Electronic Supplementary Information (ESI) for

A novel topological indium-organic framework for reversible

ammonia uptake under mild conditions and catalysis

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Experimental Section

1. Materials and Equipment

All commercially available chemicals were of analytical grade and used as received. Ligand H_2L was synthesized according to our previous work (Scheme S1).¹

In(NO₃)₃·4.5H₂O (99.9%), DMF (99.5%), hydrochloric acid (36~38%), acetone (99.5%) and carbon tetrachloride (CCl₄, 98%), were purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Benzaldehyde (BA, 99%) and trimethyl orthoformate (TMOF, 99.8%) were purchased from Aladdin Biochemical Technology Co., Ltd, Shanghai, China.

Melting point was determined with an X4 digital microscope melting-point apparatus (Beijing) and uncorrected. Elemental analyses (C, H, N) were carried out with a Elementar Vario EL cube elemental analyzer. ¹H NMR spectra in solution were recorded on a Bruker AM 400 Hz spectrometer. Chemical shifts were given in ppm. IR spectra were measured in the range 4000-400 cm⁻¹ using KBr pellets on a ThermoFisher Nicolet iS10 FT-IR spectrophotometer. Thermogravimetric analyses (TGA) were performed on a NETZSCH STA 449C thermal analyzer under a nitrogen atmosphere at a heating rate of 10°C min⁻¹. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance diffractometer equipped with Cu K_{α} radiation ($\lambda = 1.5406$ Å). The gas adsorption experiment was performed on a Micromeritics 3Flex automated micropore gas analyzer. Gas chromatography with a 0.32 mm × 30 m SE-54 capillary column and flame ionization detector (FID) was used for the analysis of the catalytic experiment.

2. Synthesis of H₂L Ligand



Scheme S1. Synthetic route of 2,2'-dimethylbiphenyl-4,4'-dicarboxylic acid (H₂L).

The synthetic route of H₂L was illustrated in Scheme S1. The commercially available 4-amino-3-methylbenzoic acid reacting with potassium iodide and iodine in 20% H₂SO₄ solution gave 3-methyl-4-iodobenzoic acid (I) in a yield of 52%.² Brief treatment of I with CH₃OH produced methyl 4-iodo-3-methylbenzoate (II) in a yield of 88%.3 By use of the Ullmann reaction II was converted into dimethyl 2,2'dimethylbiphenyl-4,4'-dicarboxylate (III) in a yield of 65% under argon atmosphere.⁴ Dimethyl 2,2'-dimethylbiphenyl-4,4'-dicarboxylate (2.0 g, 6.7 mmol) was dissolved in a mixture of THF/MeOH (50 mL, V/V = 1/1, THF = tetrahydrofuran, MeOH = methanol) and 20 mL of 2 M KOH aqueous solution. Then the mixture was stirred and refluxed for 12 hours. After cool to room temperature, THF and MeOH were removed by evaporation under vacuum. The remaining solution was acidified with 1 M HCl to give a white solid of H₂L (1.6 g, 88.4%). m.p. 213-215 °C. ¹H NMR $(DMSO-d^6, 400 \text{ MHz}) \delta$: 2.05 (s, 3H, CH₃), 7.21-7.23 (d, 1H, Ph-H⁶), 7.82-7.84 (d, 1H, Ph-H⁵), 7.91 (s, 1H, Ph-H³), 12.97 (s, 1H, CO₂H). IR (cm⁻¹): 3435(w), 2981(m), 1687(s), 1605(m), 1427(s), 1307(s), 1007(w), 772(m), 759(m). Anal. Calcd. for C₁₆H₁₄O₄ (%): C, 71.08, H, 5.26. Found: C, 71.10, H, 5.22.

3. Crystal-Structure Determination

The diffraction data for **1** were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å) at room temperature. Empirical absorption corrections were applied by using the SADABS program. The structure was solved by direct method and refined by the full-matrix least-squares based on F^2 using SHELXTL-18 program.⁵⁻⁷ All non-hydrogen atoms were refined anisotropically. The atoms C3, C4, C6, C12, C13, C15 and C16 were disordered over two positions and refined with an occupancy of 0.42(3) for C3, C4, C6, C12, C13, C15 and C16, and 0.58(3) for C3A, C4A, C6A, C12A, C13A, C15A and C16A. Hydrogen atoms were placed on calculated positions (C-H 0.96 Å) and assigned isotropic thermal parameters riding on their parent atoms. Some restraints (DFIX, SIMU, ISOR and OMIT) were used during the refinement. The solvent molecules in **1** were highly disordered and could not be modeled properly, so the SQUEEZE⁸ routine in *PLATON*⁹ was applied to obtain the solvent-free structure.

The final formulae of **1** was assigned by elemental analysis, IR, TGA and singlecrystal X-ray crystallography. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as CCDC number 2258553. Crystal data, data collection and structure refinement details for **1** were summarized in Table 1. Selected bond lengths and angles of **1** are listed in Table S2.

Empirical formula	$C_{111}H_{127}Cl_6In_8N_5O_{42}$
Formula weight	3334.46
Crystal system	trigonal
Space group	<i>R</i> -3c
<i>a</i> (Å)	18.1442(4)
<i>b</i> (Å)	18.1442(4)
<i>c</i> (Å)	81.274(6)
γ (°)	120
$V(Å^3)$	23172(2)
Ζ	6
$D_{\rm c} ({\rm g}\cdot{\rm cm}^{-3})$	1.246
μ (mm ⁻¹)	1.329
F (000)	8508
Crystal size (mm ³)	$0.20 \times 0.20 \times 0.15$
θ Range (°)	2.70-25.05
Reflections collected	74873
Independent reflections	4573 [$R_{\rm int} = 0.0637$]
Reflections observed $[I > 2\sigma(I)]$	4251
Data/restraints/parameters	4573/157/280
Goodness-of-fit on F^2	1.183
$R_1/wR_2 \left[I > 2\sigma(I)\right]$	0.0799/0.1929
R_1/wR_2 (all data)	0.0847/0.1958
Max., Min. $\Delta \rho$ (e [·] Å ⁻³)	1.945, -1.201

Table S1 Crystallographic data for InOF 1

Table S2	Selected	bond	lengths	(Å)	and angles	$(^{\circ})$	for 1
	Defected	oonu	Tenguis	(1)	and angles	V	101 1

In1-O5	2.131(5)	In1-O3 ⁱⁱⁱ	2.168(6)
In2-O4 ^{iv}	2.164(7)	In2-O1W	2.093(4)
In2-O1	2.154(6)	In2-O2 ^{vi}	2.187(7)
In2-Cl1	2.461(5)	In2-O5	2.079(6)
O5-In1-O5 ⁱ	91.5(2)	O5-In1-O3 ⁱⁱⁱ	98.0(3)
O3 ⁱⁱⁱ -In1-O3 ^v	80.3(3)	O5-In1-O3 ^v	170.3(3)
O4 ^{iv} -In2-O2 ^{vi}	84.6(4)	O5-In2-O1W	173.2(19)
O5-In2-O1	89.3(2)	O1-In2-O4 ^{iv}	177.3(3)

O1W-In2-O2vi	87.9(3)	O2 ^{vi} -In2-Cl1	176.3(3)
O1W-In2-O1	93.6(2)	O1W-In2-O4 ^{iv}	86.2(3)
O1W-In2-Cl1	91.3(2)	O5-In2-O2vi	85.8(3)
O4 ^{iv} -In2-Cl1	91.8(3)	O1-In2-O2vi	92.6(3)
O5-In2-Cl1	94.8(2)	O1-In2-Cl1	91.0(3)

Symmetry codes: i) 1-*y*, 1+*x*-*y*, *z*; iii) 5/3-*x*+*y*, *y*+1/3, *z*-1/6; iv) *x*-1/3, *x*-*y*+1/3, *z*-1/6; v) 5/3-*y*, 7/3-*x*, *z*-1/6; vi) *y*, *x*, 1/2-*z*.

4. Crystal Structure of 1



Fig. S1 The asymmetric unit of 1. Displacement ellipsoids are drawn at the 30% probability level (Hydrogen atoms were omitted for clarity).



Fig. S2 Crystal structure of **1** showing the coordination environments of In1 and In2 cations (Hydrogen and the disordered atoms were omitted for clarity).



Fig. S3 The hydrogen bond in 1.

Table S3 H	Hydrogen-b	onding	geometry	(Å,	°)	for	1.
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D-H···A	d(D-H)	d(H···A)	d(D····A)	∠D-H…A		
О5-H5…Cl1 ⁱ	0.93	2.434	3.325(4)	160		
Symmetry code: i) 2- <i>y</i> , 1+ <i>x</i> - <i>y</i> , <i>z</i> .						

5. Coordination Mode of L²⁻ Ligand



Fig. S4 The coordination mode of L^{2-} ligand in 1.

Ph/Ph	CO ₂ -/Ph
87.6(3)	17.0(2), 25.8(3)

Table S4 Dihedral angles (°) for InOF 1.

Complexes	Schläfli symbol	Ref.
$[Cu_2(pzca)_2(Mo_8O_{26})_{0.5}(H_2O)_4] \cdot H_2O$ (2)	$(8^3)_4(8^6)$	10
[Zn _{1.5} (2,5-PYDC)(ATZ)(H ₂ O)] ₂ (2)	$(4 \cdot 10^2)_2(10^2 \cdot 12)_2(4^2 \cdot 10^2 \cdot 12^2)$	11
$Cu_2(S,S,R,R-cptc)(bpe)(H_2O)_2 \cdot 2H_2O$ (1)	$(8^2 \cdot 10)(8^3)(8^4 \cdot 10 \cdot 12)$	12
$[Zn_3(bcba)_2(Hbpt)_2(H_2O)_2]_n$ (4)	$(8^3)_4(8^2 \cdot 10^2 \cdot 12^2)$	13
[Zn ₃ (otba) ₂ (bidpe) ₂ (H ₂ O) ₂] (5)	$(6\cdot 8^2)_2(6^2.8^2\cdot 10^2)$	14
$[Ag_2(NO_2)_2L] \cdot H_2O$	$(8^3)_2(8^6)$ (<i>tfa</i>)	15
$[Zn_2L(HL)(SIP)(H_2O)]\cdot 4H_2O$ (3)	$(8^3)_2(8^5\cdot 10)$ (<i>tfc</i>)	16
$\{[(CH_3)_2NH_2]_2(CdL)\}$:x(solvent) (1)	(8 ³) ₂ (8 ⁶)	17
$[Ni_2(detc)(bpea)_2 \cdot 3H_2O] \cdot 3H_2O$ (8)	$(6\cdot 8^2)(6^4\cdot 8\cdot 10)(8^3)$	18
[Cu ₂ (bpp)Cl ₂] (1)	$(5\cdot 8^2)(5^2\cdot 8^3\cdot 9)(5^2\cdot 8)$	19
${[Co_2L(4,4'-bibp)(H_2O)_4] \cdot H_2O}_n(3)$	$(6^3 \cdot 8^3)(6^3)(8^3)$	20
$[Ag_{3}(HDIBA)_{2}(H_{2}O)][(P_{2}W_{18}O_{62})_{0.5}]\cdot 4H_{2}O(4)$	$(4 \cdot 8^2)(4 \cdot 8^5)(8^3)$	21
[Cu ₂ L(1,3-BDC)] _n (1)	$(4.7.9)(7.8.9)(4.7.8.9^3)$	22
[Co ₃ (3-bpha) ₂ (1,3,5-BTC) ₂ (H ₂ O) ₄]·2H ₂ O (6)	$(8^3)_4(8^4\cdot 10^2)$	23
$[Zn_{3}L_{2}(oba)_{3}(H_{2}O)_{2}]\cdot 4H_{2}O(1)$	$(6^3)_2(6^5\cdot 8)$	24
${[Cd_2(4,4'-sdb)_2(tib)(H_2O)_3] \cdot H_2O}_n(1)$	$(6\cdot 8^2)(6^4\cdot 8^2)(8^3)$	25
${[Cu_2L(1,3-bdc)_2] \cdot 2H_2O_n(3)}$	$(4 \cdot 6 \cdot 8)_2 (6 \cdot 8^4 \cdot 10)$	26
$[Mn_3L_2(bib)_2(H_2O)_4] \cdot 4H_2O$ (2)	$(6\cdot 8^2)_2(6^2\cdot 8)_2(8\cdot 10^4\cdot 12)$	27
$[Cu_6O(TZI)_3(H_2O)_9(NO_3)]_n$ ·(H ₂ O) ₁₅ (1)	$(6\cdot 8^2)_6(6^2\cdot 8^4)_3(8^3)_2$ (<i>ntt</i>) or 3,24-(<i>rht</i>)	28
[Cu ₃ (BHB)(H ₂ O) ₃]·(DMF) ₆ (H ₂ O) _{2.5} (UTSA-20)	$(4^{12} \cdot 6^8 \cdot 8^6) (zyg)$	29
[CdL2]·H ₂ O (6)	$(8^3)_2(8^5.9)$ (cda)	30
[Ni ₂ (odip)(H ₂ O) ₄ (DMF)]·DMF·2H ₂ O (1)	$(6^2 \cdot 8)_2(6^4 \cdot 8^2)$	31
$[Cd_{3}(H_{2}O)_{2}(bmp)_{2}(DMF)(BTC)_{2}\cdot 3.5H_{2}O\cdot 1.5DMF]$ (2)	$(4 \cdot 9^2)(4^2 \cdot 8^2 \cdot 9^2)_2$	32
$[Co(OBA)(L1)_{0.5}]_n$ (1)	$(4 \cdot 8^2)_2 (6^3 \cdot 8^3)$	33
[Cd ₂ L(pycy)(Cl)]·2H ₂ O (1)	$(4 \cdot 6 \cdot 8)(4 \cdot 6^2 \cdot 8^3)(6^2 \cdot 8)$	34
[Ag ₄ (bimpy) ₂ (H ₂ O) ₂ (α-SiW ^{VI} ₁₂ O ₄₀)]·2H ₂ O (3)	$(6^2 \cdot 8)_2(6^6)$	35
${[Zn_{3}(bdc)_{2}(tib)_{2}(HCO_{2})_{2}] \cdot 4H_{2}O \cdot 0.5CH_{2}Cl_{2}}_{n}(2)$	$(8^3)_2(8^6)_2(8\cdot 10^2)$	36
$[Zn_2(L^1)(dib)(H_2O)_2]_n$ (2)	$(4.10^2)(4.6.8^4)(6^2.8)$	37
$[In_8(\mu_2-OH)_6(\mu_2-H_2O)_3L_6Cl_6]$ ·5DMF·4H ₂ O (1)	$(4 \cdot 8 \cdot 10)_3 (4 \cdot 8^3 \cdot 10^2)_3 (8^3)$	This work

 Table S5
 The reported trinodal 3,3,4-connected 3D complexes.

6. FT-IR Spectra of 1



Fig. S5 The IR spectra of 1 for as-synthesized, before and after the NH₃ adsorption.



7. PXRD Pattern of 1

Fig. S6 Simulated and experimental PXRD patterns for 1.

8. Thermogravimetric Analysis of 1



Fig. S7 TGA curve for 1.

9. Gas Sorption Experiments of 1



Fig. S8 CO_2 sorption isotherms at 195 K for 1 activated with supercritical CO_2 .



Fig. S9 CO_2 and N_2 adsorption isotherms for 1 at 273 (left) and 298 K (right).



Fig. S10 Selective separation ratio of CO_2/N_2 for 1 at 273 (left) and 298 K (right).



Fig. S11 C_2H_2 , C_2H_4 , C_2H_6 and CH_4 adsorption isotherms for 1 at 273 (left) and 298 K (right).



Fig. S12 Selective separation ratio of C₂H₂/CH₄ for 1 at 273 (left) and 298 K (right).



Fig. S13 Adsorption-desorption cycles of NH₃ by 1 at 273 (left) and 298 K (right).



Fig. S14 The PXRD patterns of 1 after the adsorption-desorption cycles of NH₃.

Calculation of adsorption heat Q_{st} for NH₃ uptake using Virial model

$$lnP = lnN + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j \qquad Q_{st} = -R \sum_{i=0}^{m} a_i N^i$$

The above virial expressions were used to fit the combined isotherm data for 1 at 273 and 298 K, respectively, where *P* is the pressure, *N* is the adsorbed amount, *T* is the temperature, a_i and b_i are virial coefficients, and *m* and *N* are the numbers of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and *R* is the universal gas constant.



Fig. S15 Virial fitting of the NH₃ adsorption isotherms for **1**. Dots are experimental data; lines are fitting curves; inset is the fitting parameters.



Fig. S16 Calculated NH₃ adsorption heats (Q_{st}) of 1 via the virial method.

		0	- 1		
MOFs	Desorption	Stability	Uptake	Temperatur	Pof
	condition	Stability	(mmol/g)	e	KCI.
MIL-101/-100	25°C and	5 avalar	10/9	200 V	20
	vacuum, 30 min	5 cycles	10/8	290 K	30
Ni_acryl_TMA	RT and vacuum	5 cycles	23.5	298 K	39
InOF 1	60°C and	10 avalas	10.4	272 V	This
	vacuum, 2 h	10 cycles	10.4	2/3 K	work
NU-1000-F-60	60°C and	3 cycles	7.6	298 K	40

Table S6 Some MOFs showing reversible NH₃ uptake at 1 bar.

	vacuum, 12 h				
SION105-Eu	75°C, 30 min	5 cycles	5.7	303 K	41
JCM-1(Cl ⁻)	85°C and 5 h	6 cycles	7.2	298 K	42
LiCl@MIL-53-(OH) ₂ -	100°C and	15 cycles	33.9	298 K	43
43.4 wt%	vacuum, 2 h	5			
[BOHmim][Zn ₂ Cl ₅]@	100°C and	5 cycles	24.12	298 K	44
MIL-101(Cr)	vacuum, 12 h				
MOF-253(Al)-NiCl ₂ -	120°C and	6 cycles	18.0	298 K	45
2	vacuum, 12 h	0 cycles	10.0	270 K	15
UiO-66-Cu ^Ⅱ	120°C and	15 cvcles	16.9	273 K	46
	vacuum, 24 h	10 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	1000	2,011	
[Cu(cyhdc)]	125°C	6 cycles	18.7	273 K	47
NHMII -53	150°C and	5 cycles	5 /	208 K	38
1 111 2-1 111 2-35	vacuum, 30 min	5 Cycles	J.T	290 IX	50
$[C_{\alpha}(\mathbf{N} \mathbf{A})_{\alpha}]$	150°C and	3 oveles	17.5	298 K	18
$[Co(NA)_2]$	vacuum, 70 min	Jeyeles	17.5		40
$MOE_{303}(A1)$	150°C and	20 cycles	10 7	208 K	/0
MOT-505(AI)	vacuum, 2 h	20 cycles	19.7	270 K	77
MEM 200 (Sa)	180°C and	5 avalas	12.1	298 K	50
WITWI-500 (SC)	vacuum, 6 h	Jeycles	13.1		50
MEM 200 (A1)	200°C and	Over 50	15 7	272 V	51
MFM-300 (AI)	vacuum, 24 h	cycles	13.7	2/3 K	31
MFM-300	200°C and	Over 20	14.0/16.1/	272 V	50
(Cr/Fe/V ^{III} /V ^{IV})	vacuum, 24 h	cycles	15.6/17.3	2/3 K	52
ECUT-36	200°C, 24 h	2 cycles	6.6	273 K	53
[Ni ₂ (adc) ₂ (dabco)]	200°C and 3 h	3 cycles	12.1	295 K	54
[M(BDC)] (M =	250°C and	2 1	170/141	2 00 V	
Cu/Zn)	vacuum, 80 min	3 cycles	1/.2/14.1	298 K	22
$[M_2(dobpdc)] (M =$	250°C and	2 1		2 00 <i>W</i>	
Mg/Ni)	vacuum, 24 h	3 cycles	25.9/20.82	298 K	56

Table S7 Hydrogen bonds between NH ₃ and μ_2 -OH ⁻ /Cl ⁻ ions in 1 calculated by DF	Τ·
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D-H…A	d(D-H) /Å	d(H···A) /Å	d(D…A) /Å	∠D-H…A /°
O12-H12…N1	1.04	1.680	2.711	173
N1-H1A…Cl5	1.02	2.643	3.352	126
N1-H1B…Cl3	1.02	2.816	3.438	120
N1-H1C…Cl1	1.03	2.714	3.700	162

D-H···A	d(D-H)	d(H···A)	d(D····A)	∠D-H…A
O12-H12…N1	1.04	2.957	3.984	172
N1-H1A····Cl5	1.02	3.344	3.896	116
N1-H1B····Cl3	1.02	3.443	3.999	116
N1-H1C…Cl1	1.03	3.411	3.889	110

Table S8 The geometry data (Å, °) for 1-opt-without hydrogen-bonds.

10. DFT Calculations

DFT calculations were carried out using CP2K code (freely available at http://www.cp2k.org),57 based on the mixed Gaussian and plane-wave scheme58 and the Quickstep module.⁵⁹ The calculation used molecularly optimized Double-Zeta-Polarization (DZVP) basis set,⁶⁰ Goedecker-Teter-Hutter Valence plus pseudopotentials,⁶¹ and the Perdew-Burke-Ernzerhof (PBE)⁶² exchange correlation functional with the D3 dispersion corrections proposed by Grimme.⁶³ The plane-wave energy cutoff was 400 Ry. The calculation was performed on Gamma point only, with no symmetry constraint. Structural optimization was performed using the Broyden-Fletcher-Goldfarb-Shannon (BFGS) optimizer, until the maximum force is below 0.00045 Ry/Bohr (0.011 eV/Å). The cluster/adsorbate systems were modelled within the repeated scheme, that is, a simulation cell containing one In7 cluster and adsorbates (NH₃). 40 Å of vacuum were included in the simulation cell to decouple the system from its periodic replicas in the direction perpendicular to the surface. All atoms were relaxed until forces were lower than 0.005 eV $Å^{-1}$.



Fig. S17 Isosurface view showing physical absorption of NH₃ in 1 with (left) and without (right) hydrogen bonds.

11. Catalytic Experiments of 1



Fig. S18 Effect of reaction conditions on the catalytic property of 1: (a) Reaction time; (b) Reaction temperature; (c) Amount of catalyst; (d) The molar ratio of BA/TMOF.



Fig. S19 The recycling tests of catalyst 1.



Fig. S20 The PXRD patterns of 1 before and after catalytic reaction.

In-MOF	<i>T</i> (°C)	Catalyst	BA/TMOF	Time	Conversion	Selectivity	Dafa	
		(mmol%)	(molar ratio)	(h)	(%)	(%)	Kels.	
[In(BDC) _{1.5} (bipy)]	60-70	10	1.95:1	4	22	NA	64	
[In ₂ (OH) ₂ (BDC) ₂ (phen) ₂]	60-70	10	1.95:1	6	56	NA	64	
[In(BTC)(H ₂ O)(bipy)]	60-70	10	1.95:1	6	60	NA	64	
[In(BTC)(H ₂ O)(phen)]	60-70	10	1.95:1	6	76	NA	64	
[In ₂ (OH) ₃ (BDC) _{1.5}]	60-70	10	1.95:1	6	68	NA	65	
[In(OH)(L)]·0.3py	100	10	1.95:1	0.5	90	NA	65	
1	70	6.9	1:1.5	4	99	96	This work	

Table S9 A comparison of the catalytic property of 1 with the known InOFs.

12. References

- 1 X. He, X. Wang, T. Xiao, S. Zhang and D. Zhu, Inorg. Chem., 2021, 60, 9.
- 2 P. Pařík, J. I. Kulhánek, M. Ludwig, R. Wagner, I. Rotrekl, D. A. Drahoňovský, L. K. Meca, M. T. Šmídková, T. S. Tobrman and D. Dvořák, *Organometallics*, 2010, 29, 4135.
- 3 C. Blaszykowski, E. Aktoudianakis, C. Bressy, D. Alberico and M. Lautens, *Org. Lett.*, 2006, **8**, 2043.
- 4 A. D. Burrows, C. G. Frost, M. F. Mahon and C. Richardson, *Chem. Commun.*, 2009, 4218.
- 5 G. M. Sheldrick, Acta Cryst., 2008, A64, 112.

- 6 G. M. Sheldrick, Acta Cryst., 2015, A71, 3.
- 7 G. M. Sheldrick, Acta Cryst., 2015, C71, 3.
- 8 A. L. Spek, Acta Cryst., 2015, C71, 9.
- 9 A. L. Spek, Acta Cryst., 2009, D65, 148.
- 10 X. Wang, N. Han, H. Lin, A. Tian, G. Liu and J. Zhang, *Dalton Trans.*, 2014, **43**, 2052.
- 11 F.-H. Zhao and J.-M. Zheng, RSC Adv., 2014, 4, 56434.
- 12 L. Cui, X.-J. Luan, C.-P. Zhang, Y.-F. Kang, W.-T. Zhang, Y.-Y. Wang and Q.-Z. Shi, *Dalton Trans.* 2013, 42, 1637.
- 13 X.-Z. Li, C. Zhao, Y. Zhang, T. Luo, Y.-H. Wen and H. Xu, *Polyhedron*, 2017, 135, 60.
- 14 H. Guo, Y. Yan, X. Guo, N. Wang and Y. Qi, J. Mol. Struct., 2016, 1108, 134.
- 15 E. Kim, D. Kim, Y.-A. Lee and O.-S. Jung. J. Coord. Chem., 2014, 67, 3532.
- 16 W.-D. Li, S.-S. Chen, S.-S. Han and Y. Zhao, J. Solid State Chem., 2020, 283, 121133.
- 17 R. Xie, Q. Wang, D. Xue, Z. Zhang, Y. Zhang and J. Bai, *Chin. J. Appl. Chem.*, 2017, **34**, 1066.
- 18 Q. Yue, Y.-Y. Wang, X.-L. Hu, W.-X. Guo and E.-Q. Gao, *CrystEngComm*, 2019, 21, 6719.
- 19 Z. Hu, B. Li, W. Ju, Y. Liang and Z. Chen, J. Chem. Sci., 2016, 128, 893.
- 20 X.-Y. Dong, C.-D. Si, Y. Fan, D.-C. Hu, X.-Q. Yao, Y.-X. Yang and J.-C. Liu, *Cryst. Growth Des.*, 2016, **16**, 2062.
- 21 X.-L. Wang, R. Zhang, X. Wang, H.-Y. Lin and G.-C. Liu, *Inorg. Chem.*, 2016, 55, 6384.
- 22 Z.-G. Kong, S.-N. Guo, B. Sun and S. W. Ng, Z. Naturforsch., 2015, 70, 857.
- 23 X.-L. Wang, X.-T. Sha, G.-C. Liu, N.-L. Chen and Y. Tian, *CrystEngComm*, 2015, 17, 7290.
- 24 B.-Q. Song, C. Qin, Y.-T. Zhang, L.-T. An, K.-Z. Shao and Z.-M. Su, *Dalton Trans.*, 2015, **44**, 2844.
- 25 H. Jia, C. Wang and F. Guo, Z. Anorg. Allg. Chem., 2014, 640, 2508.

- 26 P. Wang, L. Luo, T. Okamura, H.-P Zhou, W.-Y. Sun and Y.-P. Tian, *Polyhedron*, 2012, 44, 18.
- 27 Y.-P. Li, Y. Chai, G.-P. Yang, H.-H. Miao, L. Cui, Y.-Y. Wang and Q.-Z. Shi, *Dalton Trans.*, 2014, 43, 10947.
- 28 F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko and M. Eddaoudi, J. Am. Chem. Soc., 2008, 130, 1833.
- 29 Z. Guo, H. Wu, G. Srinivas, Y. Zhou, S. Xiang, Z. Chen, Y. Yang, W. Zhou, M. O'Keeffe and B. Chen, *Angew. Chem. Int. Ed.*, 2011, **50**, 3178.
- 30 X.-L. Yang, M.-H. Xie, C. Zou, F.-F. Sun and C.-D. Wu, *CrystEngComm*, 2011, 13, 1570.
- 31 Y. Liu, Y.-K. Lu, B. Zhang, L. Hou and Y.-Y. Wang, *Inorg. Chem.*, 2020, **59**, 7531.
- 32 Y. Zhang, W. Hu, C. Rao, D. Zhou, Y. Hu, J. Jin and M. Muddassir, J. Mol. Struct., 2021, **1227**, 129538.
- 33 Y. Liu, L. Ren and G.-H. Cui, CrystEngComm, 2021, 23, 7485.
- 34 Z.-Q. Lu, Y.-Z. Li, C. Hao, Y. Ru, S.-J. Yang, N.-D. Zhang, Y.-Q. Fu, W.-L. Wu and Y. Zhou, *Chinese J. Struct. Chem.*, 2021, 40, 1122.
- 35 Y. Zheng, W. Zhou, X. Liu, G. Yuan and J. Peng, *Electrochim. Acta*, 2021, **391**, 138930.
- 36 L. Cui, B. Zhu, K. Huang, Y. Gan, Y. Li and J. Long, J. Solid State Chem., 2020, 290, 121526.
- 37 X. Zhang, Q. Yang, M. Yun, C. Si, N. An, M. Jia, J. Liu and X. Dong, *Acta Cryst.*, 2020, **B76**, 1001.
- 38 Y. Chen, F. Zhang, Y. Wang, C. Yang, J. Yang and J. Li, *Micropor. Mesopor. Mat.*, 2018, 258, 170.
- 39 D. W. Kim, D. W. Kang, M. Kang, D. S. Choi, H. Yun, S. Y. Kim, S. M. Lee, J. H. Lee and C. S. Hong, *J. Am. Chem. Soc.*, 2022, 144, 9672.
- 40 J. Liu, Z. Lu, Z. Chen, M. Rimoldi, A. J. Howarth, H. Chen, S. Alayoglu, R. Q. Snurr, O. K. Farha and J. T. Hupp, *ACS Appl. Mater. Interfaces*, 2021, **13**, 20081.

- 41 T. N. Nguyen, I. M. Harreschou, J. H. Lee, K. C. Stylianou and D. W. Stephan, *Chem. Commun.*, 2020, **56**, 9600.
- 42 J. Lee, Y. Seo, D. W. Kang, S. Park, H. Kim, J. Kim, K. Kim, C. S. Hong, D. W. Lim and E. Lee, *RSC Adv.*, 2022, **12**, 7605.
- 43 Y. Shi, Z. Wang, Z. Li, H. Wang, D. Xiong, J. Qiu, X. Tian, G. Feng, J. Wang, Angew. Chem. Int. Ed., 2022, 61, e202212032.
- 44 G. Han, C. Liu, Q. Yang, D. Liu and C. Zhong, Chem. Eng. J., 2020, 401, 126106.
- 45 Y. Wang, Y. Shi, D. Xiong, Z. Li, H. Wang, X. Xuan and J. Wang, *Chem. Eng. J.* 2023, **474**, 145307.
- 46 Y. Ma, W. Lu, X. Han, Y. Chen, I. da Silva, D. Lee, A. M. Sheveleva, Z. Wang, J. Li, W. Li, M. Fan, S. Xu, F. Tuna, E. J. L. McInnes, Y. Cheng, S. Rudić, P. Manuel, M. D. Frogley, A. J. Ramirez-Cuesta, M. Schröder and S. Yang, J. Am. Chem. Soc., 2022, 144, 8624.
- 47 B. E. R. Snyder, A. B. Turkiewicz, H. Furukawa, M. V. Paley, E. O. Velasquez, M. N. Dods and J. R. Long, *Nature*, 2023, 613, 287.
- 48 Y. Chen, B. Shan, C. Yang, J. Yang, J. Li and B. Mu, *J. Mater. Chem. A.*, 2018, **6**, 9922.
- 49 Z. Wang, Z. Li, X. G. Zhang, Q. Xia, H. Wang, C. Wang, Y. Wang, H. He, Y. Zhao and J. Wang, ACS Appl. Mater. Interfaces, 2021, 13, 56025.
- 50 P. Lyu, A. M. Wright, A. López-Olvera, P. G. Mileo, J. A. Zárate, E. Martínez-Ahumada, V. Martis, D. R. Williams, M. Dincă, I. A. Ibarra and G. Maurin, *Chem. Mater.*, 2021, **33**, 6186.
- 51 H. G. W. Godfrey, I. da Silva, L. Briggs, J. H. Carter, C. G. Morris, M. Savage, T. L. Easun, P. Manuel, C. A. Murray, C. C. Tang, M. D. Frogley, G. Cinque, S. Yang and M. Schröder, *Angew. Chem. Int. Ed.*, 2018, 57, 14778.
- 52 X. Han, W. Lu, Y. Chen, I. da Silva, J. Li, L. Lin, W. Li, A. M. Sheveleva, H. G. W. Godfrey, Z. Lu, F. Tuna, E. J. L. McInnes, Y. Cheng, L. L. Daemen, L. J. M. McPherson, S. J. Teat, M. D. Frogley, S. Rudic, P. Manuel, A. J. Ramirez-Cuesta, S. Yang and M. Schroder, *J. Am. Chem. Soc.*, 2021, **143**, 3153.

- 53 L. J. Sun, Y. L. Fan, M. J. Yin, H. P. Zhang, H. Feng, L. J. Guo and F. Luo, *Cryst. Growth Des.*, 2020, **20**, 3605.
- 54 Z. Cao, K. N. Landström and F. Akhtar, Catalysts, 2020, 10, 1444.
- 55 Y. Chen, Y. Du, P. Liu, J. Yang, L. Li and J. Li, *Environ. Sci. Technol.*, 2020, 54, 3636.
- 56 D. W. Kim, D. W. Kang, M. Kang, J. Lee, J. H. Choe, Y. S. Chae, D. S. Choi, H. Yun and C. S. Hong, *Angew. Chem. Int. Ed.*, 2020, **59**, 22531.
- 57 J. Hutter, M. Iannuzzi, F. Schiffmann and J. Van de Vondole, WIREs Comput. Mol. Sci., 2014, 4, 15.
- 58 G. Lippert, J. Hutter and M. A. Parrinello, Mol. Phys., 1997, 92, 477.
- 59 J. Van de Vondole, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, *Comput. Phys. Commun.*, 2005, 167, 103.
- 60 J. Van de Vondole and J. Hutter, J. Chem. Phys., 2007, 127, 114105.
- 61 S. Goedecker, M. Teter and J. Hutter, J. Phys. Rev. B, 1996, 54, 1703.
- 62 J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865.
- 63 P. Hapala, G. Kichin, C. Wagner, F. S. Tautz, R. Temirov and P. Jelínek, *Phys. Rev. B*, 2014, **90**, 085421.
- 64 B. Gómez-Lor, E. Gutiérrez-Puebla, M. Iglesias, M. A. Monge, C. Ruiz-Valero and N. Snejko, *Chem. Mater.*, 2005, 17, 2568.
- 65 F. Gándara, B. Gomez-Lor, E. Gutiérrez-Puebla, M. Iglesias, M. A. Monge, D. M. Proserpio and N. Snejko, *Chem. Mater.*, 2008, **20**, 72.