS-97<sup>14</sup> and refined using SHELXL-97.<sup>15</sup> All of the atoms except for hydrogen were refined with anisotropic displacement parameters and converged for  $I > 2\sigma(I)$ . All calculations were performed using the WinGX-98 crystallographic software package.<sup>16</sup> Crystallographic data and selected bond lengths for CAUMOF-12 are summarized in Tables 1 and 2, respectively. Hydrogen atoms for the coordinated water molecules were found from the difference Fourier map and were refined. The O–H bond distances in coordinated water molecules were restrained using the DFIX command. However, those for occluded water molecules were not attached attributable to the severe disorder and partial occupancies of oxygen atoms.

### Powder X-ray diffraction

The powder XRD data were collected on a Bruker D8-Advance diffractometer using Cu K $\alpha$  radiation at room temperature with 40 kV and 40 mA. The well-ground polycrystalline CAUMOF-12 was mounted on a sample holder and scanned in the 2 $\theta$  range 5–70° with a step size of 0.02° and a step time of 0.2s.

### Nuclear magnetic resonance (NMR) spectroscopy

NMR spectra were recorded on a Varian VNS 600 MHz for <sup>1</sup>H and 150 MHz spectrometer for <sup>13</sup>C.

### Infrared spectroscopy

Infrared spectrum was recorded on a Varian 1000 FT-IR spectrometer in the 400–4000 cm<sup>-1</sup> range, with the sample embedded in a KBr matrix. IR (KBr, cm<sup>-1</sup>): 3427, 3092, 1659, 1576, 1481, 1434, 1386, 1365, 1343, 1273, 1179, 1077, 1034, 928, 768, 746, 688, 674, 600, 546, 441.

### UV-Visible spectroscopy

UV-vis spectrum was recorded with a Jasco V-630 spectrophotometer in the spectral range 190–1100 nm at room temperature.

### Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed on a Setaram LABSYS TG-DTA thermogravimetric analyzer. The polycrystalline sample of CAUMOF-12 was contained within

an alumina crucible and heated to 800 °C at a rate of 10 °C min<sup>-1</sup> under flowing argon.

### Elemental Analysis

Elemental analysis was carried out by a Carlo Erba EA1108 CHNS-O analyzer at Organic Chemistry Research Center, Sogang University. Elemental microanalysis for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>ZrO<sub>12</sub> obsd (calcd): C, 33.96% (34.07%); H, 3.11% (2.86%); N, 5.71% (5.68%).

**Table 1** Crystallographic data for Zr{[NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>}·1.3H<sub>2</sub>O (CAUMOF-12), Zr{[NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(DMF)<sub>2</sub>}·DMF and Zr{[NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(OHCH<sub>3</sub>)<sub>2</sub>}·CH<sub>3</sub>OH

Empirical formula	ZrC <sub>14</sub> H <sub>12.6</sub> N <sub>2</sub> O <sub>11.3</sub>	ZrC <sub>23</sub> H <sub>27</sub> N <sub>5</sub> O <sub>11</sub>	ZrC <sub>17</sub> H <sub>18</sub> N <sub>2</sub> O <sub>11</sub>
Formula weight	477.60	640.72	517.55
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	C2/c (No. 15)	C2/c (No. 15)	Pbca (No. 61)
a/Å	23.7011(7)	30.4402(13)	9.6801(2)
b/Å	12.1758(3)	11.6778(4)	18.9975(3)
c/Å	14.3519(6)	15.9518(6)	21.3644(3)
$\beta$ /°	105.526(2)	99.695(3)	90
V/Å <sup>3</sup>	3990.5(2)	5589.5(4)	3928.86(12)
Z	8	8	8
T/K	173.0(2)	173.0(2)	173.0(2)
$\lambda$ /Å	0.71073	0.71073	0.71073
R(F) <sup>a</sup>	0.0529	0.0419	0.0317
R <sub>w</sub> (F <sub>o</sub> <sup>2</sup> ) <sup>b</sup>	0.1534	0.0754	0.0664

$$^a R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b R_w(F^2) = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right]^{1/2}$$

**Table 2** Selected bond distances (Å) for Zr{[NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>}·1.3H<sub>2</sub>O (CAUMOF-12), Zr{[NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(DMF)<sub>2</sub>}·DMF and Zr{[NC<sub>5</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(OHCH<sub>3</sub>)<sub>2</sub>}·CH<sub>3</sub>OH

	Zr{[NC <sub>5</sub> H <sub>3</sub> (CO <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> }·1.3H <sub>2</sub> O		
Zr(1)–O(3)	2.212(4)	Zr(1)–OW(1)	2.174(4)
Zr(1)–O(5)	2.130(4)	Zr(1)–OW(2)	2.184(4)
Zr(1)–O(7)	2.195(4)	Zr(1)–N(1)	2.309(5)
Zr(1)–O(9)	2.166(4)	Zr(1)–N(2)	2.301(4)
	Zr{[NC <sub>5</sub> H <sub>3</sub> (CO <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> (DMF) <sub>2</sub> }·DMF		
Zr(1)–O(1)	2.204(2)	Zr(1)–O(9)	2.182(2)
Zr(1)–O(3)	2.122(2)	Zr(1)–O(10)	2.196(2)
Zr(1)–O(5)	2.130(2)	Zr(1)–N(1)	2.301(2)
Zr(1)–O(7)	2.181(2)	Zr(1)–N(2)	2.307(2)
	Zr{[NC <sub>5</sub> H <sub>3</sub> (CO <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> (OHCH <sub>3</sub> ) <sub>2</sub> }·CH <sub>3</sub> OH		
Zr(1)–O(1)	2.1460(16)	Zr(1)–O(9)	2.2111(17)
Zr(1)–O(3)	2.1563(16)	Zr(1)–O(10)	2.1933(18)
Zr(1)–O(5)	2.1654(17)	Zr(1)–N(1)	2.315(2)
Zr(1)–O(7)	2.1573(17)	Zr(1)–N(2)	2.3094(19)

### Gas chromatography/mass spectroscopy

Gas Chromatography/Mass spectra were measured with a Hewlett-Packard HP6890/Micromass Autospec spectrometer.

### BET surface area measurements

The surface area measurements were carried out by a

Quantachrome NOVA 1200e surface area analyzer. For the measurements of the dehydrated sample, the material was evacuated at 100 °C for 2 h before being analyzed. The gas adsorption isotherms were obtained at 77 K using N<sub>2</sub> and H<sub>2</sub>, and at 195 K using CO<sub>2</sub>. The specific surface area was estimated by the Langmuir surface area on the basis of the CO<sub>2</sub> adsorption at 195 K.

### Dehydration/rehydration experiments

The dehydration reaction was performed by heating ca. 100 mg of CAUMOF-12 at 300 °C for 5 h in vacuum. The dehydrated sample was rehydrated by immersing in water and heating to 50 °C for 1 d. After that, the product was recovered by filtration and dried in air for 1 d.

### Ligand exchange reactions

Ligand exchange reactions were carried out by transferring crystals of CAUMOF-12 into vials containing 5 mL of N,N-dimethylformamide [DMF, (CH<sub>3</sub>)<sub>2</sub>NCOH] and methanol (CH<sub>3</sub>OH). Crystals in both vials were slowly dissolved in a few days in each solvent. Colorless crystals were regrown in three weeks and a week from (CH<sub>3</sub>)<sub>2</sub>NCOH and CH<sub>3</sub>OH, respectively. Single crystal XRD was used to determine the structures of ligand-exchanged materials.

### Dimerization reaction of phenylacetylene

A 5.0 mL portion of phenylacetylene and a 0.20 g of CAUMOF-12 were added into the 10 mL of CHCl<sub>3</sub> in a 23 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and the reaction mixture was stirred at 110 °C for 24 h and cooled down to room temperature. The reaction mixture in the autoclave was analyzed through column chromatographic separation on silica gel with hexane followed by <sup>1</sup>H NMR and GC-MS measurements.

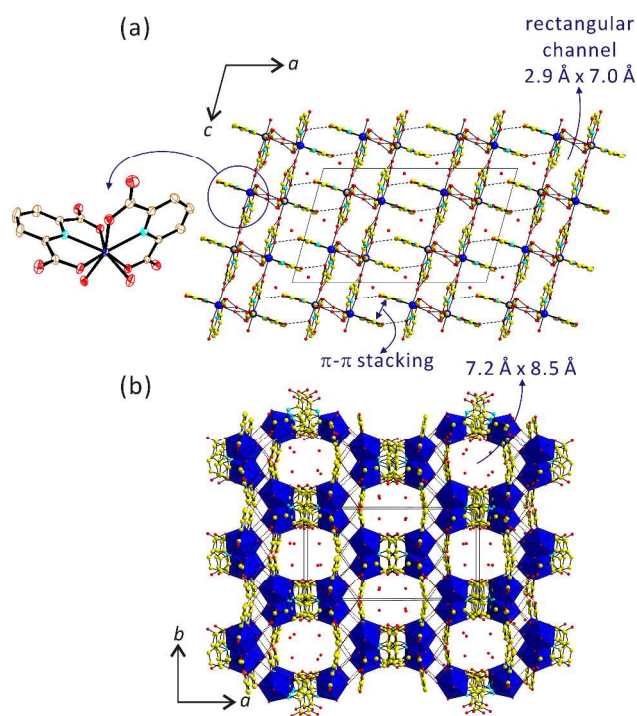
### Calculations

Density functional calculations have been carried out with GAUSSIAN 09 for the single molecule level and DMol<sup>3</sup> for the extended solid-state structure.<sup>17</sup> The DFT calculations were performed with B3LYP function in Gaussian and mixed basis are employed to describe the coordination compound. LanL2DZ is used for Zr atom and the standard basis sets of 6-311G (d, p) are used to describe the oxygen, nitrogen, carbon, and hydrogen atoms of ligands. Periodic Boundary Condition (PBC) DFT calculation performed with Perdew, Burke, and Ernzerhof (PBE) function of Generalized Gradient Approximation (GGA) was used for calculation of the solid-state structure. Geometry optimizations have been performed using DFT methods with mixed basis set at the same level. Natural bond orbital (NBO) analysis at the B3LYP/6-3111G (d, p) level gives the natural electron population and the natural charge for each atom.<sup>18</sup> In this study, we utilized the DFT calculation both in the single molecule and the extended solid-state structure to properly describe the experimental data. The point group used in the all optimization in Gaussian 09 is C<sub>1</sub>, and the space group used in DMol<sup>3</sup> is P1.

## Results and discussions

### Crystal structure description

CAUMOF-12 crystallizes in a monoclinic space group, C2/c (No. 15). Two 2,6-pyridine dicarboxylates (PDC) and two water molecules are connected to a Zr<sup>4+</sup> cation through oxygen and nitrogen atoms (see Fig. 1). The unique Zr<sup>4+</sup> cation is in an eight-coordinate dodecahedron environment with six oxygen and two nitrogen atoms. The observed bond distances of Zr–O and Zr–N are 2.130(4)–2.212(4) and 2.301(4)–2.309(5) Å, respectively. The C–O and C–N bond lengths in the carboxylate groups of the 2,6-PDC linker range over 1.208(7)–1.296(7) Å and 1.330(7)–1.343(7) Å, respectively. Bond valence sum calculations<sup>19</sup> on CAUMOF-12 resulted in a value of 4.28 for the Zr<sup>4+</sup> cation.



**Fig. 1** Ball-and-stick and polyhedral representations of CAUMOF-12 in (a) the *ac*-plane and (b) the *ab*-plane (blue, Zr; yellow, C; red, O; cyan, N). Hydrogen atoms have been omitted for clarity. Strong intermolecular hydrogen bonds give CAUMOF-12 a pseudo-three-dimensional open-framework structure.

Interestingly, the two 2,6-PDC ligands coordinated in the Zr are almost perpendicular to each other: while one of the 2,6-PDC is parallel to the *ab*-plane, another one is parallel to the *bc*-plane. Two water molecules are bonded to the Zr<sup>4+</sup> cation in *cis* positions to each other and two uncoordinated water molecules reside in the channels of CAUMOF-12. As can be seen in Fig. 1, strong intermolecular hydrogen bonds [O(4)⋯OW(1) 2.582(3) Å; O(8)⋯OW(1) 2.630(3) Å; O(10)⋯OW(2) 2.603(3) Å] occur between the coordinated water molecule in one zirconium center and the carboxylate group of 2,6-PDC ligand bonded in the adjacent zirconium,

which results in rectangular channels along the [010] direction. Density functional theory (DFT) calculations on CAUMOF-12 successfully confirm the intermolecular hydrogen bonding interactions, in which the C–O bond distances in non-coordinated carboxylate ligands revealing stronger hydrogen bonds are significantly longer than those exhibiting weaker interactions (see the Calculations section). The dimension of the large rectangular channels running down the *b*-axis is 2.9 Å × 7.0 Å. Each rectangular channel is further interlocked by fitting the 2,6-PDC “studs” perpendicular to the *c*-direction, which is attributed to another intermolecular hydrogen bonds between the carbon and the oxygen atoms in the adjacent 2,6-PDC groups [C(4)⋯O(9) 3.368(4) Å]. We also observe the  $\pi$ – $\pi$  stacking between the 2,6-PDC ligands along the [001] direction. The dimension of the channels running down the *c*-axis is 7.2 Å × 8.5 Å. Overall, all these intermolecular interactions give CAUMOF-12 a pseudo-three-dimensional open-framework structure with void space (see Fig. 1). The CALC SOLV command in PLATON<sup>20</sup> crystallographic program suggests that CAUMOF-12 contains about 12% of empty space. When the occluded water molecules are removed, the value increases to 26%.

### Gas adsorption measurements

The porous nature of CAUMOF-12 led us to monitor gas adsorption into the channels. The material was initially evacuated at 100 °C for 2 h before being analyzed to remove occluded water molecules. However, as we will discuss later in the thermogravimetric analysis section, the coordinated water molecules remain in the materials at the activation temperature, 100 °C, to maintain the intermolecular hydrogen-bondings and the subsequent porosity of the framework. To our surprise, the N<sub>2</sub> and H<sub>2</sub> diffusion into channels are not observed at 77 K, however, the adsorption capacity for CO<sub>2</sub> at 195 K is much greater for the activated sample of CAUMOF-12 (see Fig. 2). A few similar differential gas adsorptions in frameworks with channels have been reported.<sup>11,21</sup> The considerable quadruple interactions of N<sub>2</sub> with the electrostatic field gradients near the surface may result in strong interaction of the N<sub>2</sub> molecules with the channel windows, which subsequently block other molecules from passing into the pore.<sup>22</sup> However, with the CO<sub>2</sub> at 195 K, such interactions are overcome by thermal energy. Also, the observed low hydrogen uptake ability for CAUMOF-12 may be attributable to the lack of appropriate types of metal ions and linkers that can exhibit binding affinities to H<sub>2</sub> molecule. Analysis of the experimental data estimated by the Langmuir surface area on the basis of the CO<sub>2</sub> adsorption yields 420 m<sup>2</sup>/g and approximate pore diameters of 3–8 Å, which are consistent with those from crystallographic analysis. The pore size distribution plot is deposited in the ESI.

### Infrared and UV-vis spectroscopy

The infrared spectrum of CAUMOF-12 reveals the C–H and C=C stretching vibrations for the pyridine ring at ca. 3041–3137 and 1612–1731 cm<sup>-1</sup>, respectively. The bands

observed around 1375–1468 cm<sup>-1</sup> can be assigned to the COO stretches. The vibrations for the coordinated and occluded water molecules are observed around 3200 and 3550 cm<sup>-1</sup>, respectively. The assignments are consistent with those previously reported.<sup>23</sup> The UV-Vis spectrum for CAUMOF-12 shows absorption bands at 238 and 274 nm, which may be attributable to the ligand-to-metal charge transfer (LMCT) and the intraligand  $\pi \rightarrow \pi^*$  transitions. The IR and UV-Vis spectra for the reported material have been deposited in the ESI.

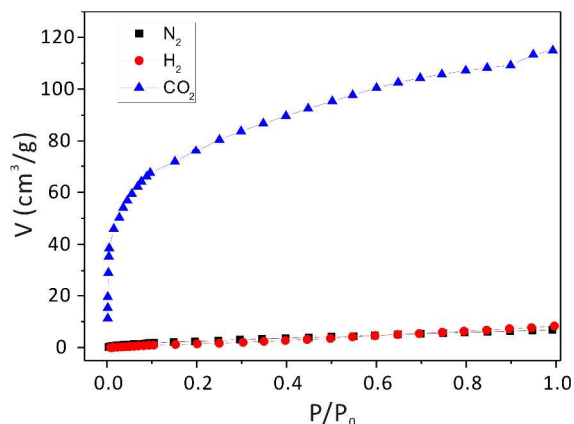


Fig. 2 Adsorption isotherms of N<sub>2</sub> (■, 77 K), H<sub>2</sub> (● (red), 77 K), and CO<sub>2</sub> (▲ (blue), 195 K) on CAUMOF-12.

### Thermogravimetric analysis

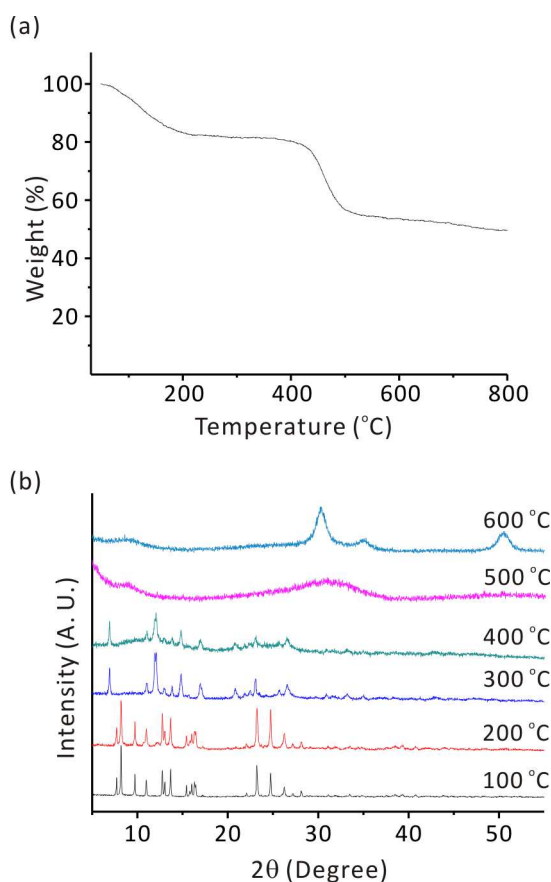
The thermal behavior of CAUMOF-12 was investigated using thermogravimetric analysis. As seen in Fig. 3a, CAUMOF-12 exhibits a weight loss of about 16.8% up to 240 °C that is attributable to the removal of water molecules from the material. Since the powder X-ray diffraction pattern obtained at 200 °C reveals similar pattern to that of as-synthesized CAUMOF-12, only occluded water molecules could be lost by 200 °C. Above the temperature, the coordinated water molecules are also removed (see Fig. 3b). However, interestingly, the framework of the material seems to be thermally stable up to 400 °C. The high thermal stability of CAUMOF-12 as a porous molecular metal-organic compound may be attributed to the flexibility of the organic linker and the strong intermolecular interactions within the framework. Above 400 °C, a thermal decomposition occurs and the material decomposes to ZrO<sub>2</sub>, which was confirmed by powder XRD data (see Figs. 3a and b).

### Reversible hydrations and ligand exchange reactions

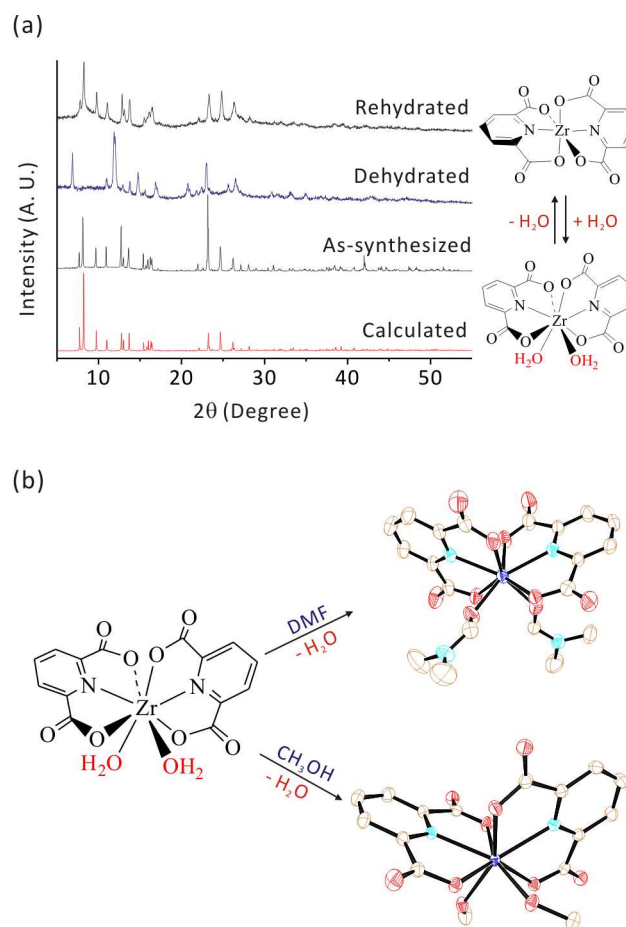
The occluded and coordinated water molecules in CAUMOF-12 are reversibly coming in and out: initially the compound is heated to 300 °C to remove the entire water molecules. The powder XRD pattern for the resulting material reveals a quite crystalline phase (see Fig. 4a). As seen in Fig. 4a, once the dehydrated material is placed in water at 50 °C for 1d, a complete rehydration occurs.

Since the loss and gain of water from the material are fully reversible, attempts have been made to exchange the

coordinated water molecules for other ligating solvents. Approximately 50 mg of CAUMOF-12 crystals were immersed in 3 mL of *N,N*-dimethylformamide (DMF) and methanol. Complete ligand exchange reactions occurred from both solvents (see Fig. 4b). Colorless crystals of  $\text{Zr}\{[\text{NC}_5\text{H}_3(\text{CO}_2)_2]_2(\text{DMF})_2\}\cdot\text{DMF}$  and  $\text{Zr}\{[\text{NC}_5\text{H}_3(\text{CO}_2)_2]_2(\text{OHCH}_3)_2\}\cdot\text{CH}_3\text{OH}$  were grown in three weeks and a week, respectively, which were identified by single crystal diffraction analyses (see Tables 1 and 2). Because crystals of both ligand-exchanged materials were grown from completely dissolved solutions, the transformations seem to occur through the dissolution and recrystallization process. Although stoichiometrically similar, both of the ligand-exchanged materials do not exhibit any porosity in the structures. In fact, neither DMF nor  $\text{CH}_3\text{OH}$  can make hydrogen-bonding interactions with adjacent molecules.



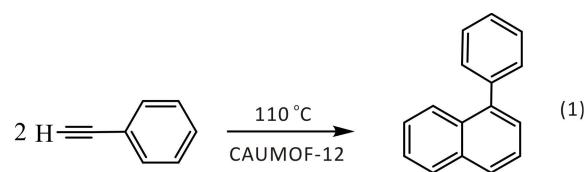
**Fig. 3** (a) Thermogravimetric analysis diagram and (b) powder X-ray diffraction (PXRD) patterns at different temperatures for CAUMOF-12.



**Fig. 4** (a) Powder X-ray diffraction patterns exhibiting reversible dehydration/rehydration. (b) A scheme showing ligand exchange reactions for CAUMOF-12.

### Dimerizations of phenylacetylene

Because CAUMOF-12 revealed facile ligand exchange reactions, we thought that the two labile water ligands in *cis* configuration could be utilized. Thus, a 5.0 mL portion (52.64 mmol) of phenylacetylene was added into a  $\text{CHCl}_3$  (10.0 mL) solution containing 0.20 g (0.41 mmol) of CAUMOF-12. The reaction mixture in a sealed container was stirred at 110 °C for 24 h and cooled down to room temperature. Interestingly, an unconventional dimerization product, 1-phenylnaphthalene was exclusively obtained from the reaction, although the yield was low (8.2%) based on gas chromatography analysis (see eq. 1 and the ESI).



When the temperature increased to 180 °C, however, 1-phenylnaphthalene and the cyclotrimerization products, 1,2,4-triphenylbenzene and 1,3,5-triphenylbenzene, were obtained in 58.5, 16.1, and 20.5% yields, respectively. It is worth to

note that normal dimerization products of phenylacetylene catalyzed by transition metals are known to be 1,3-diphenylbut-1-yn-3-ene, (*E*)-1,4-diphenylbut-1-yn-3-ene, and (*Z*)-1,4-diphenylbut-1-yn-3-ene.<sup>24</sup> To exclude any possibility of photodimerization of phenylacetylene, the same reaction was performed in the absence of CAUMOF-12; however, no oligomer was observed at all from the reaction. We believe that the selective formation of 1-phenylnaphthalene from the reaction of CAUMOF-12 with phenylacetylene may be attributable to the steric crowdedness arising from the 2,6-PDC ligands as well as the *cis* configuration of labile H<sub>2</sub>O ligands around the zirconium. It should be also noted that the reaction possibly occurred on the surface of CAUMOF-12, because the channels of CAUMOF-12 are not larger enough for phenylacetylene to diffuse into. Similar dimerization reaction of phenylacetylene was observed before from the close-packed surface of mpg-C<sub>3</sub>N<sub>4</sub>.<sup>25</sup> Once the reaction temperature increases to 180 °C, cyclotrimerization products such as 1,2,4-triphenylbenzene and 1,3,5-triphenylbenzene are obtained by the catalytic reaction of CAUMOF-12 with phenylacetylene. At higher temperatures, more coordination sites around Zr are available by fast movement of ancillary ligands. Similar thermally induced cyclotrimerizations of terminal alkynes at higher temperatures have been observed before from the organometallic compounds revealing a selective dimerization at lower temperatures.<sup>24k</sup> Also, the catalyst is recyclable: powder X-ray diffraction data for the recovered zirconium complex after the dimerization reaction show the same pattern as that of CAUMOF-12. The <sup>1</sup>H NMR and GC-Mass spectra for the obtained oligomers have been deposited in the ESI.

### Electronic structure calculations

DFT calculations have been carried out using the DMol<sup>3</sup> to calculate the electronic structure of CAUMOF-12.<sup>17a,17b</sup> The partial density of states (PDOS) plot obtained by performing spin-polarized generalized gradient approximation (GGA) calculations for CAUMOF-12 is shown in Figure 5.<sup>26</sup> As seen in Fig. 5, the lower filled band is mainly composed of  $\pi$  orbitals from the 2,6-PDC ligands. The empty higher band is contributed by approximately 85% of ligand  $\pi^*$  orbitals and 15% of zirconium d orbitals. Thus, the observed absorption bands in UV-Vis spectrum are believed to be attributed to the ligand-to-ligand charge transfer (LLCT) and the ligand-to-metal charge transfer (LMCT).

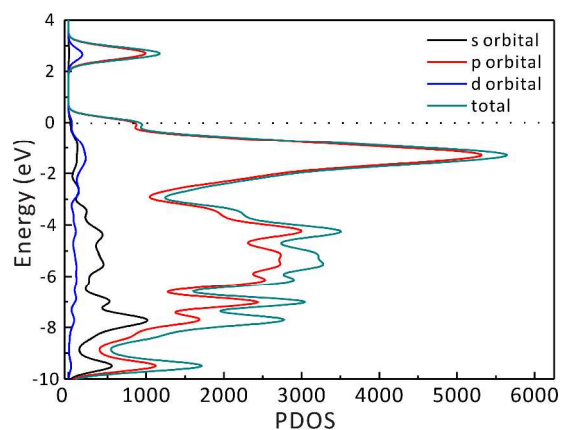


Fig. 5 The partial density of states (PDOS) plot for CAUMOF-12 obtained from DFT calculations. The dotted line represents Fermi level.

### Conclusions

We have synthesized a novel zirconium-organic molecular porous material, CAUMOF-12, containing intermolecular hydrogen bonds through a hydrothermal reaction. The structure of the reported material has been determined by single-crystal X-ray diffraction. CAUMOF-12 exhibits a pseudo-three-dimensional open-framework structure with void space attributed to intermolecular interactions. The existence of the intermolecular interactions within the framework of CAUMOF-12 is successfully confirmed by calculations. The material reveals a differential gas adsorption property and high thermal stability. The reported compound also shows a reversible dehydration/rehydration phenomenon as well as facile ligand exchange reactions. 1-phenylnaphthalene is exclusively obtained from the reaction of CAUMOF-12 with excess phenylacetylene.

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### Notes and references

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- † Electronic Supplementary Information (ESI) available: X-ray crystallographic file in CIF format, experimental and calculated powder XRD patterns, <sup>1</sup>H and <sup>13</sup>C NMR, infrared and UV-Vis spectra, pore size distribution plot, and band structure for CAUMOF-12, and GC-MS and NMR spectra for the oligomerization products of phenylacetylene. See DOI: 10.1039/b000000x/

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