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**Hysteretic Gas and Vapor Sorption in Flexible Interpenetrated
Lanthanide-based Metal-Organic Frameworks with Coordinated
Molecular Gating via Reversible Single-Crystal to Single-Crystal
Transformation for Enhanced Selectivity**

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Abstract

A series of flexible 3-fold interpenetrated lanthanide-based metal organic frameworks (MOFs) with formula $[\text{Ln}(\text{HL})(\text{DMA})_2] \cdot \text{DMA} \cdot 2\text{H}_2\text{O}$ where $\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Er}$; $\text{DMA} = \text{dimethylacetamide}$ and $\text{H}_4\text{L} = 5,5'-(2,3,5,6\text{-tetramethyl-1,4-phenylene})\text{bis}(\text{methylene})\text{bis}(\text{azanediyl})\text{diisophthalic acid}$, have been prepared. $[\text{Sm}(\text{HL})(\text{DMA})_2] \cdot \text{DMA} \cdot 2\text{H}_2\text{O}$ was studied as an exemplar of the series. The activated $\text{Sm}(\text{HL})(\text{DMA})_2$ framework exhibited reversible single-crystal to single-crystal (SCSC) structural transformations in response to adsorption and desorption of guest molecules. X-ray single crystal structural analysis showed that activation of $[\text{Sm}(\text{HL})(\text{DMA})_2] \cdot \text{DMA} \cdot 2\text{H}_2\text{O}$ by heat treatment to form $\text{Sm}(\text{HL})(\text{DMA})_2$, involves closing of $13.8 \times 14.8 \text{ \AA}$ channels with coordinated DMA molecules rotating into the interior of the channels with a change from *trans* to *cis* Sm coordination and unit cell volume shrinkage of $\sim 20\%$, to a void volume of 3.5% . Solvent exchange studies with CH_2Cl_2 gave $[\text{Sm}(\text{HL})(\text{DMA})_2] \cdot 2.8\text{CH}_2\text{Cl}_2$ which, at 173 K , had a structure similar to *trans*- $[\text{Sm}(\text{HL})(\text{DMA})_2] \cdot \text{DMA} \cdot 2\text{H}_2\text{O}$. CH_2Cl_2 vapor sorption on activated *cis*- $[\text{Sm}(\text{HL})(\text{DMA})_2]$ results in gate opening and the fully loaded structure has a similar pore volume to *trans*- $[\text{Sm}(\text{HL})(\text{DMA})_2] \cdot 2.8\text{CH}_2\text{Cl}_2$ structure at 173 K . Solvent exchange and heat treatment studies also provided evidence for intermediate framework structural phases. Structural, thermodynamic and kinetic aspects of the molecular gating mechanism were studied. The dynamic and structural response of the endothermic gate opening process is driven by the

enthalpy of adsorption, entropic effects and Fickian diffusion along the pores produced during framework structure development thus relating structure and function of the material. Exceptionally high CO₂ selectivity was observed at elevated pressure compared with CH₄, H₂, O₂ and N₂ due to molecular gate opening of *cis*-[Sm(HL)(DMA)₂] for CO₂, but not for the other gases. The CO₂ adsorption induced structural transformation of *cis*-[Sm(HL)(DMA)₂] to *trans*-[Sm(HL)(DMA)₂] and hysteretic desorption behavior allows capture at high pressure, with storage at lower pressure.

1. INTRODUCTION

Metal-organic frameworks (MOFs)¹⁻⁴ are a subclass of porous coordination polymers, which have shown great potential for applications in gas storage⁵⁻⁷, gas separation⁸⁻¹⁰, sequestration^{9,11,12}, luminescence^{13,14}, catalysis^{15,16}, magnetism¹⁷, and biomedicine.^{18,19} MOFs have extensive structural variability due to the availability of a wide range of both the organic and inorganic components, which can be used in various approaches including appropriate structure-predicting design,²⁰⁻²² organic group functionalization²³⁻²⁶, and post-synthesis modification.^{27,28} In addition to the structural variability, framework flexibility is also a distinguishing characteristic compared with other porous materials²⁹, which is derived not only from the organic linker, but also from variable coordination geometry. The flexibility of MOFs can be observed as single-crystal to single-crystal (SCSC) transformations in response to guest removal and reintroduction without losing their structural integrity.³⁰ These interesting structural transformations of MOFs involve bonds forming and breaking,³¹ dimensionality increasing and decreasing³², unit cell volume expansion and contraction,³³ layers slipping³⁴ and interpenetrated networks shifting,³⁵ accompanied by a change of porosity. In contrast, structural flexibility often gives rise to the loss of framework long-range order during the activation procedure of ‘as-synthesized’ MOFs, which involves removal of disordered guest molecules in the framework. Several strategies have been developed to preserve the permanent porosity in MOFs, such as supercritical carbon dioxide activation³⁶ and freeze drying methods.³⁷

Structural interpenetration may occur in the crystal growth process and may stabilize the framework, while frequently involving the degradation or even disappearance of porosity. Despite being unpredictable, intriguingly, some reports showed that the occurrence and shifting degree of interpenetration in MOFs can be artificially controlled by modulating the synthesis methodology.³⁸⁻⁴¹ In this sense, interpenetration in flexible MOFs can be a reasonable approach for meeting the systematic stability requirement in response to removal of guest molecules. In addition to these novel discoveries, in some cases, interpenetration can also enhance the gas selectivity by better overlap of attractive potential fields or adsorption induced structural transformation during the sorption process.^{42,43}

The introduction of flexibility into metal–organic frameworks is also a potentially effective method for enhancing gas selectivity by making use of both the adaptable framework and specific interactions with guests.^{29,38,44-46} In recent years, a number of flexible interpenetrated MOFs have presented favorable gas separation capacity, involving gas-induced structural transformation mechanisms, such as breathing and gate-opening effects.^{38,47-50} These structural transformation phenomena can be observed both at low/high pressure and at low/ambient temperature, usually along with a stepwise and/or hysteretic sorption^{34,38,45-47,51,52} to enhance the selectivity of a certain gas over others.^{31,42,53,54} Although molecular simulation methods have been widely adopted to fill the gaps left by poor crystal data,^{55,56} there are still only few reports providing details of specific structural transformations during the gas

sorption process. Thus, it is desirable and challenging to build precise relationships between the structural transformations and sorption behaviors to link structure and function.

Lanthanides have large coordination spheres and variable coordination geometries. When coupled with flexible ligands, lanthanides provide the possibility for the synthesis of MOFs with both flexible frameworks and coordination geometries, potentially giving both structural and chemical diversity. A wide range of MOFs have been made with rigid tetracarboxylate linker ligands, for example, the isostructural NOTT 100-109 series, which have unsaturated copper centers when activated.^{57,58} A new long tetracarboxylate ligand, H_4L , (= 5,5'-(2,3,5,6-tetramethyl-1,4-phenylene) -*bis*(methylene)-*bis*(azanediyl) diisophthalic acid), which has rotational freedom around the $-CH_2-NH-$ bonds between aromatic groups providing flexibility has been synthesized (Scheme S1) and used to prepare a series of isostructural flexible 3-fold interpenetrated lanthanide-based MOFs ($[Ln(HL)(DMA)_2] \cdot DMA \cdot 2H_2O$) with three-dimensional networks and one-dimensional channels. The ligand has amine groups that decorate the pore walls, and may influence the adsorption and selectivity for CO_2 . On removal of the guest molecules, coordinated DMA molecules rotate to close the channel and act as a molecular gate. To the best of our knowledge, these MOFs are the first materials where a coordinated molecule serves as a rotational molecular gate for a pore channel. In addition to the above SCSC transformation, this material also exhibits an

intermediate framework structure in responding to chloroalkane molecules (CH_2Cl_2 , CHCl_3 and $\text{C}_2\text{H}_4\text{Cl}_2$) regardless of its original framework structural state ‘as synthesized’ $\text{trans-}[\text{Sm}(\text{HL})(\text{DMA})_2]\cdot\text{DMA}\cdot 2\text{H}_2\text{O}$ or activated $\text{cis-}[\text{Sm}(\text{HL})(\text{DMA})_2]$. Importantly, we use CO_2 gas as a molecular adsorption probe to perform this structural transformation process and provide thermodynamic and kinetic evidence to further understand the mechanism associated with the stepwise and hysteretic sorption. Moreover, the CH_2Cl_2 adsorption isotherms show analogous stepwise and hysteretic sorption characteristics. X-ray diffraction results provide a detailed description of the structural transformation during the sorption process. Stepwise and hysteretic CO_2 adsorption characteristics contrast with the low uptakes of CH_4 , H_2 , O_2 and N_2 , giving exceptionally high selectivity at high pressure.

2. EXPERIMENTAL SECTION

2.1 Materials used

All reagents and solvents were commercially available and further details are given in Supporting Information.

2.2 Materials Synthesis

Synthesis of the ligand

The tetracarboxylate linker used for the synthesis of the series of MOFs is shown in Scheme 1 and the synthesis route is given in Supporting Information.

Scheme 1. (5,5'-(2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene) bis(azanediyl) diisophthalic acid (H₄L)

Synthesis of diethyl 5-aminoisophthalate: 5-aminoisophthalic acid (18.12 g, 0.1 mol) was dissolved in 200 mL of anhydrous ethanol and then 20 mL of concentrated H₂SO₄ was added to the solution. The solution was stirred under reflux for 12 h at 373 K. The pH value was adjusted to 7.0 using a 10 wt% Na₂CO₃ aqueous solution and this was followed by a filtration step. The organic solvent was removed from the filtrate using a rotary evaporator and the crude product was extracted with diethyl ether. The organic layer was then dried with Na₂SO₄, and the solvent was removed with a rotary evaporator. The resulting product was dried under vacuum at 338 K (19.50 g, 82% yield).

Synthesis of 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene:

1,2,4,5-tetramethylbenzene (13.44 g, 0.1 mol) and paraformaldehyde (6.00 g, 0.2 mol) were added to 60 mL of HBr/HOAc (33 wt%) aqueous solution and stirred at 358 K until a white solid precipitate was observed. The solution was kept at 358 K for 20 min and was then heated to 368 K for 12 h. 100 mL of deionized water was added into the above solution. The resulting product obtained after filtration was washed with deionized water and air-dried at 338 K (26.50 g, 83% yield).

Synthesis of 1: tetraethyl 5,5'-(2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene) bis(azanediyl)diisophthalate.

Diethyl 5-aminoisophthalate (7.12 g, 30.0 mmol) was dissolved in 100 mL acetonitrile, followed by the addition of 5.53 g (40.0 mmol) K₂CO₃. The solution was cooled below 283 K in an ice water bath prior to the drop-wise addition of 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (4.80 g, 15.0 mmol, in 150 mL acetonitrile). After the addition, the solution was kept below 283 K for 1 h and stirred for 16 h at room temperature. The solvent was removed under vacuum. The crude product was extracted with CHCl₃ and washed with H₂O several times. The organic layer was then dried with Na₂SO₄, and the solvent was removed with a rotary evaporator. Recrystallization of the crude solid in ethyl acetate and methanol afforded a white product. This product was dried under vacuum at 338 K (6.20 g, 65% yield). ¹H NMR (600 MHz, CDCl₃): δ (ppm): 8.05 (s, 2H), 7.50 (s, 4H), 4.40 (m, 8H), 4.34 (d, 4H), 3.76 (s, 2H), 2.32 (s, 12H), 1.41 (t, 12H), See Supporting Information, Figure S1.

Synthesis of 2: 5,5'-(2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene) bis(azanediyl) diisophthalic acid (H₄L).

150 mL NaOH (2 M) aqueous solution was added to the solution of **1** (6.20 g, 9.80 mmol) in 200 mL methanol/tetrahydrofuran (THF) (1:1 v/v) and the solution was stirred under reflux for 24 h at 373 K. The organic solvent was removed with a rotary evaporator at 338 K. The pH value was adjusted to 3-4 using concentrated HCl and a pale yellow precipitate formed. The resulting solution was cooled overnight at 278 K and the precipitate was collected by filtration, washed with water and diethyl ether, and then dried under vacuum at 338 K (4.85 g, 95% yield). ¹H NMR (600 MHz, DMSO-*d*₆): δ (ppm): 12.96 (b, 4H), 7.73 (s, 2H), 7.49 (d, 2H), 6.11 (s, 2H), 4.19 (s, 4H), 2.25 (s, 12H), see Figure S2. IR data (KBr, cm⁻¹): 3409 (b), 2923 (w), 1711 (w),

1682 (m), 1606 (s), 1508 (w), 1428 (w), 1382 (w), 1297 (w), 1262 (m), 1210 (w), 1096 (w), 992 (w), 798 (w), 762 (m), 674 (m), see Figure S3.

Synthesis of the Ln-MOFs

A mixture of the organic ligand H₄L (0.10 mmol) and Ln(NO₃)₃·6H₂O (0.20 mmol) (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er) and a mixed solvent (DMA/H₂O, 10/2 mL for La³⁺ complex, DMA/H₂O, 6/6 mL for Ce³⁺ and Pr³⁺ complex and 6/6 mL with 2 drops of HNO₃ for the other metal ion species) was placed in a Teflon-lined stainless steel autoclave (20 mL) and heated at 373 K for 3 days.

Characterization data for the full series of isostructural flexible 3-fold interpenetrated lanthanide-based metal organic frameworks (MOFs) with formula [Ln(HL)(DMA)₂]·DMA·2H₂O where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Er; and H₄L = 5,5'-(2,3,5,6-tetramethyl-1,4-phenylene)-bis(methylene)-bis(azanediyl) diisophthalic acid, are given in Supporting Information, Section 1.3.2. The data for *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O are given below.

[Sm(HL)(DMA)₂]·DMA·2H₂O: Yield: 0.039 g (42%) based on H₄L. Elemental analysis for C₄₀H₅₈N₅SmO₁₄ (M_r = 965.26) (%): calcd: H 5.85, C 49.77, N 7.26; found: H 5.51, C 48.75, N 7.12. IR data (KBr, cm⁻¹): 3436 (b), 2917 (w), 2847 (w), 1617 (s), 1537 (s), 1432 (m), 1382 (m), 1283 (w), 1258 (w), 1147 (w), 1099 (w), 1052 (w), 1024 (w), 780 (m), 723 (w), 666 (w), 596 (w), See Figure S5.

2.3 Characterization Methods used

C, H, and N analyses were carried out on an Elementar Analysensysteme Vario EL III elemental analyzer. ¹H NMR spectra were recorded on a Bruker AVANCE III (600 MHz) spectrophotometer. Infrared spectra were recorded a Thermo Fisher Nicolet 6700 FTIR Spectrometer in transmittance mode. Thermogravimetric analysis (TGA) was obtained using a Netzsch STA 449 F3 unit under a flow of nitrogen (20

mL min⁻¹) at a heating rate of 10 K min⁻¹ under a nitrogen atmosphere in the temperature range 303–1073 K. SEM micrographs were taken using a Hitachi S-4800 scanning electron microscope with an accelerating voltage of 3 kV.

Powder X-ray Diffraction (PXRD)

Measurements were carried using a Bruker axs D8 Advance $\theta/2\theta$ diffractometer equipped with CuK α ($\lambda = 1.5418$ Å), with a scan speed of 2° min⁻¹ and a step size of 0.02° in 2θ at room temperature. The variable temperature experiments were performed using a PANalytical X'Pert PRO MRD diffractometer with CuK α radiation ($\lambda = 1.5418$ Å) fitted with an Anton Parr HTK1200 oven between 303 and 573 K under static air. The powder patterns were recorded with a PIXcel3D detector in the range 5–20° (2θ) with a scan speed of 2° min⁻¹ and a step size of 0.02° in 2θ . The temperature ramp between two profiles was 10 K min⁻¹ and the holding time for each temperature was 5 min before the profiles were recorded.

Single crystal X-ray diffraction

Single crystal X-ray diffraction data were collected on a Bruker Smart CCD diffractometer using a ω -scan method with graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) at 293 K. Absorption corrections were collected using multi-scan technique. The structures were solved by direct methods and developed by difference Fourier techniques using the SHELXTL software package.

Crystal data

Trans-[Sm(HL)(DMA)₂]·DMA·2H₂O: C₃₆H₄₃N₄O₁₀Sm, $M = 842.09$ g mol⁻¹, monoclinic, space group: C2/c, $a = 32.84(3)$, $b = 8.998(8)$ Å, $c = 34.21(3)$ Å, $T = 293$ K, $V = 9119(14)$ Å³, $\beta = 115.564(11)^\circ$, $Z = 8$, total reflections = 22613, independent reflections = 7876, $GOF = 1.049$, $R_1[F_0 > 2\sigma(F_0)] = 0.0639$, $wR_2 = 0.1432$ for all data (see Table S2).

***Cis*-[Sm(HL)(DMA)₂]:** C₃₆H₄₃N₄O₁₀Sm, M = 842.09 g mol⁻¹, monoclinic, space group: C2/c, *a* = 32.14(2), *b* = 9.156(6) Å, *c* = 26.864(18) Å, β = 112.859(7)°, T = 293 K, *V* = 7285(8) Å³, *Z* = 8, total reflections = 21958, independent reflections = 6376, *GOF* = 1.051, *R*_I[*F*₀ > 2σ(*F*₀)] = 0.0625, *wR*₂ = 0.1434 for all data (see Table S2).

***Trans*-[Sm(HL)(DMA)₂]·2.8CH₂Cl₂ (173 K):** C₃₆H₄₃N₄O₁₀Sm, M = 842.09 g mol⁻¹, monoclinic, space group: C2/c, *a* = 32.599(5), *b* = 8.8449(14) Å, *c* = 26.246(8) Å, β = 116.457(2)°, T = 173(2) K, *V* = 8840(3) Å³, *Z* = 8, total reflections = 29796, independent reflections = 7782, *GOF* = 1.048, *R*_I[*F*₀ > 2σ(*F*₀)] = 0.0507, *wR*₂ = 0.0929 for all data (Table S3).

***Trans*-[La(HL)(DMA)₂]·DMA·2H₂O:** C₃₆H₄₃N₄O₁₀La, M = 830.65 g mol⁻¹, monoclinic, space group: C2/c, *a* = 32.985(7), *b* = 8.9901(18) Å, *c* = 34.432(7) Å, β = 115.591(2)°, T = 293 K, *V* = 9209(3) Å³, *Z* = 8, total reflections = 25159, independent reflections = 8103, *GOF* = 1.127, *R*_I[*F*₀ > 2σ(*F*₀)] = 0.0554, *wR*₂ = 0.1480 for all data (see Table S4).

2.4 Adsorption measurements

a) Isotherm studies

Gas sorption isotherms were measured using an Intelligent Gravimetric Analyzer (IGA-001, Hiden Isochema, Warrington, UK). The system is an ultra-high vacuum (UHV) system comprising of a fully computer controlled microbalance with both pressure and temperature regulation systems. The microbalance had a long-term stability of ± 1 μg with a weighing resolution of 0.2 μg. The pressure transducers had ranges of 0–0.1 and 0–2 MPa. Carbon dioxide sorption at 195 K was carried out using a solid carbon dioxide–acetone bath. Gas sorption isotherms between 273 K and 333 K were obtained using a circulating water–ethylene glycol bath controlled by a computer using IGA software. The CH₂Cl₂ used to generate the vapor for the

isotherm measurements was degassed fully by repeated evacuation and vapor equilibration cycles of the liquid supply side of the vapor reservoir. The gas or vapor pressure was gradually increased to the desired value over a time-scale of ~30 s, to prevent disruption of the microbalance. Therefore, the period over which the pressure change occurred was very small compared with the adsorption kinetics allowing isotherm adsorption kinetics to be measured for each pressure step. The sample temperature was measured using a thermocouple located 5 mm from the sample. The sample was out gassed to constant weight at $< 10^{-6}$ Pa and 393 K prior to commencing adsorption measurements. Surface excess adsorption isotherms were determined for high pressure CO₂ adsorption using the buoyancy correction based on the crystallographic density for the desolvated framework material.

Saturated vapor pressures were calculated using the Antoine equation:

$$\log p_0 = A - \frac{B}{T + C} \quad (1)$$

where p_0 is the saturated vapor pressure (Torr), T is the temperature (°C), and A, B, and C are adsorbate dependent constants. The parameters used for each adsorptive are as follows: CH₂Cl₂ (233–313 K) (A) 7.4092, (B) 1325.9, (C) 252.6; carbon dioxide (77–303 K) (A) 7.81024, (B) 995.705, (C) 293.475.⁵⁹

b) Temperature Swing Experiments.

Kinetic studies of the framework transformation of *cis*-[Sm(HL)(DMA)₂] to *trans*-[Sm(HL)(DMA)₂] were studied. The sample was allowed to equilibrate and the amount of CO₂ adsorbed on the sample was 0.6 mmol g⁻¹ at equilibrium. Meanwhile, the circulation bath was set to the desired temperature (313, 303, 293 or 273 K). The liquid circulation bath system was equilibrated using a plug to block the liquid overflow. After the sample has reached equilibrium, the heater was removed quickly and replaced by the water bath. This operation took ~30 s and the desired sample

temperatures (293–313 K) were reached within 60–90 seconds. This time scale was very short, compared to the kinetic equilibration times for the framework transformation. The cooling to 273 K took longer, while the adsorption kinetics were much faster and followed the qualitative trend with temperature. However, the kinetics parameters were not quantifiable because of the relatively slow thermal equilibration.

3. RESULTS AND DISCUSSION

3.1 Structure Characterization

The experimental and simulated PXRD patterns of *trans*-[Ln(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er) are shown in Supplementary Information (Figures S6a and b). The peak positions for all the materials are in good agreement indicating that all the *trans*-[Ln(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O MOFs are isostructural. Single-crystal X-ray diffraction results reveal that *trans*-[Ln(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O crystallize in the monoclinic space group C2/c for Ln = Sm, La and Tb (Table S1). *Trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O was selected as a representative example of the series for detailed crystal structure analysis and adsorption studies.

The solvothermal reaction of H₄L with Sm(NO₃)₃ $\cdot$ 6H₂O in an acidic (HNO₃) mixture of H₂O/DMA (v/v = 1/1) at 373 K for 3 days afforded the colorless, needle-shaped crystals of solvated framework [Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O. The single-crystal X-ray structure of [Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O shows an infinite three-dimensional (3D) (4,4)-connected framework constructed from mononuclear

Sm^{3+} nodes each linked to four others by four ligands HL^{3-} (Figure 1). The framework structure is 3-fold interpenetrated and consists of three identical crystallographically independent networks.

As illustrated in Figure 1a, each Sm^{3+} exhibits 8-coordination through two bidentate carboxylate groups, two monodentate carboxylate groups and a pair of DMA molecules to form a 4-connected node (see Figure S11). Each ligand HL^{3-} binds to four separate Sm^{3+} centers and acts as a 4-connected linker (Figure 1b). Additionally, the middle phenyl ring of ligand HL^{3-} is significantly tilted toward end phenyl rings with dihedral angles of 78.71° and 84.94° , respectively. It is apparent that the middle aromatic ring in the linker is perpendicular to the plane consisting of the terminal aromatic groups.

Each single network consists of infinite 2D layers. For a single layer, the ligand HL^{3-} bridges two Sm^{3+} through its adjacent carboxylate groups and forms infinite helical chains along the *c*-axis. The Sm atoms are almost coplanar with Sm–Sm–Sm angles of $162.485(18)^\circ$, while the Sm–Sm distances through the carboxylate groups alternately vary from 8.6396(69) to 8.8604(79) Å (Figure 1c). The metal carboxylate chains are bridged by HL^{3-} linkers to form a 2D layer network (Figure 1d), and the remaining carboxylic binding sites of HL^{3-} ligands extend downward and upward to link the adjacent layers, leading to the formation of a 3D framework (Figure 1e). From the viewpoint of network topology, the structure is a rare binodal (4,4)-connected *umc* network.

To understand the construction of the resultant 3D 3-fold interpenetrated framework of $[\text{Sm}(\text{HL})(\text{DMA})_2]\cdot\text{DMA}\cdot 2\text{H}_2\text{O}$, it is necessary to simplify the chemical composition of the networks. The individual 3D motif can be reduced as a (4,4)-connected network if the ligand HL^{3-} is defined as a four-connected node linking to four Sm^{3+} , and the Sm^{3+} is viewed as a four-connected node (Figure 2a). A single layer shows two types of micropores viewed along the *a*-axis. However, the layer is further connected by ligands HL^{3-} to generate a 3D framework (Figure 2b) and the bigger voids (marked in Figure 2c) are divided into small ones. Similarly, the geometric construction transformation along the *b*-axis is observed (Figure S7a, Supporting Information). Furthermore, the three-dimensional framework consisting of 2D layers and HL^{3-} linkers exhibits square channels along the *c*-axis (Figures 1e and S7b).

Figure 1. X-ray crystal structures of a single network of $[\text{Sm}(\text{HL})(\text{DMA})_2] \cdot \text{DMA} \cdot 2\text{H}_2\text{O}$. The coordination environments of (a) the Sm^{3+} node and (b) ligand HL^{3-} . (c) The metal chain linked by ligands HL^{3-} along the b -axis. (d) The two-dimensional layer network formed by the metal chains and ligands HL^{3-} viewed along the b -axis. (e) The three-dimensional framework viewed along the c -axis. (Sm, orange; O, red; N, blue; C, grey; H atoms and guest molecules are omitted for clarity).

Figure 2. Simplified views of a single network of $[\text{Sm}(\text{HL})(\text{DMA})_2] \cdot \text{DMA} \cdot 2\text{H}_2\text{O}$. (a) The four-connected Sm^{3+} node and HL^{3-} node. (b) The single 2D layer and 3D network. (c) The layer and network along a -axis.

Figure 3. Simplified view of the 3-fold interpenetration framework of $[\text{Sm}(\text{HL})(\text{DMA})_2] \cdot \text{DMA} \cdot 2\text{H}_2\text{O}$.

The three independent networks are shown in red, blue and yellow, respectively. The geometrical configurations of these three networks are identical and they are related to each other by a translational vector of 9.00 Å along *b*-axis. Simplified views of the 3-fold interpenetrated framework structure are shown in Figure S8.

Due to the interpenetration in [Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O, the channels in a single 3D network are mainly filled by the other two 3D networks (Figure 3). These three interpenetrated networks are related by a single translational vector with the shortest interpenetration vector [0,1,0] of 9.00 Å. Interestingly, even after 3-fold interpenetration [Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O still possesses some void space along the *b*-axis (Figure 4a). The resulting 3-fold interpenetration framework exhibits 13.8 $\times$ 14.8 Å channels along the *b*-axis (Figure 4).

The structure of [La(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O is very similar to that of [Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O with virtually identical coordination geometries (Figure S11). The dihedral angles between the center aromatic and terminal aromatic rings were 78.75° and 84.97° for [La(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O; and 78.71° and 84.94° for [Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O. The corresponding dihedral angles for [Sm(HL)(DMA)₂] $\cdot$ 2.8CH₂Cl₂ (173 K) were 78.69° and 89.85°, respectively and this shows a small amount of conformational flexibility. The PLATON⁶⁰ pore volumes were 0.217 cm³ g⁻¹ (26.0%), 0.21 cm³ g⁻¹ (25.9%) and 0.19 cm³ g⁻¹ (24.1%) for [La(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O, [Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O and [Sm(HL)(DMA)₂] $\cdot$ 2.8CH₂Cl₂ (173 K), respectively.

3.2 Structural Transformations

In the structural transformation from *trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O to *cis*-[Sm(HL)(DMA)₂], the channels are transformed into discontinuous voids during the desolvation process. Viewed along the *b*-axis, the channel windows are clearly blocked off by the coordinated DMA molecules in *cis*-[Sm(HL)(DMA)₂]. During the desolvation process, the shortest interpenetration vector of the 3-fold interpenetration frameworks elongates from 9.00 to 9.16 Å along the *b*-axis. Viewed along the same direction, for a single network, the approximate diameter of the channel window varies from 24.2 $\times$ 14.0 to 14.6 $\times$ 14.6 Å, coupled with the intersection angle varying from 95.6° to 86.7°. For a detailed view, two C–N–C angles vary from 125.0(9)° (C(21)–N(2)–C(16)) and 125.3(8)° (C(6)–N(1)–C(9)) in *trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O to 119.6(8)° (C(21)–N(2)–C(20)) and 124.9(8)° (C(6)–N(1)–C(9)) in *cis*-[Sm(HL)(DMA)₂]. The Sm–O bond lengths for DMA and bidentate and monodentate carboxylate coordination were similar in *cis*-[Sm(HL)(DMA)₂] and *trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O.

The coordination geometries of Sm³⁺ centers change markedly and one coordinated DMA molecule in the *trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O framework rotates to the *a*-axis to close the channels along the *b*-axis in *cis*-[Sm(HL)(DMA)₂] framework with the intersection angle between two Sm–O bonds changing from 151.21° in *trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O to 76.30° in *cis*-[Sm(HL)(DMA)₂]. Therefore, the structural transformation can be described as

trans-[Sm(HL)(DMA)₂]·DMA·2H₂O changing to activated *cis*-[Sm(HL)(DMA)₂]. Generally, the structural transformations induced by guest removal are classified into three categories: crystalline to amorphous state transformations with the framework collapsing and crystal to crystal transformations with and without the cleavage and regeneration of coordination bonds.³⁰ The structural transformation of *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O upon guest removal is shown in Figure 5. Simplified views of the change in interpenetration on desolvation of *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O and resolution of *cis*-[Sm(HL)(DMA)₂] are shown in Figure S9. Single crystals remained physically intact after heating for 4 h at 393 K under vacuum, but a significant phase transformation took place and a new single-crystal form *cis*-[Sm(HL)(DMA)₂] was formed (Figures 4 and 5). The single-crystal structure determination of the desolvated *cis*-[Sm(HL)(DMA)₂] shows that the monoclinic crystal structure and C2/c space group are maintained, while the unit cell volume shrinks by ~20% (Table S2). Detailed illustrations in Figure 5 show that although no change occurs in the coordination bonds of Sm³⁺ centers, two O atoms from a monodentate carboxylate group and a DMA molecule almost exchange the coordination positions to the Sm³⁺ center and the distance between two adjacent Sm³⁺ along the *a*-axis shortens markedly, which is the leading cause of the shrinkage of unit cell volume from 9119(14) to 7285(8) Å³ (Figure 5).

a)

b)

Figure 4. Perspective views of the framework of *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O. Connolly surface representation of the 3-fold interpenetration framework structure and channels (orange) of *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O along the (a) *b*-axis and (b) *c*-axis with Connolly probe diameter 2.4 Å. (Sm, light blue, O, red; N, blue; C, grey; H, white; guest molecules are omitted for clarity).

The rotatable coordinated DMA molecule in *cis*-[Sm(HL)(DMA)₂], which is almost orthogonal to the *b*-axis, points toward the interior of the channel and cuts it into discontinuous voids (Figure 5), coupled with a significant decrease of void volume to only 3.5% calculated by PLATON,⁶⁰ much lower than that of the *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O framework (25.9%). Thus, guest removal leads to the structural transformation of *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O, in which the framework undergoes a marked change of coordination geometry for Sm³⁺ centers, which shrinks both the void and unit cell volumes, while maintaining the overall framework connectivity.

Figure 5. The structural transformations between *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O and *cis*-[Sm(HL)(DMA)₂].

3.2.1 Heat Treatment Studies

The experimental PXRD profiles for *trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O and *cis*-[Sm(HL)(DMA)₂] were in good agreement with the corresponding simulated profiles calculated from single crystal structure data (see Figure S6a). The conversion of *trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O into the fully desolvated *cis*-[Sm(HL)(DMA)₂] with heat treatment temperature (HTT) under atmospheric pressure was monitored using PXRD studies and is shown in Figures S12a and b (Supporting Information). At 433 K, close to the boiling point of DMA (439 K), strong reflections at $2\theta = 6.5^\circ$ (intermediate phase) and 7.4° (*cis*-[Sm(HL)(DMA)₂]) were observed with the former peak being absent at 473 K confirming complete transformation to *cis*-[Sm(HL)(DMA)₂] and the coexistence of three correlative structures. The first sharp weight loss occurs at 438 K in the TGA profile of *trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O (Figure S15). The phase transformation continued until the new phase of *cis*-[Sm(HL)(DMA)₂] was completely formed at 473 K, corresponding to the end of the initial weight loss in the TGA profile. It is evident that crystallinity is maintained throughout the conversion of *trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O to *cis*-[Sm(HL)(DMA)₂] and the latter is stable after cooling to ambient conditions. The *trans*-[Ln(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O (Ln= Sm, La, Pr, Nd, Eu, Gd, Tb, Dy, Er) series have very similar PXRD (Figure S6b) and TGA (Figure S16) profiles.

Guest Exchange Studies.

Scheme 2. Framework Structural Transformations involving Solvent Guest Exchange and Heat Treatment.

Figure 6. PXRD profiles for *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O, *cis*-[Sm(HL)(DMA)₂], DMA soaked *cis*-[Sm(HL)(DMA)₂], CH₂Cl₂ soaked *cis*-[Sm(HL)(DMA)₂] and CH₂Cl₂ soaked *cis*-[Sm(HL)(DMA)₂] with air drying (ad). Intensities have been rescaled to avoid the overlap of peaks.

Flexible frameworks may display intermediate structural states.^{34,45,61} This aspect was studied by solvent exchange with *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O and soaking *cis*-[Sm(HL)(DMA)₂] in various solvents (see Scheme 2 and sample nomenclature in Table S5). The DMA (B. Pt. = 439 K) soaked *cis*-[Sm(HL)(DMA)₂] sample had a similar PXRD profile to *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O (see Figure 6). Hence, the framework *trans* to *cis* structural transformation on activation by heat treatment is reversed by soaking in DMA.

The single crystal structure of *trans*-[Sm(HL)(DMA)₂] $\cdot$ 2.8CH₂Cl₂ at 173 K was very similar to the structure of *trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O (Figures S10 and S11) and hence the simulated PXRD profiles are very similar (Figure S13a). The PXRD profiles of solvent exchanged samples *trans*-[Sm(HL)(DMA)₂] $\cdot$ CH₂Cl₂ and *cis*-[Sm(HL)(DMA)₂] $\cdot$ CH₂Cl₂ were similar irrespective of the starting *cis* or *trans*-[Sm(HL)(DMA)₂] framework structure, with relatively broad peaks indicative of lower crystallinity (see Figures 6 and S13c). Drying *trans*-[Sm(HL)(DMA)₂] $\cdot$ CH₂Cl₂ and *cis*-[Sm(HL)(DMA)₂] $\cdot$ CH₂Cl₂ in air gave *trans*-[Sm(HL)(DMA)₂] $\cdot$ CH₂Cl₂-ad and *cis*-[Sm(HL)(DMA)₂] $\cdot$ CH₂Cl₂-ad, respectively. The PXRD profiles of both air dried samples were similar in terms of peak positions and only show small differences in relative intensities (Figure S13d). Air drying leads to loss of volatile CH₂Cl₂, which changes the framework structure as shown in the PXRD profiles (see Figure 6, S13c and d). The major changes in the PXRD profiles due to air drying are the increased intensity of the peak at 6.75° and the marked decrease in intensity of the peak at 6° to form a vestigial peak (see Figure S13d). The latter peak is present in the simulated profile for the single crystal structure of *trans*-[Sm(HL)(DMA)₂] $\cdot$ 2.8 CH₂Cl₂(173K) (Figure S13d) while the former is indicative of an intermediated framework structure. The PXRD profiles of both air dried samples do not have peaks at 7.4° observed for the *cis*-[Sm(HL)(DMA)₂] framework (Figure 6). Furthermore, strong PXRD peaks observed at 13.26° in *cis*-[Sm(HL)(DMA)₂] and 11.45° and 12.48° in *trans*-[Sm(HL)(DMA)₂] framework

structures were absent from the PXRD profiles of both *cis*- and *trans*-[Sm(HL)(DMA)₂] $\cdot$ CH₂Cl₂-ad (Figure 6 and S12d). It is evident that the CH₂Cl₂ exchange framework structure after air drying is independent of the initial [Sm(HL)(DMA)₂] framework structure and the *cis* and *trans* framework structures are not present in significant amounts.

The CHCl₃ and C₂H₄Cl₂ exchanged *cis*-[Sm(HL)(DMA)₂] air dried samples were also studied as well as CH₂Cl₂. These solvents are volatile (dichloromethane (B. Pt. = 312.8 K), chloroform (B. Pt. = 334.3 K), and 1,2-dichloroethane (B. Pt. = 357 K)) and have different sizes/shapes. However, the PXRD profiles for *cis*-[Sm(HL)(DMA)₂] $\cdot$ CH₂Cl₂-ad, *cis*-[Sm(HL)(DMA)₂] $\cdot$ CHCl₃-ad and *cis*-[Sm(HL)(DMA)₂] $\cdot$ C₂H₄Cl₂-ad, were very similar (Figures S13b, d and e, Supporting Information). The results above suggest that loss of volatile solvent has led to a stable intermediate phase with only vestigial peaks assignable to the *trans*-[Sm(HL)(DMA)₂] framework.

The stable intermediate framework [Sm(HL)(DMA)₂] $\cdot$ CH₂Cl₂ phase PXRD peak at 6.75° is different from the intermediate peak observed in heat treatment of *trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O (intermediate peak at 6.5°), (Figures S12a and b, and, S13d and f, Supporting Information).

3.3 Gas Sorption Properties

Flexible MOFs may display some intriguing gas and vapor sorption properties including stepwise and selective adsorption, hysteretic desorption and breathing,

gate-opening and shape-memory effects.^{34,38,45,48,51,53} Single crystal to single crystal transformations with gating characteristics for adsorption/desorption were related to sorption isotherms for flexible coordination polymers.⁴⁵ The gating mechanism involved rotation of pillars and slippage of layers and is therefore, different to the *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O to *cis*-[Sm(HL)(DMA)₂] gating mechanism. The detailed transport and structure-function relationships for the molecular gating mechanism in the *cis*-[Sm(HL)(DMA)₂] / *trans*-[Sm(HL)(DMA)₂] porous system has been investigated by relating structural, thermodynamic and kinetic aspects in order to bridge the critical gap between the macroscopic data and the transport behavior at the molecular level.

Trans-[Sm(HL)(DMA)₂]·DMA·2H₂O was heat treated at 393 K under ultra-high vacuum for 4 h to give a fully desolvated (activated) *cis*-[Sm(HL)(DMA)₂]. High pressure surface excess adsorption isotherms were measured for CO₂, CH₄, H₂, O₂ and N₂ adsorption on *cis*-[Sm(HL)(DMA)₂]. Notably, there are only very low surface excess values for CH₄, H₂, O₂ or N₂ by the material at 273 K below 20 bar (Figure 7a).

In contrast to the adsorption isotherms observed for CH₄, H₂, O₂ and N₂, the adsorption isotherm for CO₂ at 273 K exhibits a gradual step starting at a pressure of ~5 bar with surface excess uptake of ~>0.67 mmol g⁻¹ (Figure 7a). The maximum CO₂ surface excess capacity for *cis*-[Sm(HL)(DMA)₂] was 3.81 mmol g⁻¹ at 273 K and 20 bar ($p/p_0 = 0.57$), equivalent to ~3.2 CO₂ molecules per formula unit (FU).

(a)

(b)

(c)

(d)

Figure 7. Adsorption isotherms for *cis*-[Sm(HL)(DMA)₂] and variation of CO₂ thermodynamic parameters Q_{st} and ΔS as a function of amount adsorbed. (a) Comparisons of CO₂, CH₄, H₂, N₂ and O₂ surface excess sorption isotherms at 273 K; (b) CO₂ surface excess sorption isotherms at various temperatures between 273 and 333 K; (c) The isosteric adsorption enthalpies (Q_{st}) and entropies (ΔS) of CO₂ for *cis*-[Sm(HL)(DMA)₂] were calculated from the CO₂ isotherms at low CO₂ surface excess uptakes (≤ 0.5 mmol g⁻¹) for 273 – 333 K and for higher CO₂ surface excess uptakes (≥ 0.7 mmol g⁻¹) for 273 – 313 K, respectively; (d) CH₂Cl₂ sorption isotherm at 293 K; the inset figure shows the isotherm in the low pressure region at the start of gate opening.

The desorption isotherm exhibits a broad hysteresis loop, but all of the adsorbed CO₂ was released under vacuum. The presence of the distinct sorption step in *cis*-[Sm(HL)(DMA)₂] indicates that CO₂ molecules are able to induce a structural transformation to *trans*-[Sm(HL)(DMA)₂] framework. The desorption of CO₂ may be influenced by the amine groups that decorate the pore walls in the expanded framework observed in the structure of the ‘as-synthesized’ framework (*trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O). However, the Q_{st} for CO₂ adsorption on *cis*-[Sm(HL)(DMA)₂] was lower (23–29 kJ mol⁻¹) than observed for direct observation of CO₂ binding for amine functional groups (37–40 kJ mol⁻¹) in a functionalized Zn nanoporous MOF.⁶²

The CO₂ sorption isotherms were measured at various temperatures to gain insight into the sorption system (Figure 7b). Between 293 and 313 K, the CO₂ adsorption isotherms show the analogous adsorption step with different inflection points corresponding to the different structural transformation onset pressures (Figure

7b). Each structural transformation pressure is lower than the corresponding phase restoration pressure.^{34,38,45-47,52} The CO₂ sorption isotherms for temperature range 273 – 313 K show that all the steps take place at approximately the same surface excess of ~0.60 mmol g⁻¹, equivalent to ~0.5 CO₂ molecules per FU. Comparison of CO₂ sorption isotherms at 273, 293 and 303 K shows that relative pressures for the appearance of the adsorption step are similar (Figure S17). These results suggest that the structural transformation is highly dependent on temperature and pressure, but occurs at a specific amount of CO₂ adsorbed, which is related to the relative pressure for subcritical adsorption. At 333 K, no apparent adsorption step or major hysteresis was observed in the isotherm (Figure 7b). However, this does not preclude the development of a structural transformation phenomenon at higher (> 20 bar) pressures. Similar CO₂ isotherm steps are observed for other materials in the MOF series, for example, *cis*-[Tb(HL)(DMA)₂] materials (Figure S19). The CO₂ sorption isotherm at 273 K gives a maximum surface excess of ~3.81 mmol g⁻¹ (0.168 g g⁻¹) at 20 bar (p/p_0 ~0.57) and the isotherm is close to reaching a plateau although some further uptake may occur up to $p/p_0 = 1$. This surface excess uptake corresponds to an adsorbed CO₂ volume of 0.162 cm³ g⁻¹ assuming a CO₂ density of 1.032 g cm⁻³ (CO₂ liquid density at 253 K⁶³) and is equivalent to ~77% of the PLATON pore volume of *trans*-[Sm(HL)(DMA)₂].DMA·2H₂O. Small cavities exist between each two adjacent Sm³⁺ centers in the framework (Figure 4), which are possibly too small to be accessible for guest molecules, but still contribute to the void volume. Accordingly,

the framework structure at 273 K and 20 bar pressure in CO₂ atmosphere is very similar to that of the fully open *trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O framework structure.

The factors which influence isotherm hysteresis were investigated by measuring two additional CO₂ isotherms at 293 K for 0 – 1 and 0 – 5 bar, respectively (Figure S18). The maximum surface excess uptakes for both isotherms were below the amount (0.6 mmol g⁻¹ at 6 bar and 293 K), which initiates structural transformation (Figure 7b). A small amount of isotherm hysteresis was observed in both these isotherms. Thus, the flexible framework of *cis*-[Sm(HL)(DMA)₂] has minor isotherm hysteresis for the CO₂ isotherms even below the onset of the isotherm step corresponding to the structural framework transformation from *cis* to *trans*-[Sm(HL)(DMA)₂].

3.3.1 CO₂ Adsorption Thermodynamics

The isosteric adsorption enthalpies (Q_{st}) and entropies (ΔS) were calculated from the CO₂ isotherms measured at 273 – 333 K using the isostere (Figures 7c, and S20 and Table S6). The initial Q_{st} was ~29 kJ mol⁻¹ for a surface coverage of 0.1 mmol g⁻¹, which is comparable to the previously reported values (25 – 35 kJ mol⁻¹) for porous materials.⁶ A gradual decrease was observed before the adsorption isotherm step with Q_{st} decreasing to ~27 kJ mol⁻¹ at ~0.5 mmol g⁻¹. When the surface coverage increased to 0.7 mmol g⁻¹, Q_{st} decreases abruptly to ~23 kJ mol⁻¹ and simultaneously ΔS increases sharply from ~ -90 to ~ -75 J K⁻¹ mol⁻¹. This is consistent with widening

of the pores and increasing disorder. Subsequently, Q_{st} and ΔS are both relatively constant for surface coverage up to 1.5 mmol g⁻¹. The significant decrease of Q_{st} is attributed to the endothermic phase transformation process, which competes with the exothermic adsorption process.⁶⁴ The corresponding results shows that ΔS increases for the adsorption system (CO₂ – *cis*-[Sm(HL)(DMA)₂] host) and then maintains a more disordered state due to the continuous phase transformation.⁶⁵ Thus, all the above results are in good agreement with the CO₂-induced framework transformation from *cis* to *trans*-[Sm(HL)(DMA)₂].

3.4 CH₂Cl₂ Vapor Sorption Properties

The CH₂Cl₂ sorption experiments were performed to further explore the unique structural transformation and sorption characteristics (Figure 7d). Similarly, the CH₂Cl₂ sorption isotherm at 293 K also shows an adsorption step and a broad hysteric loop. At $p/p_0 = 0.04$ (CH₂Cl₂ uptake capacity of ~0.22 mmol g⁻¹), the onset of gate opening is shown by the upward isotherm curvature. Differences in the amounts adsorbed to initiate structural transformation, may be explained by the difference in molecular volume of CO₂ and CH₂Cl₂ sorbates. Adsorption increases very steeply for $p/p_0 = 0.04$ to 0.17. In this relative pressure range, *cis*-[Sm(HL)(DMA)₂] undergoes a continuous structural framework transformation. The adsorption behavior can be explained by the host–guest and guest–guest interactions and the resulting expansion of the framework and pore volume upon adsorption of CH₂Cl₂ guest molecules. At $p/p_0 = 1.00$, the CH₂Cl₂ uptake capacity was ~2.95 mmol g⁻¹, which corresponds to a total pore volume of 0.19 cm³ g⁻¹ assuming a

CH₂Cl₂ density of 1.33 g cm⁻³. This vapor adsorption total pore volume is in agreement with the PLATON pore volume of 0.19 cm³ g⁻¹ obtained for *trans*-[Sm(HL)(DMA)₂] $\cdot$ CH₂Cl₂ (173 K). The PLATON pore volume for *trans*-[Sm(HL)(DMA)₂] $\cdot$ DMA $\cdot$ 2H₂O was similar (0.21 cm³ g⁻¹). The structural transformation was reversible with hysteretic adsorption isotherm behavior. The adsorbed CH₂Cl₂ molecules were released on reducing the pressure to $p/p_0 = 0.04$ and completely desorbed under vacuum as shown in the desorption isotherm in Figure 7d.

Combining the results of X-ray analyses and CH₂Cl₂ sorption experiments, the results suggest a novel adsorption mechanism in which adsorption induces structural transformations associated with the molecular gate effect (Figure 8) leading to stepwise and hysteretic adsorption. Below $p/p_0 = 0.04$, the CH₂Cl₂ molecules adsorb without any significant structural change, consistent with the observed isotherm in the low pressure region (Figure 7d inset). The coordinated DMA molecules present in *cis*-[Sm(HL)(DMA)₂] form a gate for the channel along the ***b***-axis. At $p/p_0 = 0.04$, the threshold for gate-opening is reached, equivalent to ~ 0.2 CH₂Cl₂ molecules per FU. As the pressure increases further, the structure of the flexible framework begins to transform, coupled with the opening of the pore structure and increased CH₂Cl₂ uptake. In this pressure range, the *cis*-[Sm(HL)(DMA)₂] structure changes and closed DMA molecular gates progressively rotate to the orientation of the ***b***-axis, opening the pore channels. Furthermore, due to expansion of the *cis*-[Sm(HL)(DMA)₂] framework and increase of available void volume, the CH₂Cl₂ uptake capacity (~ 2.5 CH₂Cl₂

molecules per FU) is close to the saturation uptake capacity of ~ 2.8 CH_2Cl_2 molecules per FU for *trans*-[Sm(HL)(DMA)₂] $\cdot 2.8\text{CH}_2\text{Cl}_2$ (173 K). The small difference between the theoretical and experiment results can be explained by the presence of small cavities between each two adjacent Sm^{3+} centers (Figure 4). Therefore, it is proposed that the material exhibits virtually the same *trans* framework structure as that of *trans*-[Sm(HL)(DMA)₂] $\cdot 2.8\text{CH}_2\text{Cl}_2$ (173 K) at p/p_0 close to 1.0 in CH_2Cl_2 atmosphere.

Figure 8. The structural transformations of the channel in *cis*-[Sm(HL)(DMA)₂] induced by CH₂Cl₂ adsorption. The structural transformation giving the gate-opening behavior and the expansion of framework involves coordinated DMA molecules, which close off the channel by rotating to the *b*-axis. The DMA coordination around the Sm changes from *cis* (O–Sm–O = 76.30°) in *cis*-[Sm(HL)(DMA)₂] to *trans* (O–Sm–O = 151.21°) in *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O. The resulting framework has greater void volume and therefore, is able to accommodate more guest molecules. Three independent networks are shown in red, blue and yellow, respectively. Except for the channel along the *b*-axis and two coordinated DMA molecules, the other sections and atoms of the framework are omitted for clarity.

3.5 Adsorption kinetics for CO₂

3.5.1 Temperature swing kinetics

Adsorption kinetic profiles for CO₂ on *cis*-[Sm(HL)(DMA)₂] were measured at 20 bar for rapid cooling to 273, 293, 303 and 313 K, respectively, from initial starting conditions of 333 K and 20 bar. The CO₂ sorption isotherms indicated that the uptake capacity at 333 K and 20 bar was close to that of the threshold for structural transformation. Thus, in order to understand the adsorption kinetics during the structural transformation process, the sample was allowed to reach adsorption

equilibrium at an surface excess uptake of 0.6 mmol g⁻¹ of CO₂ at 333 K and 20 bar and this was selected as the initial state prior to structural transformation. The experimental temperature was then changed to 273, 293, 303 and 313 K, respectively. The graphs of $(M_t - M_i)/(M_f - M_i)$ versus time for adsorption of CO₂ on *cis*-[Sm(HL)(DMA)₂] are shown in Figure 9. Here, M_t is the uptake at time t, M_f is the equilibrium uptake and M_i is the initial uptake prior to temperature change. The adsorption kinetics profiles for 273, 293, 303 and 313 K become faster as the change in equilibrium amount increases with decreasing temperature. The time of $(M_t - M_i)/(M_f - M_i) = 0.5$ ($t_{1/2}$) varies from 293 s for 273 K to 4991 s for 313 K (Table S7). All the kinetic profiles were described by a double exponential model (Figure S21). The final uptakes for the kinetic profiles are compared with the isotherm uptakes in Table S8 and Figure S22. It is evident that the final uptakes from the kinetic profiles are in good agreement with the isotherm uptakes thereby confirming the accuracy of the measurements.

Figure 9. A comparison of $(M_t - M_i)/(M_f - M_i)$ versus time profiles for CO₂ adsorption on *cis*-[Sm(HL)(DMA)₂] starting at an initial surface excess uptake of 0.6 mmol g⁻¹, 20 bar and 333 K for temperature change to 273, 293, 303 and 313 K

3.5.2 Isothermal kinetics

The CO₂ isotherm up to 20 bar at 273 K covers the isotherm step for the transition of *cis*-[Sm(HL)(DMA)₂] to *trans*-[Sm(HL)(DMA)₂] frameworks and adsorption kinetics were investigated in detail to study the dynamics of the structural change and gating opening process. In the case of porous materials with essentially fixed structures, linear driving force (LDF)^{66,67}, combined barrier resistance/Fickian diffusion⁶⁸ and Fickian⁶⁹ and stretched exponential⁷⁰ models have been used to describe diffusion of molecules into these materials. However, the change in the structure of *cis*-[Sm(HL)(DMA)₂] involving gate opening in response to adsorption makes the description of the diffusion of molecules into *cis*-[Sm(HL)(DMA)₂] much more complex.

The stretched exponential (SE) kinetic model has been used to describe adsorption kinetics for a wide range of porous materials and does not require any assumptions regarding particle shape/size.⁷¹ The kinetic adsorption/desorption profiles measured in gravimetric studies are for a sample with a particle size distribution and hence, represent a distribution of adsorption characteristics. It is very difficult to control the particle size and shape in the synthesis of MOF crystals. This model is described by the following equation:

$$\frac{M_t}{M_e} = 1 - e^{-(kt)^\beta} \quad (2)$$

where M_t is the mass increase at time t during the mass relaxation process following the pressure increment, M_e is the mass increase at equilibrium for pressure increment, k is the mass transfer rate constant (s^{-1}) and t is the time (s). The exponent parameter (β) reflects the width of the distribution of relaxation times and is material dependent. The Linear Driving Force (LDF) model⁷⁰ is a special case of the SE model when $\beta = 1$ with a single relaxation time. The process is one-dimensional with a distribution of relaxation times when $\beta = 0.5$. All the kinetic profiles, both prior to and during the isotherm gating step, can be described by this kinetic model (Figures 10a, b and c and, S23, Supporting Information). It is apparent that values of the kinetic parameter (k) are faster and the exponent is smaller, prior to the isotherm step. The values for β before the isotherm step are close to that expected for a one-dimensional process.

The SE model also provides good descriptions of Fickian diffusion into porous materials⁷¹ and overlaps with these and related combined barrier resistance /diffusion models (Figure S22). The stretched exponential function is an approximation for uniformly convergent sums of exponentials.⁷² The Fickian diffusion description depends on the shape and size of particles with different equations required for specific particle shapes.⁶⁹ An average particle size/dimension has to be used and this is essentially a scaling factor.

The particles of both *trans*-[Sm(HL)(DMA)₂]-DMA·2H₂O and *cis*-[Sm(HL)(DMA)₂] have needle-like morphology and therefore, can be described as approximately cylindrical in shape. Fick's law for isothermal diffusion into a cylinder particle is given by the equation below⁷³:

$$\frac{M_t}{M_e} = 1 - 4 \sum_{n=1}^{\infty} \left(\frac{1}{\zeta_n^2} \right) \exp \left(- \frac{D \zeta_n^2 t}{a^2} \right) \quad (3)$$

where D is diffusivity ($\text{m}^2 \text{s}^{-1}$), a is radius of the cylinder (m) and ζ_n the roots of the equation $J_n(x)$ where $J_n(x)$ is the Bessel function for zero order and have values of 2.405, 5.520, 8.654, 11.792, 14.931 --- for $n = 1, 2, 3, 4, 5$ --- etc. The kinetic profile for the 4000–6000 mbar pressure increment can be described by equation (3). This indicates that diffusion along the pores is the mechanism involved in the dynamics of structural change in response to adsorption. The 6000–8000 and 8000–10000 mbar steps deviate from the above description.

Figure S23 shows that the particle shape changes as a result of adsorption of carbon dioxide. Fick's law for isothermal diffusion into a homogeneous spherical particle, which is given by the equation below⁶⁹:

$$\frac{M_t}{M_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left(\frac{1}{n^2} \right) \exp\left(-\frac{Dn^2\pi^2t}{r^2} \right) \quad (4)$$

where r is the particle radius. The kinetic profile for the 8000–10000 mbar pressure increment can be described by equation (4) as shown in Figure 10c. The subtle change in the shape of the kinetic profile is ascribed to particle fragmentation. The 6000–8000 mbar kinetic profile is intermediate between equations (3) and (4).

The crystals of *cis*-[Sm(HL)(DMA)₂] and *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O both have needle morphology with the axis of the needle being the C2 *b* crystallographic axis. CO₂ adsorption results in a change in morphology from needle shaped crystals to irregular shaped particles with more equivalent dimensions, which can be described as approximately spherical shaped particles (Figure S14). The biggest change in the transition from *cis* to *trans* [Sm(HL)(DMA)₂] framework is in the *c* crystallographic axis, which increases from to 26.864(18) to 34.21(3) Å (Table S2). The change in this dimension during adsorption is the most likely cause of the change in particle morphology due to fracturing at faults and dislocations etc., in the crystals. The Fickian diffusion coefficients calculated for pressure increment 4000–6000 mbar and 8000–10000 mbar at 273 K were $\sim 2.25 \times 10^{-14}$ and $\sim 6.8 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$, respectively. These values are much lower than those obtained for intra-crystalline

CO₂ diffusion into metal organic framework ($8 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ at 295 K for IRMOF-1⁷⁴, $1.86 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ at 273 K for CPM-5⁷⁵ and $7 \times 10^{-13} - 20 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ for diffusion along pores NPC-4 at 273 K.⁷¹ This suggests that the structural response of the framework is the rate determining step in the kinetic process.

(a)

(b)

(c)

Figure 10. Adsorption kinetic profiles for CO₂ adsorption on *cis*-[Sm(HL)(DMA)₂] at 273 K for various pressure increments (a) 1000–2000 mbar, (b) 4000–6000 mbar and (c) 8000–10000 mbar.

3.6 Selectivity Studies

Commonly, highly selective hysteretic sorption of CO₂ is found for flexible MOF materials, which have breathing or gate-opening behavior.^{53,54,76} In some cases, the initial MOF materials are non-porous without void space to accommodate the guest molecules, while the framework becomes porous by guest-induced structural transformations on increasing the pressure. A partially interpenetrated MOF NOTT-202a showed extremely high single-component gas adsorption selectivity ratios for CO₂ over other small gases, coupled with microscopic CO₂–host ordering in

the micropores below the triple point of CO₂ (216.7 K).⁴² At a higher temperature, however, the selectivity in capturing and separating CO₂ from a gaseous mixture declined sharply to ~CO₂/CH₄ of 2.92 at 273 K and 1.41 at 293 K with the disappearance of hysteresis behavior, reflecting a significant limitation in practical applications.

To examine the sorption selectivity and capability of *cis*-[Sm(HL)(DMA)₂] single-component gas sorption experiments were carried out on CO₂, CH₄, H₂, O₂ and N₂ at 273 K below 20 bar, respectively (Figure 7a). The isotherms have low uptakes with fast kinetics. In contrast, the CO₂ isotherm exhibits relatively high surface excess capacity of 3.81 mmol g⁻¹ at 20 bar with stepwise sorption and a broad hysteresis loop. At low pressure, prior to the isotherm step, there is a relatively strong initial interaction between the CO₂ molecules and the host framework as shown by the Q_{st} ~29 kJ mol⁻¹ at low surface coverage. Q_{st} decreases rapidly to ~23 kJ mol⁻¹ as the *cis*-[Sm(HL)(DMA)₂] framework expands. The large polarizability (29.11×10^{25} cm³) and quadrupole moment (4.30×10^{26} esu cm²) of CO₂^{24,54,77} interacts with the pore surface of *cis*-[Sm(HL)(DMA)₂] including the amine groups in the linker. The isosteric enthalpy of adsorption is large enough to drive the endothermic structural transformation with an increase in disorder in the system. The selectivity ratio of CO₂ in *cis*-[Sm(HL)(DMA)₂], obtained from Henry's law, was 6/1, 68/1, 24/1 and 45/1 for CH₄, H₂, O₂ and N₂, respectively (Tables S10 and 11, Figures S26 and 27). Below the isotherm step, at a pressure of 4 bar, the CO₂ isotherm shows type-I characteristics

with a plateau in conjunction with gradually decreasing selectivity ratios (Figure S25). Above this pressure, the *cis*-[Sm(HL)(DMA)₂] continues adsorbing CO₂ with the highest selectivity ratio of 17/1, 36/1, 22/1 and 22/1 for CO₂/CH₄, CO₂/H₂, CO₂/O₂ and CO₂/N₂ in this pressure range, respectively (Figure S25). Intriguingly, remarkable hysteretic desorption is maintained to 4 bar with 20% CO₂ being released, compared with 62%, 82%, 75% and 69% for CH₄, H₂, O₂ and N₂, respectively. The selectivity ratios are enhanced by the hysteretic CO₂ desorption coupled with structural transformation yielding high values at 27/1 for CO₂/CH₄, 172/1 for CO₂/H₂, 82/1 for CO₂/O₂ and 42/1 for CO₂/N₂ (Table S11). Additionally, almost all of the trapped gases can be recovered under vacuum, indicating that *cis*-[Sm(HL)(DMA)₂] can be regenerated without extra activation procedures. Thus, *cis*-[Sm(HL)(DMA)₂] exhibits high selectivity for CO₂ capture and trapping of CO₂ at ambient temperature. The selectivity at high pressure is enhanced by the framework structural transformation of *cis*-[Sm(HL)(DMA)₂] to *trans*-[Sm(HL)(DMA)₂], which gives additional CO₂ capacity, while the other gases (CH₄, N₂ etc) do not transform the *cis*-[Sm(HL)(DMA)₂] framework structure.

4. CONCLUSIONS

The flexible 3-fold interpenetrated *trans* and *cis*-[Sm(HL)(DMA)₂] structures exhibit unique and reversible structural transformations upon removal and reintroduction of guest molecules and an intermediate structural state was also observed in response to adsorption of various chloroalkane (CHCl₃, C₂H₄Cl₂ and

CH₂Cl₂) molecules. The ‘as-synthesized’ MOF *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O was fully activated at 393 K under vacuum to give a new single-crystal form *cis*-[Sm(HL)(DMA)₂]. The activated *cis*-[Sm(HL)(DMA)₂] material underwent structural transformation during adsorption of CO₂ and CH₂Cl₂. The CO₂ and CH₂Cl₂ isotherms provide comprehensive experimental evidence for the connection between the structural changes and the observed stepwise and hysteretic sorption features. A detailed characterization of the structures of *trans*-[Sm(HL)(DMA)₂]·DMA·2H₂O and *cis*-[Sm(HL)(DMA)₂] indicate that the mechanism involves coordinated DMA molecules acting as molecular gates by switching from *cis* to *trans* coordination around the Sm to open the framework thereby providing additional adsorption capacity. The endothermic structural transformation for adsorption of carbon dioxide is driven by the enthalpy of adsorption and entropic effects. Kinetic studies indicate that the mechanism involves CO₂ diffusion along the pores developed as the structural change progresses. The adsorption induced structural transformation of *cis*-[Sm(HL)(DMA)₂] and hysteretic desorption behavior allows capture of CO₂ at high pressure, but storage and transport at lower pressure. Adsorption of CH₄, H₂, O₂ and N₂ do not result in the structural transformation of *cis*-[Sm(HL)(DMA)₂]. This gives rise to exceptional adsorption selectivity of *cis*-[Sm(HL)(DMA)₂] for CO₂ over other permanent gases (CH₄, H₂, O₂ and N₂) at high pressure and ambient temperature. The reversible and selective molecular gating characteristics of these frameworks

highlight potential sorption applications such as gas separation or molecular recognition.

■ ASSOCIATED CONTENT

Details of additional characterization data for the ligands and MOFs in the series are given in section given in Supporting Information, section S1. Additional crystal structure descriptions and scanning electron micrographs are given in sections S2 and S3 respectively. Thermogravimetric analysis is presented in Section S4. Gas adsorption data are included in sections S5–S11 and includes gas adsorption isotherms, isosteric adsorption enthalpy calculation procedures, kinetic data and equilibrium selectivity information. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 952124 - 952126 and 1019366 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/.

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Notes

The authors declare no competing financial interest.

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Graphical Abstract