Abstract: Solvothermal reactions of a predesigned amphiphilic ligand, 4′-tert-butyl-biphenyl-3,5-dicarboxylate (BBPDC), with Zn(NO₃)₂, Co(NO₃)₂, and Cu(NO₃)₂ gave rise to three isostructural mesh-adjustable molecular sieves (MAMSS), MAMS-2, MAMS-3, and MAMS-4, respectively. The three new MAMSSs all exhibit temperature-tuned molecular sieving effect. There exists a linear relationship between mesh size and temperature, \( D = D₀ + αT \) (\( D₀ \), mesh size at temperature \( T \); \( D₀ \), mesh size at 0 K; and \( α \), constant). Constants \( D₀ \) and \( α \) are characteristics of a ligand in a certain structure, independent of the choice of metal. As a result, all of the three MAMSSs based on the BBPDC ligand have a \( D₀ \) of 2.83 and an \( α \) of 0.0073.

Introduction

Molecular sieves are porous materials that can selectively adsorb molecules on the basis of their sizes. They have been widely used in shape/size selective catalysis and separation. Conventionally, molecular sieves are made of inorganic zeolites. Due to the rigidity of the bonds in such materials, a molecular sieve is made with a fixed mesh size. This is beneficial when the mesh size precisely fits the separation needs. However, when the size difference of the two gases is very small, a molecular sieve with the precise mesh size is not always readily available. In such cases, mesh-adjustable molecular sieves (MAMSSs) that can always meet the separation needs are highly desirable.

In order to make a MAMS, two factors—permanent porosity and flexibility of the pores—must be taken into account. Although a titanasilicate zeolite was reported to possess discrete mesh sizes based on the degree of dehydration of this material at various temperatures, these two factors would seem irreconcilable for inorganic zeolites due to their robust frameworks.

As a new type of zeolitic analogues, porous metal—organic frameworks (MOFs) have in the past decade become a burgeoning research field due to their potential applications in gas storage, catalysis, magnetism, and gas separation. In particular, the dynamic features of porous MOFs have distinguished themselves from traditional inorganic zeolites and afforded the possibility to construct frameworks with flexible pores.

Recently, we reported the first MOF-based mesh-adjustable molecular sieve, MAMS-1, built from the amphiphilic ligand 5-tert-butyl-1,3-benzenedicarboxylate (BBDC) (scheme 1a). The mesh range of MAMS-1 falls between 2.9 and 5.0 Å. When the temperature is precisely controlled, any mesh size within this range can be accurately attained. In addition, a linear relationship between mesh size and temperature, \( D = D₀ + αT \) (eq 1: \( D \), mesh size at temperature \( T \); \( D₀ \), mesh size at 0 K; and \( α \), constant).

Scheme 1. (a) 5-tert-Butyl-1,3-benzenedicarboxylate (BBDC) and (b) 4′-tert-Butyl-biphenyl-3,5-dicarboxylate (BBPDC)

and α, constant), was discovered. Moreover, mechanistic studies of the molecular gating effect of MAMS-1, which is controlled by the tert-butyl groups of the BBDC ligand, suggest that D0 and α can be tuned by ligand design. This implies the possibility of a MAMS that will be versatile in gas separation even at ambient temperatures. In order to test the feasibility of the hypothesis and explore new MAMSs for gas separation, herein we present a new ligand 4’-tert-butyl-biphenyl-3,5-dicarboxylate (BBPDC) (Scheme 1b), which has one more phenyl ring than BBDC. As expected, solvothermal reactions of BBPDC with \( \text{Zn(NO}_3\text{)}_2 \), \( \text{Co(NO}_3\text{)}_2 \), and \( \text{Cu(NO}_3\text{)}_2 \) give rise to MAMS-2, MAMS-3, MAMS-4, respectively. The three new MAMSs are isostructural but quite different from the structure of MAMS-1, and all display a temperature-induced molecular sieving effect similar to that observed in MAMS-1 but with different \( D_0 \) and α values for eq 1. This also allows the assessment of the effect of the choice of metal (Zn, Co, or Cu) on the slope (α) and in (D0) of the linear relationship between mesh size and temperature; there is none. Thus, the most likely means to tune \( D_0 \) and α values in eq 1 is through ligand design.

**Experimental Section**

**General Information.** Commercially available reagents were used as received without further purification. Elemental analyses (C, H, and N) were obtained from Canadian Microanalytical Service Ltd. Thermal gravimetric analysis (TGA) was performed under \( \text{N}_2 \) on a PerkinElmer TGA 7 and a Beckman Coulter SA3100 surface area analyzer was utilized for the gas adsorption measurements. NMR data were collected on a Bruker 300 MHz spectrometer.

**Synthesis of 4’-tert-Butyl-biphenyl-3,5-dicarboxylic Acid (H2BBPDC).** To a 500 mL Schlenk flask, dimethyl-5-bromoisophtalate (2 g, 0.015 mol), 4’-tert-butyl-phenyl boronic acid (4 g, 0.015 mol), CsF (2.3 g), and Pd(PPh3)4 (0.2 g) were added. The reaction was amplified to gram quantity using multiple tubes. Anal. Calcd for MAMS-2: C 55.22%, H 5.87%, N 4.31%; found: C 55.63%, H 5.39%, N 3.86%.

**Synthesis of MAMS-3.** A mixture of 20 mg of \( \text{Zn(NO}_3\text{)}_2 \cdot \text{H}_2\text{O} \) and 10 mg of H2BBPDC in 1.5 mL of dimethylformamide (DMF) solvent was sealed in a Pyrex glass tube (i.d. 8 mm/o.d. 10 mm) and heated to 120 °C at a rate of 1 °C/min. After staying at 120 °C for 24 h, it was cooled to 35 °C at a rate of 0.1 °C/min. The resulting colorless crystals were washed with DMF twice to give pure MAMS-3 (\( \text{Zn}_2(\text{H}_2\text{O})_6(\text{BBPDC})_2 \cdot 3\text{DMF} \), yield = 85% based on H2BBPDC). The reaction was amplified to gram quantity using multiple tubes. Anal. Calcd for MAMS-3: C 57.20%, H 6.30%, N 4.17%; found: C 58.85%, H 6.16%, N 4.15%.

**Synthesis of MAMS-4.** A mixture of 20 mg of Cu(NO3)2·3H2O and 10 mg of H2BBPDC in 1.5 mL of dimethylacetamide (DMA) solvent was sealed in a Pyrex glass tube (i.d. 8 mm/o.d. 10 mm) and heated to 120 °C at a rate of 1 °C/min. After staying at 120 °C for 24 h, it was cooled to 35 °C at a rate of 0.1 °C/min. The resulting violet crystals were washed with DMA twice to give pure MAMS-4 (\( \text{Cu}_2(\text{H}_2\text{O})_6(\text{BBPDC})_2 \cdot 3\text{DMA} \), yield = 80% based on BBPDC ligand). The reaction was amplified to gram quantity using multiple tubes. Anal. Calcd for MAMS-4: C 55.43%, H 5.89%, N 4.31%; found: C 55.13%, H 5.54%, N 4.58%.

**Single-Crystal X-ray Crystallography.** Single crystal X-ray data were collected on a Bruker Smart Apex diffractometer equipped with an Oxford Cryostream low-temperature device and a fine-focus sealed-tube X-ray source (Mo Kα radiation, λ = 0.71073 Å, graphite monochromated) operating at 45 kV and 35 mA. Frames were collected with 0.3° intervals in θ and 0.05 s/frame such that a hemisphere of data was collected. Raw data collection and refinement were done using SMART. Data reduction was performed using SAINT+ and corrected for Lorentz and polarization effects. Adsortion corrections were applied using the SADABS routine.11 The structure was solved by direct methods and refined by least-squares on \( F^2 \) with anisotropic displacement parameters for SHELX-97.12 Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2Ueq of the attached atom.

**References**


In all cases solvent molecules were highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful; contributions to scattering due to these solvent molecules were removed using the SQUEEZE routine of PLATON and refined further using the data generated.12

**Gas Adsorption Measurements.** Gas adsorption measurements were performed using a Beckman Coulter SA 3100 surface area and pore size analyzer. The samples were held under a dynamic vacuum (~10^-3 torr) at 300 °C for MAMS-2 and MAMS-3, or 170 °C for MAMS-4, for 5 h to remove the free guest solvent molecules (DMF or DMA) and coordinated aqua ligands. Before the measurement, the sample was evacuated again by using the “outgas” function of the surface area analyzer for 1 h at 300 °C for MAMS-2 and MAMS-3 or 170 °C for MAMS-4. A sample of about 100.0 mg was used for N2 (99.999%) adsorption measurement and was maintained at 77 K with liquid nitrogen. In the hydrogen storage measurement, high purity hydrogen (99.9995%) and a 100.0 mg sample were used. The regulator and pipe were flushed with hydrogen before they were connected to the analyzer. The internal lines of the instrument were flushed three times by utilizing the “flushing lines” function of the program to ensure the purity of H2. Similar to the procedures used for H2 measurement at 77 K, highly pure O2 (99.99%), CO (99.99%), CH4 (99.997%), C2H4 (99.5%), iso-C4H10 (99.5%), SF6 (99.8%), and CO2 (99.99%) were used for their respective gas adsorption measurements. All the gases used for the measurements were purchased from Linde Gas LLC (Cincinnati, OH). The temperatures at 87, 113, 143, 195, and 231 K were maintained with a liquid argon bath, isopentane gas, dry ice bath, and acetonitrile, respectively.13,14 To prevent condensation of C3H6 at 195 K, the pressure range was below 110 torr; to prevent condensation of C2H4 at 231 K, the pressure range was below 466 torr; to prevent condensation of CH4, CO, and CO2 and 108 torr for C3H6; at 241 K, P0 was 757 torr for C2H4 and CO2 and 108 torr for C3H6; at 295 K, P0 was 757 torr for H2 and N2, 441 torr for CO, 18.3238(1) 18.4472(4) 18.4472(4) 18.5706(1)

### Results and Discussion

**Crystal Structure Description.** Single-crystal X-ray studies reveal that the three new MAMSs are isostructural, and all of them crystallize in the space group P3c1 (Table 1). They adopt the well-known M4(COO)4 paddlewheel as their secondary motif. However, as for cobalt, MAMS-3 represents one of the very few instances of MOFs possessing the dicobalt paddlewheel SBU.3c,15 Selected interatomic distances are listed in Table 2. The M⋯M distance varies from 2.647 for Cu to 2.951 Å for Zn. For all of the three MAMSs, the longer the M⋯M distance, the shorter the M⋯aqua distance. The trend of the interatomic distances seems to suggest that the stronger the M⋯M interaction (if any), the weaker the M⋯aqua bonding.

Each paddlewheel SBU connects four BBPDC ligands, while every BBPDC ligand connects two paddlewheel SBUs expanding into a 2-D layer with the hydrophilic paddlewheel SBUs sandwiched by two hydrophobic BBPDC layers (Figure 1). In each layer, every three paddlewheel SBUs are connected by three BBPDC ligands to form the triangular hydrophilic holes (Figure 1). In each hydrophobic cage, there are six vertical slits with the narrowest opening size of 9.71 Å.

![Figure 1. Structure of a 2-D sandwich layer.](image)

### Table 1. Crystal Data and Structure Refinement of MAMS-2, MAMS-3, and MAMS-4

<table>
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<tr>
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<th>MAMS-2 (Zn)</th>
<th>MAMS-3 (Co)</th>
<th>MAMS-4 (Cu)</th>
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<td>19.3238(1)</td>
<td>18.4472(4)</td>
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<td>19.3238(1)</td>
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<td>0.0665, 0.203</td>
<td>0.0731, 0.2152</td>
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</table>

### Table 2. Selected Bonding Distances in MAMS-2, MAMS-3, and MAMS-4

<table>
<thead>
<tr>
<th></th>
<th>MAMS-2 (Zn)</th>
<th>MAMS-3 (Co)</th>
<th>MAMS-4 (Cu)</th>
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<tbody>
<tr>
<td>M⋯M distances (Å)</td>
<td>2.951</td>
<td>2.876</td>
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<td>M⋯aqua bonding distances (Å)</td>
<td>1.869</td>
<td>1.978</td>
<td>2.016</td>
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</table>

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(atom-to-atom distance; \( \sim 6.6 \) Å when considering van der Waals radii\(^{17} \)) for MAMS-2, 9.87 Å (atom-to-atom distance; \( \sim 6.8 \) Å when considering van der Waals radii\(^{17} \)) for MAMS-3, and 9.60 Å (atom-to-atom distance; \( \sim 6.5 \) Å when considering van der Waals radii\(^{17} \)) for MAMS-4 (Figure 3a).

Every layer interacts with adjacent layers through van der Waals interaction among tert-butyl groups between the adjacent layers (Figure 4) to form a graphic structure. The triangular hydrophilic holes of each layer pack along \( c \) direction to form 1-D triangular hydrophilic channels with edge length of 7.82 Å for MAMS-2, 8.07 Å for MAMS-3, and 7.90 Å for MAMS-4 (metal atom-to-metal atom distances: \( \sim 4.9 \) Å for MAMS-2, \( \sim 4.8 \) Å for MAMS-3, and \( \sim 4.9 \) Å for MAMS-4 when considering van der Waals radii\(^{17} \)) after removal of the aqua ligands. The hydrophobic cages of each layer pack along \( c \) direction with the tert-butyl groups from the adjacent layers inserting into the vertical slits of the hydrophobic cages (Figure 3b). Viewed from the \( c \) direction, it can be inferred that the hydrophobic cages should be the main storage space for gas molecules, while the hydrophilic channels should act as passages to allow gas molecules to enter the cages through the space between the adjacent tert-butyl groups. These groups may serve as gates at the intersections of the hydrophilic channels and hydrophobic cages (Figure 5).

**Thermal Gravimetric Analysis (TGA).** As shown in Figure 6, the first 24.6% (cald, 26.0%) weight loss of MAMS-2 from about 300 to 420 °C corresponds to the loss of three unbound DMF guest molecules and two coordinated aqua ligands. Decomposition of the BBPDC ligands starts from around 430 °C and ends at 650 °C with an overall weight loss of 56.4% (cald, 57.2%). As for MAMS-3, the loss of three unbound DMA guest molecules and two coordinated aqua ligands also starts from around 300 °C and ends at about 420 °C (cald, 29.5%; found, 28.0%), which is followed by the decomposition of the BBPDC ligands with an overall weight loss of 55.0% (cald, 55.6%). Finally for MAMS-4, the loss of three unbound DMF.

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that if temperatures can be tuned continuously and precisely, any two molecules with a size difference can be separated by MAMS-2, as seen in MAMS-1.

With these considerations in mind, we decided to explore the possibility of using MAMS-2 in separations important to the petroleum refinery and petrochemical industry. Not surprisingly, MAMS-2 can distinguish methane from ethylene at 143 K, ethylene from propylene at 195 K, and propylene from isobutane at 231 K (Figure 7d-f).

Gas adsorption studies on activated MAMS-3 and activated MAM-4 reveal almost the same phenomena as discovered in MAMS-2 (see Supporting Information). The temperature-induced molecular-sieving effects of the three MAMSs are very similar to that of MAMS-1. However, unlike MAMS-1 where a significant amount of isobutane can enter the hydrophilic channels (~5.1 Å) and then enter the gas storage space at room temperature,9 the relative smaller sizes of the channels of the three new MAMSs (~4.9 Å) preclude the entrance of isobutane (kinetic diameter 5.0 Å)18 leading to very limited uptake. A drawing of temperature versus size of the molecule allowed to enter the gate is given in Figure 8. The gate opening, \( D \), and temperature, \( T \), can be related by a linear equation, \( D = 0.0073T + 2.83 \), with a correlation coefficient of 0.996 (Figure 8). This is very close to the linear equation found in MAMS-1, \( D = 0.0076T + 2.76 \). The equation can be used to predict if a gas molecule will be allowed to enter the gate at a certain temperature. It can also be used to find the best temperature for the separation of a mixture. The opening of the gates at 77 K is extrapolated to be 3.4 Å, consistent with the experimental observation that all gas molecules except hydrogen are rejected by the new MAMSs.

**Proposed Mechanism Studies.** The mechanistic details of these unprecedented temperature-controlled gas-selective adsorption phenomena can be deduced from the crystal structures and adsorption data of the new MAMSs.
These temperature-dependent molecular-gating effects do not arise from simple thermal expansion of the framework. As shown in Figure 9, the unit cell parameters of the three new MAMSs remain almost constant while the temperature changes from 113 to 273 K. This assessment is also supported by the temperature independence of powder X-ray diffraction (PXRD). Although MAMS-2 lose crystallinity after activation,19 the PXRD patterns of activated MAMS-3 and MAMS-4 reveal their framework integrities and no peak shifts have been observed when temperature changes (Figure S15, 16).

The hydrophobic cages are not accessible when the hydrophilic channels are closed, which not only can be inferred from the crystal structure, but is also consistent with gas adsorption data. An inactivated sample had very low uptake of H2 at 77 K (Figure S1, 3, 9). A partially activated sample was inactive for gas uptake. The DMF (or DMA) guests and bound aqua ligands must be removed completely for MAMSs to be active for gas adsorption.

Figure 7. Gas adsorption isotherms of MAMS-2 at six different temperatures (note: $P_0$ represents a relative standard as specified in the Experimental Section).

Figure 8. Temperature and gate-opening relationship of MAMS-2. ▲, estimated values based on experimental data; ---, linear fit.

Figure 9. Crystal lattice parameters of MAMSs at different temperatures: sideways arrows represent $a$ or $b$ axis; upright arrows represent $c$ axis; MAMS-2 (black); MAMS-3 (red); MAMS-4 (green).

The hydrophilic channels alone are not responsible for the gas uptake. In fact, they account for only a very small part of the adsorption. As the gas adsorption data at 77 K suggests, only H2 can enter the hydrophobic gas storage space, showing a significant uptake. At 77 K, other gas molecules stay in the hydrophilic channels and the uptake of these gases is very low, as shown by adsorption studies.

Gas molecules must go through the hydrophilic channel to access the hydrophobic cages. As previously mentioned, activation of the hydrophilic channels is a prerequisite for gas adsorption on MAMSs. Further evidence for the hydrophilic channels being the only passage to the main gas storage space is provided by the observation that when the kinetic diameter of the gas molecule (for example, isobutane, 5.0 Å, and SF6, 5.5 Å) exceeded the size of the hydrophilic channels (~4.8–4.9 Å considering van der Waals radii), no meaningful uptake was observed in an adsorption study (Figure S2, 8, 14) even at room temperature. The upper limit of the channel is also consistent with an adsorption study on

propylene (4.5 Å), which is allowed to enter MAMS-2 at 231 K (Figure 7). Through the interface between the hydrophobic and hydrophilic channels, gas molecules enter the hydrophobic gas storage cages, which account for the majority of gas uptake. The interface is controlled by a tert-butyl group of a BBPDC ligand which inserts in each vertical slit of the cage acting as a gate. The opening of this gate is controlled by thermal motion. When temperature is raised, the van der Waals interaction among the tert-butyl groups is reduced, leading to wider gate-opening (Figure 10). As shown in Figure 8, the gate opening, \( D \), and temperature, \( T \), have a linear relationship, \( D = 0.0073T + 2.83 \), with a correlation coefficient of 0.996 (Figure 8) for the three new MAMSs, implying that the choice of metal is irrelevant to the mesh adjustment. This is very close to the linear equation found in MAMS-1, \( D = 0.0076T + 2.76 \). This means that in the linear relationship between mesh size and temperature, \( D = D_0 + \alpha T \) (\( D \), mesh size at temperature \( T \) K; \( D_0 \), mesh size at 0 K; and \( \alpha \), constant), \( D_0 \) and \( \alpha \) are dominated by the tert-butyl group. Changing the tert-butyl group to other functional groups such as a methyl or isopropyl group can lead to different values for \( D_0 \) and \( \alpha \).

Conclusions

In summary, by designing a new amphiphilic ligand, BBPDC, and placing it in solvothermal reactions with M(NO₃)₂ (M = Zn, Co, Cu), three new graphitic MOF structures, MAMS-2, MAMS-3, and MAMS-4, generated by the packing of sand-winged layers through van der Waals interaction, were obtained. In each layer, the hydrophilic dimetal paddlewheel cluster layer is sandwiched by two hydrophobic BBPDC layers; every three dimetal paddlewheel clusters are connected to form triangular hydrophilic holes, and every six triangular hydrophilic holes are enclosed to form a hydrophobic cage which serves as the main space for gas storage. Packing of the sandwiched layers generates one-dimensional triangular hydrophilic channels, every six of which surround the hydrophobic cages, which are not accessible without activation. Gas molecules enter the hydrophobic gas storage cages through the hydrophilic channels, and gates in the hydrophobic/hydrophilic interface. The gates are formed by the BBPDC groups inserted in the vertical slits of the hydrophobic cages via van der Waals interaction, which is readily weakened by thermal motion. As temperature increases, the gates of the new MAMSs open linearly, giving rise to molecular sieves with adjustable meshes that can separate any two gases with kinetic diameters in the range of 2.9–4.6 Å, corresponding to the size limits of most commercially relevant gases. There exists a linear relationship between mesh size and temperature, \( D = D_0 + \alpha T \) (\( D \), mesh size at temperature \( T \) K; \( D_0 \), mesh size at 0 K; and \( \alpha \), constant), \( D_0 \) and \( \alpha \) are only related to the tert-butyl group and are not affected by the choice of metal. Changing the tert-butyl group to other functional groups such as methyl group or isopropyl group is expected to lead to different values for \( D_0 \) and \( \alpha \).

Acknowledgment. This work was supported by the U.S. Department of Energy (DE-FC36-07GO17033) and the U.S. National Science Foundation (CHE-0449634). H.-C.Z. acknowledges the Research Corporation for a Cottrell Scholar Award, and Air Products for a Faculty Excellence Award.

Supporting Information Available: Crystallographic information files (CIFs) of MAMS-2, MAMS-3, MAMS-4, gas adsorption isotherm graphics, and PXRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.