Supporting materials

Hexnuclear, octanuclear, dodecanuclear, hexadecnuclear polyoxomolybdenum(V)-based porous materials for selective adsorptions of gases

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Figure and Table Options

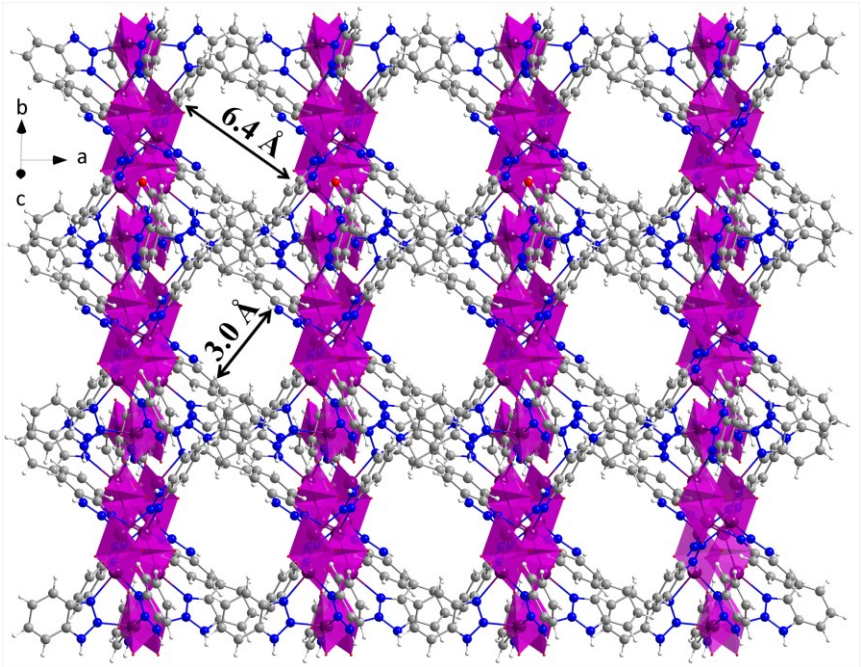

Fig. S1. Channels in **1** viewed along (0,1,1) direction with an area of 6.4×3.0 Å^2.

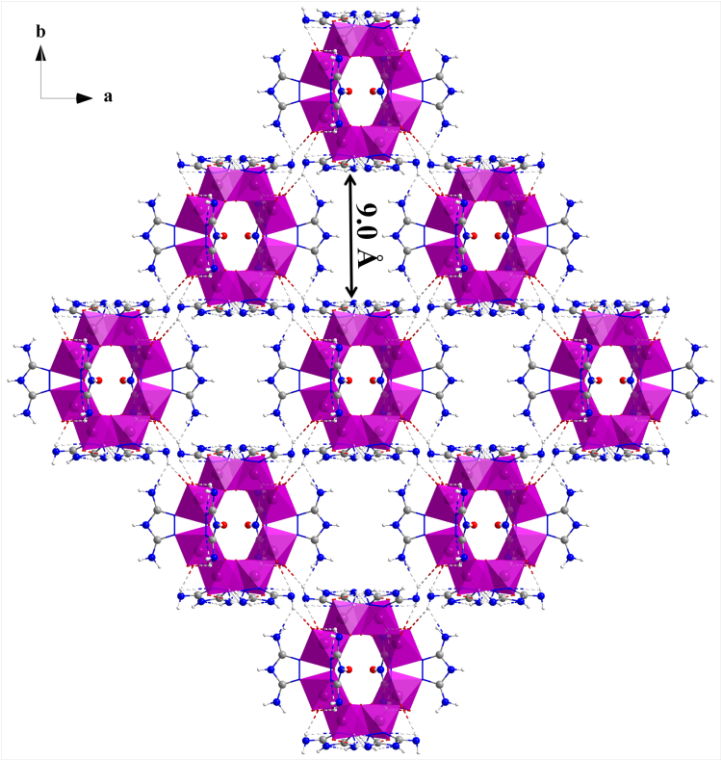

Fig. S2. Channels in **2** viewed along *c* axis with an area of 9.0 × 4.4 Å^2.

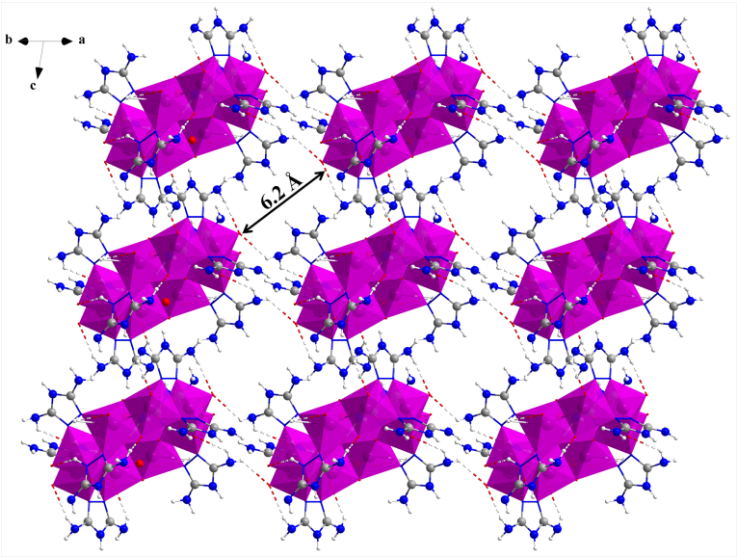

Fig. S3. Channels in **2** viewed along (1,1,0) direction with an area of 6.2×4.0 Å^2.

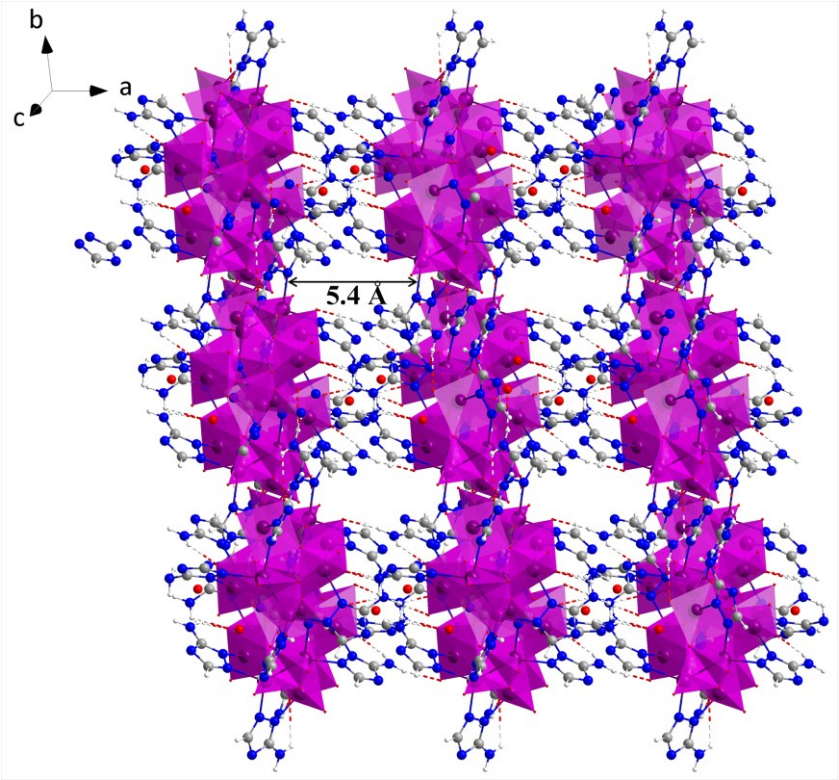

Fig. S4. Channels in **3** viewed along (1,1,1) direction with an area of 5.4×3.4 Å^2.

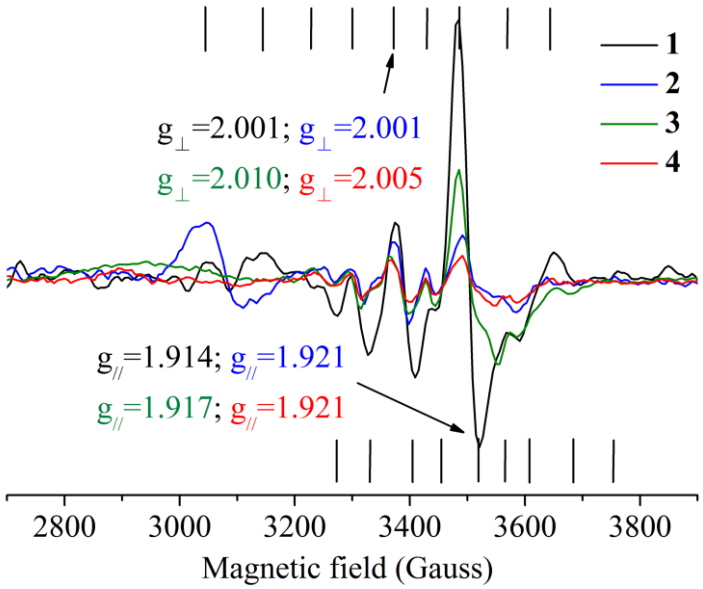

Fig. S5. Solid EPR spectra of **1** – **4** at 110 K respectively.

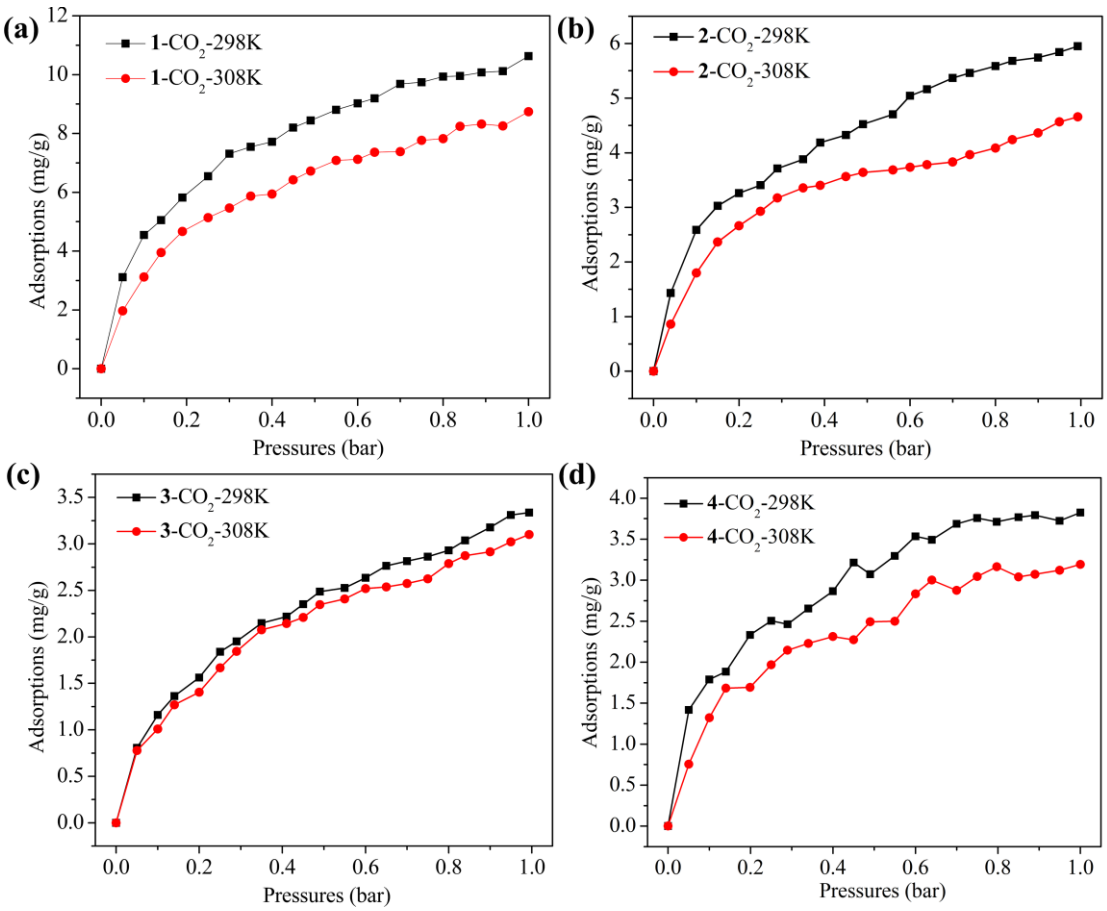

Fig. S6. CO_2 adsorption isotherms for **1** (a), **2** (b), **3** (c) and **4** (d) at different temperatures (298 and 308 K) under the low pressure respectively.

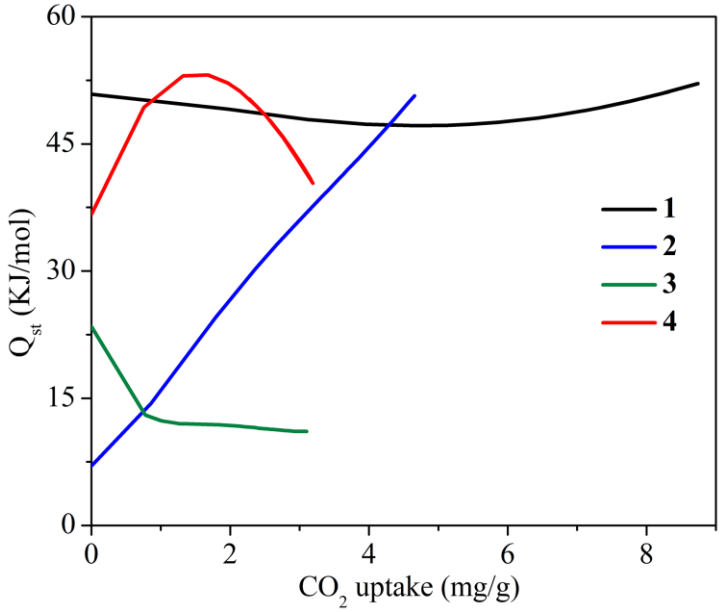

Fig. S7. Isosteric heats of adsorptions (Q_{st}) plotted against CO_2 uptakes for **1** – **4** respectively.

Q_{st} Analyses

To extract the coverage-dependent isosteric heat of adsorption, the adsorption data were modeled with a virial-type expression[1] composed of parameters a_i and b_i, which are independent from temperature:

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1)$$

$$Q_{st} = -\mathrm{R}\sum_{i=0}^{m} a_i N^i \qquad (2)$$

Where P is pressure, N is the amount adsorbed (or uptake), T is temperature, m and n determine the number of terms that required describing the isotherm adequately, and R is the universal gas constant. The Q_{st} was calculated by fitting the adsorption data at different temperatures in the pressure range of 0 ~ 1 bar.

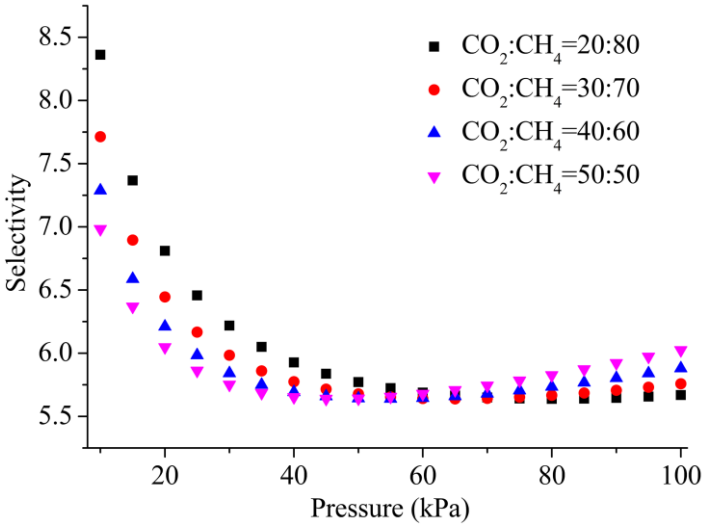

Fig. S8. IAST selectivity of CO_2/CH_4 mixture with different molar ratios for **1**.

Calculation of CO_2/CH_4 selectivity

The ideal adsorbed solution theory (IAST) developed by Myers and Praunitz was used to quantify the selectivities to CO_2/CH_4 gas mixtures with different molar ratios for **1**. Pure component isotherm of CO_2 and CH_4 at 298 K were fitted to the single-site Langmuir-Freundlich (LF) model:

$$N = a \times \frac{bp^c}{1 + bp^c}$$

where *a* represents the saturation adsorption capacities; *b* is the affinity constants; *p* is the pressure of the bulk gas at equilibrium with the adsorbed phase; *c* is the deviations from an ideal homogeneous surface.

The adsorption selectivity is defined as

$$S = \frac{x_1/x_2}{y_1/y_2}$$

where x is the molar fraction in the adsorbed phase and y is the molar fraction in the gas phase.

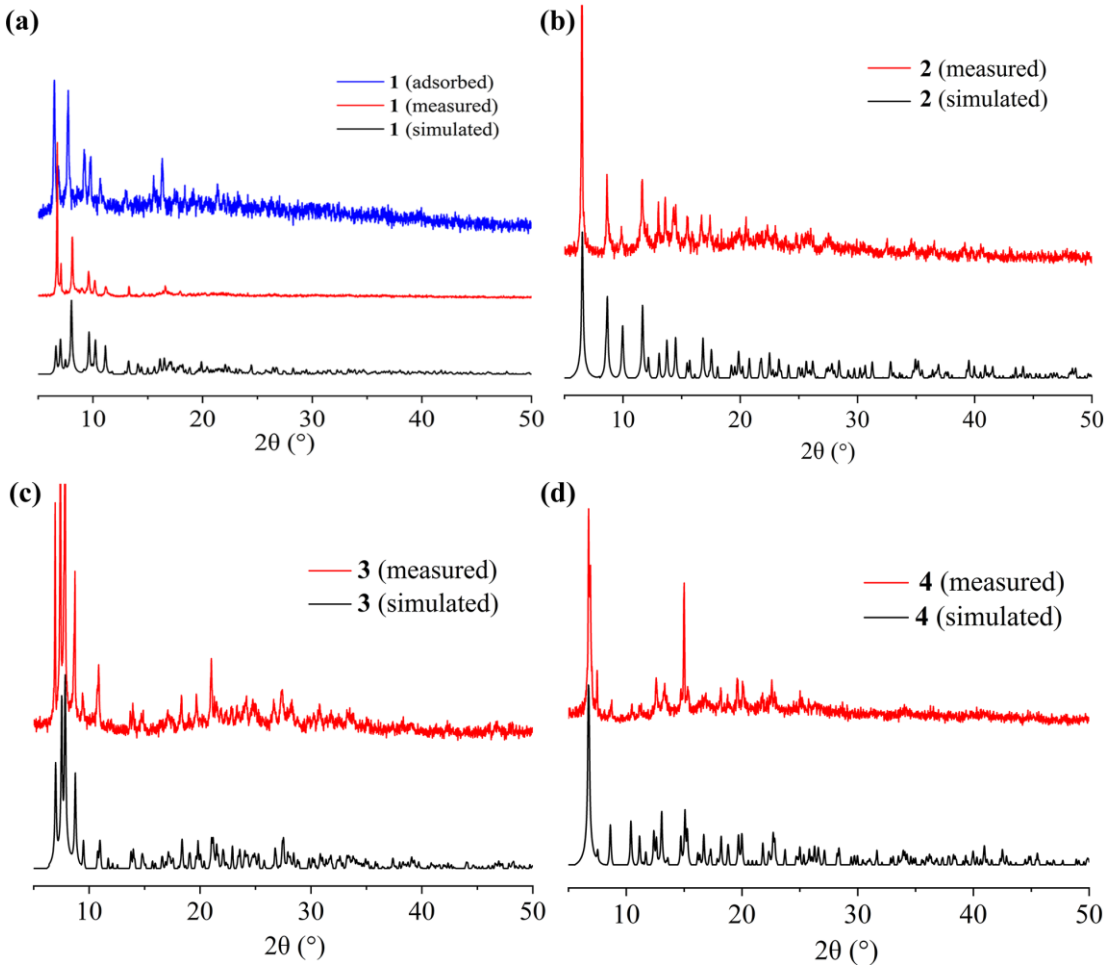

Fig. S9. Calculated and simulated PXRD patterns of **1(ad.), 1** – **4** respectively.

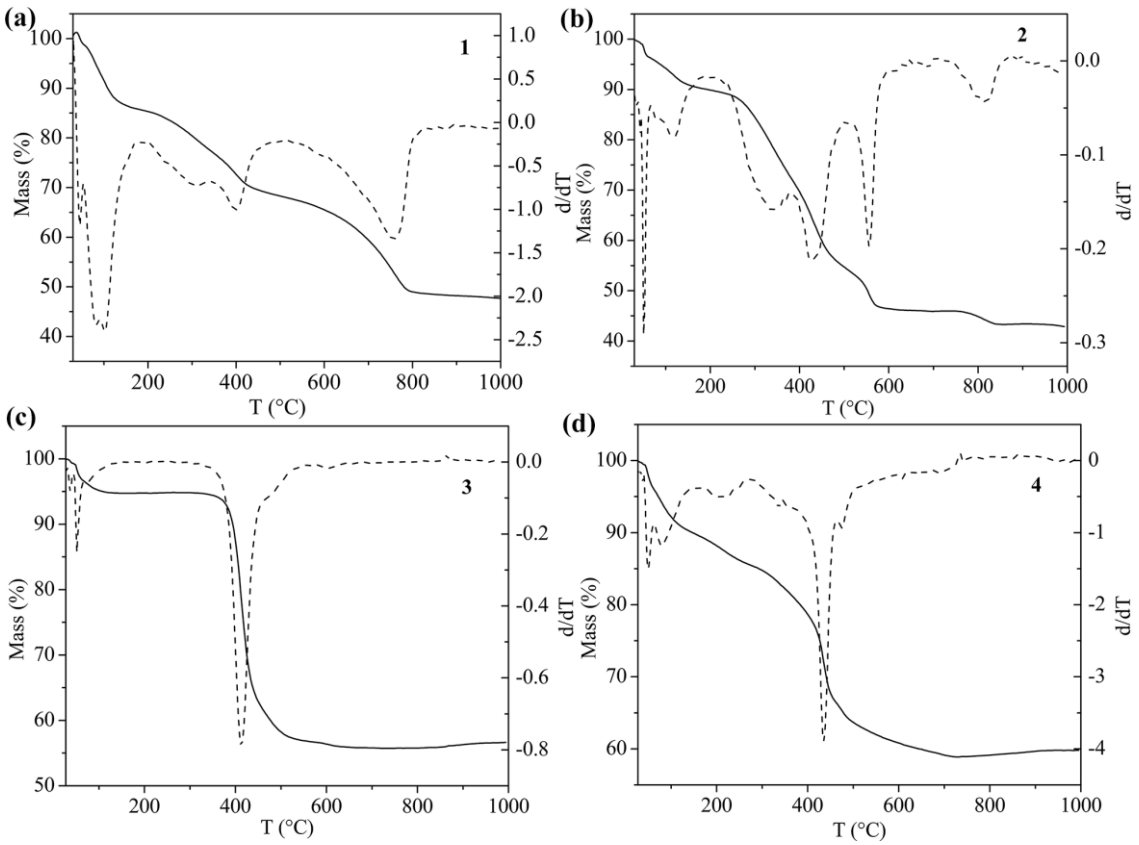

Fig. S10. TG-DTG curves of **1** – **4** respectively.

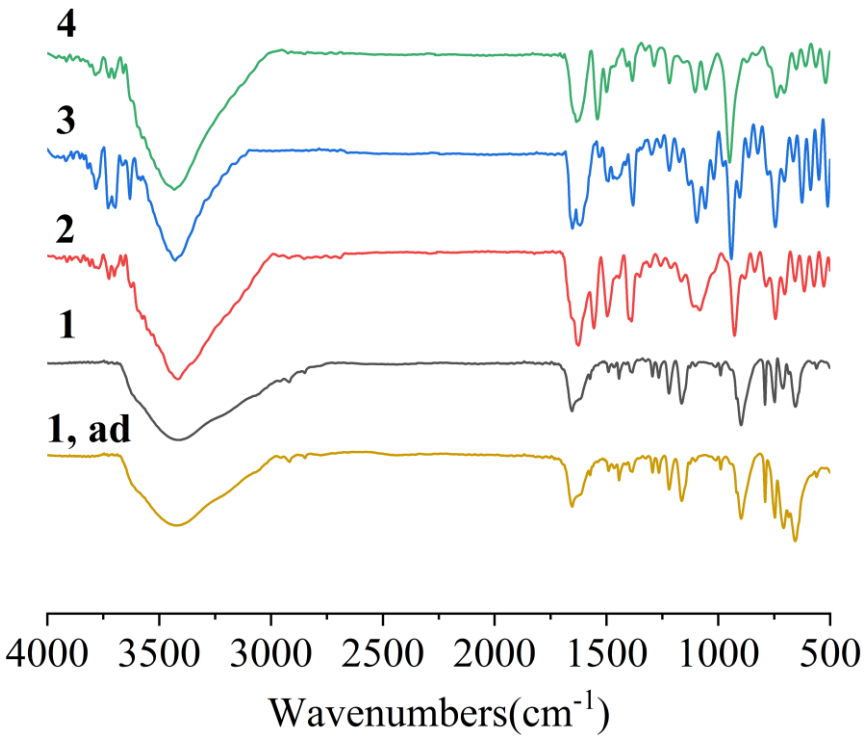

Fig. S11. IR spectra of **1(ad), 1** – **4** respectively.

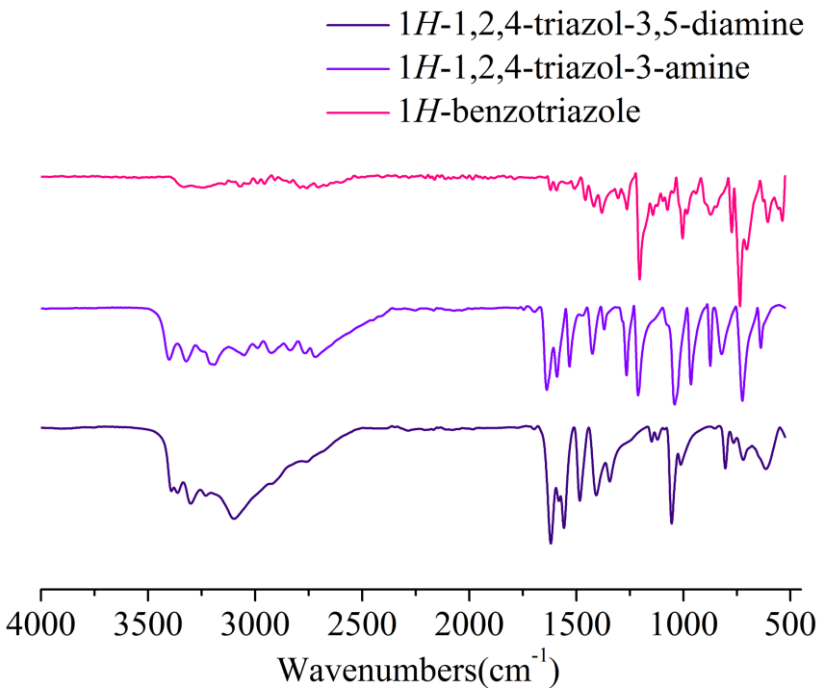

Fig. S12. IR spectra of 1*H*-benzotriazole, 1*H*-1,2,4-triazol-3-amine and 1*H*-1,2,4-triazole-3,5-diamine ligands respectively.

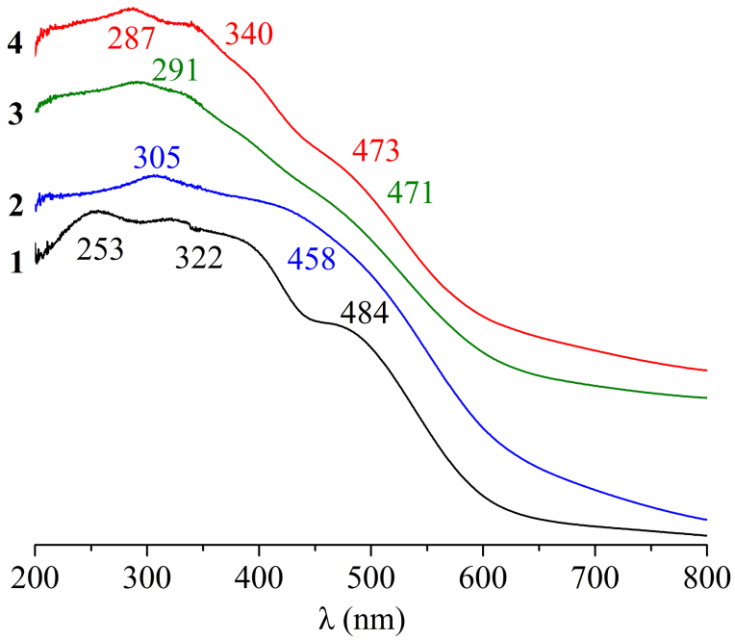

Fig. S13. Solid-state UV-vis reflective spectra for **1** – **4** respectively.

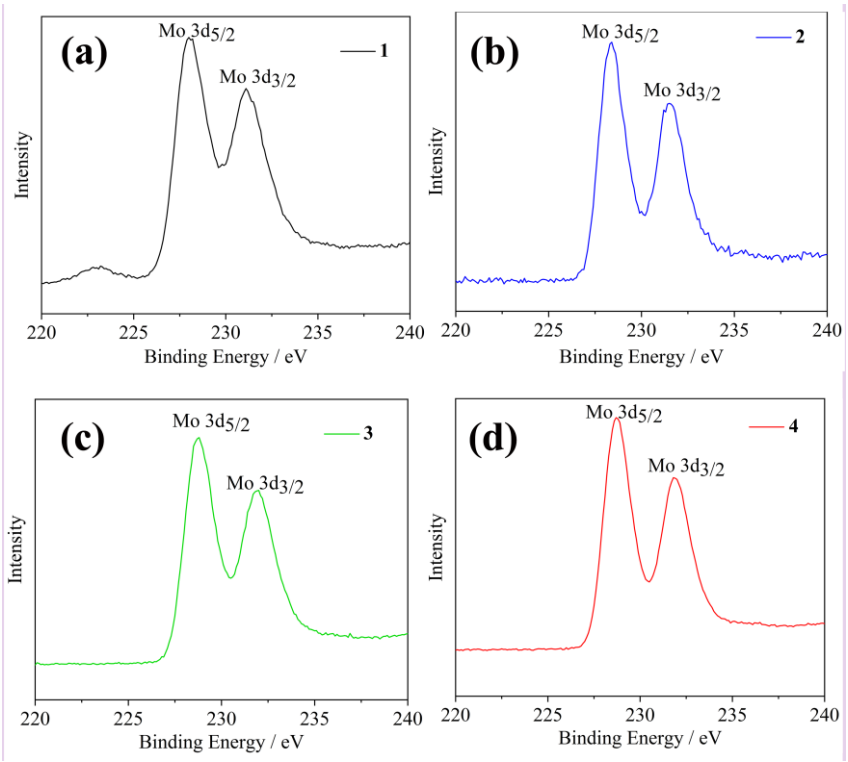

Fig. S14. X-ray photoelectron spectra for **1** – **4** respectively.

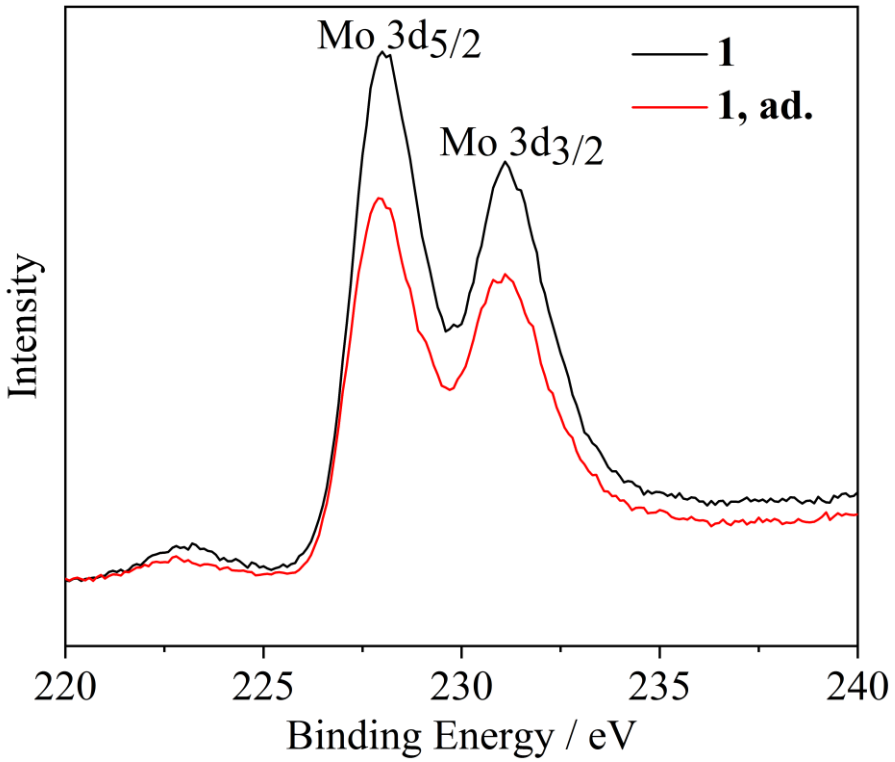

Fig. S15. X-ray photoelectron spectroscopy for **1** before and after adsorptions respectively.

X-ray photoelectron spectroscopy

Figures S14 and 15 show the X-ray photoelectron spectra of **1** – **4**, especially those of **1** before and after O_2 adsorption experiments. The species of Mo were observed in **1** – **4**, with binding energies of the Mo $3d_{5/2}$ corresponding to 228.0, 228.2, 228.7 and 228.7 eV respectively, where the peaks at 228 ~ 229 eV correspond to Mo(V) in complexes **1** – **4**.[2] The Mo $3d_{3/2}$ photoelectron binding energies of 231.1, 231.3, 232.0 and 231.9 eV also corresponded to Mo(V) for **1** – **4** respectively. Moreover, it can be seen the Mo spectra of $3d_{5/2}$ and $3d_{3/2}$ for compound **1** remain before and after the adsorptions.

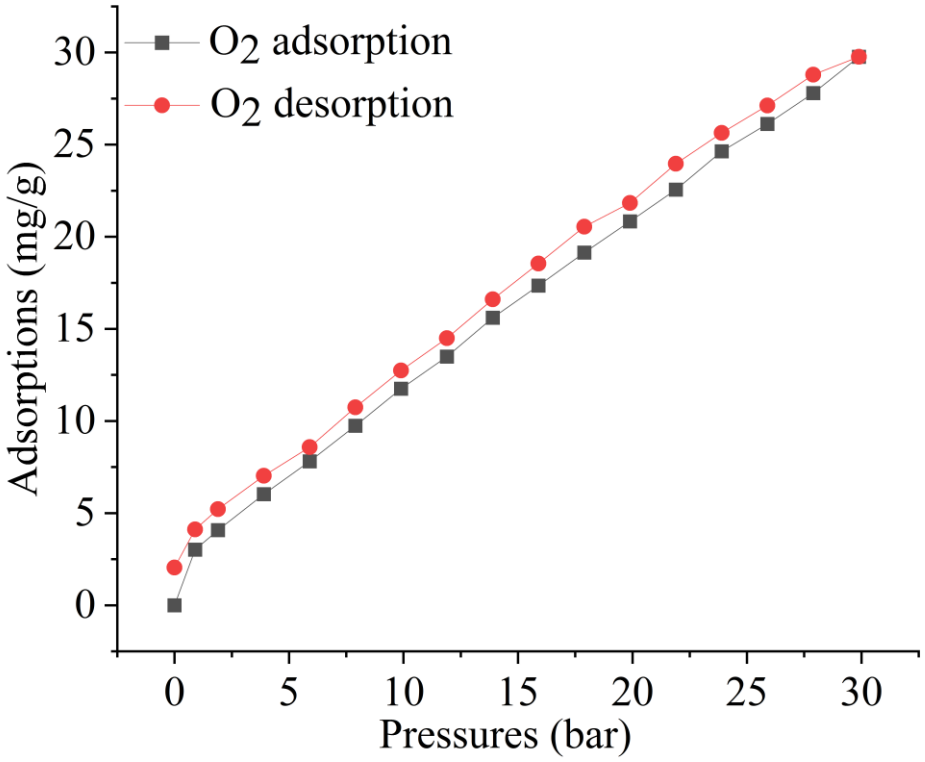

Fig. S16. O_2 adsorption and desorption isotherms for **1** at 298K.

Table S1. Comparisons of synthetic pH values for **1**, **2**, **3** and **4** with the other Mo_{12}, Mo_8 and Mo_6 POMs.

Categories	Complexes	Suitable pH values
Mo_{12}	$Na_4[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(3\text{-}trz)_8]\cdot 14H_2O$ (**3**)	**6.0**
	$Cs_2[Mo_{12}O_{12}S_{12}(OH)_{12}(C_8H_4O_4)]\cdot 15H_2O\cdot 6DMF$[3]	5.0
	$K_3[Mo_{12}O_{12}S_{12}(OH)_{12}(C_9H_3O_6)]\cdot 22H_2O$[3]	5.5
	$Na_4[(HPO_4)_2Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_2]\cdot 27H_2O$[4]	5.0
	$Cs_2[Mo_{12}S_{12}O_{12}(OH)_{12}(C_7H_{10}O_4)]\cdot 22H_2O$[5]	5.0
Mo_8	$[Mo_8O_8(\mu_2\text{-}O)_{12}(Hdatrz)_8]\cdot 28H_2O$ (**2**)	**8.9**
	$Na_8[Mo_{16}O_{16}(\mu_2\text{-}O)_{16}(\mu_2\text{-}OH)_{16}(3\text{-}trz)_8]\cdot 29H_2O$ (**4**)	**8.0**
	$[Cu(bix)][(Cubix)(\delta\text{-}Mo_8O_{26})_{0.5}]$[6]	3.0
	$(H_2bix)_2(\beta\text{-}Mo_8O_{26})_{0.5}(\beta\text{-}Mo_8O_{26})_{0.5}\cdot 3H_2O$[6]	4.0
	$[Cu(bpp)][Cu(bpp)(R\text{-}Mo_8O_{26})_{0.5}]\cdot 3H_2O$[6]	4.5
	$[(V_2O_2)(H_2PMo_8V_4O_{40})]\cdot 2(en)\cdot 12H_2O$[7]	3.7
	$(NH_4)_5[Mo_8(OH)_2O_{24}(\mu_8\text{-}PO_4)](H_2O)_2$[8]	4.2
	$[N(CH_3)_4]_2[Mo_8S_8O_8(OH)_8(C_2O_4)]\cdot 13H_2O$[5]	5.0
	$Li_2[Mo_8S_8O_8(OH)_8(C_2O_4)]\cdot 18.5H_2O$[5]	5.0
	$(Him)_4[Mo_8O_{26}(im)_2]$[9]	4.7 ~ 5.0
Mo_6	$[Mo_6O_6(\mu_2\text{-}O)_9(Hbtz)_6]\cdot 21H_2O$ (**1**)	**10.9**
	$(NH_4)Na_2[As^{III}Mo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8H_2O$[10]	4.0
	$\{[Sm(H_2O)_5]_2(TeMo_6O_{24})\}\cdot 6H_2O$[11]	2.7
	$(H_2bpp)[Ag\{AlMo_6(OH)_6O_{18}\}]\cdot 2.5H_2O$[12]	2.4

List of abbreviations: DMF = *N*,*N*-dimethylformamide; bix = 1,4-bis(imida-zole-1-ylmethyl)benzene; bpp = 1,3-bis(4-pyridyl)propane; en = ethylenediamine; im = imidazole.

Table S2. Crystallographic data and structural refinements for complexes $[Mo_6O_6(\mu_2\text{-}O)_9(Hbtz)_6]\cdot 21H_2O$ (**1**), $[Mo_8O_8(\mu_2\text{-}O)_{12}(Hdatrz)_8]\cdot 28H_2O$ (**2**), $Na_4[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(3\text{-}trz)_8]\cdot 14H_2O$ (**3**) and $Na_8[Mo_{16}O_{16}(\mu_2\text{-}O)_{16}(\mu_2\text{-}OH)_{16}(3\text{-}trz)_8]\cdot 29H_2O$ (**4**) respectively.

Identification codes	**1**	**2**	**3**	**4**
Empirical formula	$C_{36}H_{31}Mo_6N_{18}O_{16}$	$C_{16}H_{42}Mo_8N_{40}O_{22}$	$C_{16}H_{47}Mo_{12}N_{32}Na_4O_{42}$	$C_{16}H_{88}Mo_{16}N_{32}Na_8O_{77}$
Formula weight	1547.43	1914.41	2603.09	3680.14
Temperature/K	99.98(1)	99.90(6)	100.00(1)	100.00(1)
Crystal system	triclinic	monoclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	*C 2/m*	$P\bar{1}$	*F ddd*
a/Å	11.1739(2)	18.2829(9)	11.8391(3)	14.9900(2)
b/Å	12.6845(3)	20.7000(9)	11.9219(2)	31.7213(4)
c/Å	27.1349(6)	10.4480(5)	25.7883(6)	46.9852(6)
α/°	83.745(2)	90	98.134(2)	90
β/°	81.094(2)	102.276(5)	97.651(2)	90
γ/°	84.215(2)	90	91.857(2)	90
Volume/Å^3	3763.17(1)	3863.7(3)	3566.31(1)	22341.6(5)
Z	2	2	2	8
ρ_{calc}g/cm^3	1.366	1.646	2.424	2.188
μ/mm^{-1}	8.442	10.967	17.920	15.510
F(000)	1506.0	1860.0	2502.0	14272.0
Crystal size/mm^3	0.10 × 0.05 × 0.02	0.15 × 0.10 × 0.10	0.10 × 0.10 × 0.05	0.10 × 0.10 × 0.05
Radiation (Å)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.624 to 148.328	6.536 to 128.684	6.994 to 142.498	6.724 to 151.802

Index ranges	$-12 \le h \le 13$, $-15 \le k \le 15$, $-33 \le l \le 33$	$-21 \le h \le 21$, $-17 \le k \le 24$, $-12 \le l \le 12$	$-14 \le h \le 14$, $-13 \le k \le 14$, $-31 \le l \le 31$	$-18 \le h \le 17$, $-39 \le k \le 35$, $-57 \le l \le 30$
Reflections collected	47835	10565	39596	19930
Independent reflections	14696 (R_{int} = 0.0499, R_σ = 0.0467)	3261 (R_{int} = 0.0372, R_σ = 0.0379)	13354 (R_{int} = 0.0398, R_σ = 0.0462)	5475 (R_{int} = 0.0206, R_σ = 0.0196)
Data/restraints/parameters	14696/250/628	3261/2/203	13354/7/856	5475/78/302
Goodness–of–fit on F^2	1.051	1.059	1.037	1.048
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0789, wR_2 = 0.2210	R_1 = 0.0421, wR_2 = 0.1234	R_1 = 0.0764, wR_2 = 0.1987	R_1 = 0.0434, wR_2 = 0.1331
Final R indexes [all data]	R_1 = 0.0892, wR_2 = 0.2310	R_1 = 0.0475, wR_2 = 0.1270	R_1 = 0.0903, wR_2 = 0.2098	R_1 = 0.0461, wR_2 = 0.1357
Largest diff. peak/hole/e·Å^{-3}	1.71/-1.49	1.19/-0.96	2.03/-1.20	1.21/-1.40

Table S3. Selected bond distances (Å) and angles (°) in $[Mo_6O_6(\mu_2\text{-}O)_9(Hbtz)_6]\cdot 21H_2O$ (**1**).

Atom–Atom	Length/Å	Atom–Atom	Distances/Å
Mo1–Mo2	2.5919(7)	Mo3–Mo4	2.5725(1)
Mo1–O1	1.706(5)	Mo3–O4	1.945(5)
Mo1–O2	2.059(5)	Mo3–O8	2.000(7)
Mo1–O3	1.977(5)	Mo3–O10	1.963(7)
Mo1–O7	1.971(6)	Mo3–N2	2.246(6)
Mo1–N16	2.243(6)	Mo3–N5	2.252(8)
Mo1–N13	2.220(6)	Mo3–O13	1.721(6)
Mo2–O3	1.985(6)	Mo5–O6	1.974(6)
Mo2–O4	2.028(5)	Mo5–O9	1.932(6)
Mo2–O5	1.711(5)	Mo5–O11	1.960(7)
Mo2–O7	1.964(5)	Mo5–O15	1.726(7)
Mo2–N1	2.233(7)	Mo5–N7	2.228(1)
Mo2–N4	2.236(6)	Mo5–N10	2.229(8)
Mo6–Mo5	2.5672(9)	Mo4–O8	2.001(7)
Mo6–O2	1.941(5)	Mo4–O9	1.961(6)
Mo6–O6	1.965(6)	Mo4–O10	1.975(6)
Mo6–O11	1.949(6)	Mo4–O14	1.708(7)
Mo6–N14	2.268(7)	Mo4–N11	2.275(8)
Mo6–O12	1.720(6)	Mo4–N8	2.234(1)
Mo6–N17	2.260(7)		

Atom–Atom–Atom	Angle/°	Atom–Atom–Atom	Angle/°
O1–Mo1–Mo2	105.64(1)	O4–Mo3–N5	75.8(2)
O1–Mo1–O2	159.5(2)	O8–Mo3–Mo4	50.02(2)
O1–Mo1–O3	104.5(2)	O8–Mo3–N2	168.3(2)
O1–Mo1–O7	105.2(2)	O8–Mo3–N5	89.3(3)
O1–Mo1–N16	88.9(2)	O10–Mo3–Mo4	49.42(2)
O1–Mo1–N13	88.9(2)	O10–Mo3–O8	99.2(3)
O2–Mo1–Mo2	94.81(1)	O10–Mo3–N2	86.0(2)
O2–Mo1–N16	75.9(2)	O10–Mo3–N5	166.1(2)
O2–Mo1–N13	75.6(2)	N2–Mo3–Mo4	135.10(2)
O3–Mo1–Mo2	49.27(2)	N2–Mo3–N5	83.7(3)
O3–Mo1–O2	89.0(2)	N5–Mo3–Mo4	138.91(2)
O3–Mo1–N16	88.9(2)	O13–Mo3–Mo4	105.4(2)
O3–Mo1–N13	163.4(2)	O13–Mo3–O4	156.1(3)
O7–Mo1–Mo2	48.69(1)	O13–Mo3–O8	102.7(3)
O7–Mo1–O2	87.9(2)	O13–Mo3–O10	101.9(3)
O7–Mo1–O3	97.2(2)	O13–Mo3–N2	86.3(3)
O7–Mo1–N16	162.5(2)	O13–Mo3–N5	86.8(3)
O7–Mo1–N13	88.5(2)	O6–Mo5–Mo6	49.17(2)
N16–Mo1–Mo2	137.72(1)	O6–Mo5–N7	166.2(4)
N13–Mo1–Mo2	136.82(2)	O6–Mo5–N10	88.0(3)
N13–Mo1–N16	81.5(2)	O9–Mo5–Mo6	95.23(2)
O3–Mo2–Mo1	49.01(1)	O9–Mo5–O6	90.4(2)

O3–Mo2–O4	89.3(2)	O9–Mo5–O11	91.0(2)
O3–Mo2–N1	164.5(2)	O9–Mo5–N7	76.3(4)
O3–Mo2–N4	89.0(2)	O9–Mo5–N10	77.0(3)
O4–Mo2–Mo1	95.24(1)	O11–Mo5–Mo6	48.77(2)
O4–Mo2–N1	76.1(2)	O11–Mo5–O6	97.7(2)
O4–Mo2–N4	76.5(2)	O11–Mo5–N7	86.4(4)
O5–Mo2–Mo1	105.83(2)	O11–Mo5–N10	166.8(3)
O5–Mo2–O3	104.8(2)	O15–Mo5–Mo6	106.6(3)
O5–Mo2–O4	158.9(2)	O15–Mo5–O6	103.8(3)
O5–Mo2–O7	105.1(2)	O15–Mo5–O9	158.2(3)
O5–Mo2–N1	87.9(2)	O15–Mo5–O11	103.2(3)
O5–Mo2–N4	88.0(2)	O15–Mo5–N7	88.0(5)
O7–Mo2–Mo1	48.93(2)	O15–Mo5–N10	86.8(3)
O7–Mo2–O3	97.2(2)	N7–Mo5–Mo6	134.7(4)
O7–Mo2–O4	88.2(2)	N7–Mo5–N10	85.4(4)
O7–Mo2–N1	87.8(2)	N10–Mo5–Mo6	136.8(2)
O7–Mo2–N4	163.4(2)	O8–Mo4–Mo3	49.96(2)
N1–Mo2–Mo1	136.44(2)	O8–Mo4–N11	88.0(3)
N1–Mo2–N4	82.5(2)	O8–Mo4–N8	165.6(4)
N4–Mo2–Mo1	137.68(2)	O9–Mo4–Mo3	95.81(1)
O2–Mo6–Mo5	98.17(2)	O9–Mo4–O8	90.8(2)
O2–Mo6–O6	92.4(2)	O9–Mo4–O10	91.9(2)
O2–Mo6–O11	92.8(2)	O9–Mo4–N11	75.9(3)
O2–Mo6–N14	76.1(2)	O9–Mo4–N8	75.8(4)
O2–Mo6–N17	74.9(2)	O10–Mo4–Mo3	49.00(2)
O6–Mo6–Mo5	49.48(2)	O10–Mo4–O8	98.8(3)
O6–Mo6–N14	167.4(2)	O10–Mo4–N11	166.2(3)
O6–Mo6–N17	88.2(2)	O10–Mo4–N8	87.1(4)
O11–Mo6–Mo5	49.15(2)	O14–Mo4–Mo3	107.3(3)
O11–Mo6–O6	98.4(3)	O14–Mo4–O8	104.2(3)
O11–Mo6–N14	87.5(3)	O14–Mo4–O9	156.9(3)
O11–Mo6–N17	166.3(2)	O14–Mo4–O10	102.9(3)
N14–Mo6–Mo5	136.31(2)	O14–Mo4–N11	87.0(3)
O12–Mo6–Mo5	106.0(2)	O14–Mo4–N8	87.2(5)
O12–Mo6–O2	155.8(3)	N11–Mo4–Mo3	137.4(2)
O12–Mo6–O6	102.6(3)	N8–Mo4–Mo3	135.5(4)
O12–Mo6–O11	103.5(3)	N8–Mo4–N11	83.7(4)
O12–Mo6–N14	86.7(3)	Mo6–O2–Mo1	132.0(3)
O12–Mo6–N17	86.6(3)	Mo1–O3–Mo2	81.7(2)
N17–Mo6–Mo5	137.29(2)	Mo3–O4–Mo2	132.3(3)
N17–Mo6–N14	83.9(2)	Mo6–O6–Mo5	81.4(2)
O4–Mo3–Mo4	98.45(1)	Mo2–O7–Mo1	82.4(2)
O4–Mo3–O8	93.5(2)	Mo3–O8–Mo4	80.0(3)
O4–Mo3–O10	92.6(2)	Mo5–O9–Mo4	133.5(3)
O4–Mo3–N2	75.7(2)	Mo3–O10–Mo4	81.6(2)

Table S4. Selected hydrogen bond distances (Å) and angles (°) in $[Mo_6O_6(\mu_2\text{-}O)_9(Hbtz)_6]\cdot 21H_2O$ (**1**).

	D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
	O1w–H1w···O13	0.87	1.81	2.371(8)	121
	N3–H3···O1w	0.88	1.65	2.447(8)	149
	N18–H18···O1w[a]	0.88	1.69	2.467(7)	145
Intra	C9–H9···O5	0.95	2.59	3.162(1)	119
	C22–H22···N9[b]	0.95	2.62	3.560(2)	167
Intra	C27–H27···O1	0.95	2.56	3.147(9)	120
Intra	C33–H33···O1	0.95	2.60	3.179(9)	120

Symmetry codes: (a) x, -1 + y, z; (b) 1 – x, 1 – y, 1 – z.

Table S5. Selected bond distances (Å) and angles (°) in $[Mo_8O_8(\mu_2\text{-}O)_{12}(Hdatrz)_8]\cdot 28H_2O$ (**2**).

Atom–Atom	Length/Å	Atom–Atom	Length/Å
Mo1–Mo2	2.5639(6)	Mo2–O5	2.195(3)
Mo1–O3	2.155(2)	Mo2–O1	1.941(4)
Mo1–O1	1.946(4)	Mo2–O2	1.951(4)
Mo1–O2	1.954(4)	Mo2–O6	1.702(4)
Mo1–O4	1.701(4)	Mo2–N4	2.137(5)
Mo1–N9	2.182(4)	Mo2–N5[1]	2.195(5)
Mo1–N1	2.167(5)		

Atom–Atom–Atom	Angle/°	Atom–Atom–Atom	Angle/°
O3–Mo1–Mo2	104.2(1)	O1–Mo2–Mo1	48.8(1)
O3–Mo1–N9	77.41(7)	O1–Mo2–O5	86.56(3)
O3–Mo1–N1	74.59(7)	O1–Mo2–O2	93.67(6)
O1–Mo1–Mo2	48.64(1)	O1–Mo2–N4	161.83(6)
O1–Mo1–O3	88.42(6)	O1–Mo2–N5[1]	86.60(7)
O1–Mo1–O2	93.41(6)	O2–Mo2–Mo1	49.02(1)
O1–Mo1–N9	86.09(6)	O2–Mo2–O5	92.27(4)
O1–Mo1–N1	163.01(6)	O2–Mo2–N4	84.47(7)
O2–Mo1–Mo2	48.91(2)	O2–Mo2–N5[1]	168.27(7)
O2–Mo1–O3	89.00(7)	O6–Mo2–Mo1	96.72(2)
O2–Mo1–N9	166.41(6)	O6–Mo2–O5	157.76(7)
O2–Mo1–N1	86.10(8)	O6–Mo2–O1	105.84(7)
O4–Mo1–Mo2	97.78(3)	O6–Mo2–O2	104.98(8)
O4–Mo1–O3	158.04(7)	O6–Mo2–N4	92.06(8)
O4–Mo1–O1	106.29(7)	O6–Mo2–N5[1]	86.17(8)
O4–Mo1–O2	105.89(7)	N4–Mo2–Mo1	133.38(3)
O4–Mo1–N9	87.22(7)	N4–Mo2–O5	75.48(4)
O4–Mo1–N1	90.12(8)	N4–Mo2–N5[1]	91.62(7)
N9–Mo1–Mo2	134.14(2)	N5[1]–Mo2–Mo1	134.50(3)
N1–Mo1–Mo2	134.83(4)	Mo1–O3–Mo1[2]	120.5(2)
N1–Mo1–N9	90.42(8)	Mo2[1]–O5–Mo2	118.3(2)
O5–Mo2–Mo1	105.24(1)	Mo2–O1–Mo1	82.55(5)
O5–Mo2–N5[1]	76.03(5)	Mo2–O2–Mo1	82.07(5)

Symmetric codes: [1] $1-x, y$, [2] $1-z; x, 1-y, z$.

Table S6. Selected hydrogen bond distances (Å) and angles (°) in $[Mo_8O_8(\mu_2\text{-}O)_{12}(Hdatrz)_8]\cdot 28H_2O$ (**2**).

	D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
	O1w–H1w···N10	0.87	2.17	2.798(9)	128
	O1w–H1w···O3[a]	0.87	2.52	2.865(8)	105
	N3–H3A···N7[b]	0.88	2.48	3.260(9)	149
	N7–H7A···O4[b]	0.88	2.35	3.055(7)	138
	N7–H7A···O6[b]	0.88	2.54	3.093(7)	122
Intra	N7–H7B···O2	0.88	2.56	3.090(7)	120
Intra	N8–H8B···O6[c]	0.90	2.33	3.063(8)	140
	N10–H10···O1w	0.88	1.94	2.798(9)	166
Intra	N11–H11A···O4	0.88	2.44	3.133(7)	137

Symmetry codes: (a) $1 - x, y, 2 - z$; (b) $\frac{1}{2} - x, 3/2 - y, 1 - z$; (c) $1 - x, y, 1 - z$.

Table S7. Selected bond distances (Å) and angles (°) in $Na_4[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(3\text{-}trz)_8]\cdot 14H_2O$ (**3**).

Atom–Atom	Length/Å	Atom–Atom	Length/Å
Mo11–Mo12	2.5806(1)	Mo10–N25	2.188(1)
Mo11–O5	1.969(8)	Mo3–O7	1.950(8)
Mo11–O8	1.965(9)	Mo3–O4	2.131(1)
Mo11–O4	1.982(9)	Mo3–O12	1.924(9)
Mo11–O10	2.286(8)	Mo3–O17	2.216(1)
Mo11–O23	1.690(9)	Mo3–O22	1.672(1)
Mo11–N6	2.154(1)	Mo3–N14	2.191(1)
Mo4–Mo3	2.5783(1)	Mo8–Mo7	2.5869(2)
Mo4–O2	1.994(9)	Mo8–O2	2.061(8)
Mo4–O5	2.286(8)	Mo8–O9	1.980(9)
Mo4–O7	1.970(8)	Mo8–O11	1.976(8)
Mo4–O12	1.973(9)	Mo8–O24	1.697(9)
Mo4–O15	1.661(1)	Mo8–N18	2.176(1)
Mo4–N21	2.164(1)	Mo8–N22	2.167(1)
Mo6–Mo5	2.5748(1)	Mo9–O10	1.962(8)
Mo6–O2	2.103(8)	Mo9–O1	2.101(1)
Mo6–O6	1.974(9)	Mo9–O13	2.213(9)
Mo6–O9	2.217(8)	Mo9–O14	1.904(1)
Mo6–O20	1.701(9)	Mo9–O19	1.692(1)
Mo6–O21	1.916(9)	Mo9–N2	2.185(1)
Mo6–N17	2.156(1)	Mo7–O3	2.078(8)
Mo12–O5	1.958(8)	Mo7–O9	1.972(8)
Mo12–O3	2.091(9)	Mo7–O11	1.985(9)
Mo12–O8	1.914(8)	Mo7–O26	1.689(1)
Mo12–O11	2.215(8)	Mo7–N29	2.196(1)
Mo12–O16	1.692(9)	Mo7–N26	2.088(2)
Mo12–N30	2.198(1)	Mo1–Mo2	2.5914(2)
Mo5–O6	1.975(8)	Mo1–O1	2.055(9)
Mo5–O7	2.300(7)	Mo1–O13	1.982(1)
Mo5–O1	2.003(9)	Mo1–O17	1.971(1)
Mo5–O21	1.943(9)	Mo1–N9	2.130(1)
Mo5–O25	1.666(9)	Mo1–O27	1.663(1)
Mo5–N10	2.172(1)	Mo1–N1	2.201(1)
Mo10–Mo9	2.5760(1)	Mo2–O4	2.059(9)
Mo10–O6	2.271(8)	Mo2–O13	1.940(1)
Mo10–O3	1.992(9)	Mo2–O17	1.987(1)
Mo10–O10	1.961(8)	Mo2–O28	1.676(1)
Mo10–O14	1.974(9)	Mo2–N5	2.143(1)
Mo10–O18	1.686(9)	Mo2–N13	2.143(2)

Atom–Atom–Atom	Angle/°	Atom–Atom–Atom	Angle/°
O5–Mo11–Mo12	48.7(2)	N14–Mo3–O17	78.8(5)
O5–Mo11–O4	91.0(3)	O2–Mo8–Mo7	97.7(3)
O5–Mo11–O10	82.3(3)	O2–Mo8–N18	78.1(4)
O5–Mo11–N6	163.6(4)	O2–Mo8–N22	81.0(4)
O8–Mo11–Mo12	47.5(2)	O9–Mo8–Mo7	49.0(2)
O8–Mo11–O5	94.7(3)	O9–Mo8–O2	75.9(3)
O8–Mo11–O4	154.3(4)	O9–Mo8–N18	82.9(4)
O8–Mo11–O10	78.7(3)	O9–Mo8–N22	156.6(4)
O8–Mo11–N6	86.2(4)	O11–Mo8–Mo7	49.4(3)
O4–Mo11–Mo12	138.2(2)	O11–Mo8–O2	94.7(3)
O4–Mo11–O10	77.3(3)	O11–Mo8–O9	94.8(4)
O4–Mo11–N6	81.5(4)	O11–Mo8–N18	172.8(4)
O10–Mo11–Mo12	85.48(2)	O11–Mo8–N22	83.7(4)
O23–Mo11–Mo12	99.2(3)	O24–Mo8–Mo7	102.0(4)
O23–Mo11–O5	103.3(4)	O24–Mo8–O2	159.4(4)
O23–Mo11–O8	101.9(4)	O24–Mo8–O9	113.3(4)
O23–Mo11–O4	101.1(4)	O24–Mo8–O11	102.6(4)
O23–Mo11–O10	174.2(4)	O24–Mo8–N18	84.6(4)
O23–Mo11–N6	92.5(4)	O24–Mo8–N22	89.7(5)
N6–Mo11–Mo12	133.5(3)	N18–Mo8–Mo7	130.4(3)
N6–Mo11–O10	81.8(4)	N22–Mo8–Mo7	132.9(3)
O2–Mo4–Mo3	138.2(2)	N22–Mo8–N18	95.7(4)
O2–Mo4–O5	77.9(3)	O10–Mo9–Mo10	48.9(2)
O2–Mo4–N21	81.3(4)	O10–Mo9–O1	87.7(3)
O5–Mo4–Mo3	85.41(2)	O10–Mo9–O13	94.6(3)
O7–Mo4–Mo3	48.5(2)	O10–Mo9–N2	164.2(4)
O7–Mo4–O2	91.0(3)	O1–Mo9–Mo10	101.1(2)
O7–Mo4–O5	82.3(3)	O1–Mo9–O13	70.0(4)
O7–Mo4–O12	94.8(3)	O1–Mo9–N2	76.4(4)
O7–Mo4–N21	162.8(4)	O13–Mo9–Mo10	143.4(2)
O12–Mo4–Mo3	47.8(3)	O14–Mo9–Mo10	49.5(3)
O12–Mo4–O2	154.9(3)	O14–Mo9–O10	97.0(4)
O12–Mo4–O5	78.7(3)	O14–Mo9–O1	94.2(4)
O12–Mo4–N21	86.1(4)	O14–Mo9–O13	160.0(4)
O15–Mo4–Mo3	99.5(3)	O14–Mo9–N2	84.3(4)
O15–Mo4–O2	99.8(4)	O19–Mo9–Mo10	102.7(4)
O15–Mo4–O5	174.5(4)	O19–Mo9–O10	103.8(4)
O15–Mo4–O7	102.9(4)	O19–Mo9–O1	155.5(4)
O15–Mo4–O12	102.6(4)	O19–Mo9–O13	87.4(5)
O15–Mo4–N21	93.6(4)	O19–Mo9–O14	105.5(5)
N21–Mo4–Mo3	133.7(3)	O19–Mo9–N2	90.9(5)

N21–Mo4–O5	81.1(3)	N2–Mo9–Mo10	133.8(3)
O2–Mo6–Mo5	101.4(2)	N2–Mo9–O13	80.2(4)
O2–Mo6–O9	70.2(3)	O3–Mo7–Mo8	98.7(2)
O2–Mo6–N17	75.5(4)	O3–Mo7–N29	76.8(4)
O6–Mo6–Mo5	49.3(2)	O3–Mo7–N26	80.7(4)
O6–Mo6–O2	87.3(3)	O9–Mo7–Mo8	49.2(3)
O6–Mo6–O9	94.9(3)	O9–Mo7–O3	95.8(3)
O6–Mo6–N17	162.8(4)	O9–Mo7–O11	94.8(4)
O9–Mo6–Mo5	144.2(2)	O9–Mo7–N29	172.3(4)
O20–Mo6–Mo5	102.3(3)	O9–Mo7–N26	84.3(4)
O20–Mo6–O2	155.7(4)	O11–Mo7–Mo8	49.1(2)
O20–Mo6–O6	103.9(4)	O11–Mo7–O3	76.2(3)
O20–Mo6–O9	87.2(4)	O11–Mo7–N29	81.7(4)
O20–Mo6–O21	104.1(4)	O11–Mo7–N26	156.7(4)
O20–Mo6–N17	92.3(4)	O26–Mo7–Mo8	101.5(4)
O21–Mo6–Mo5	48.6(3)	O26–Mo7–O3	158.2(5)
O21–Mo6–O2	95.8(3)	O26–Mo7–O9	103.4(4)
O21–Mo6–O6	96.6(4)	O26–Mo7–O11	111.7(5)
O21–Mo6–O9	161.4(4)	O26–Mo7–N29	84.2(5)
O21–Mo6–N17	84.7(4)	O26–Mo7–N26	91.0(5)
N17–Mo6–Mo5	133.0(3)	N29–Mo7–Mo8	129.3(4)
N17–Mo6–O9	80.0(4)	N26–Mo7–Mo8	133.5(3)
O5–Mo12–Mo11	49.1(2)	N26–Mo7–N29	96.1(5)
O5–Mo12–O3	87.6(3)	O1–Mo1–Mo2	98.1(2)
O5–Mo12–O11	95.2(3)	O1–Mo1–N9	81.3(4)
O5–Mo12–N30	164.3(4)	O1–Mo1–N1	77.3(4)
O3–Mo12–Mo11	100.8(2)	O13–Mo1–Mo2	48.0(3)
O3–Mo12–O11	71.1(3)	O13–Mo1–O1	75.6(4)
O3–Mo12–N30	76.7(4)	O13–Mo1–N9	156.6(4)
O8–Mo12–Mo11	49.1(3)	O13–Mo1–N1	82.5(5)
O8–Mo12–O5	96.7(3)	O17–Mo1–Mo2	49.4(3)
O8–Mo12–O3	93.7(3)	O17–Mo1–O1	95.6(3)
O8–Mo12–O11	160.3(4)	O17–Mo1–O13	93.7(4)
O8–Mo12–N30	84.7(4)	O17–Mo1–N9	84.7(5)
O11–Mo12–Mo11	144.2(2)	O17–Mo1–N1	172.5(4)
O16–Mo12–Mo11	102.0(3)	N9–Mo1–Mo2	134.0(4)
O16–Mo12–O5	104.0(4)	N9–Mo1–N1	96.2(5)
O16–Mo12–O3	156.6(4)	O27–Mo1–Mo2	102.3(4)
O16–Mo12–O8	104.8(4)	O27–Mo1–O1	158.1(5)
O16–Mo12–O11	87.4(4)	O27–Mo1–O13	113.0(5)
O16–Mo12–N30	90.7(5)	O27–Mo1–O17	103.6(5)
N30–Mo12–Mo11	133.8(3)	O27–Mo1–N9	89.9(6)

N30–Mo12–O11	79.7(4)	O27–Mo1–N1	83.9(5)
O6–Mo5–Mo6	49.3(2)	N1–Mo1–Mo2	128.8(4)
O6–Mo5–O7	82.4(3)	O4–Mo2–Mo1	98.1(2)
O6–Mo5–O1	90.6(4)	O4–Mo2–N5	80.5(4)
O6–Mo5–N10	162.8(4)	O4–Mo2–N13	77.6(4)
O7–Mo5–Mo6	85.4(2)	O13–Mo2–Mo1	49.4(3)
O1–Mo5–Mo6	138.5(3)	O13–Mo2–O4	94.2(4)
O1–Mo5–O7	78.1(3)	O13–Mo2–O17	94.5(4)
O1–Mo5–N10	81.2(4)	O13–Mo2–N5	84.6(5)
O21–Mo5–Mo6	47.7(3)	O13–Mo2–N13	171.8(4)
O21–Mo5–O6	95.7(4)	O17–Mo2–Mo1	48.8(3)
O21–Mo5–O7	79.6(3)	O17–Mo2–O4	76.4(4)
O21–Mo5–O1	155.7(4)	O17–Mo2–N5	156.8(4)
O21–Mo5–N10	86.1(4)	O17–Mo2–N13	83.4(5)
O25–Mo5–Mo6	99.1(4)	O28–Mo2–Mo1	101.7(5)
O25–Mo5–O6	103.0(4)	O28–Mo2–O4	159.3(5)
O25–Mo5–O7	174.5(4)	O28–Mo2–O13	103.3(5)
O25–Mo5–O1	100.3(4)	O28–Mo2–O17	112.6(5)
O25–Mo5–O21	101.0(4)	O28–Mo2–N5	90.1(5)
O25–Mo5–N10	93.3(5)	O28–Mo2–N13	84.8(6)
N10–Mo5–Mo6	133.6(4)	N5–Mo2–Mo1	133.8(3)
N10–Mo5–O7	81.2(4)	N13–Mo2–Mo1	130.9(4)
O6–Mo10–Mo9	85.6(2)	N13–Mo2–N5	94.2(5)
O3–Mo10–Mo9	138.5(2)	Mo4–O2–Mo6	123.9(4)
O3–Mo10–O6	78.8(3)	Mo4–O2–Mo8	131.5(4)
O3–Mo10–N25	81.0(4)	Mo8–O2–Mo6	104.3(4)
O10–Mo10–Mo9	49.0(2)	Mo11–O5–Mo4	133.3(4)
O10–Mo10–O6	82.7(3)	Mo12–O5–Mo11	82.2(3)
O10–Mo10–O3	90.8(3)	Mo12–O5–Mo4	143.9(4)
O10–Mo10–O14	94.8(4)	Mo6–O6–Mo5	81.4(3)
O10–Mo10–N25	163.1(4)	Mo6–O6–Mo10	144.6(4)
O14–Mo10–Mo9	47.2(3)	Mo5–O6–Mo10	133.5(4)
O14–Mo10–O6	78.7(4)	Mo4–O7–Mo5	132.6(4)
O14–Mo10–O3	155.9(4)	Mo3–O7–Mo4	82.3(3)
O14–Mo10–N25	87.2(4)	Mo3–O7–Mo5	144.4(4)
O18–Mo10–Mo9	99.1(3)	Mo10–O3–Mo12	124.8(4)
O18–Mo10–O6	173.9(4)	Mo10–O3–Mo7	131.1(4)
O18–Mo10–O3	99.9(4)	Mo7–O3–Mo12	103.9(4)
O18–Mo10–O10	103.3(4)	Mo12–O8–Mo11	83.4(3)
O18–Mo10–O14	101.6(4)	Mo8–O9–Mo6	103.0(4)
O18–Mo10–N25	92.6(4)	Mo7–O9–Mo6	133.8(4)
N25–Mo10–Mo9	134.3(3)	Mo7–O9–Mo8	81.8(3)

N25–Mo10–O6	81.3(4)	Mo1–O13–Mo9	103.1(4)
O7–Mo3–Mo4	49.2(2)	Mo2–O13–Mo9	135.1(5)
O7–Mo3–O4	86.7(3)	Mo2–O13–Mo1	82.7(4)
O7–Mo3–O17	95.0(3)	Mo11–O4–Mo3	123.5(5)
O7–Mo3–N14	161.0(5)	Mo11–O4–Mo2	132.4(5)
O4–Mo3–Mo4	100.9(2)	Mo2–O4–Mo3	103.6(4)
O4–Mo3–O17	70.3(4)	Mo10–O10–Mo11	133.2(4)
O4–Mo3–N14	74.3(5)	Mo10–O10–Mo9	82.1(3)
O12–Mo3–Mo4	49.4(3)	Mo9–O10–Mo11	144.1(4)
O12–Mo3–O7	97.1(4)	Mo5–O1–Mo9	124.0(4)
O12–Mo3–O4	94.5(4)	Mo5–O1–Mo1	131.2(5)
O12–Mo3–O17	160.0(4)	Mo1–O1–Mo9	104.6(4)
O12–Mo3–N14	84.6(5)	Mo8–O11–Mo12	134.0(4)
O17–Mo3–Mo4	144.2(2)	Mo8–O11–Mo7	81.5(3)
O22–Mo3–Mo4	102.8(4)	Mo7–O11–Mo12	102.7(4)
O22–Mo3–O7	105.1(4)	Mo3–O12–Mo4	82.8(3)
O22–Mo3–O4	155.9(4)	Mo1–O17–Mo3	133.9(4)
O22–Mo3–O12	104.5(5)	Mo1–O17–Mo2	81.8(4)
O22–Mo3–O17	87.5(4)	Mo9–O14–Mo10	83.2(4)
O22–Mo3–N14	92.6(5)	Mo2–O17–Mo3	103.1(4)
N14–Mo3–Mo4	133.7(4)	Mo6–O21–Mo5	83.7(3)

Table S8. Selected hydrogen bond distances (Å) and angles (°) in $Na_4[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(3\text{-}trz)_8]\cdot 14H_2O$ (**3**).

	D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
Intra	N8–H8A···O8	0.88	1.99	2.743(2)	143
Intra	N8–H8B···O25[a]	0.88	2.48	3.212(2)	141
Intra	N12–H12A···O21	0.88	1.98	2.750(2)	144
Intra	N16–H16A···O12	0.88	2.52	3.060(2)	121
	N16–H16A···N28[b]	0.88	2.59	3.400(3)	153
	N16–H16B···O18[b]	0.88	2.28	2.920(2)	129
	N16–H16A···O19[b]	0.88	2.46	3.180(2)	139
Intra	N20–H20A···O21	0.88	2.57	3.139(1)	123
Intra	N20–H20B···O16[c]	0.88	2.28	3.056(1)	148
Intra	N20–H20B···O23[c]	0.88	2.49	3.069(2)	124
Intra	N24–H24A···O12	0.88	1.99	2.740(2)	143
Intra	N28–H28A···O14	0.88	2.01	2.789(2)	146
	N28–H28B···O15[d]	0.88	2.47	3.229(2)	145
Intra	N32–H32A···N20[a]	0.88	2.19	3.050(2)	164
	C5–H5···O28[e]	0.95	2.48	3.340(3)	151
	C13–H13···O24[f]	0.95	2.33	3.230(2)	156

Symmetry codes: (a) x, -1 + y, z; (b) 1 + x, y, z; (c) x, 1 + y, z; (d) -1 + x, y, z; (e) 2 – x, 1 – y, 1 – z; (f) 1 – x, 1 – y, -z.

Table S9. Selected bond distances (Å) and angles (°) in $Na_8[Mo_{16}O_{16}(\mu_2\text{-}O)_{16}(\mu_2\text{-}OH)_{16}(3\text{-}trz)_8]\cdot 29H_2O$ (**4**).

Atom–Atom	Length/Å	Atom–Atom	Length/Å
Mo2–Mo1	2.5595(8)	Mo3–N1	2.184(5)
Mo2–O6	1.951(4)	Mo1–O6	1.949(4)
Mo2–O4	2.160(4)	Mo1–O2	2.170(4)
Mo2–O3	2.106(5)	Mo1–O1	2.110(4)
Mo2–O5	1.956(5)	Mo1–O5	1.951(4)
Mo2–N2	2.216(5)	Mo1–O9	1.693(5)
Mo2–O10	1.693(4)	Mo1–N5	2.214(7)
Mo3–Mo4	2.5527(7)	Mo4–O8	1.950(4)
Mo3–O4	2.162(4)	Mo4–O2	2.191(4)
Mo3–O8	1.948(4)	Mo4–O1	2.112(4)
Mo3–O3	2.106(4)	Mo4–O7	1.937(4)
Mo3–O7	1.942(4)	Mo4–O12	1.696(5)
Mo3–O11	1.693(5)	Mo4–N6	2.195(6)

Atom–Atom–Atom	Angle/°	Atom–Atom–Atom	Angle/°
O6–Mo2–Mo1	48.95(1)	O6–Mo1–N5	162.8(2)
O6–Mo2–O4	89.08(1)	O2–Mo1–Mo2	100.90(1)
O6–Mo2–O3	87.45(2)	O2–Mo1–N5	74.6(2)
O6–Mo2–O5	95.33(2)	O1–Mo1–Mo2	137.01(1)
O6–Mo2–N2	163.44(2)	O1–Mo1–O2	70.76(1)
O4–Mo2–Mo1	98.60(1)	O1–Mo1–N5	83.8(2)
O4–Mo2–N2	75.54(2)	O5–Mo1–Mo2	49.15(1)
O3–Mo2–Mo1	136.05(1)	O5–Mo1–O2	88.91(2)
O3–Mo2–O4	71.70(1)	O5–Mo1–O1	159.27(2)
O3–Mo2–N2	81.98(2)	O5–Mo1–N5	87.0(3)
O5–Mo2–Mo1	48.98(1)	O9–Mo1–Mo2	99.52(2)
O5–Mo2–O4	85.19(2)	O9–Mo1–O6	105.2(2)
O5–Mo2–O3	156.69(2)	O9–Mo1–O2	159.6(2)
O5–Mo2–N2	89.54(2)	O9–Mo1–O1	94.1(2)
N2–Mo2–Mo1	138.50(1)	O9–Mo1–O5	104.6(2)
O10–Mo2–Mo1	100.38(2)	O9–Mo1–N5	90.6(3)
O10–Mo2–O6	105.69(2)	N5–Mo1–Mo2	136.2(2)
O10–Mo2–O4	160.8(2)	O8–Mo4–Mo3	49.07(1)
O10–Mo2–O3	96.3(2)	O8–Mo4–O2	86.82(1)
O10–Mo2–O5	105.1(2)	O8–Mo4–O1	89.03(2)
O10–Mo2–N2	88.2(2)	O8–Mo4–N6	161.5(2)
O4–Mo3–Mo4	98.16(1)	O2–Mo4–Mo3	100.20(1)
O4–Mo3–N1	75.69(2)	O2–Mo4–N6	74.8(2)
O8–Mo3–Mo4	49.13(1)	O1–Mo4–Mo3	137.99(1)
O8–Mo3–O4	87.83(2)	O1–Mo4–O2	70.32(1)
O8–Mo3–O3	88.56(2)	O1–Mo4–N6	83.7(2)
O8–Mo3–N1	162.9(2)	O7–Mo4–Mo3	48.94(1)
O3–Mo3–Mo4	137.39(1)	O7–Mo4–O8	95.32(2)

O3–Mo3–O4	71.66(1)	O7–Mo4–O2	89.27(2)
O3–Mo3–N1	82.05(2)	O7–Mo4–O1	158.90(2)
O7–Mo3–Mo4	48.75(1)	O7–Mo4–N6	85.8(2)
O7–Mo3–O4	85.56(2)	O12–Mo4–Mo3	99.54(2)
O7–Mo3–O8	95.19(2)	O12–Mo4–O8	105.3(2)
O7–Mo3–O3	156.78(1)	O12–Mo4–O2	160.2(2)
O7–Mo3–N1	88.13(1)	O12–Mo4–O1	93.9(2)
O11–Mo3–Mo4	100.48(1)	O12–Mo4–O7	104.8(2)
O11–Mo3–O4	161.2(2)	O12–Mo4–N6	92.2(3)
O11–Mo3–O8	106.04(2)	N6–Mo4–Mo3	134.78(2)
O11–Mo3–O3	95.6(2)	Mo1–O6–Mo2	82.05(1)
O11–Mo3–O7	105.2(2)	Mo2–O4–Mo3	102.39(1)
O11–Mo3–N1	89.1(2)	Mo3–O8–Mo4	81.81(1)
N1–Mo3–Mo4	136.87(1)	Mo1–O2–Mo4	101.98(2)
O6–Mo1–Mo2	49.00(1)	Mo2–O3–Mo3	106.20(2)
O6–Mo1–O2	88.38(1)	Mo1–O1–Mo4	106.71(2)
O6–Mo1–O1	88.11(2)	Mo1–O5–Mo2	81.88(1)
O6–Mo1–O5	95.55(2)	Mo4–O7–Mo3	82.31(2)

Table S10. Selected hydrogen bond distances (Å) and angles (°) in $Na_8[Mo_{16}O_{16}(\mu_2\text{-}O)_{16}(\mu_2\text{-}OH)_{16}(3\text{-}trz)_8]\cdot 29H_2O$ (**4**).

	D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
Intra	O1–H1···O8[a]	0.76	1.97	2.692(5)	160
Intra	O1–H1···O8[b]	0.76	2.54	2.851(6)	113
	O2–H2···O2w	0.88	2.14	2.941(7)	150
	O2w–H2w···N3[c]	0.87	1.96	2.827(6)	172
Intra	O3–H3···O6[a]	0.84	1.86	2.691(5)	168
	O3w–H3w···O5[c]	0.84	2.00	2.843(9)	176
	O4–H4···O2w	0.85	2.51	3.048(7)	123
	O4–H4···N3[c]	0.85	2.27	3.082(6)	161
	N4–H22···O7[c]	0.88	2.22	2.800(1)	123

Symmetric codes: (a) $5/4 - x, y, 5/4 - z$; (b) $5/4 - x, 5/4 - y, z$; (c) $1 - x, 1 - y, 1 - z$.

Table S11. Bond valence calculations for POMs **1** – **4** respectively.

Complexes	Atoms	N	$\sum S_{ij}$	Δ
$[Mo_6O_6(\mu_2\text{-}O)_9(Hbtz)_6]\cdot 21H_2O$ (**1**)	Mo1	5+	5.145	0.145
	Mo2	5+	5.181	0.181
	Mo3	5+	5.245	0.245
	Mo4	5+	5.208	0.208
	Mo5	5+	5.369	0.369
	Mo6	5+	5.319	0.319
		5+	**5.245_{av}**	**0.245_{av}**
$[Mo_8O_8(\mu_2\text{-}O)_{12}(Hdatrz)_8]\cdot 28H_2O$ (**2**)	Mo1	5+	5.317	0.317
	Mo2	5+	5.309	0.309
		5+	**5.313_{av}**	**0.313_{av}**
$Na_4[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(3\text{-}trz)_8]\cdot 14H_2O$ (**3**)	Mo1	5+	5.581	0.581
	Mo2	5+	5.642	0.642
	Mo3	5+	5.322	0.322
	Mo4	5+	5.429	0.429
	Mo5	5+	5.420	0.420
	Mo6	5+	5.248	0.248
	Mo7	5+	5.495	0.495
	Mo8	5+	5.360	0.360
	Mo9	5+	5.307	0.307
	Mo10	5+	5.295	0.295
	Mo11	5+	5.347	0.347
	Mo12	5+	5.277	0.277
		5+	**5.393_{av}**	**0.393_{av}**
$Na_8[Mo_{16}O_{16}(\mu_2\text{-}O)_{16}(\mu_2\text{-}OH)_{16}(3\text{-}trz)_8]\cdot 29H_2O$ (**4**)	Mo1	5+	5.206	0.206
	Mo2	5+	5.210	0.210
	Mo3	5+	5.302	0.302
	Mo4	5+	5.225	0.225
		5+	**5.236_{av}**	**0.236_{av}**

Table S12. Detail calibrated adsorption data of O_2, CH_4, H_2, N_2 and CO_2 for $[Mo_6O_6(\mu_2\text{-}O)_9(Hbtz)_6]\cdot 21H_2O$ (**1**) at 298 K.

Gases	O_2		CO_2		CH_4		N_2		H_2	
Temperature (^oC)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)
25.0	0	0	0	0	0	0	0	0	0	0
	0.9	3.02036	0.9	8.98546	0.9	2.35408	0.9	2.35408	0.9	1.0482
	1.9	4.07172	1.9	12.34362	1.9	2.87971	1.9	2.87971	1.9	1.46448
	3.9	6.03101	3.9	15.76731	3.9	2.95609	3.9	2.85609	3.9	1.67429
	5.899	7.81108	5.899	18.88886	5.899	2.96028	5.899	2.93028	5.899	1.77095
	7.899	9.73785	7.899	21.54057	7.899	2.98234	7.899	2.98234	7.899	1.7949
	9.892	11.74674	9.892	24.20783	9.892	3.05572	9.892	3.15572	9.892	2.08097
	11.896	13.49734	11.896	26.36884	11.896	3.06827	11.896	3.26827	11.896	2.07146
	13.898	15.60089	13.898	27.44793	13.898	3.09947	13.898	3.09947	13.898	1.96403
	15.894	17.34734	15.894	28.95	15.894	3.02285	15.894	3.02285	15.894	1.66834
	17.897	19.14292	17.897	31.27345	17.897	2.96875	17.897	2.96875	17.897	1.48302
	19.893	20.83209	19.893	31.5933	19.893	2.9558	19.893	2.8158	19.893	2.00387
	21.898	22.5602	21.898	33.77469	21.898	3.06817	21.898	2.96817	21.898	2.15909
	23.896	24.63723	23.896	33.51867	23.896	3.09245	23.896	2.99245	23.896	2.99101
	25.894	26.12388	25.894	35.19543	25.894	3.08822	25.894	2.98822	25.894	2.83133
	27.894	27.79929	27.894	35.33227	27.894	3.011	27.894	2.911	27.894	2.88893
	29.894	29.76862	29.894	36.86083	29.894	2.98035	29.894	2.88035	29.894	3.58588

Table S13. Detail calibrated adsorption data of O_2, CH_4, H_2, N_2 and CO_2 for $[Mo_8O_8(\mu_2\text{-}O)_{12}(Hdatrz)_8]\cdot 28H_2O$ (**2**) at 298 K.

Gases		O_2		CO_2		CH_4		N_2		H_2
Temperature (^oC)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)
25.0	0	0	0	0	0	0	0	0	0	0
	0.9	3.26541	0.9	2.44609	0.9	1.67802	0.9	1.74055	0.9	1.26597
	1.891	4.80697	1.891	3.93266	1.891	2.07676	1.891	1.81401	1.891	1.33681
	3.891	7.61611	3.891	4.9746	3.891	2.00507	3.891	1.96901	3.891	1.91252
	5.900	10.6488	5.900	5.90545	5.900	0.90745	5.900	1.89869	5.900	1.98547
	7.899	13.42143	7.899	6.52245	7.899	1.22231	7.899	1.98688	7.899	2.29344
	9.899	15.67771	9.899	6.94787	9.899	1.58798	9.899	2.19758	9.899	2.76436
	11.900	19.20053	11.900	7.21367	11.900	2.10685	11.900	2.05402	11.900	1.97806
	13.896	21.02197	13.896	7.2307	13.896	2.0055	13.896	1.95927	13.896	2.31509
	15.900	24.49838	15.900	7.30199	15.900	1.51232	15.900	2.01193	15.900	1.96378
	17.895	27.08844	17.895	7.25238	17.895	1.62389	17.895	1.96524	17.895	2.10285
	19.897	29.6585	19.897	7.40219	19.897	1.80925	19.897	2.03112	19.897	1.94762
	21.896	32.57412	21.896	7.26068	21.896	1.31063	21.896	2.05687	21.896	2.36093
	23.896	35.34812	23.896	7.31659	23.896	1.18058	23.896	2.07603	23.896	2.05783
	25.898	37.88831	25.898	7.29275	25.898	1.3402	25.898	2.12725	25.898	2.08429
	27.895	40.19806	27.895	7.46985	27.895	1.37488	27.895	1.92451	27.895	2.02783
	29.892	42.81752	29.892	8.18262	29.892	0.96674	29.892	1.73984	29.892	2.3886

Table S14. Detail calibrated adsorption data of O_2, CH_4, H_2, N_2 and CO_2 for $Na_4[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(3\text{-}trz)_8]\cdot 14H_2O$ (**3**) at 298 K.

Gases		O_2		CO_2		CH_4		N_2		H_2
Temperature (^oC)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)
25.0	0	0	0	0	0	0	0	0	0	0
	0.893	2.50124	0.893	3.77367	0.893	1.78037	0.893	1.66078	0.893	1.1967
	1.890	3.26684	1.890	3.31444	1.890	1.82716	1.890	2.17723	1.890	1.1027
	3.900	4.72207	3.900	4.31341	3.900	2.67594	3.900	2.27906	3.900	1.70016
	5.890	6.18244	5.890	5.63293	5.890	2.9985	5.890	2.45472	5.890	1.62839
	7.900	7.81876	7.900	6.24564	7.900	3.49606	7.900	2.46063	7.900	1.51916
	9.892	9.20356	9.892	6.19706	9.892	4.00321	9.892	2.76315	9.892	1.82
	11.899	10.95991	11.899	6.97734	11.899	4.39461	11.899	2.85427	11.899	1.4468
	13.900	12.29355	13.900	7.39546	13.900	4.61269	13.900	2.84211	13.900	2.2151
	15.897	13.90065	15.897	7.55481	15.897	4.87352	15.897	2.77733	15.897	2.11732
	17.897	15.40797	17.897	8.10015	17.897	4.96758	17.897	2.60398	17.897	1.53418
	19.897	16.73484	19.897	7.8353	19.897	4.80213	19.897	2.77791	19.897	1.79702
	21.896	18.49816	21.896	7.84133	21.896	4.63769	21.896	2.8935	21.896	2.09948
	23.893	19.90997	23.893	7.8569	23.893	4.74399	23.893	2.89466	23.893	1.76251
	25.894	21.46479	25.894	7.86312	25.894	4.88507	25.894	2.89389	25.894	1.74418
	27.896	22.96248	27.896	7.8654	27.896	4.90019	27.896	2.74383	27.896	1.80475
	29.893	24.2697	29.893	7.87559	29.893	4.91564	29.893	2.76731	29.893	1.8183

Table S15. Detail calibrated adsorption data of O_2, CH_4, H_2, N_2 and CO_2 for $Na_8[Mo_{16}O_{16}(\mu_2\text{-}O)_{16}(\mu_2\text{-}OH)_{16}(3\text{-}trz)_8]\cdot 29H_2O$ (**4**) at 298 K.

Gases	O_2		CO_2		CH_4		N_2		H_2	
Temperature (^oC)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)
25.0	0	0	0	0	0	0	0	0	0	0
	0.890	2.52594	0.890	5.12816	0.890	5.12816	0.890	0.95956	0.890	0.95956
	1.890	3.24996	1.890	6.90345	1.890	6.90345	1.890	1.73884	1.890	1.73884
	3.900	5.27142	3.900	9.18453	3.900	9.18453	3.900	1.48188	3.900	1.48188
	5.890	6.8601	5.890	10.83894	5.890	10.83894	5.890	1.09128	5.890	1.09128
	7.900	8.78391	7.900	12.01897	7.900	12.01897	7.900	2.2308	7.900	2.2308
	9.899	10.56792	9.899	12.19072	9.899	12.19072	9.899	1.64253	9.899	1.64253
	11.898	12.35951	11.898	12.20179	11.898	12.04179	11.898	1.93485	11.898	1.93485
	13.897	14.05107	13.897	12.30908	13.897	12.15908	13.897	1.27842	13.897	1.27842
	15.895	15.54922	15.895	12.39084	15.895	14.39084	15.895	2.30201	15.895	2.30201
	17.900	17.26034	17.900	12.89373	17.900	14.89373	17.900	1.24712	17.900	1.24712
	19.895	19.09354	19.895	12.80611	19.895	14.80611	19.895	1.52512	19.895	1.52512
	21.895	20.76321	21.895	12.71431	21.895	14.71431	21.895	1.99431	21.895	1.99431
	23.896	22.59773	23.896	12.70224	23.896	15.14224	23.896	1.73929	23.896	1.73929
	25.899	24.27387	25.899	12.68929	25.899	15.08929	25.899	1.82826	25.899	1.82826
	27.895	25.84537	27.895	12.64519	27.895	14.64519	27.895	2.22378	27.895	2.22378
	29.896	27.51	29.896	12.46768	29.896	14.46768	29.896	1.47732	29.896	1.47732

Table S16. Solid ^{13}C NMR spectral data (ppm) of **1** – **4** respectively.

Compound	δ (−C1)	δ (−C2)	δ (−C3)
1	146.41, 143.01	125.04, 123.10	115.82
2	162.61	–	–
3	163.10	154.85, 142.72	–
4	162.61	151.94	–

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