Supporting materials

Binuclear, tetranuclear and hexadecnuclear thio- oxomolybdenum(V/IV) glycolates with selective adsorptions of gases

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Figure and Table Options

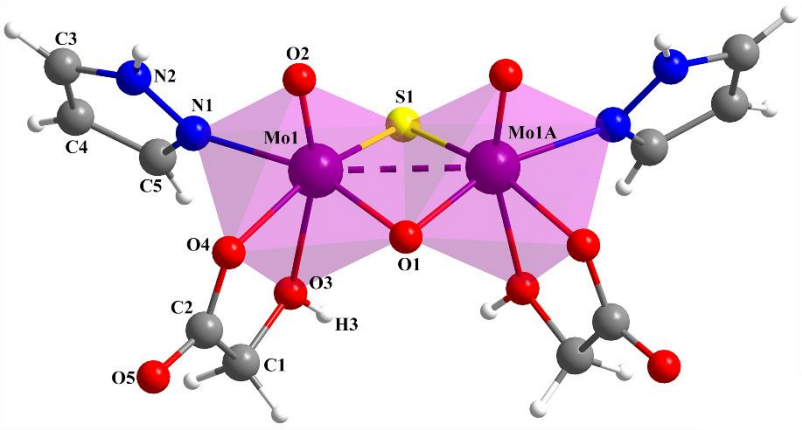

Figure S1. Polyhedral representation of **1**.

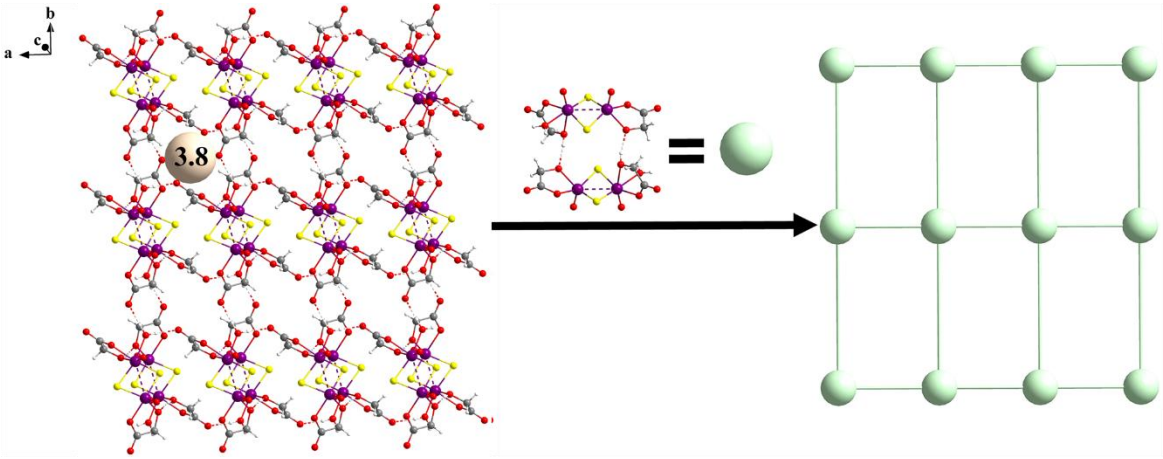

Figure S2. Forming a circular cavity of 3.8 Å approximately in **2** and its corresponding simplified topological nets, green sphere represents a complete tetramer.

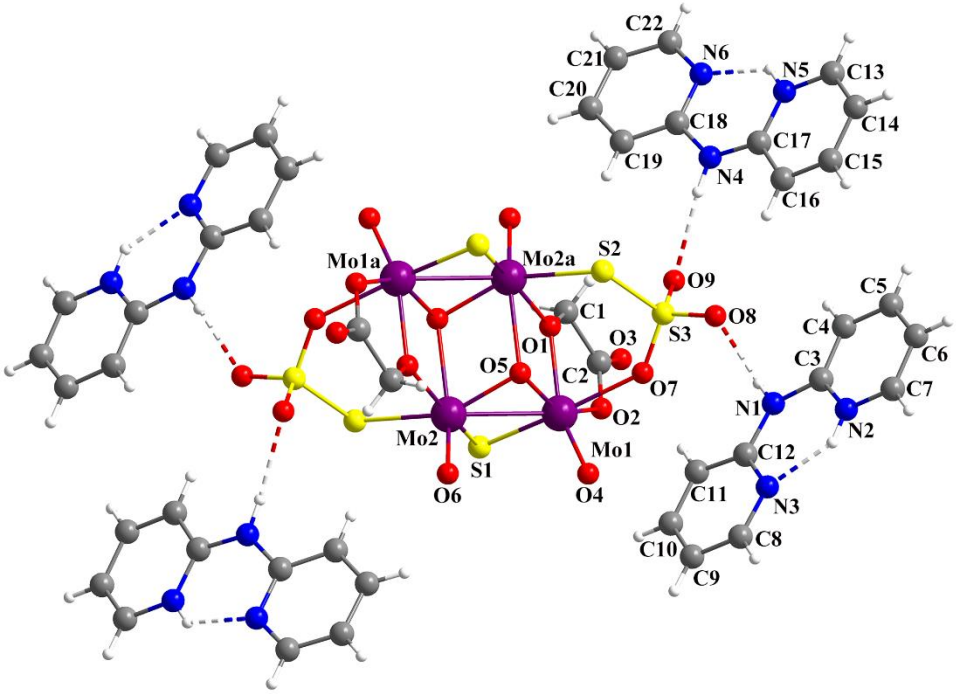

Figure S3. View of the main structure of **3**. Symmetric code: *a* (*-x*, *-y*, *-z*).

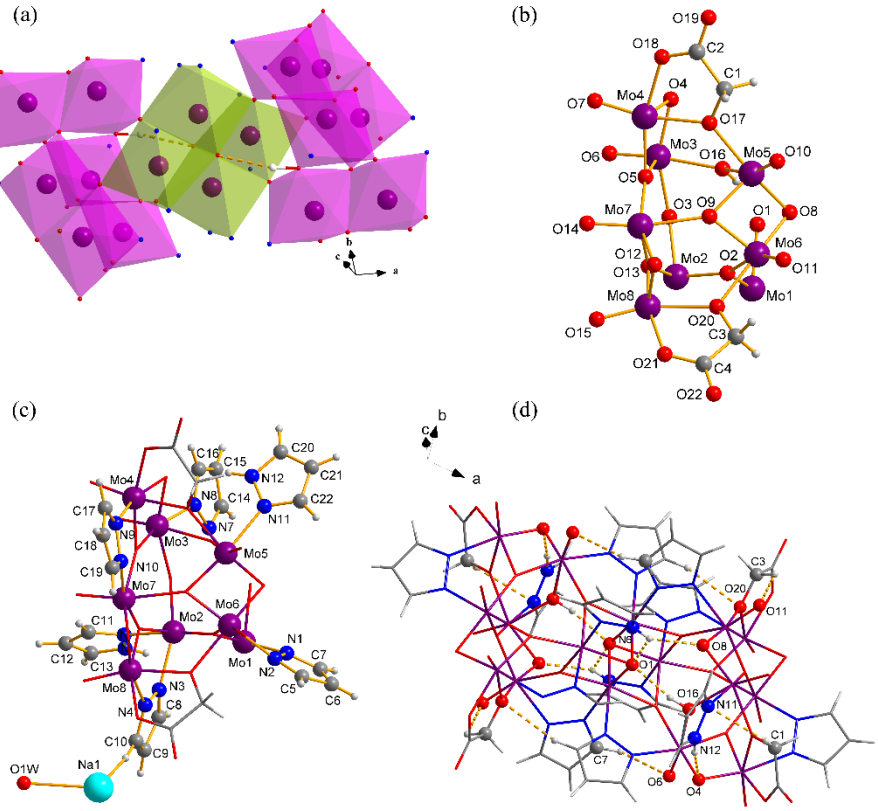

Figure S4. (a) Polyhedral representation of **4**. (b) The skeleton connection in **4-part 2**. (c) Highlighted pz/Hpz ligands in **4-part 2**. (d) Highlighted intramolecular hydrogen bonds in **4**.

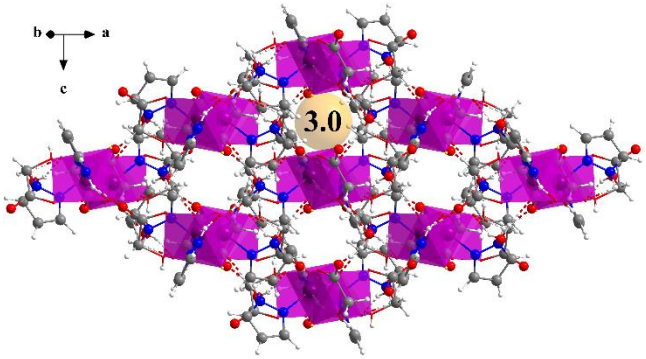

Figure S5. 3D holes exist in **1** viewed along (1,1,0) direction with a diameter of 3.0 Å approximately. Atomic color: molybdenum, violet; oxygen, red; nitrogen, blue; carbon, gray; hydrogen, white.

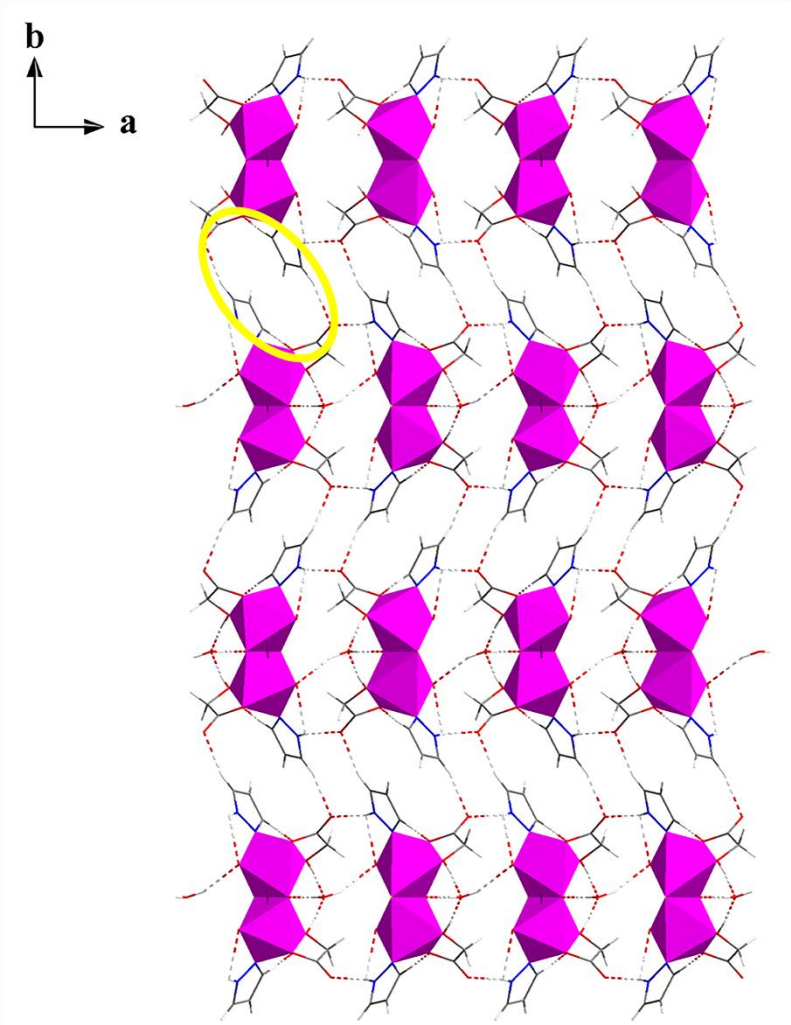

Figure S6. Packing diagram of **1** in *c*-axis direction, forming an "8"-shaped cavity of 6.4 × 2.8 $Å^2$ approximately.

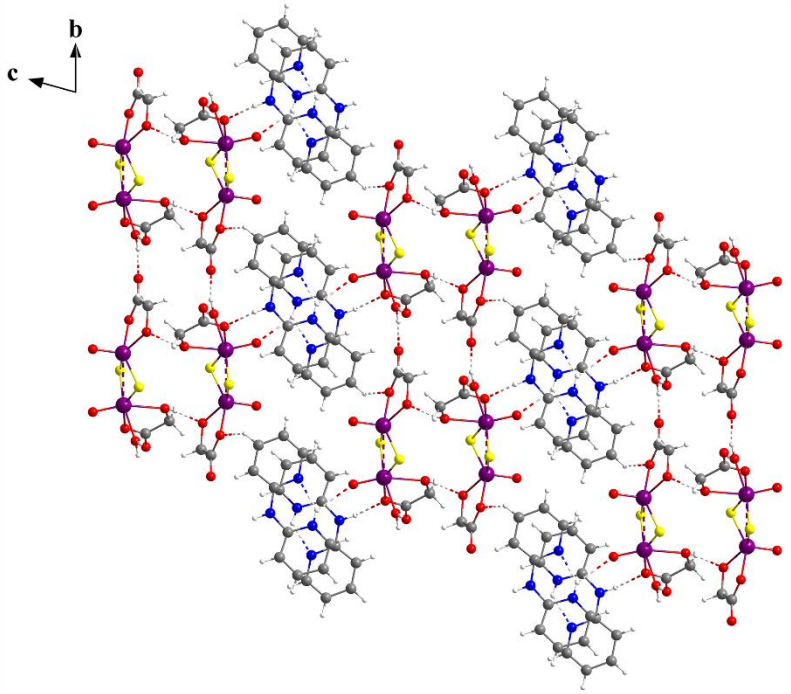

Figure S7. Packing diagram of **2** viewed from *a*-axis direction.

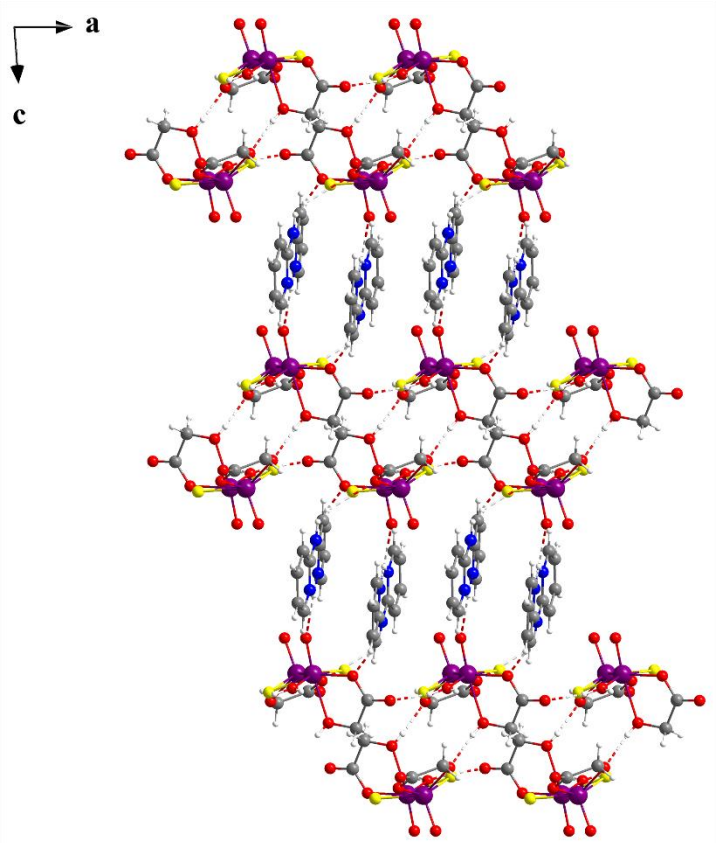

Figure S8. Packing diagram of **2** viewed from *b*-axis direction.

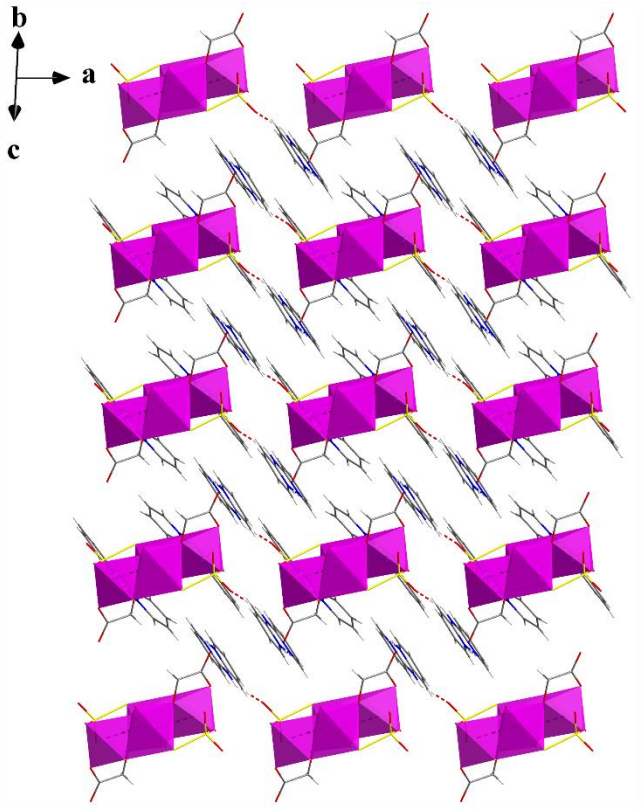

Figure S9. Packing diagram of **3** viewed from (0, 1, 1) direction.

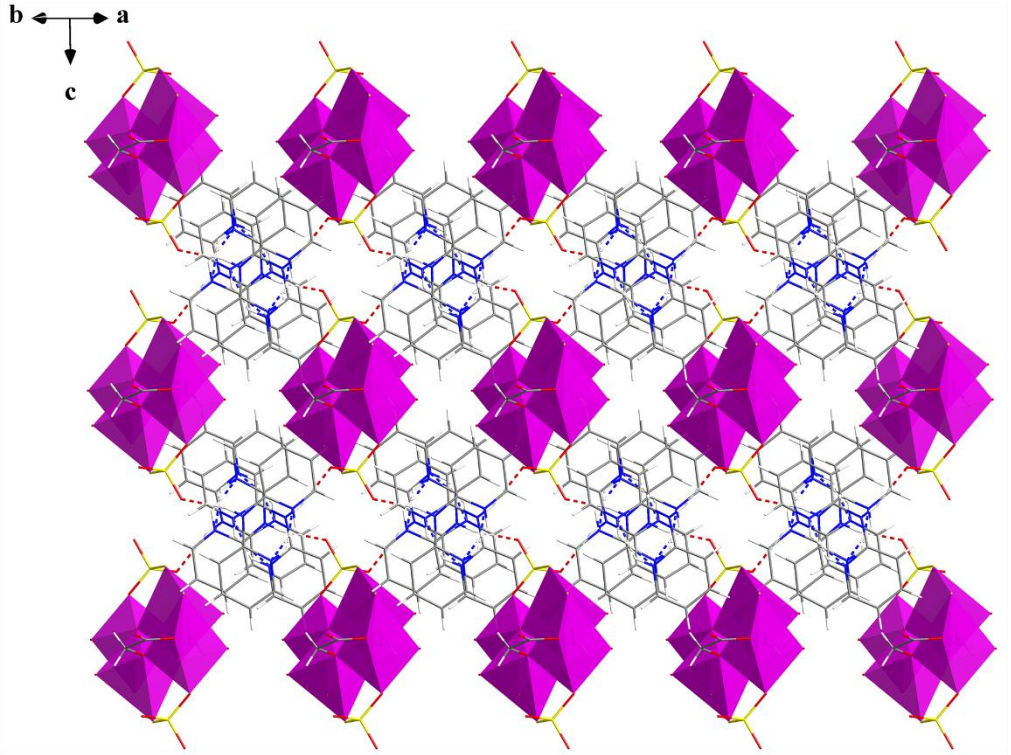

Figure S10. Packing diagram of **3** viewed from (1, 1, 0) direction.

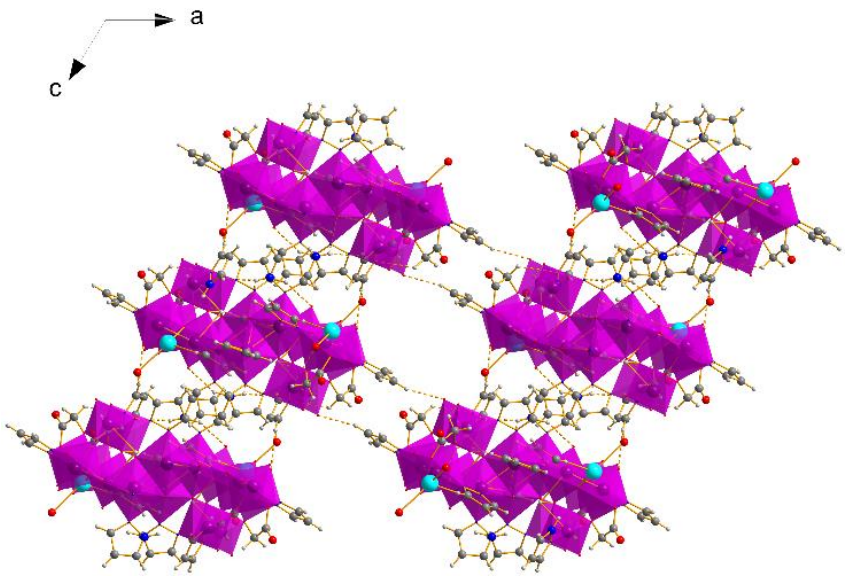

Figure S11. Packing diagram of **4** viewed from *b*-axis direction.

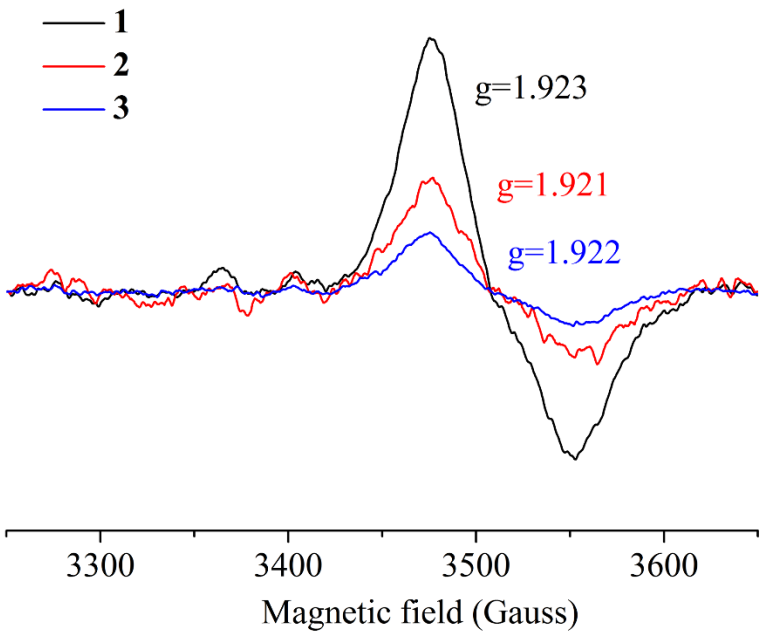

Figure S12. Solution EPR spectra of **1** ~ **3** in DMSO solvents at 110 K respectively.

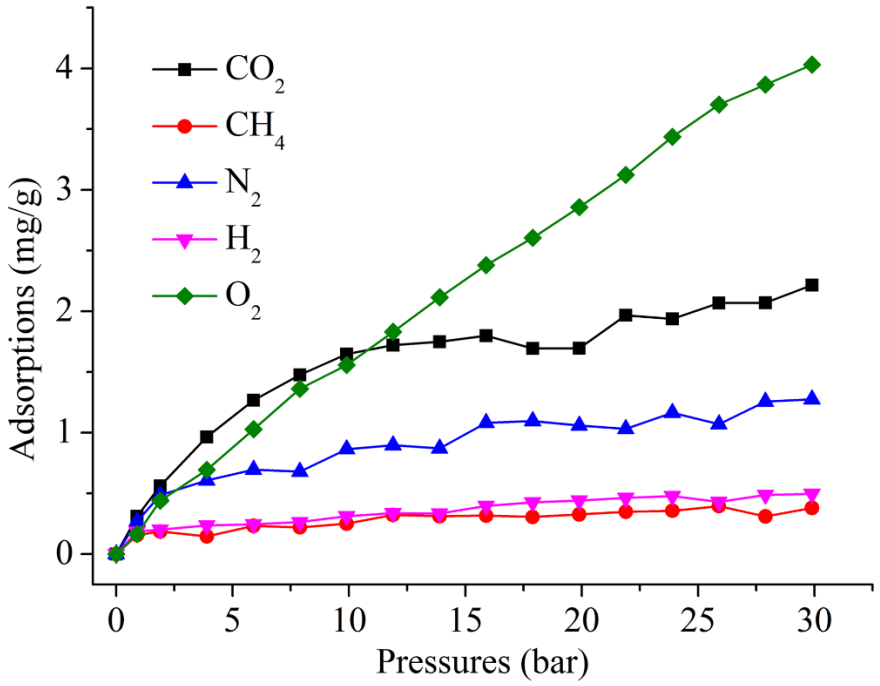

Figure S13. O_2, CO_2, N_2, CH_4 and H_2 adsorptions for **1** at different pressures at 298 K, respectively.

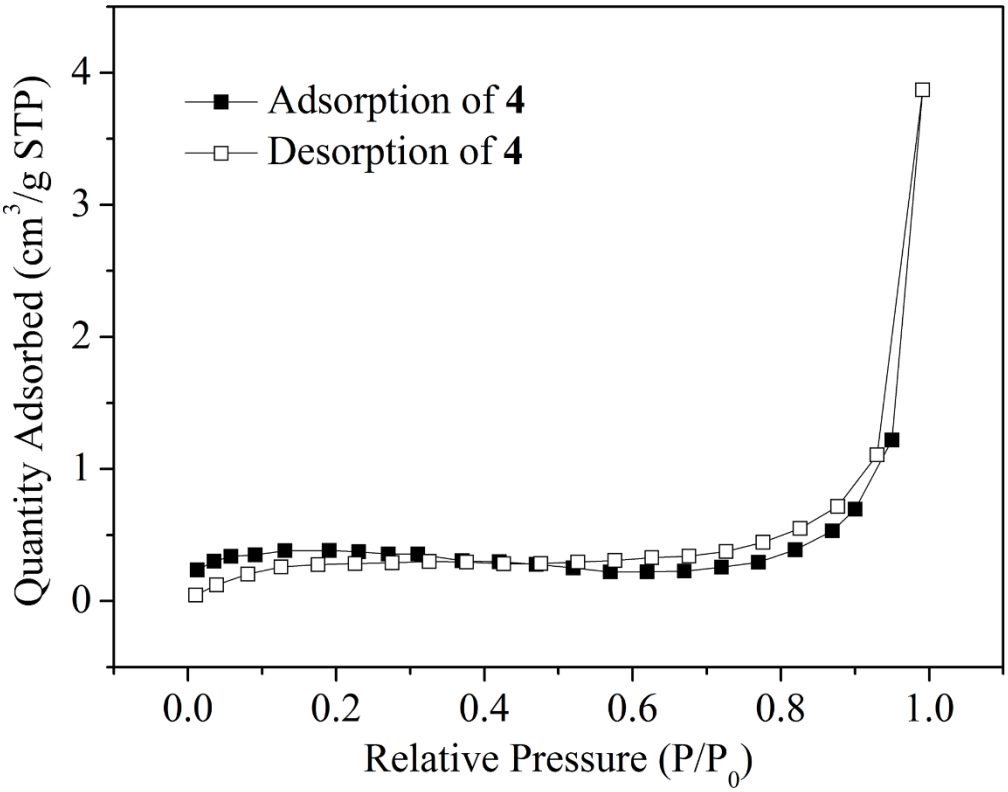

Figure S14. N_2 adsorption-desorption isotherms of $Na_2[Mo_{16}O_{12}(\mu_2\text{-}O)_6(\mu_2\text{-}OH)_2(\mu_3\text{-}O)_{12}(glyc)_4(Hpz)_4(pz)_8]\cdot 28H_2O$ (**4**) at low pressure.

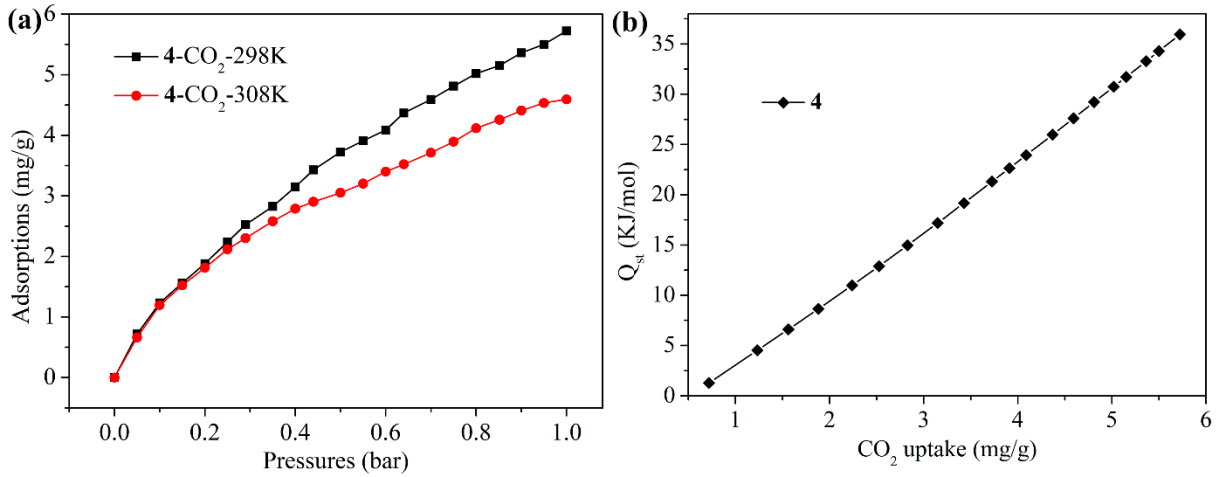

Figure S15. (a) CO_2 adsorption isotherms for **4** at different temperatures (298 and 308 K) under the low pressure; (b) Isosteric heat of adsorption (Q_{st}) plotted against CO_2 uptake for **4**.

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 temperature in the pressure range of 0 ~ 1 bar.

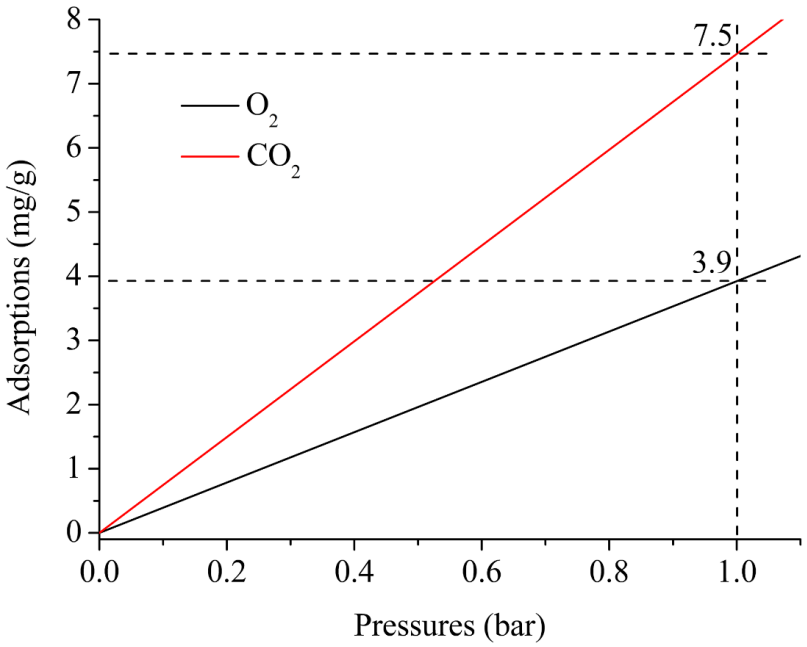

Figure S16. O_2 and CO_2 adsorption isotherms for **4** at 298 K and pressures of up to 1 bar.

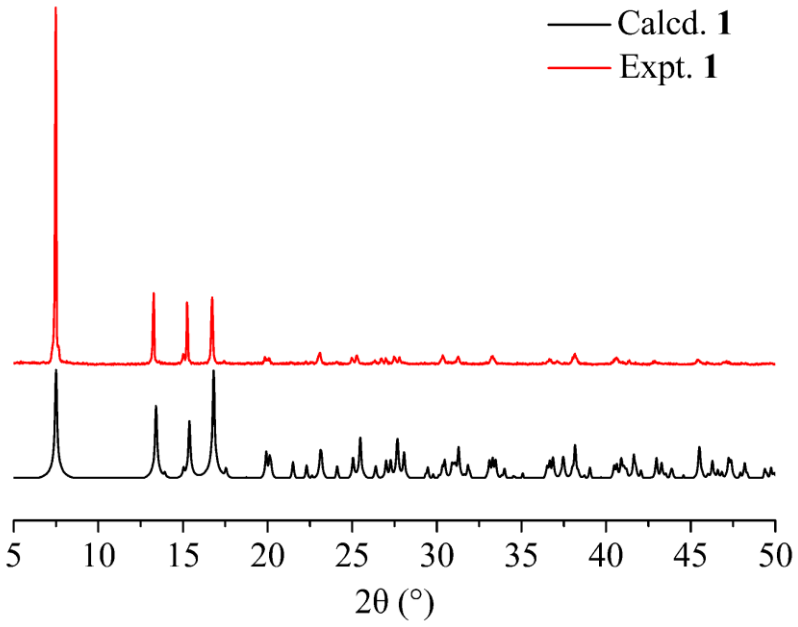

Figure S17. Calculated and simulated PXRD patterns of compound **1**.

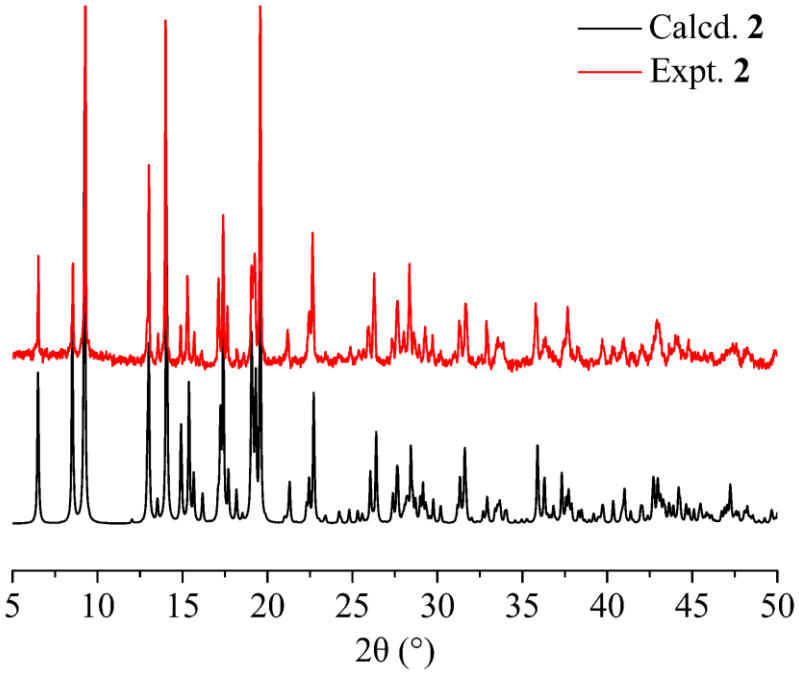

Figure S18. Calculated and simulated PXRD patterns of compound **2**.

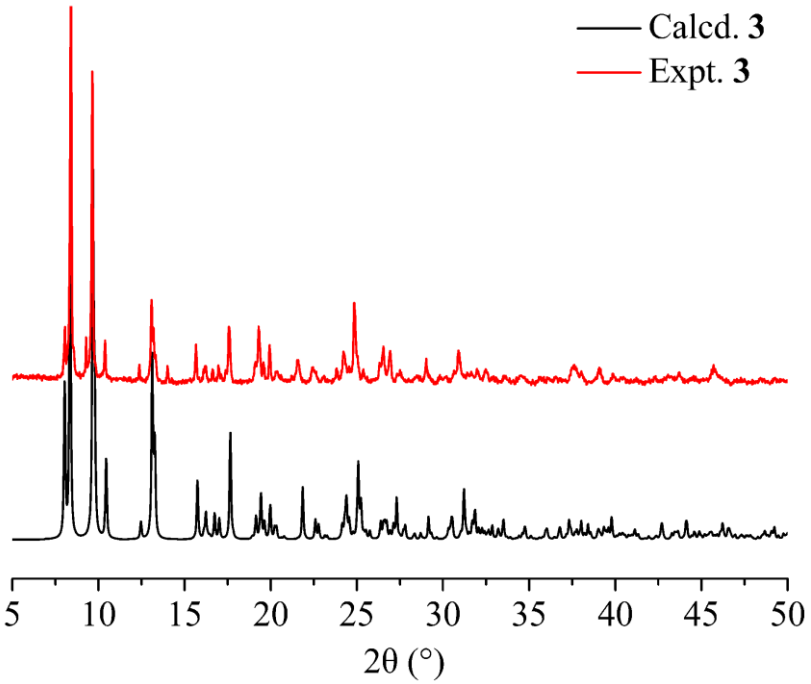

Figure S19. Calculated and simulated PXRD patterns of compound **3**.

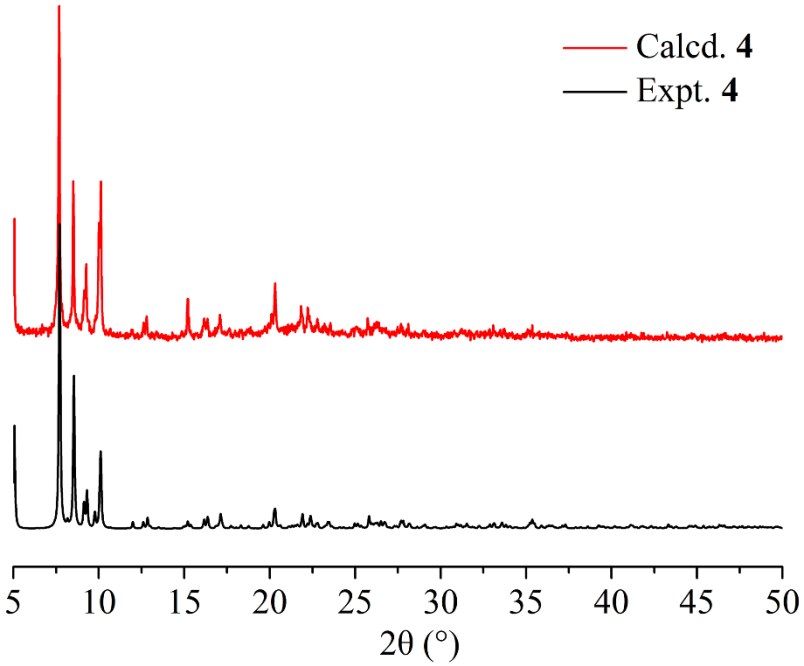

Figure S20. Calculated and simulated PXRD patterns of compound **4**.

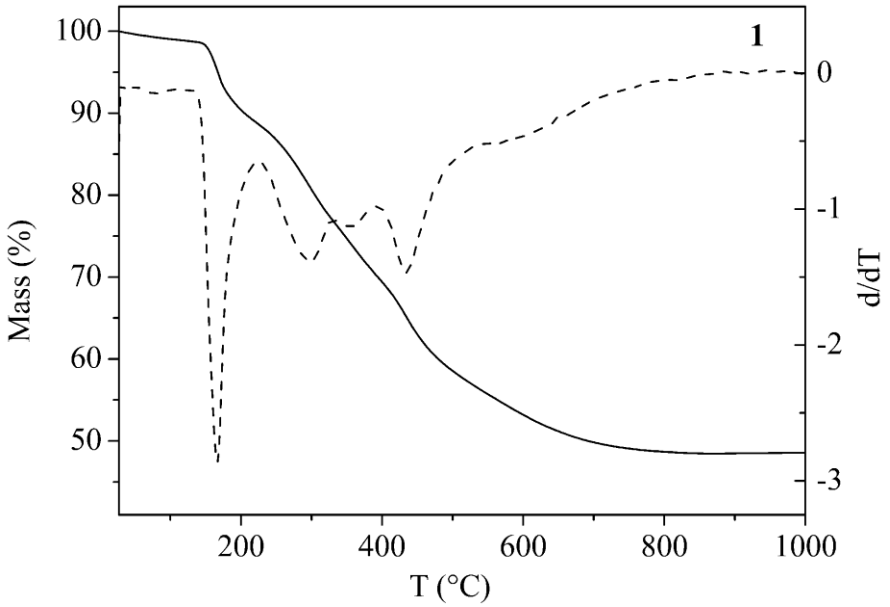

Figure S21. TG-DTG curves of compound **1**.

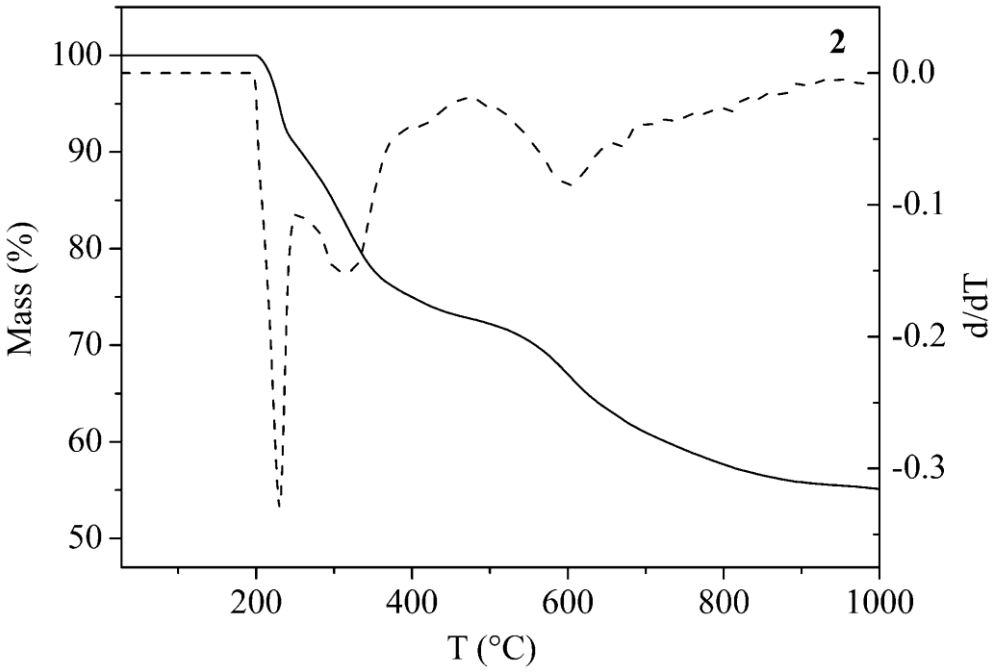

Figure S22. TG-DTG curves of compound **2**.

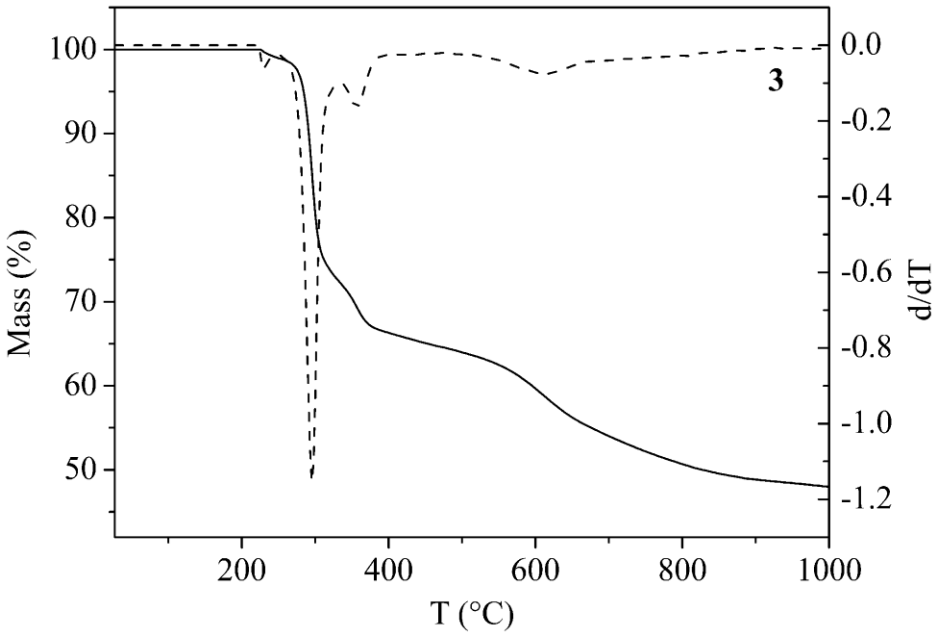

Figure S23. TG-DTG curves of compound **3**.

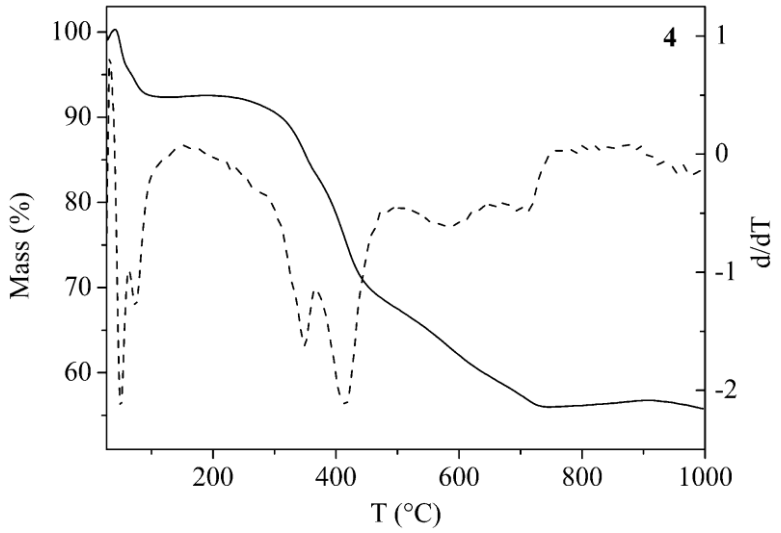

Figure S24. TG-DTG curves of compound **4.**

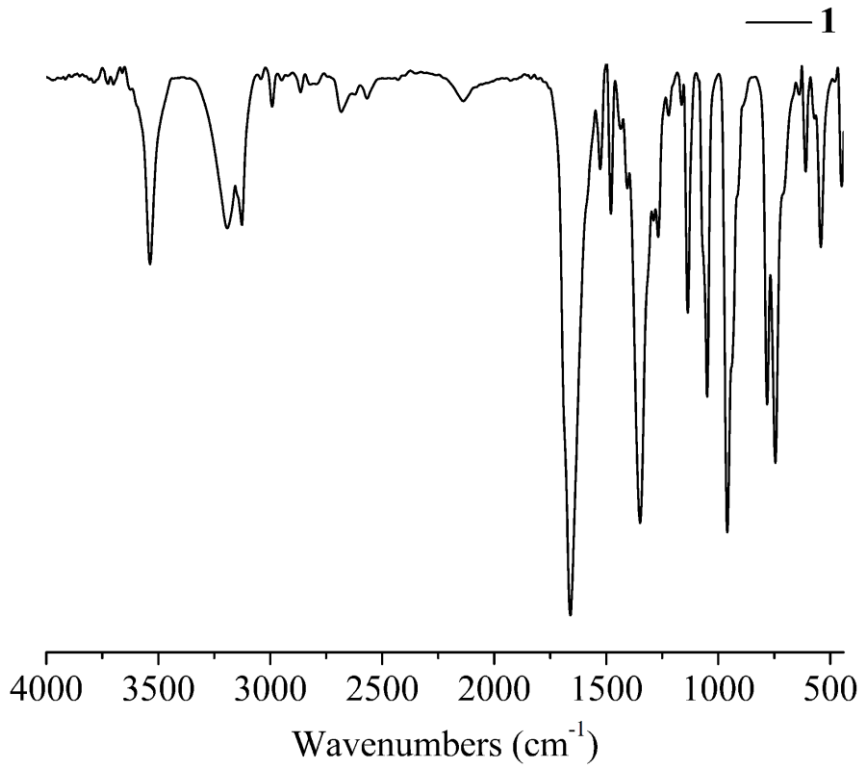

Figure S25. IR spectrum of compound **1**.

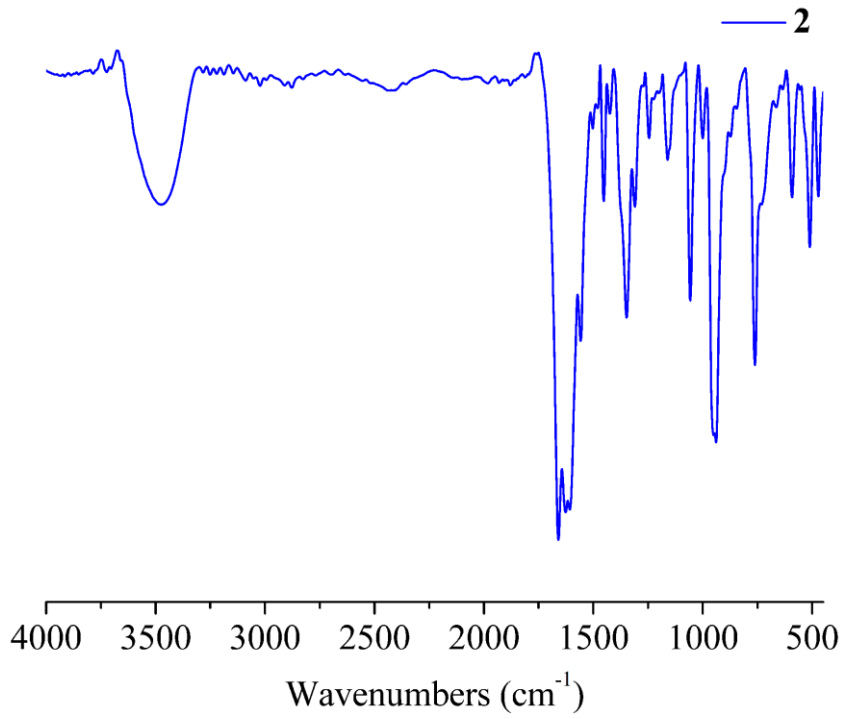

Figure S26. IR spectrum of compound **2**.

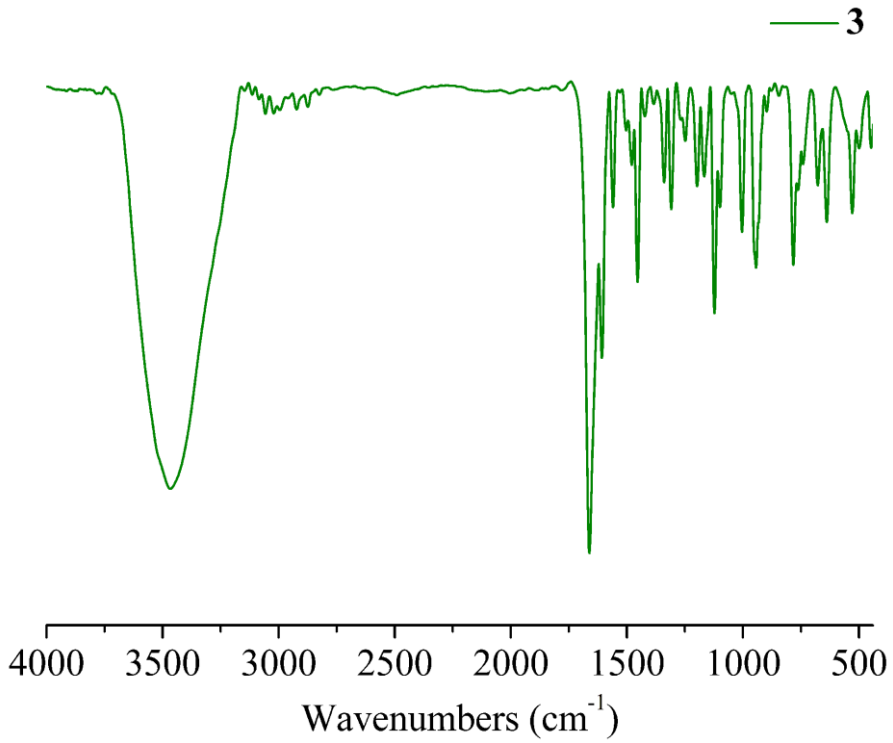

Figure S27. IR spectrum of compound **3**.

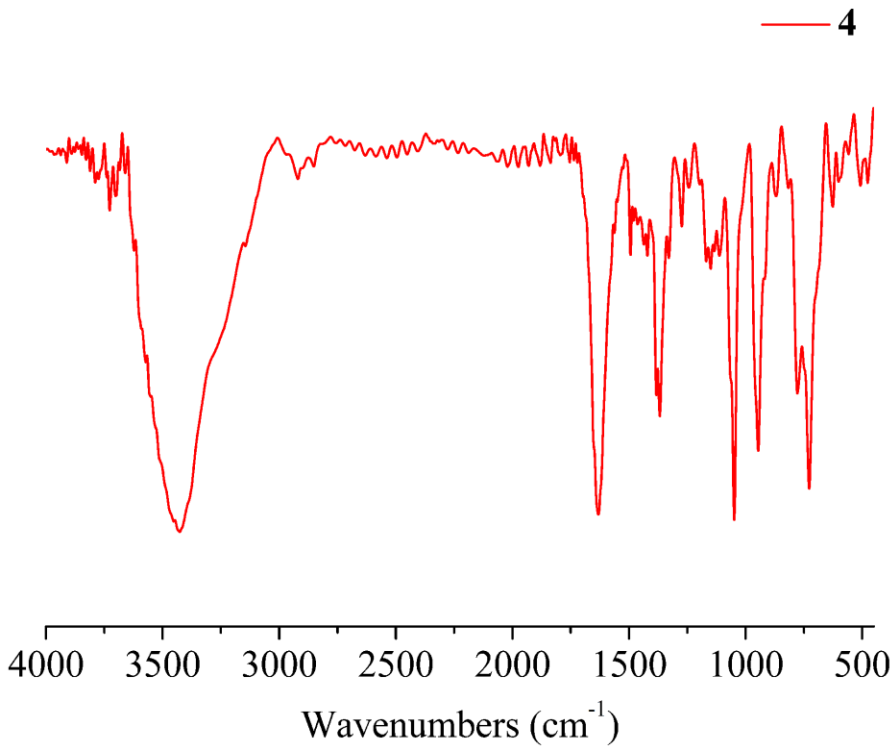

Figure S28. IR spectrum of compound **4**.

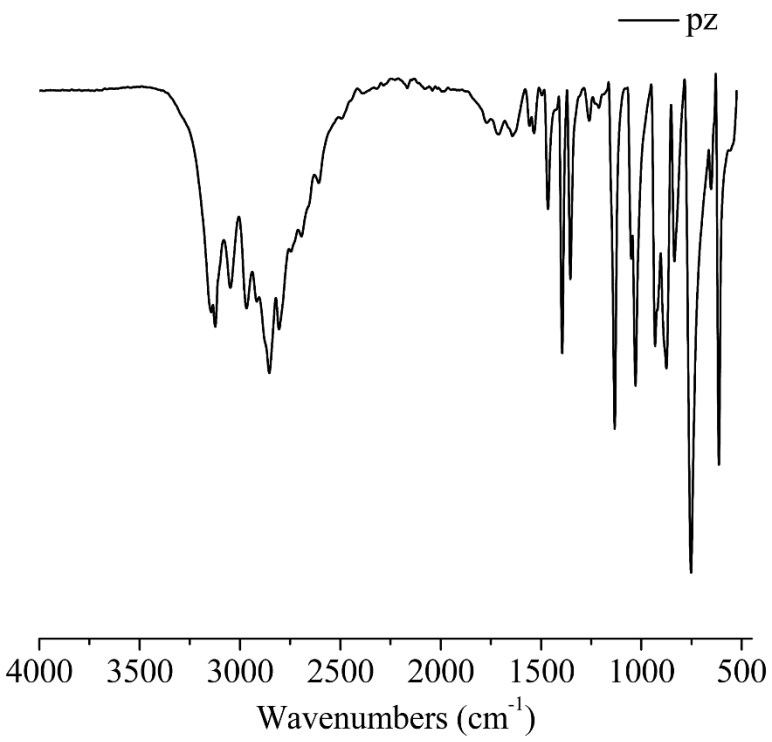

Figure S29. IR spectrum of pyrazole ligands.

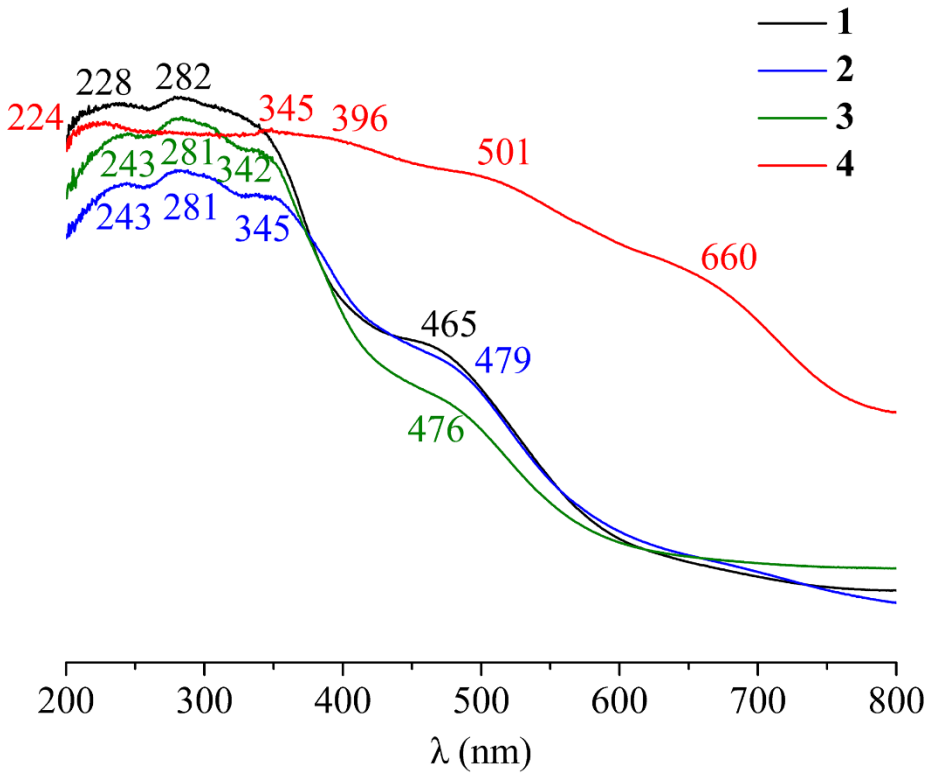

Figure S30. Solid-state UV-vis reflective spectra for **1** ~ **4**.

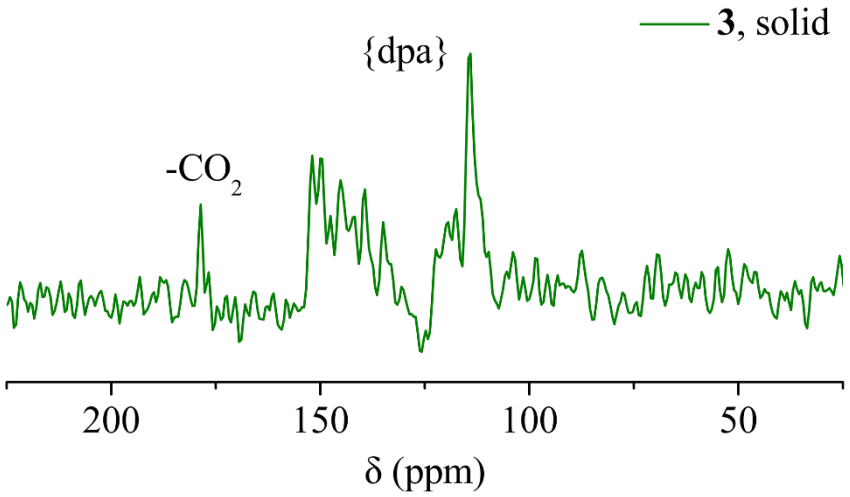

Figure S31. Solid-state ^{13}C NMR spectrum for **3**.

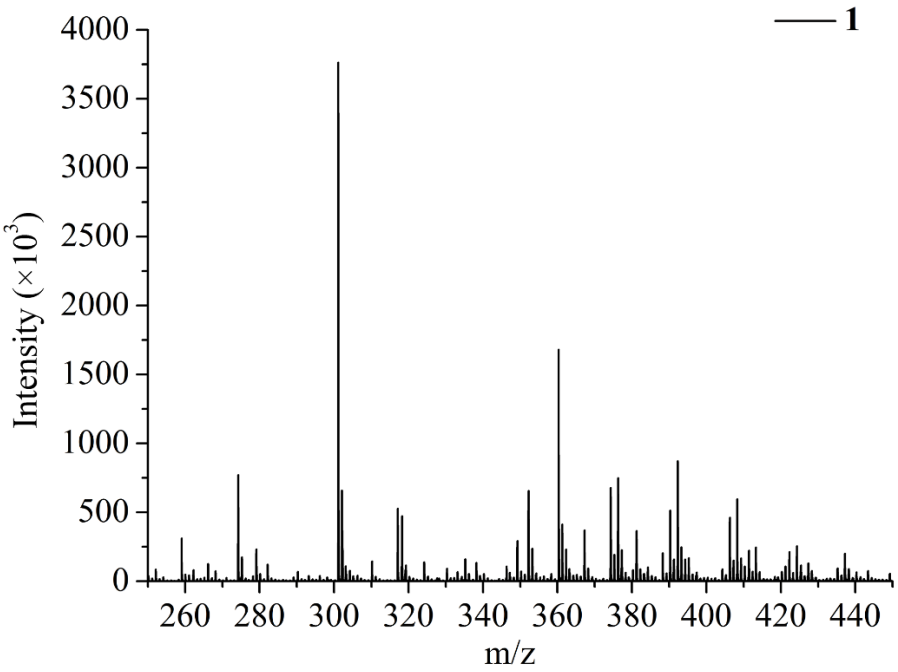

Figure S32. Positive ion electrospray ionization mass spectra (ESI-MS) of **1** in MeOH solution.

Table S1. Crystallographic data and structural refinements for complexes $[Mo_2O_2(\mu_2\text{-}O)(\mu_2\text{-}S)(Hglyc)_2(Hpz)_2]\cdot H_2O$ (**1**), $(Hdpa)[Mo_2O_2(\mu_2\text{-}S)_2(Hglyc)(glyc)(H_2O)]$ (**2**), $(Hdpa)_4[Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}S)_2(glyc)_2(S_2O_3)_2]$ (**3**) and $Na_2[Mo_{16}O_{12}(\mu_2\text{-}O)_6(\mu_2\text{-}OH)_2(\mu_3\text{-}O)_{12}(glyc)_4(Hpz)_4(pz)_8]\cdot 28H_2O$ (**4**) respectively.

Identification codes	**1**	**2**	**3**	**4**
Empirical formula	$C_{10}H_{16}Mo_2N_4O_{10}S$	$C_{14}H_{17}Mo_2N_3O_9S_2$	$C_{44}H_{44}Mo_4N_{12}O_{18}S_6$	$C_{44}H_{50}Mo_{16}N_{24}Na_2O_{46}$
Formula weight	576.2	627.3	1605.03	3232.1
Temperature/K	100.00(1)	230.00(1)	100.00(2)	100.00(1)
Crystal system	orthorhombic	triclinic	triclinic	monoclinic
Space group	*Pnma*	*P* $\bar{1}$	*P* $\bar{1}$	*C* 2/*c*
a/Å	13.1969(3)	6.8529(3)	11.1684(2)	43.6195(7)
b/Å	23.5561(7)	10.7593(4)	11.2139(2)	13.7952(1)
c/Å	5.9279(2)	14.1435(6)	11.8751(2)	20.6277(3)
α/ °	90	74.526(3)	104.928(1)	90
β/ °	90	85.918(3)	103.841(1)	121.411(2)
γ/ °	90	89.947(3)	98.2450(4)	90
Volume/Å^3	1842.79(9)	1002.31(7)	1361.60(4)	10593.5(3)
Z	4	2	1	4
ρ_{calc}g/cm^3	2.077	2.079	1.957	2.027
μ/mm^{-1}	12.766	12.704	10.264	15.783
F(000)	1136.0	620.0	800.0	6176.0
Crystal size/mm^3	0.1 × 0.1 × 0.05	0.35 × 0.1 × 0.02	0.3 × 0.2 × 0.05	0.1 × 0.05 × 0.03
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/ °	7.506 to 154.864	6.502 to 143.176	8.048 to 149.66	4.748 to 146.146

Index ranges	$-11 \leq h \leq 16$, $-29 \leq k \leq 27$, $-7 \leq l \leq 7$	$-8 \leq h \leq 7$, $-12 \leq k \leq 13$, $-17 \leq l \leq 17$	$-11 \leq h \leq 13$, $-14 \leq k \leq 13$, $-14 \leq l \leq 11$	$-53 \leq h \leq 53$, $-13 \leq k \leq 17$, $-25 \leq l \leq 25$
Reflections collected	6129	7558	13703	30981
Independent reflections	1873 (R_{int} = 0.0219, R_{σ} = 0.0220)	3887 (R_{int} = 0.0807, R_{σ} = 0.0754)	5299 (R_{int} = 0.0338, R_{σ} = 0.0392)	10101 (R_{int} = 0.0431, R_{σ} = 0.0424)
Data/restraints/parameters	1873/0/131	3887/4/277	5299/0/387	10101/1/598
Goodness–of–fit on F^2	1.178	1.141	1.045	1.044
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0348, wR_2 = 0.0957	R_1 = 0.0598, wR_2 = 0.1808	R_1 = 0.0461, wR_2 = 0.1098	R_1 = 0.0469, wR_2 = 0.1243
Final R indexes [all data]	R_1 = 0.0376, wR_2 = 0.0973	R_1 = 0.0806, wR_2 = 0.2167	R_1 = 0.0469, wR_2 = 0.1103	R_1 = 0.0584, wR_2 = 0.1322
Largest diff. peak/hole/e $\cdot$Å^{-3}	0.46/-0.91	2.02/-1.95	3.25/-1.20	1.59/-0.92

Table S2. Selected hydrogen bond distances (Å) and angles (°) in $[Mo_2O_2(\mu_2\text{-}O)(\mu_2\text{-}S)(Hglyc)_2(Hpz)_2]\cdot H_2O$ (**1**).

	D–H ···A	D–H(Å)	H ···A(Å)	D ···A(Å)	D–H ···A(°)
	O1w–H1wA···O1[a]	0.87	1.74	2.597(6)	170
Intra	N2–H2···O2	0.88	2.52	2.896(5)	106
	N2–H2···O5[b]	0.88	1.98	2.761(5)	147
	O1w–H1wB···O2[c]	0.87	2.36	3.191(4)	160
Intra	O3–H3···O1w	0.84	1.81	2.645(4)	172
	C3–H3A···O5[d]	0.95	2.28	3.162(5)	153
	C5–H5···O4[a]	0.95	2.24	3.146(5)	159

Symmetry codes: (a) *x*, *y*, -1 + *z*; (b) -½ + *x*, *y*, 3/2 – *z*; (c) ½ + *x*, 3/2 – *y*, ½ – *z*; (d) ½ – *x*, 1 – *y*, -½ + *z*.

Table S3. Selected hydrogen bond distances (Å) and angles (°) in $(Hdpa)[Mo_2O_2(\mu_2\text{-}S)_2(Hglyc)(glyc)(H_2O)]$ (**2**).

	D–H ···A	D–H(Å)	H ···A(Å)	D ···A(Å)	D–H ···A(°)
Intra	N1–H1···O5	0.87	2.09	2.900(1)	154
Intra	N2–H2···N3	0.87	1.94	2.618(1)	134
	N2–H2···O8[a]	0.87	2.35	3.041(1)	137
	O4–H4···S1[b]	0.86(3)	2.85(7)	3.477(7)	132(8)
	O4–H4···O1[b]	0.86(3)	1.78(5)	2.574(9)	154(9)
	O1w–H1wA···O3[c]	0.85	1.75	2.588(1)	167
	O1w–H1wB···O6[d]	0.85	1.75	2.596(1)	172
	C1–H1A···O9[b]	0.98	2.59	3.450(1)	146
	C12–H12···O2[c]	0.94	2.54	3.074(2)	116

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

Table S4. Selected hydrogen bond distances (Å) and angles (°) in $(Hdpa)_4[Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}S)_2(glyc)_2(S_2O_3)_2]$ (**3**).

	D–H ···A	D–H(Å)	H ···A(Å)	D ···A(Å)	D–H ···A(°)
Intra	N1–H1···O8	0.86	2.01	2.821(7)	156
Intra	N2–H2···N3	0.86	1.9	2.575(6)	135
Intra	N4–H4A···O9	0.86	2.21	3.009(7)	155
Intra	N5–H5···N6	0.86	1.96	2.627(6)	134
Intra	C1–H1A···O9	0.90(6)	2.57(6)	3.115(7)	120(4)
	C7–H7···O5[a]	0.93	2.23	3.106(7)	158
	C9–H9···O2[b]	0.93	2.58	3.032(7)	110
Intra	C11–H11···O7	0.93	2.42	3.333(7)	167
	C13–H13···O4[c]	0.93	2.39	3.292(7)	164
	C14–H14···O2[d]	0.93	2.55	3.158(7)	124
	C19–H19···O6[e]	0.93	2.49	3.242(7)	138
	C20–H20···O3[f]	0.93	2.58	3.315(7)	136
	C23–H23···O3[d]	0.93	2.36	3.183(7)	148

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

Table S5. Selected hydrogen bond distances (Å) and angles (°) in $Na_2[Mo_{16}O_{12}(\mu_2\text{-}O)_6(\mu_2\text{-}OH)_2(\mu_3\text{-}O)_{12}(glyc)_4(Hpz)_4(pz)_8]\cdot 28H_2O$ (**4**).

	D–H ···A	D–H(Å)	H ···A(Å)	D ···A(Å)	D–H ···A(°)
Intra	N6–H6···O1[a]	0.88	2.41	2.871(7)	113
Intra	N6–H6···O8[a]	0.88	2.3	3.123(9)	156
Intra	N12–H12···O4	0.88	2.29	3.158(1)	168
Intra	O16–H16···O1	0.87(6)	1.96(6)	2.797(7)	161(7)
Intra	C1–H1A···N11	0.99	2.62	3.219(1)	119
Intra	C3–H3A···O11	0.99	2.35	2.878(8)	113
Intra	C7–H7···O6[a]	0.95	2.48	3.223(1)	135
Intra	C14–H14···O20[a]	0.95	2.58	3.506(1)	164
	C18–H18···O10[b]	0.95	2.48	3.387(1)	159
	C22–H22···O1w[c]	0.95	2.55	3.381(2)	146
	C22–H22···O7[d]	0.95	2.5	3.178(9)	129

Symmetric codes: (a) $½ - x$, $½ - y$, $1 - z$; (b) $1 - x$, y, $3/2 - z$; (c) x, $1 - y$, $½ + z$; (d) x, $-y$, $½ + z$.

Table S6. Bond valence calculations for complexes **1** ~ **4** respectively.

Complexes	Atoms	N	$\sum S_{ij}$	|d|
$[Mo_2O_2(\mu_2\text{-}O)(\mu_2\text{-}S)(Hglyc)_2(Hpz)_2]\cdot H_2O$ (**1**)	**Mo**	**5+**	**5.317**	**0.317**
	Mo1	5+	5.080	0.080
$(Hdpa)[Mo_2O_2(\mu_2\text{-}S)_2(Hglyc)(glyc)(H_2O)]$ (**2**)	Mo2	5+	5.199	0.199
		5+	**5.140_{av}**	**0.140_{av}**
	Mo1	5+	5.245	0.245
$(Hdpa)_4[Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}S)_2(glyc)_2(S_2O_3)_2]$ (**3**)	Mo2	5+	5.077	0.077
		5+	**5.161_{av}**	**0.161_{av}**
	Mo1	4+	3.959	0.041
	Mo2	4+	4.269	0.269
		4+	**4.114_{av}**	**0.114_{av}**
	Mo3	5+	5.433	0.433
	Mo4	5+	5.335	0.335
$Na_2[Mo_{16}O_{12}(\mu_2\text{-}O)_6(\mu_2\text{-}OH)_2(\mu_3\text{-}O)_{12}(glyc)_4(Hpz)_4(pz)_8]\cdot 28H_2O$ (**4**)	Mo5	5+	5.213	0.213
	Mo6	5+	5.279	0.279
	Mo7	5+	5.252	0.252
	Mo8	5+	5.202	0.202
		5+	**5.286_{av}**	**0.286_{av}**

Table S7. Selected bond distances (Å) and angles (°) in $[Mo_2O_2(\mu_2\text{-}O)(\mu_2\text{-}S)(Hglyc)_2(Hpz)_2]\cdot H_2O$ (**1**).

Atom–Atom	**Length/Å**	**Atom–Atom**	**Length/Å**
Mo(1)–Mo(1)[1]	2.6741(6)	Mo(1)–O(2)	1.684(3)
Mo(1)–S(1)	2.3312(11)	Mo(1)–O(4)	2.085(3)
Mo(1)–O(3)	2.260(3)	Mo(1)–N(1)	2.222(3)
Mo(1)–O(1)	1.936(3)		

Atom–Atom–Atom	**Angle/°**	**Atom–Atom–Atom**	**Angle/°**
S(1)–Mo(1)–Mo(1)[1]	55.00(2)	N(1)–Mo(1)–Mo(1)[1]	145.40(9)
O(3)–Mo(1)–Mo(1)[1]	100.56(7)	N(1)–Mo(1)–S(1)	90.65(9)
O(3)–Mo(1)–S(1)	85.41(8)	N(1)–Mo(1)–O(3)	78.3(1)
O(1)–Mo(1)–Mo(1)[1]	46.32(8)	Mo(1)–S(1)–Mo(1)[1]	69.99(4)
O(1)–Mo(1)–S(1)	97.58(9)	Mo(1)–S(1)–Mo(1)[1]	83.0(1)
O(1)–Mo(1)–O(3)	87.6(1)	Mo(1)–O(1)–Mo(1)[1]	87.4(2)
O(1)–Mo(1)–O(4)	83.7(1)	O(2)–Mo(1)–O(4)	96.6(1)
O(1)–Mo(1)–N(1)	163.1(1)	O(2)–Mo(1)–N(1)	87.1(1)
O(2)–Mo(1)–Mo(1)[1]	97.5(1)	O(4)–Mo(1)–Mo(1)[1]	129.96(9)
O(2)–Mo(1)–S(1)	105.5(1)	O(4)–Mo(1)–S(1)	156.63(9)
O(2)–Mo(1)–O(3)	161.9(1)	O(4)–Mo(1)–O(3)	71.3(1)
O(2)–Mo(1)–O(1)	104.8(2)		

Symmetric codes: [1] x, 3/2 – y, z.

Table S8. Selected bond distances (Å) and angles (°) in (Hdpa)[$Mo_2O_2(\mu_2$-$S)_2$(Hglyc)(glyc)(H_2O)] (**2**).

Atom–Atom	**Length/Å**	**Atom–Atom**	**Length/Å**
Mo(2)–Mo(1)	2.8050(9)	Mo(2)–O(8)	1.672(6)
Mo(2)–S(1)	2.305(2)	Mo(1)–S(1)	2.307(2)
Mo(2)–S(2)	2.301(3)	Mo(1)–S(2)	2.314(3)
Mo(2)–O(4)	2.265(6)	Mo(1)–O(2)	2.064(7)
Mo(2)–O(1w)	2.178(6)	Mo(1)–O(7)	1.676(7)
Mo(2)–O(5)	2.145(6)	Mo(1)–O(1)	2.027(6)

Atom–Atom–Atom	**Angle/°**	**Atom–Atom–Atom**	**Angle/°**
S(1)–Mo(2)–Mo(1)	52.57(6)	O(1)–Mo(1)–S(2)	141.0(2)
S(2)–Mo(2)–Mo(1)	52.77(6)	O(1)–Mo(1)–O(2)	75.7(3)
S(2)–Mo(2)–S(1)	102.74(8)	Mo(2)–S(1)–Mo(1)	74.93(8)
O(4)–Mo(2)–Mo(1)	99.36(7)	Mo(2)–S(2)–Mo(1)	74.86(9)
O(4)–Mo(2)–S(1)	87.26(7)	O(8)–Mo(2)–S(2)	101.9(3)
O(4)–Mo(2)–S(2)	87.3(2)	O(8)–Mo(2)–O(4)	162.0(3)
O(1w)–Mo(2)–Mo(1)	136.72(8)	O(8)–Mo(2)–O(1w)	90.9(4)
O(1w)–Mo(2)–S(1)	84.18(8)	O(8)–Mo(2)–O(5)	93.5(3)
O(1w)–Mo(2)–S(2)	163.0(2)	S(1)–Mo(1)–Mo(2)	52.51(6)
O(1w)–Mo(2)–O(4)	77.5(3)	S(1)–Mo(1)–S(2)	102.30(8)
O(5)–Mo(2)–Mo(1)	139.43(9)	S(2)–Mo(1)–Mo(2)	52.37(7)
O(5)–Mo(2)–S(1)	156.21(9)	O(2)–Mo(1)–Mo(2)	131.68(8)
O(5)–Mo(2)–S(2)	86.89(9)	O(2)–Mo(1)–S(1)	149.5(2)
O(5)–Mo(2)–O(4)	71.3(2)	O(2)–Mo(1)–S(2)	81.00(9)
O(5)–Mo(2)–O(1w)	81.2(2)	O(7)–Mo(1)–Mo(2)	102.7(2)
O(8)–Mo(2)–Mo(1)	98.5(2)	O(7)–Mo(1)–S(1)	105.4(3)
O(8)–Mo(2)–S(1)	105.4(3)	O(7)–Mo(1)–S(2)	106.9(3)
O(1)–Mo(1)–Mo(2)	131.88(8)	O(7)–Mo(1)–O(2)	102.4(3)
O(1)–Mo(1)–S(1)	83.85(9)	O(7)–Mo(1)–O(1)	108.4(3)

Table S9. Selected bond distances (Å) and angles (°) in $(Hdpa)_4[Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}S)_2(glyc)_2(S_2O_3)_2]$ (**3**).

Atom–Atom	**Length/Å**	**Atom–Atom**	**Length/Å**
Mo(1)–Mo(2)	2.7167(5)	Mo(2)–S(1)	2.3254(2)
Mo(1)–S(1)	2.3250(2)	Mo(2)–S(2)[1]	2.4883(4)
Mo(1)–O(5)	1.956(3)	Mo(2)–O(5)	1.984(3)
Mo(1)–O(1)	2.117(3)	Mo(2)–O(5)[1]	2.299(3)
Mo(1)–O(2)	2.060(3)	Mo(2)–O(1)[1]	2.113(3)
Mo(1)–O(7)	2.247(4)	Mo(2)–O(6)	1.678(4)
Mo(1)–O(4)	1.682(4)		

Atom–Atom–Atom	**Angle/°**	**Atom–Atom–Atom**	**Angle/°**
S(1)–Mo(1)–Mo(2)	54.26(3)	Mo(1)–S(1)–Mo(2)	71.49(4)
O(5)–Mo(1)–Mo(2)	46.82(1)	O(5)–Mo(2)–Mo(1)	45.99(9)
O(5)–Mo(1)–S(1)	99.53(1)	Mo(1)–O(5)–Mo(2)	87.18(3)
O(5)–Mo(1)–O(1)	74.40(3)	Mo(1)–O(5)–Mo(2)[1]	108.27(4)
O(5)–Mo(1)–O(2)	148.53(3)	Mo(2)–O(5)–Mo(2)[1]	107.17(5)
O(5)–Mo(1)–O(7)	87.69(3)	Mo(2)[1]–O(1)–Mo(1)	109.50(5)
O(1)–Mo(1)–Mo(2)	90.75(9)	O(5)[1]–Mo(2)–S(1)	96.52(8)
O(1)–Mo(1)–S(1)	94.62(1)	O(5)–Mo(2)–S(1)	98.72(1)
O(1)–Mo(1)–O(7)	78.20(4)	O(5)–Mo(2)–S(2)[1]	152.57(1)
O(2)–Mo(1)–Mo(2)	137.28(9)	O(5)1–Mo(2)–S(2)[1]	80.29(9)
O(2)–Mo(1)–S(1)	86.66(1)	O(5)–Mo(2)–O(5)[1]	72.83(5)
O(2)–Mo(1)–O(1)	74.36(3)	O(5)–Mo(2)–O(1)[1]	85.23(3)
O(2)–Mo(1)–O(7)	82.36(3)	O(1)[1]–Mo(2)–Mo(1)	131.12(1)
O(7)–Mo(1)–Mo(2)	134.32(9)	O(1)[1]–Mo(2)–S(1)	162.10(1)
O(7)–Mo(1)–S(1)	168.16(1)	O(1)[1]–Mo(2)–S(2)[1]	89.72(1)
O(4)–Mo(1)–Mo(2)	103.02(2)	O(1)[1]–Mo(2)–O(5)[1]	67.82(2)
O(4)–Mo(1)–S(1)	103.53(3)	O(6)–Mo(2)–Mo(1)	102.33(3)
O(4)–Mo(1)–O(5)	105.96(6)	O(6)–Mo(2)–S(1)	105.15(3)
O(4)–Mo(1)–O(1)	161.41(6)	O(6)–Mo(2)–S(2)[1]	103.24(4)
O(4)–Mo(1)–O(2)	102.41(5)	O(6)–Mo(2)–O(5)[1]	158.33(5)
O(4)–Mo(1)–O(7)	83.23(6)	O(6)–Mo(2)–O(5)	103.76(6)
S(1)–Mo(2)–Mo(1)	54.25(3)	O(6)–Mo(2)–O(1)[1]	90.69(5)
S(1)–Mo(2)–S(2)[1]	78.72(4)	O(5)[1]–Mo(2)–Mo(1)	90.58(8)
S(2)[1]–Mo(2)–Mo(1)	130.79(4)		

Symmetric codes: [1] *-x*, *-y*, *-z*.

Table S10. Selected bond distances (Å) and angles (°) in $Na_2[Mo_{16}O_{12}(\mu_2\text{-}O)_6(\mu_2\text{-}OH)_2(\mu_3\text{-}O)_{12}(glyc)_4(Hpz)_4(pz)_8]\cdot 28H_2O$ (**4**).

Atom–Atom	Length/Å	Atom–Atom	Length/Å
Mo(1)–Mo(1)^1	2.6340(9)	Mo(4)–O(5)	1.960(4)
Mo(1)–Mo(2)	2.5588(7)	Mo(4)–O(17)	2.182(5)
Mo(1)–Mo(2)^1	2.5620(7)	Mo(4)–O(4)	1.953(5)
Mo(1)–O(3)^1	2.035(4)	Mo(4)–O(18)	2.105(5)
Mo(1)–O(2)	2.011(4)	Mo(4)–O(7)	1.674(5)
Mo(1)–O(1)^1	2.065(4)	Mo(4)–N(9)	2.175(6)
Mo(1)–O(1)	2.067(4)	Mo(7)–O(13)	1.989(5)
Mo(1)–N(7)^1	2.195(5)	Mo(7)–O(9)	2.232(5)
Mo(1)–N(1)	2.184(5)	Mo(7)–O(12)	1.944(5)
Mo(2)–O(3)	1.971(4)	Mo(7)–O(14)	1.697(5)
Mo(2)–O(2)	1.940(4)	Mo(7)–N(10)	2.134(6)
Mo(2)–O(1)^1	2.061(4)	Mo(5)–O(16)	2.084(4)
Mo(2)–O(13)	2.114(5)	Mo(5)–O(9)	1.976(5)
Mo(2)–N(3)	2.132(5)	Mo(5)–O(8)	1.935(5)
Mo(2)–N(5)	2.196(5)	Mo(5)–O(17)	2.129(5)
Mo(3)–Mo(4)	2.5944(7)	Mo(5)–O(10)	1.700(5)
Mo(3)–O(3)	2.052(4)	Mo(5)–N(11)	2.232(6)
Mo(3)–O(5)	1.988(5)	Mo(8)–O(13)	1.958(4)
Mo(3)–O(16)	2.190(4)	Mo(8)–O(20)	2.205(5)
Mo(3)–O(6)	1.670(5)	Mo(8)–O(12)	1.976(5)
Mo(3)–O(4)	1.955(4)	Mo(8)–O(21)	2.110(5)
Mo(3)–N(8)	2.135(6)	Mo(8)–O(15)	1.686(5)
Mo(6)–Mo(5)	2.5778(7)	Mo(8)–N(4)	2.163(6)
Mo(6)–O(2)	2.100(4)	Mo(6)–O(11)	1.682(5)
Mo(6)–O(20)	2.195(4)	Mo(6)–N(2)	2.164(6)
Mo(6)–O(9)	1.981(5)	Mo(7)–Mo(8)	2.5753(8)
Mo(6)–O(8)	1.940(4)	Mo(7)–O(5)	2.063(4)

Atom–Atom–Atom	Angle/°	Atom–Atom–Atom	Angle/°
Mo(2)^1–Mo(1)–Mo(1)^1	58.99(2)	O(13)–Mo(8)–Mo(7)	49.79(3)
Mo(2)–Mo(1)–Mo(1)^1	59.10(2)	O(13)–Mo(8)–O(20)	90.88(7)
Mo(2)–Mo(1)–Mo(2)^1	118.09(2)	O(13)–Mo(8)–O(12)	96.45(9)
O(3)^1–Mo(1)–Mo(1)^1	96.41(2)	O(13)–Mo(8)–O(21)	162.7(2)
O(3)^1–Mo(1)–Mo(2)^1	49.14(2)	O(13)–Mo(8)–N(4)	83.65(9)
O(3)^1–Mo(1)–Mo(2)	140.35(2)	O(20)–Mo(8)–Mo(7)	95.60(2)
O(3)^1–Mo(1)–O(1)^1	88.79(7)	O(12)–Mo(8)–Mo(7)	48.41(4)
O(3)^1–Mo(1)–O(1)	99.41(7)	O(12)–Mo(8)–O(20)	82.59(9)
O(3)^1–Mo(1)–N(7)^1	81.42(8)	O(12)–Mo(8)–O(21)	89.4(2)
O(3)^1–Mo(1)–N(1)	90.07(9)	O(12)–Mo(8)–N(4)	167.4(2)
O(2)–Mo(1)–Mo(1)^1	92.94(2)	O(21)–Mo(8)–Mo(7)	137.80(5)
O(2)–Mo(1)–Mo(2)	48.44(2)	O(21)–Mo(8)–O(20)	73.75(8)
O(2)–Mo(1)–Mo(2)^1	135.66(2)	O(21)–Mo(8)–N(4)	87.1(2)
O(2)–Mo(1)–O(3)^1	170.15(7)	O(15)–Mo(8)–Mo(7)	98.82(8)
O(2)–Mo(1)–O(1)^1	99.58(7)	O(15)–Mo(8)–O(13)	105.2(2)

O(2)–Mo(1)–O(1)	84.20(7)	O(15)–Mo(8)–O(20)	163.1(2)
O(2)–Mo(1)–N(7)[1]	93.67(8)	O(15)–Mo(8)–O(12)	100.5(2)
O(2)–Mo(1)–N(1)	80.46(9)	O(15)–Mo(8)–O(21)	89.6(2)
O(1)–Mo(1)–Mo(1)[1]	50.36(1)	O(15)–Mo(8)–N(4)	91.6(2)
O(1)1–Mo(1)–Mo(1)[1]	50.43(1)	N(4)–Mo(8)–Mo(7)	133.42(4)
O(1)–Mo(1)–Mo(2)	88.06(2)	N(4)–Mo(8)–O(20)	84.80(9)
O(1)[1]–Mo(1)–Mo(2)[1]	88.02(1)	N(10)–Mo(7)–O(9)	83.2(2)
O(1)[1]–Mo(1)–Mo(2)	51.60(3)	O(5)–Mo(4)–Mo(3)	49.39(3)
O(1)–Mo(1)–Mo(2)[1]	51.53(2)	O(5)–Mo(4)–O(17)	87.42(8)
O(1)[1]–Mo(1)–O(1)	100.79(4)	O(5)–Mo(4)–O(18)	161.34(9)
O(1)[1]–Mo(1)–N(7)[1]	87.68(7)	O(5)–Mo(4)–N(9)	83.8(2)
O(1)–Mo(1)–N(7)[1]	171.49(7)	N(10)–Mo(7)–Mo(8)	135.71(6)
O(1)[1]–Mo(1)–N(1)	164.37(7)	O(17)–Mo(4)–Mo(3)	93.62(2)
O(1)–Mo(1)–N(1)	94.77(7)	O(5)–Mo(7)–N(10)	83.8(2)
N(7)[1]–Mo(1)–Mo(1)[1]	138.10(3)	O(4)–Mo(4)–Mo(3)	48.44(3)
N(7)[1]–Mo(1)–Mo(2)[1]	130.44(4)	O(4)–Mo(4)–O(5)	96.16(9)
N(7)[1]–Mo(1)–Mo(2)	96.70(4)	O(4)–Mo(4)–O(17)	83.64(9)
N(1)–Mo(1)–Mo(1)[1]	145.11(4)	O(4)–Mo(4)–O(18)	86.2(2)
N(1)–Mo(1)–Mo(2)	128.32(5)	O(4)–Mo(4)–N(9)	161.5(2)
N(1)–Mo(1)–Mo(2)[1]	102.95(4)	O(14)–Mo(7)–O(12)	104.9(2)
N(1)–Mo(1)–N(7)[1]	76.74(9)	O(18)–Mo(4)–Mo(3)	134.47(5)
Mo(1)–Mo(2)–Mo(1)[1]	61.91(2)	O(18)–Mo(4)–O(17)	74.42(8)
O(3)–Mo(2)–Mo(1)	100.56(3)	O(18)–Mo(4)–N(9)	88.1(2)
O(3)–Mo(2)–Mo(1)[1]	51.37(3)	O(14)–Mo(7)–O(9)	168.8(2)
O(3)–Mo(2)–O(1)[1]	101.78(7)	O(7)–Mo(4)–Mo(3)	103.79(7)
O(3)–Mo(2)–O(13)	89.67(7)	O(7)–Mo(4)–O(5)	106.8(2)
O(3)–Mo(2)–N(3)	162.67(9)	O(7)–Mo(4)–O(17)	162.2(2)
O(3)–Mo(2)–N(5)	86.73(8)	O(7)–Mo(4)–O(4)	104.9(2)
O(2)–Mo(2)–Mo(1)[1]	96.92(3)	O(7)–Mo(4)–O(18)	90.3(2)
O(2)–Mo(2)–Mo(1)	50.87(3)	O(7)–Mo(4)–N(9)	92.7(2)
O(2)–Mo(2)–O(3)	98.66(7)	O(13)–Mo(7)–O(9)	84.21(7)
O(2)–Mo(2)–O(1)[1]	102.13(7)	N(9)–Mo(4)–Mo(3)	133.01(6)
O(2)–Mo(2)–O(13)	81.75(7)	N(9)–Mo(4)–O(17)	77.9(2)
O(2)–Mo(2)–N(3)	95.14(8)	O(14)–Mo(7)–N(10)	91.8(2)
O(2)–Mo(2)–N(5)	171.5(2)	Mo(1)[1]–O(3)–Mo(3)	129.0(2)
O(1)[1]–Mo(2)–Mo(1)[1]	51.74(1)	Mo(2)–O(3)–Mo(1)[1]	79.49(5)
O(1)[1]–Mo(2)–Mo(1)	51.74(1)	Mo(2)–O(3)–Mo(3)	148.8(2)
O(1)[1]–Mo(2)–O(13)	167.09(6)	Mo(1)–O(2)–Mo(6)	130.0(2)
O(1)[1]–Mo(2)–N(3)	85.41(9)	Mo(2)–O(2)–Mo(1)	80.69(6)
O(1)[1]–Mo(2)–N(5)	83.01(9)	Mo(2)–O(2)–Mo(6)	148.4(2)
O(13)–Mo(2)–Mo(1)[1]	140.59(1)	Mo(1)[1]–O(1)–Mo(1)	79.21(4)
O(13)–Mo(2)–Mo(1)	132.39(2)	Mo(2)[1]–O(1)–Mo(1)	76.73(5)
O(13)–Mo(2)–N(3)	82.0(2)	Mo(2)[1]–O(1)–Mo(1)[1]	76.66(4)
O(13)–Mo(2)–N(5)	91.81(9)	Mo(3)–O(5)–Mo(7)	149.1(2)
N(3)–Mo(2)–Mo(1)	96.28(5)	Mo(4)–O(5)–Mo(3)	82.16(7)
N(3)–Mo(2)–Mo(1)[1]	137.02(6)	Mo(4)–O(5)–Mo(7)	128.3(2)
N(3)–Mo(2)–N(5)	78.45(9)	Mo(7)–O(13)–Mo(2)	146.4(2)
N(5)–Mo(2)–Mo(1)	134.74(6)	Mo(8)–O(13)–Mo(2)	125.3(2)

N(5)–Mo(2)–Mo(1)[1]	91.54(5)	Mo(8)–O(13)–Mo(7)	81.45(7)
O(3)–Mo(3)–Mo(4)	139.37(2)	Mo(5)–O(16)–Mo(3)	133.8(2)
O(3)–Mo(3)–O(16)	76.37(6)	Mo(6)–O(20)–Mo(8)	124.6(2)
O(3)–Mo(3)–N(8)	83.49(8)	O(13)–Mo(7)–Mo(8)	48.76(2)
O(5)–Mo(3)–Mo(4)	48.45(3)	O(13)–Mo(7)–O(5)	89.55(8)
O(5)–Mo(3)–O(3)	91.53(8)	Mo(6)–O(9)–Mo(7)	133.5(2)
O(5)–Mo(3)–O(16)	81.90(8)	Mo(5)–O(9)–Mo(6)	81.28(8)
O(5)–Mo(3)–N(8)	164.03(9)	Mo(5)–O(9)–Mo(7)	141.6(2)
O(16)–Mo(3)–Mo(4)	89.22(2)	Mo(5)–O(8)–Mo(6)	83.38(8)
O(6)–Mo(3)–Mo(4)	98.17(7)	Mo(7)–O(12)–Mo(8)	82.13(8)
O(6)–Mo(3)–O(3)	96.0(2)	Mo(5)–O(17)–Mo(4)	127.6(2)
O(6)–Mo(3)–O(5)	100.8(2)	O(13)–Mo(7)–N(10)	166.8(2)
O(6)–Mo(3)–O(16)	172.1(2)	O(9)–Mo(7)–Mo(8)	92.45(2)
O(6)–Mo(3)–O(4)	103.7(2)	O(5)–Mo(7)–O(9)	76.58(7)
O(6)–Mo(3)–N(8)	94.8(2)	Mo(4)–O(4)–Mo(3)	83.19(8)
O(4)–Mo(3)–Mo(4)	48.38(4)	O(16)–Mo(5)–Mo(6)	97.94(2)
O(4)–Mo(3)–O(3)	157.54(9)	O(16)–Mo(5)–O(17)	79.90(8)
O(4)–Mo(3)–O(5)	95.20(9)	O(16)–Mo(5)–N(11)	76.08(9)
O(4)–Mo(3)–O(16)	83.39(8)	O(9)–Mo(5)–Mo(6)	49.44(4)
O(4)–Mo(3)–N(8)	84.2(2)	O(9)–Mo(5)–O(16)	88.71(7)
N(8)–Mo(3)–Mo(4)	132.55(4)	O(9)–Mo(5)–O(17)	92.96(9)
N(8)–Mo(3)–O(16)	82.18(8)	O(9)–Mo(5)–N(11)	164.7(2)
O(2)–Mo(6)–Mo(5)	102.88(1)	O(8)–Mo(5)–Mo(6)	48.39(3)
O(2)–Mo(6)–O(20)	76.33(6)	O(8)–Mo(5)–O(16)	85.92(8)
O(2)–Mo(6)–N(2)	76.52(8)	O(8)–Mo(5)–O(9)	95.60(9)
O(20)–Mo(6)–Mo(5)	136.84(3)	O(8)–Mo(5)–O(17)	163.25(9)
O(9)–Mo(6)–Mo(5)	49.28(3)	O(8)–Mo(5)–N(11)	85.0(2)
O(9)–Mo(6)–O(2)	90.12(7)	O(17)–Mo(5)–Mo(6)	142.38(3)
O(9)–Mo(6)–O(20)	87.67(8)	O(17)–Mo(5)–N(11)	82.9(2)
O(9)–Mo(6)–N(2)	165.69(9)	O(10)–Mo(5)–Mo(6)	99.62(7)
O(8)–Mo(6)–Mo(5)	48.23(4)	O(10)–Mo(5)–O(16)	162.0(2)
O(8)–Mo(6)–O(2)	91.20(7)	O(10)–Mo(5)–O(9)	105.8(2)
O(8)–Mo(6)–O(20)	167.21(8)	O(10)–Mo(5)–O(8)	102.8(2)
O(8)–Mo(6)–O(9)	95.28(9)	O(10)–Mo(5)–O(17)	88.6(2)
O(8)–Mo(6)–N(2)	80.1(2)	O(10)–Mo(5)–N(11)	88.9(2)
O(11)–Mo(6)–Mo(5)	99.75(7)	N(11)–Mo(5)–Mo(6)	133.42(5)
O(11)–Mo(6)–O(2)	157.3(2)	O(12)–Mo(7)–Mo(8)	49.47(5)
O(11)–Mo(6)–O(20)	87.9(2)	O(12)–Mo(7)–O(5)	159.87(8)
O(11)–Mo(6)–O(9)	105.6(2)	O(12)–Mo(7)–O(13)	96.48(9)
O(11)–Mo(6)–O(8)	103.2(2)	O(12)–Mo(7)–O(9)	84.92(8)
O(11)–Mo(6)–N(2)	88.7(2)	O(12)–Mo(7)–N(10)	86.3(2)
N(2)–Mo(6)–Mo(5)	128.32(5)	O(14)–Mo(7)–Mo(8)	98.13(7)
N(2)–Mo(6)–O(20)	94.00(9)	O(14)–Mo(7)–O(5)	92.9(2)
O(5)–Mo(7)–Mo(8)	138.06(3)	O(14)–Mo(7)–O(13)	99.9(2)

Symmetric codes: [1] ½ – *x*, ½ – *y*, 1 – *z*.

Table S11. Detail calibrated adsorption data of O_2, N_2 and CO_2 for $Na_2[Mo_{16}O_{12}(\mu_2\text{-}O)_6(\mu_2\text{-}OH)_2(\mu_3\text{-}O)_{12}(glyc)_4(Hpz)_4(pz)_8]\cdot 28H_2O$ (**4**) at 298 K.

Gases	O_2		CO_2		CH_4		N_2		H_2	
Temperature (°C)	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	3.4998	0.892	6.6610	0.892	1.85039	0.890	1.6038	0.892	0.892
	1.890	5.2060	1.890	9.3815	1.890	2.69209	1.900	2.6457	1.890	1.890
	3.900	8.1738	3.892	12.4707	3.892	3.11232	3.891	3.3619	3.892	3.892
	5.898	10.9607	5.896	15.3245	5.896	3.39305	5.900	3.3120	5.896	5.896
	7.895	13.5227	7.894	16.9496	7.894	3.84454	7.900	3.7706	7.894	7.894
	9.900	16.2109	9.895	18.1760	9.895	4.13023	9.900	3.7187	9.895	9.895
	11.900	18.7349	11.892	20.2010	11.892	4.05501	11.898	3.5520	11.892	11.892
	13.896	21.4256	13.895	20.6612	13.895	4.48924	13.895	2.8474	13.895	13.895
	15.896	24.2378	15.899	20.5404	15.899	4.24398	15.896	2.3342	15.899	15.899
	17.890	26.7388	17.899	22.4261	17.899	4.49908	17.894	3.1299	17.899	17.899
	19.896	29.7496	19.894	22.5480	19.894	4.17718	19.898	3.3014	19.894	19.894
	21.894	32.2922	21.895	23.1963	21.895	4.04903	21.894	3.3090	21.895	21.895
	23.894	34.7491	23.891	23.7147	23.891	4.39791	23.894	3.1755	23.891	23.891
	25.893	37.0642	25.895	23.3122	25.895	4.41047	25.895	2.3057	25.895	25.895
	27.891	39.5402	27.894	23.1564	27.894	4.34825	27.897	2.8725	27.894	27.894
	29.891	42.2306	29.890	21.2955	29.890	4.26905	29.894	2.6617	29.890	29.890

Table S12. Comparisons of O_2 adsorption data for **4** with some other adsorbents at different conditions.

Adsorbents	Species	Amounts ($mmol \cdot g^{-1}$)	Pressure (bar)	Temperature (K)
4		0.123	1	298
		1.320	30	298
MOF-177[2]	MOF	0.18	1	298
SNU-50'[3]		34.6	0.70	87
SNU-9[4]		12.3	0.61	87
Zeolite 5A[5]	Zeolite	0.10	0.96	303
SBFO[6]		0.31	1	723
$SrCo_{0.8}Fe_{0.2}O_{3-\delta}$[7]		0.40	1	773
COP-1[8]	COP	0.12	1.3	298
COP-2[8]		0.20	1.3	298
COP-3[8]		0.17	1.3	298
COP-4[8]		0.18	1.3	298
AgF[9]	salt	0.0075	1	295
AgCl[9]		0.0067	1	295
$AgBr/SiO_2$[9]		0.243	1	295

Table S13. Comparisons of CO_2 adsorption data for **4** with the other typical MOFs at 298 K.

Adsorbents	Amounts ($mmol \cdot g^{-1}$)	Pressure (bar)
4	0.170	1
	0.484	30
Mg-MOF-1[10]	0.614	1
MOF-253[11]	1.409	1
$[Fe(III)(Tp)(CN)_3]_2Co(II)$[12]	0.682	1
$Co(doborDC)_2(py)$[13]	0.364	1
$Ni_3(pzdc)_2(7H\text{-}ade)_2(H_2O)_4$[14]	2.228	1
HKUST-1[15]	4.182	1
SNU-50[3]	3.114	1
ZIF-78[16]	2.068	1
IMOF-3[17]	1.955	1
Cd-ADA-1[18]	0.773	1

List of abbreviations: Tp = hydrotris(pyrazolyl)borate; doborDC = 1,12-dihydroxy-carbonyl-1,12-dicarba-closo-dodecaborane, py = pyridine; pzdc = 2,3-pyrazinedicarboxylate, ade = adenine.

Table S14. Solid ^{13}C NMR spectral data (ppm) of **1** ~ **4**.

Compound	δ (−CO_2)	δ (−CO)	δ (−CH)
1	175.23	61.69	108.27, 133.98, 143.69
2	181.86, 186.79	65.61, 69.72	117.15, 136.03, 140.06, 143.11, 146.65, 151.47
3	178.60	−	114.72 ~ 152.22
4	183.48	74.79	105.84 ~ 144.66

References

1. J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304–1315.
2. Y. Li and R. T. Yang, *Langmuir*, 2007, **23**, 12937–12944.
3. T. K. Prasad, D. H. Hong and M. P. Suh, *Chem.–Eur. J.*, 2010, **16**, 14043–14050.
4. H. J. Park and M. P. Suh, *Chem. Commun.*, 2010, **46**, 610–612.
5. M. Mofarahi and M. Seyyedi, *J. Chem. Eng. Data*, 2009, **54**, 916–921.
6. T. Masunaga, J. Izumi and N. Miura, *Chem. Eng. Sci.*, 2012, **84**, 108–112.
7. Y. He, X. Zhu, Q. Li and W. Yang, *AICHE J.*, 2009, **55**, 3125–3133.
8. Z. Xiang, X. Zhou, C. Zhou, S. Zhong, X. He, C. Qin and D. Cao, *J. Mater. Chem.*, 2012, **22**, 22663–22669.
9. A. Jayaraman and R. T. Yang, *Chem. Eng. Sci.*, 2005, **60**, 625–634.
10. A. Mallick, S. Saha, P. Pachfule, S. Roy and R. Banerjee, *J. Mater. Chem.*, 2010, **20**, 9073–9080.
11. E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe Romo, H. Furukawa, J. R. Long and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 14382–14384.
12. Y. J. Zhang, T. Liu, S. Kanegawa and O. Sato, *J. Am. Chem. Soc.*, 2010, **132**, 912–913.
13. Y. S. Bae, A. M. Spokoyny, O. K. Farha, R. Q. Snurr, J. T. Hupp and C. A. Mirkin, *Chem. Commun.*, 2010, **46**, 3478–3480.
14. K. C. Stylianou, J. E. Warren, S. Y. Chong, J. Rabone, J. Bacsa, D. Bradshaw and M. J. Rosseinsky, *Chem. Commun.*, 2011, **47**, 3389–3391.
15. A. O. Yazaydin, A. I. Benin, S. A. Faheem, P. Jakubczak, J. J. Low, R. R. Willis and R. Q. Snurr, *Chem. Mat.*, 2009, **21**, 1425–1430.
16. A. Phan, C. J. Doonan, F. J. Uribe Romo, C. B. Knobler, M. O'Keeffe and O. M. Yaghi, *Accounts Chem. Res.*, 2010, **43**, 58–67.
17. F. Debatin, A. Thomas, A. Kelling, N. Hedin, Z. Bacsik, I. Senkovska, S. Kaskel, M. Junginger, H. Mueller, U. Schilde, C. Jaeger, A. Friedrich and H. J. Holdt, *Angew. Chem.–Int. Edit.*, 2010, **49**, 1258–1262.
18. P. Pachfule, T. Panda, C. Dey and R. Banerjee, *Crystengcomm*, 2010, **12**, 2381–2389.