Supporting materials

Isolated molybdenum-based microporous POMs for selective adsorption of gases

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Figure and Table Options

Figure S1. Perspective view of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**, a), free and disordered water molecules are omitted for clarity. 2D packing diagrams of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**) in *a* (b), *b* (c) and *c* (d) axes.

Figure S2. Perspective view of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**, a), free and disordered water molecules are omitted for clarity. (b) A complete molecular of **2**. 2D packing diagrams of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**) in *a* (c) and *c* (d) axes.

Figure S3. Perspective view of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**), free and disordered water molecules are omitted for clarity. (a) Main structure of $[Mo_4O_4(\mu_2\text{-}O)_6(Htrz)_4]$ species. (b) Main structure of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]$ species. (c) Complete composite structure of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]$ in **3**. Packing diagrams of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**) in *a* (d) and *b* (e) axes.

Figure S4. Perspective view of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\ 62H_2O$ (**4**, a), free and disordered water molecules are omitted for clarity. (b) Holes with maximum diameter of 5.1 Å exist in each complete unit. (c) 2D layered diagram of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\ 62H_2O$ (**4**) in *b* axis.

Figure S5. (a) Perspective view of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**) before conducting mask command. (b) Highlighted hydrogen bonds between protonated N atoms and free water molecules. (c) Perspective view of **1** before solvent mask, thermal ellipsoids are drawn by ORTEP and represent 30% probability surfaces.

Figure S6. (a) Perspective view of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**) before conducting mask command. (b) Highlighted hydrogen bonds between C atoms, protonated N atoms and free water molecules. (c) Perspective view of **2** before solvent mask, thermal ellipsoids are drawn by ORTEP and represent 30% probability surfaces.

Figure S7. (a) Perspective view of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**) before conducting mask command. (b) Highlighted hydrogen bonds between protonated N atoms and free water molecules. (c) Perspective view of **3** before solvent mask, thermal ellipsoids are drawn by ORTEP and represent 30% probability surfaces.

Figure S8. (a) Perspective view of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\ 62H_2O$ (**4**) before conducting mask command. (b) Highlighted hydrogen bonds between protonated N atoms and free water molecules. (c) Perspective view of **4** before solvent mask, thermal ellipsoids are drawn by ORTEP and represent 30% probability surfaces.

Figure S9. Gases adsorption isotherms of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**) at 298 K at different pressures for O_2 (a), CO_2 (b), H_2 (c), CH_4 (d), N_2 (e) respectively.

Figure S10. Gases adsorption isotherms of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**) at 298 K at different pressures for O_2 (a), CO_2 (b), H_2 (c), CH_4 (d), N_2 (e) respectively.

Figure S11. Gases adsorption isotherms of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\ 62H_2O$ (**4**) at 298 K at different pressures for O_2 (a), CO_2 (b), H_2 (c), CH_4 (d), N_2 (e) respectively.

Figure S12. O_2, CO_2 and CH_4 adsorption isotherms for **1**, **2** and **4** (a ~ c) respectively at 298 K and pressures of up to 1 bar.

Figure S13. N_2 adsorption−desorption isotherms of **1**, **2** and **4** at 77 K respectively.

Figure S14. (a) TGA of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**); (b) TGA of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**); (c) TGA of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\ 62H_2O$ (**4**) respectively.

Figure S15. Powder XRD curves for $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot nH_2O$ (n = 22, **1**; n = 92, **2**) and $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\ 62H_2O$ (**4**) under different circumstances respectively.

Figure S16. IR spectra of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot nH_2O$ (n = 22, **1**; n = 92, **2**) and $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\ 62H_2O$ (**4**) respectively.

Figure S17. FT-IR spectrum of 1H-1,2,3-triazole $[C_2H_3N_3]$ originated from Spectral Database for Organic Compounds SDBS. URL for this compound: https://sdbs.db.aist.go.jp/sdbs/cgi-bin/landingpage?sdbsno=41390.

Figure S18. Diffused reflectance spectra of solid $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot nH_2O$ (n = 22, **1**; n = 92, **2**) and $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\ 62H_2O$ (**4**) respectively.

Figure S19. EPR spectra of solid **1**, **2** and **4** at 100 K respectively.

Figure S20. Solution ^{13}C NMR spectrum of pure trz.

Table S1. Crystallographic data and structural refinements for complexes $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot nH_2O$ (n = 22, **1**; n = 92, **2**), $[Mo_4O_4(\mu_2\text{-}O)_6(Htrz)_4]\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**) and $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\cdot 62H_2O$ (**4**) respectively.

Table S2. Hydrogen bond distances (Å) and angles (°) in $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**) before solvent mask.

Table S3. Hydrogen bond distances (Å) and angles (°) in $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**) before solvent mask.

Table S4. Hydrogen bond distances (Å) and angles (°) in $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**) before solvent mask.

Table S5. Hydrogen bond distances (Å) and angles (°) in $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\cdot 62H_2O$ (**4**) before solvent mask.

Table S6. Solvent mask values are calculated based on the unit cells for compounds **1** ~ **4** respectively.

Table S7. Selected bond distances (Å) and angles (°) in $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**) after solvent mask and final refinements.

Table S8. Selected bond distances (Å) and angles (°) in $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**) after solvent mask and final refinements.

Table S9. Selected bond distances (Å) and angles (°) in $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**) after solvent mask and final refinements.

Table S10. Selected bond distances (Å) and angles (°) in $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\cdot 62H_2O$ (**4**) after solvent mask and final refinements.

Table S11. Detail calibrated adsorption data of O_2, N_2, H_2, CO_2 and CH_4 for $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**) at 298 K.

Table S12. Detail calibrated adsorption data of O_2, N_2, H_2, CO_2 and CH_4 for $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**) at 298 K.

Table S13. Detail calibrated adsorption data of O_2, N_2, H_2, CO_2 and CH_4 for $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\cdot 62H_2O$ (**4**) at 298 K.

Table S14. Bond valence calculations for complexes $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot nH_2O$ (n = 22, **1**; n = 92, **2**), $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**) and $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\cdot 62H_2O$ (**4**) respectively.

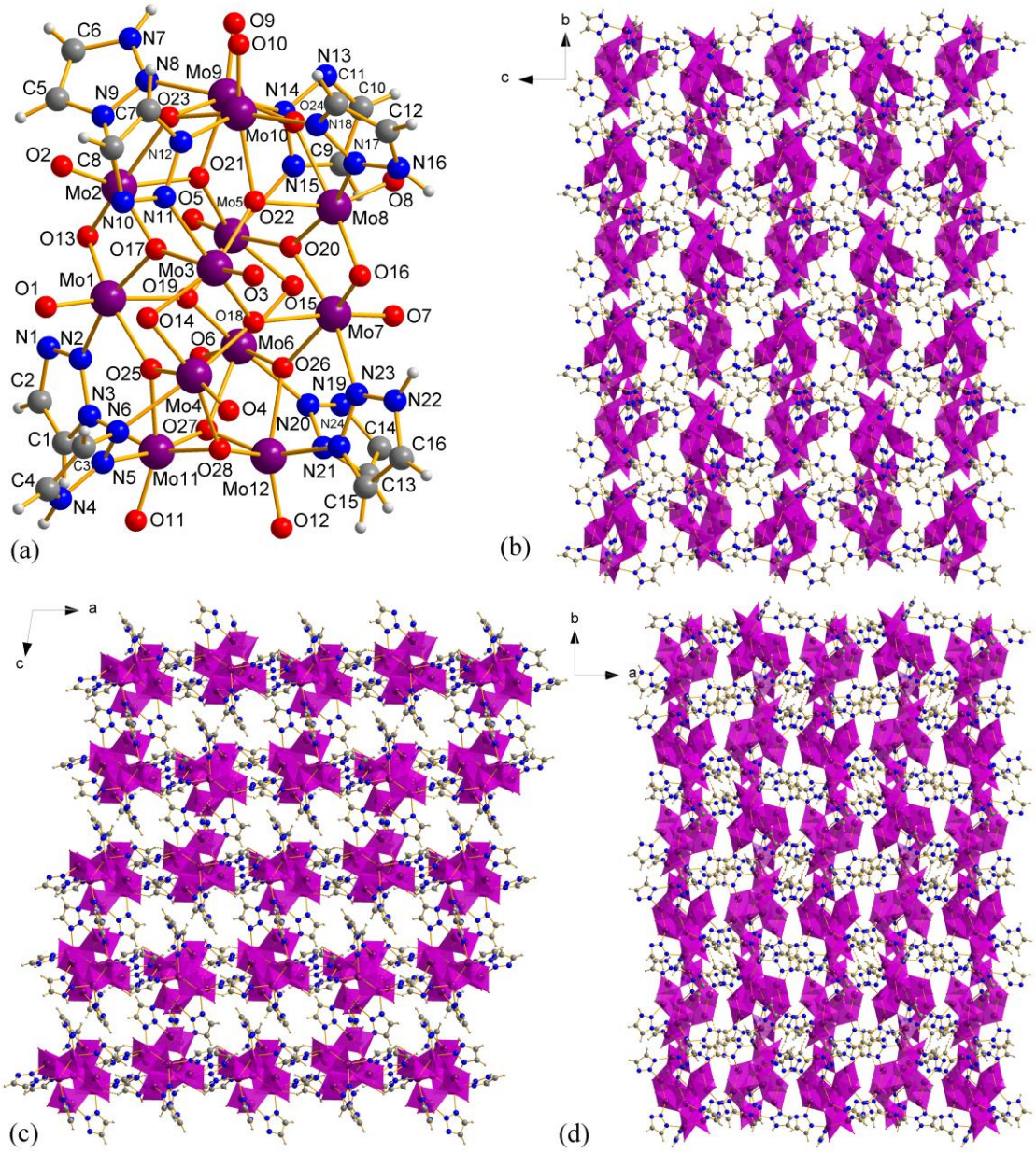


Figure S1. Perspective view of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**, a), free and disordered water molecules are omitted for clarity. 2D packing diagrams of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**) in *a* (b), *b* (c) and *c* (d) axes.

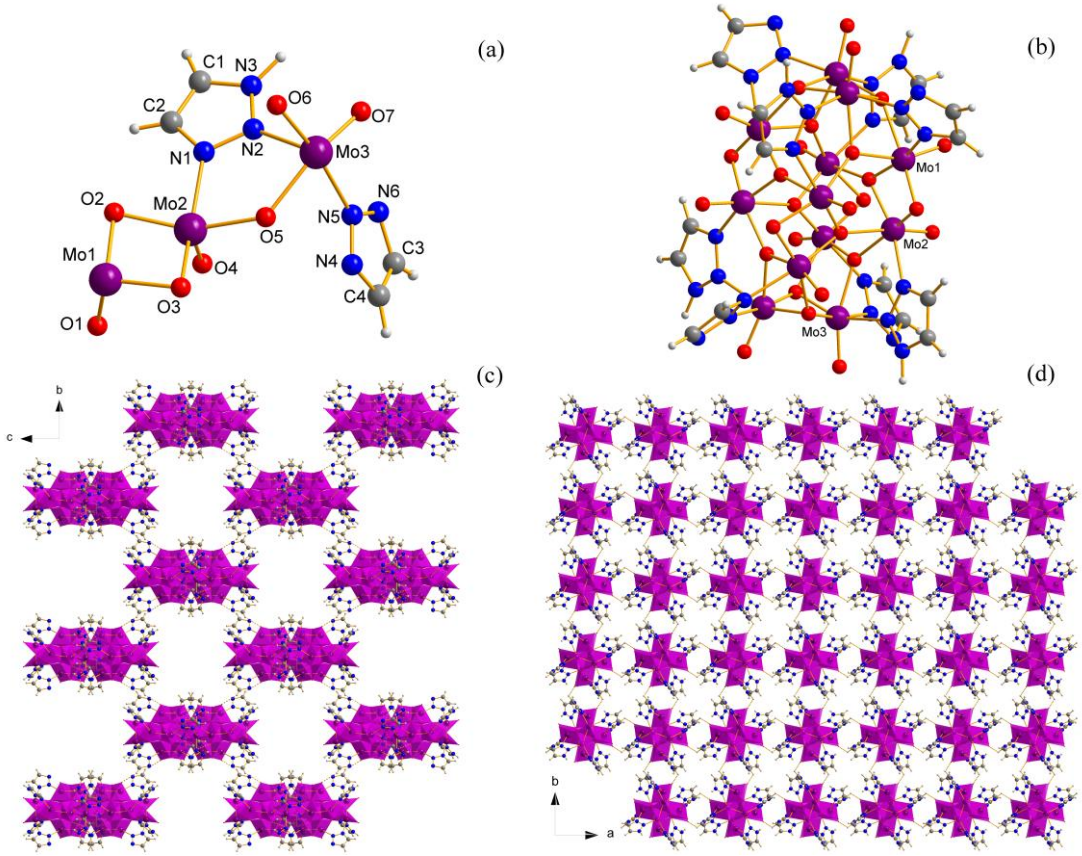


Figure S2. Perspective view of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**, a), free and disordered water molecules are omitted for clarity. (b) A complete molecular of **2**. 2D packing diagrams of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**) in *a* (c) and *c* (d) axes.

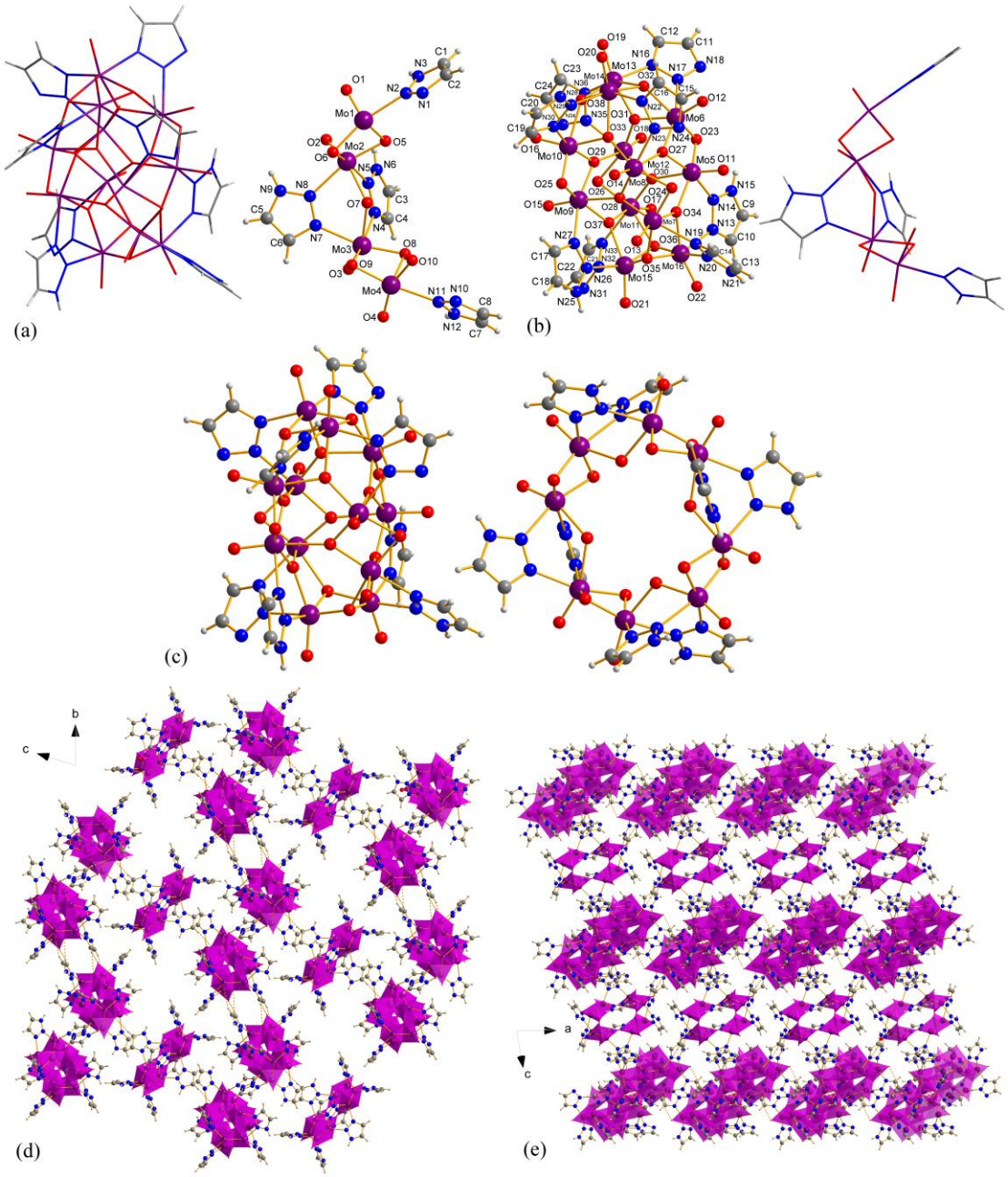


Figure S3. Perspective view of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**), free and disordered water molecules are omitted for clarity. (a) Main structure of $[Mo_4O_4(\mu_2\text{-}O)_6(Htrz)_4]$ species. (b) Main structure of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]$ species. (c) Complete composite structure of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]$ in **3**. Packing diagrams of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**) in *a* (d) and *b* (e) axes.

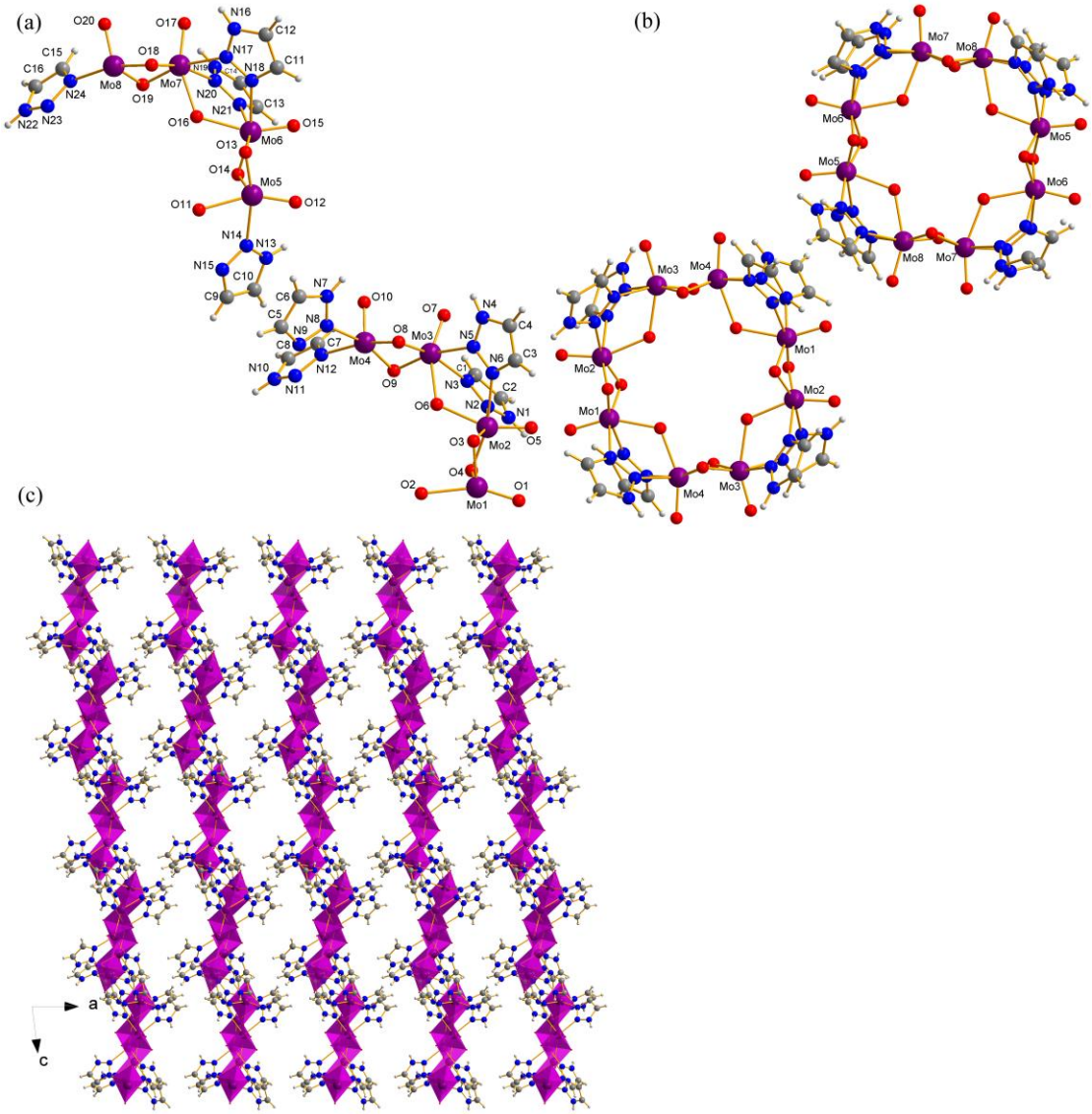


Figure S4. Perspective view of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\cdot 62H_2O$ (**4**, a), free and disordered water molecules are omitted for clarity. (b) Holes with maximum diameter of 5.1 Å exist in each complete unit. (c) 2D layered diagram of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\cdot 62H_2O$ (**4**) in *b* axis.

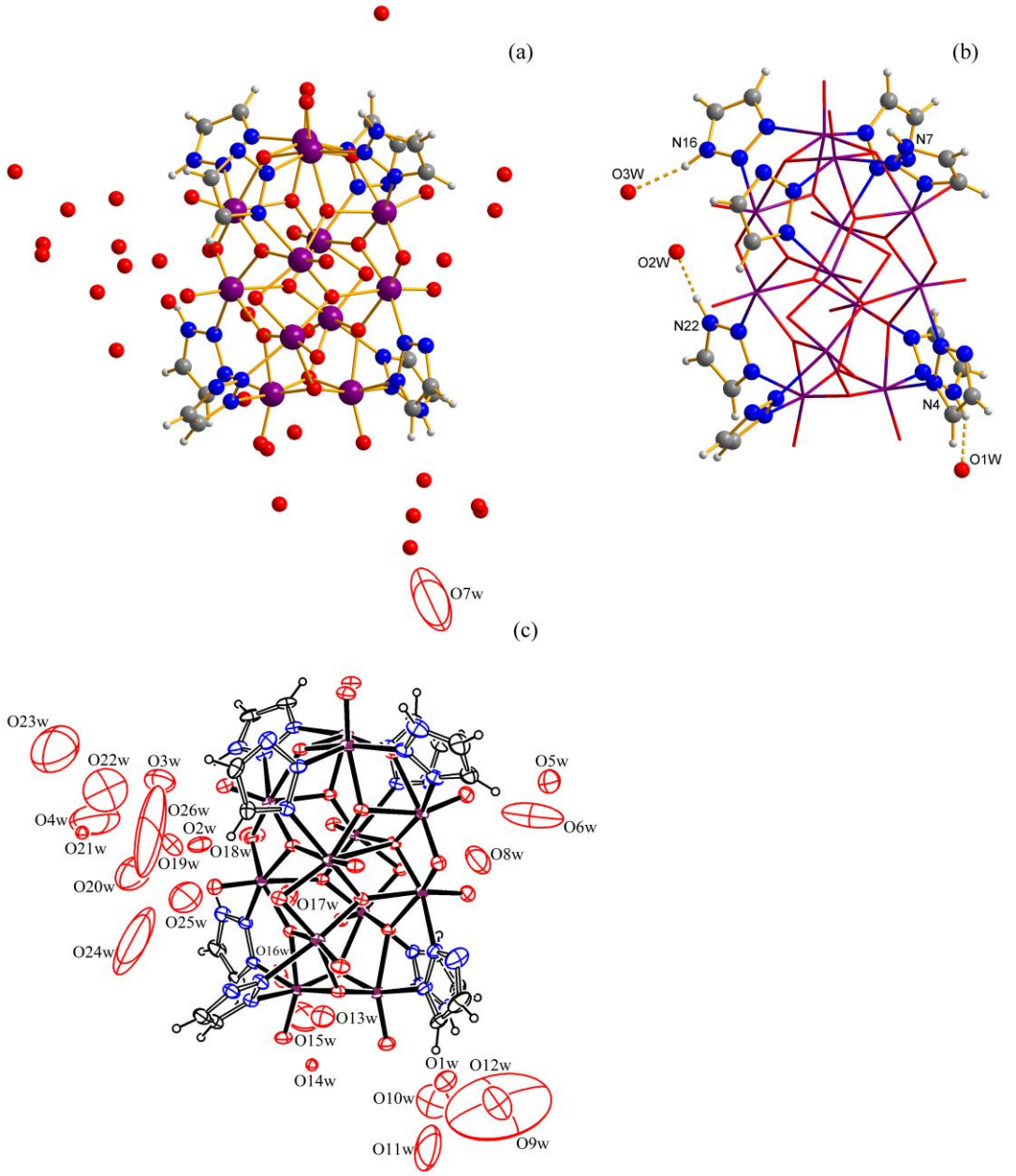


Figure S5. (a) Perspective view of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**) before conducting mask command. (b) Highlighted hydrogen bonds between protonated N atoms and free water molecules. (c) Perspective view of **1** before solvent mask, thermal ellipsoids are drawn by ORTEP and represent 30% probability surfaces.

Distribution of 1H-1,2,3-triazoles: two atoms which coordinated with central molybdenum are identified as nitrogen and the other three are all designated as carbon atoms in trzs. After refinements, one carbon atom has the smallest U_{eq} value compared with the other two and there is a pair of obvious Q peaks located at the left and right of its periphery, which this carbon can be further revised as nitrogen atom. There is only one far Q peak around the other two atoms, which is obviously hydrogen atom on carbon. Then hydrogen atoms on carbon atoms are generated geometrically and

refined isotropically, while hydrogen atoms on three nitrogen in eight trzs are confirmed by forming intramolecular hydrogen bonds with surrounding water molecules, namely, N16, N22 and N4 in Figure S5b. The fourth hydrogen is added by a distinct Q peak around N7 and also having hydrogen bond with free water molecular. In addition, there is no Q peak around nitrogen atoms in the other coordinated four trzs, which are all defined as deprotonated states. All hydrogen bonds in **1** before solvent mask are listed in Table S2.

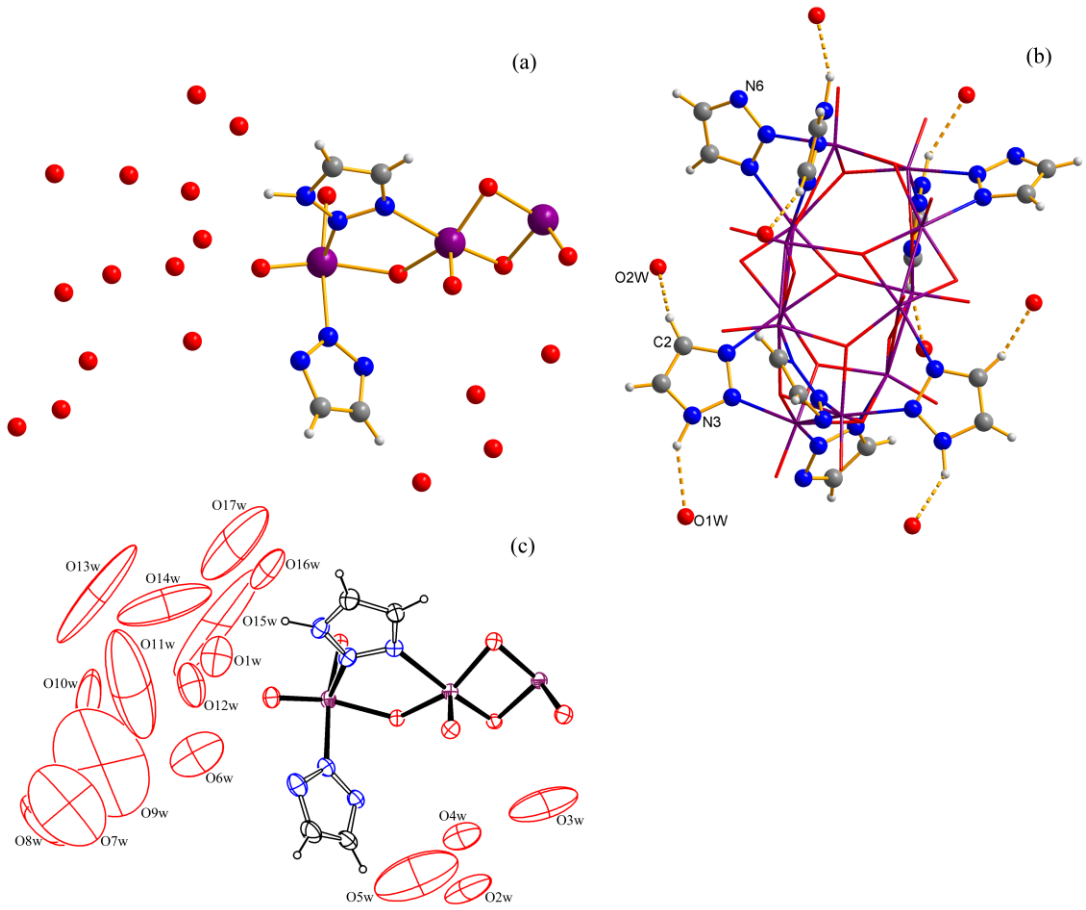


Figure S6. (a) Perspective view of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**) before conducting mask command. (b) Highlighted hydrogen bonds between C atoms, protonated N atoms and free water molecules. (c) Perspective view of **2** before solvent mask, thermal ellipsoids are drawn by ORTEP and represent 30% probability surfaces.

The distribution of 1H-1,2,3-triazoles in **2** is the same as **1**. Hydrogen atom on N3 in trz is confirmed through the surrounding Q peak and forming intramolecular hydrogen bond with free water molecule O1w in Figure S6b. All hydrogen bonds before solvent mask are listed in Table S3. There is no Q peak around N6, which is defined as deprotonated state and further satisfy charge conservation.

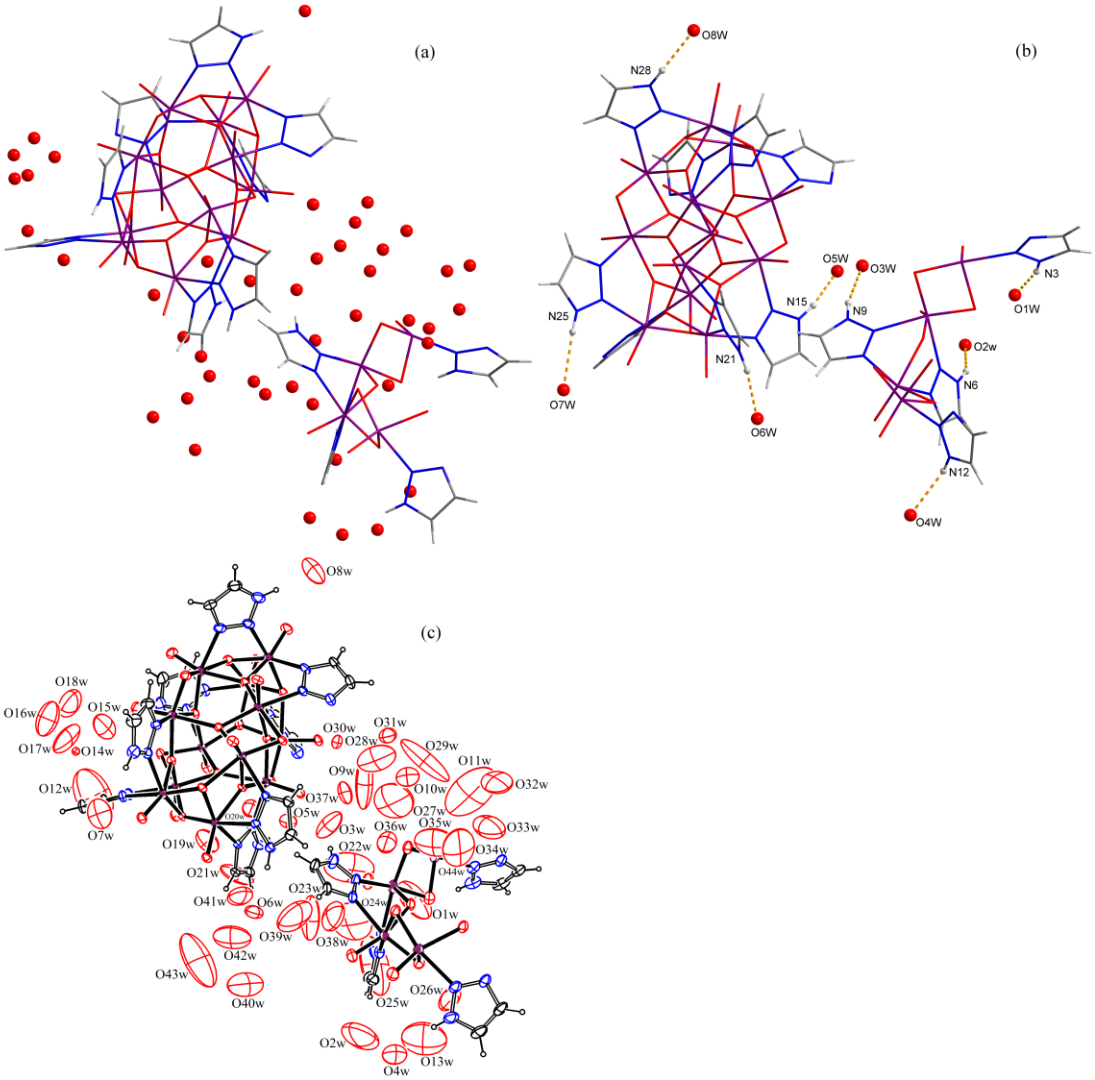


Figure S7. (a) Perspective view of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**) before conducting mask command. (b) Highlighted hydrogen bonds between protonated N atoms and free water molecules. (c) Perspective view of **3** before solvent mask, thermal ellipsoids are drawn by ORTEP and represent 30% probability surfaces.

There are about 44 free and disordered water molecules in **3** before conducting mask command in Figure S7a. The distribution of 1H-1,2,3-triazoles in **3** is the same as **1** and **2**. Hydrogen atoms in trzs are confirmed through the surrounding Q peak, and forming intramolecular hydrogen bonds with free water molecules mainly in Figure S7b. All hydrogen bonds in **3** before solvent mask are listed in Table S4.

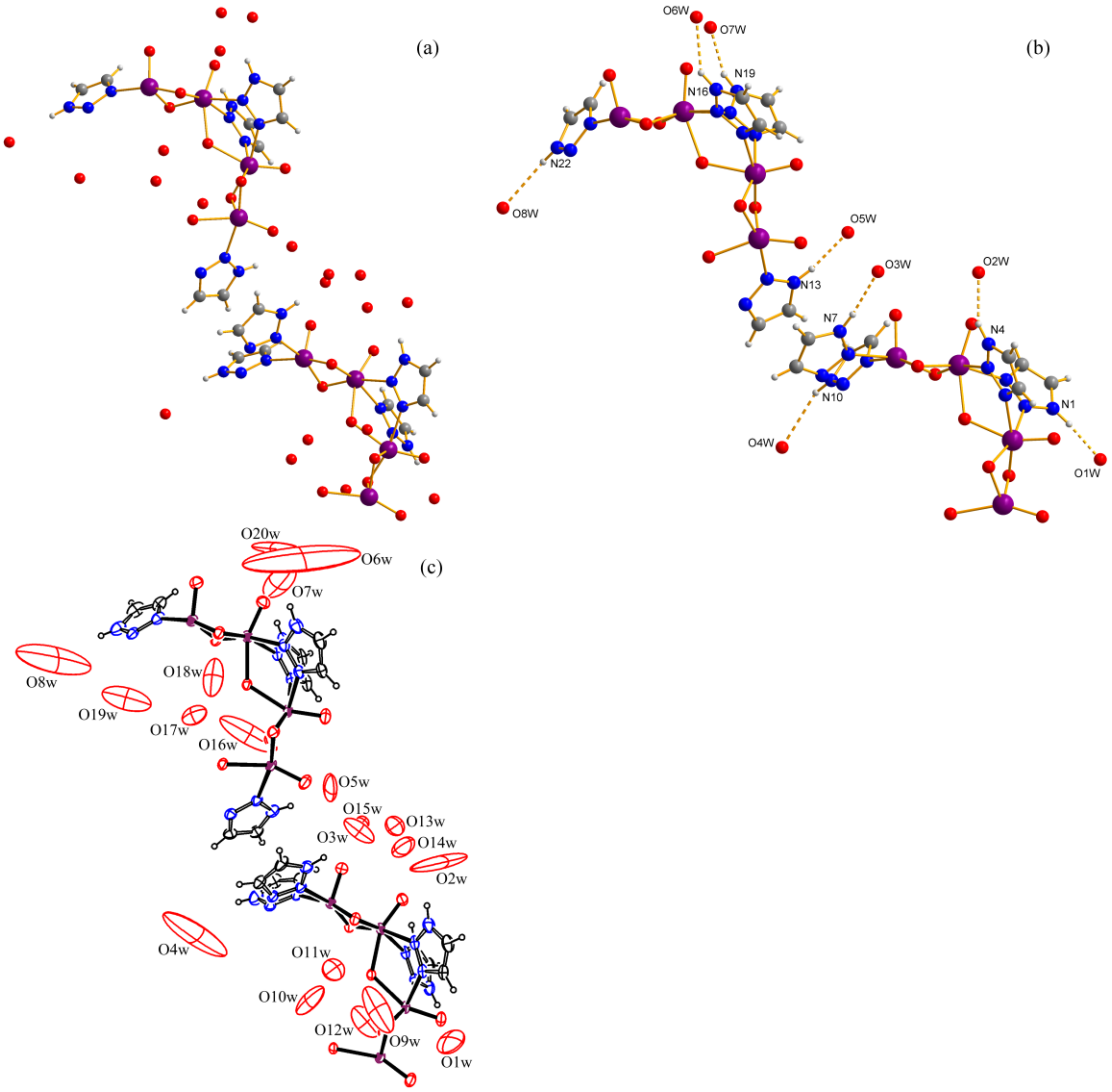


Figure S8. (a) Perspective view of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\ 62H_2O$ (**4**) before conducting mask command. (b) Highlighted hydrogen bonds between protonated N atoms and free water molecules. (c) Perspective view of **4** before solvent mask, thermal ellipsoids are drawn by ORTEP and represent 30% probability surfaces.

The distribution of 1H-1,2,3-triazoles in **4** is the same as **1** ~ **3**. Hydrogen atoms on all N atoms in trzs are confirmed through forming intramolecular hydrogen bonds with free water molecules in Figure S7b. All hydrogen bonds before solvent mask are listed in Table S5.

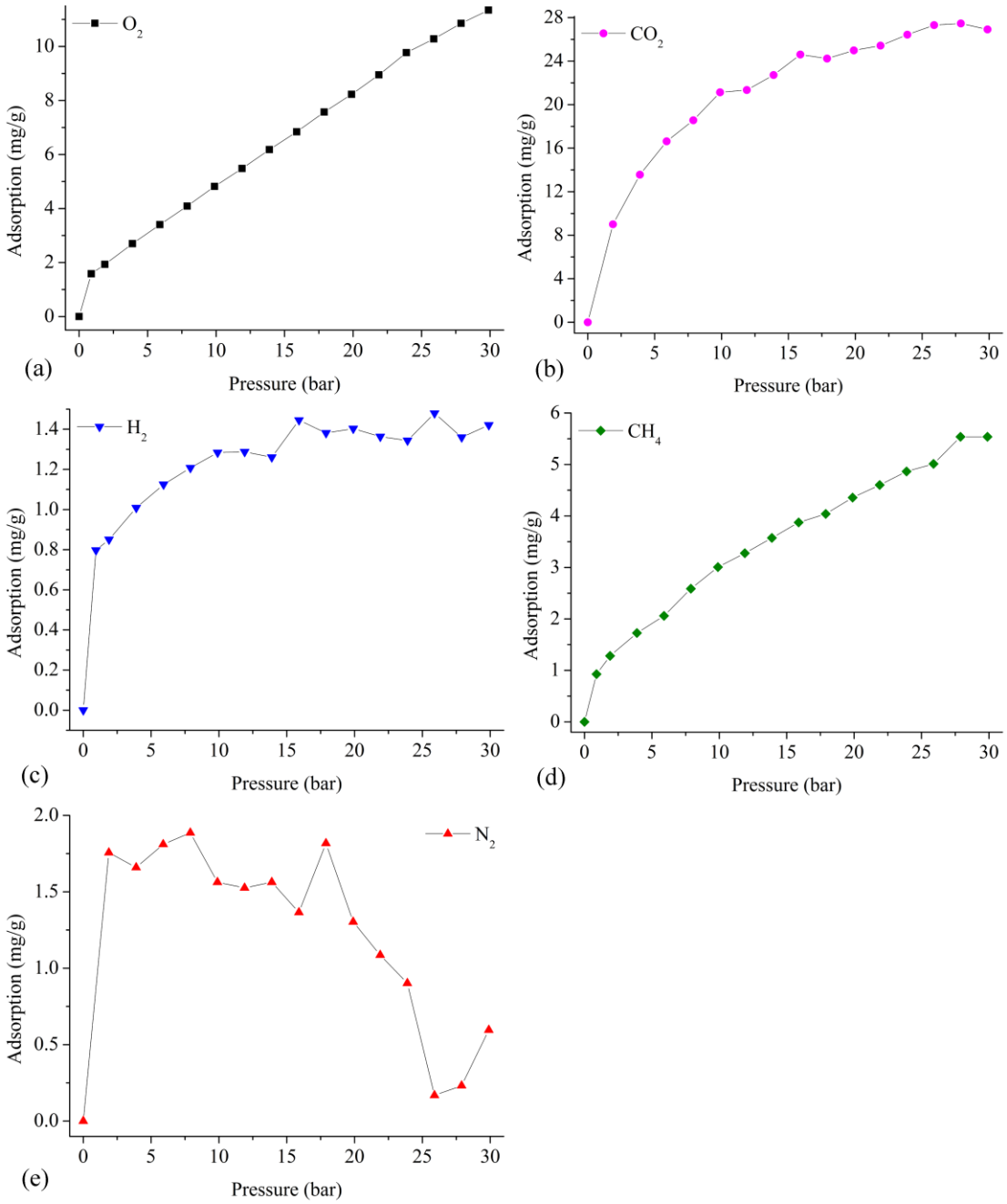


Figure S9. Gases adsorption isotherms of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**) at 298 K at different pressures for O_2 (a), CO_2 (b), H_2 (c), CH_4 (d), N_2 (e) respectively.

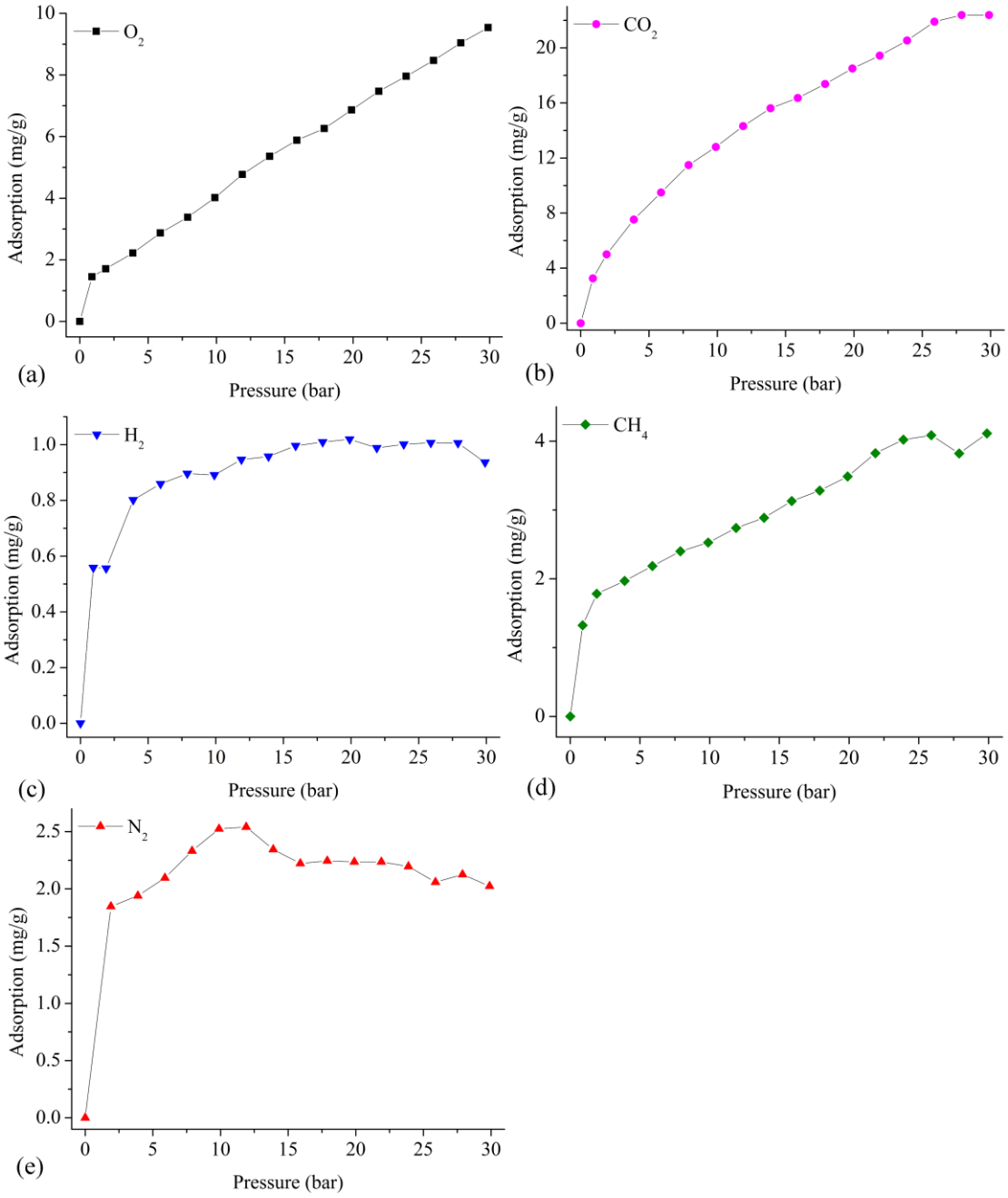


Figure S10. Gases adsorption isotherms of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**) at 298 K at different pressures for O_2 (a), CO_2 (b), H_2 (c), CH_4 (d), N_2 (e) respectively.

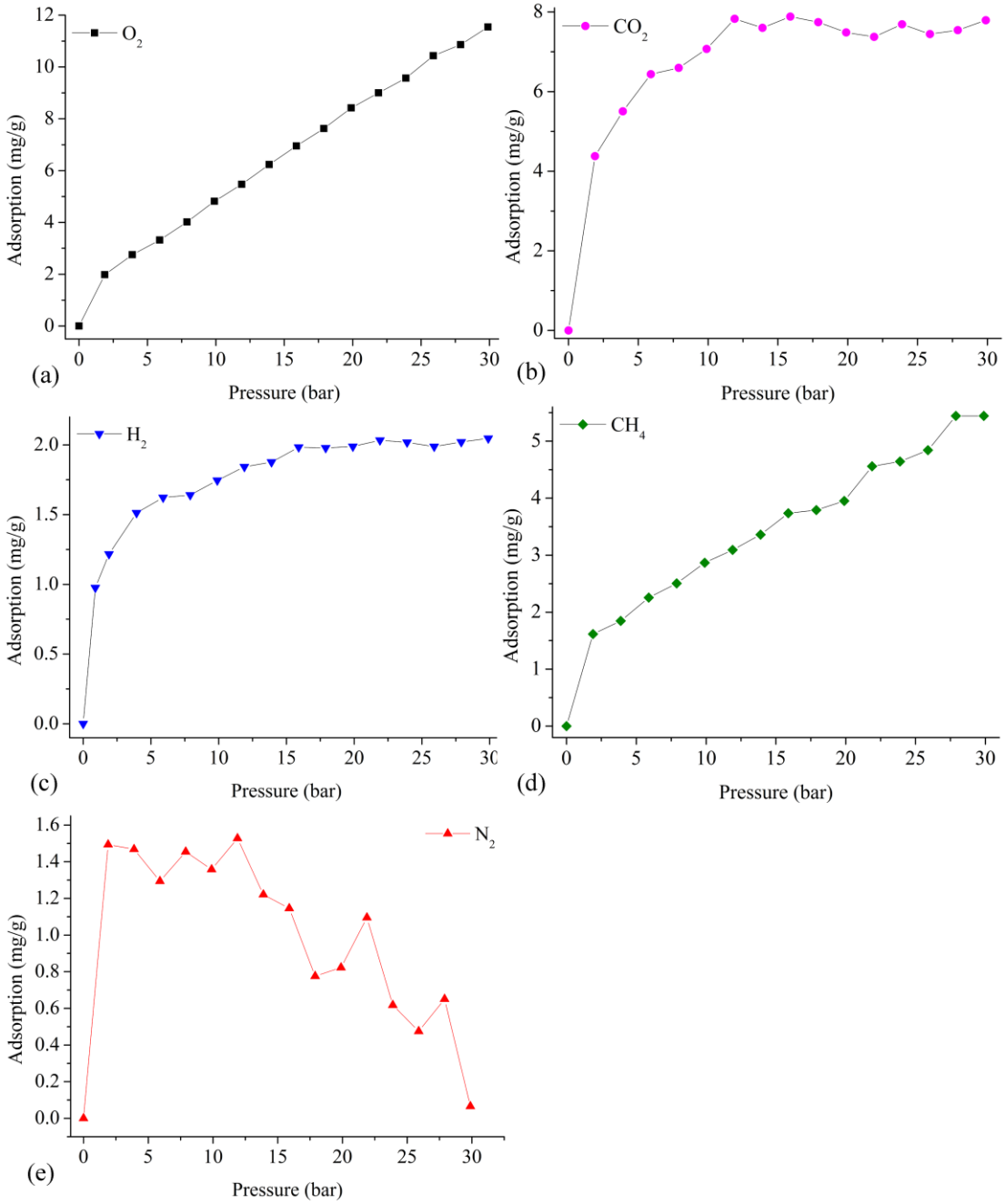


Figure S11. Gases adsorption isotherms of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\cdot 62H_2O$ (**4**) at 298 K at different pressures for O_2 (a), CO_2 (b), H_2 (c), CH_4 (d), N_2 (e) respectively.

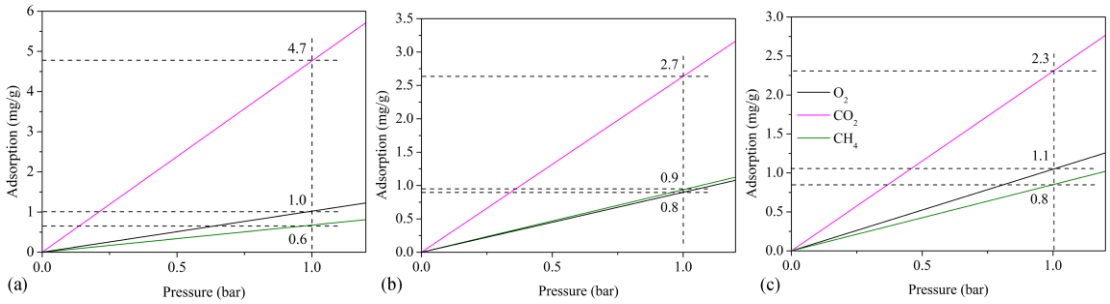


Figure S12. O_2, CO_2 and CH_4 adsorption isotherms for **1**, **2** and **4** (a ~ c) respectively at 298 K and pressures of up to 1 bar.

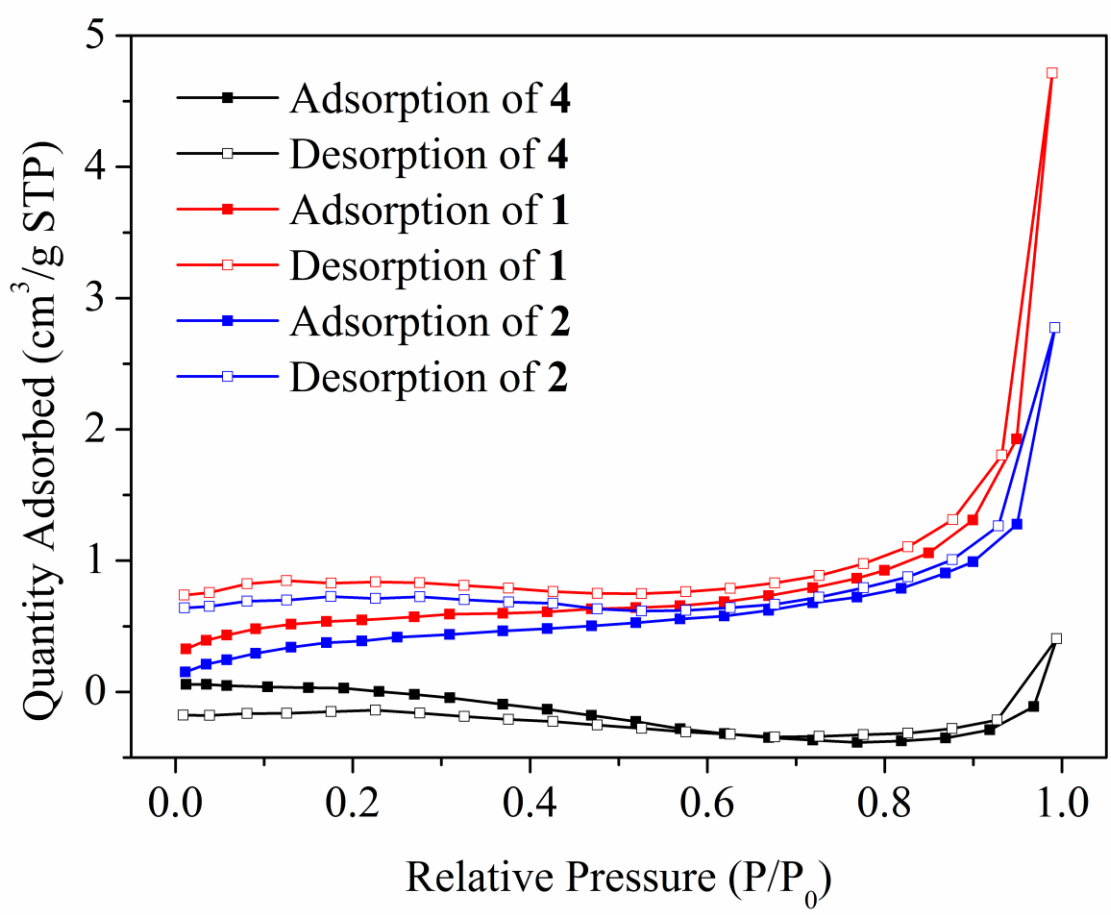


Figure S13. N_2 adsorption−desorption isotherms of **1**, **2** and **4** at 77 K respectively.

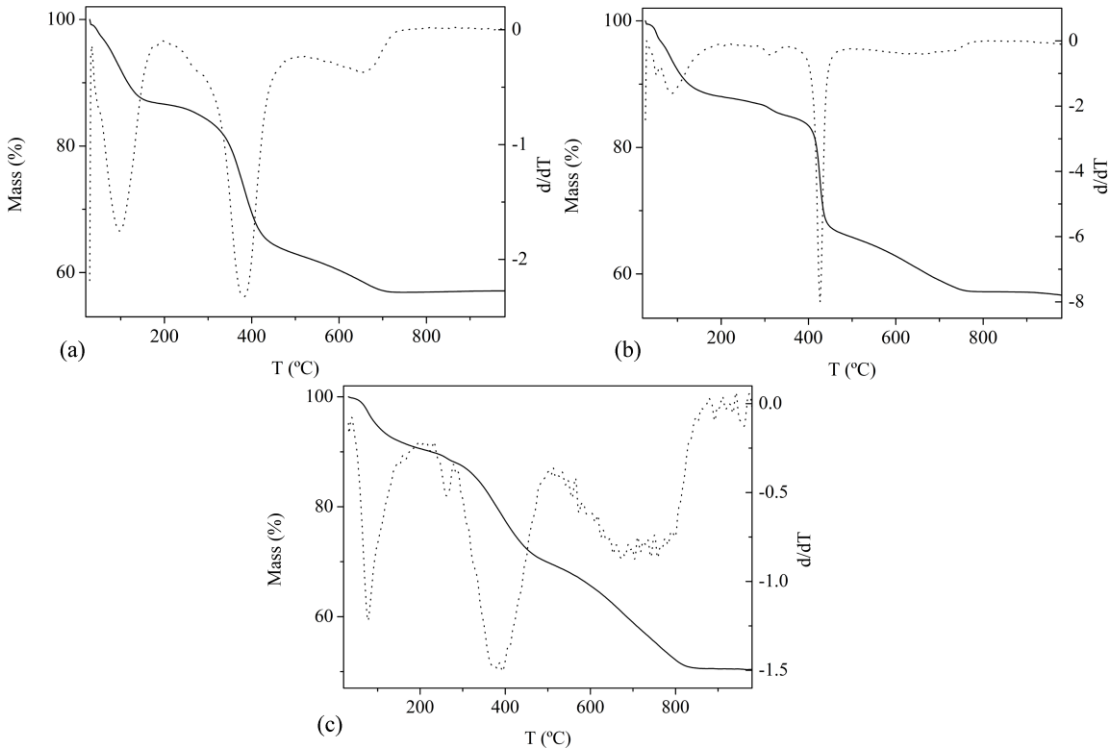


Figure S14. (a) TGA of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**); (b) TGA of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**); (c) TGA of $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]$ $62H_2O$ (**4**) respectively.

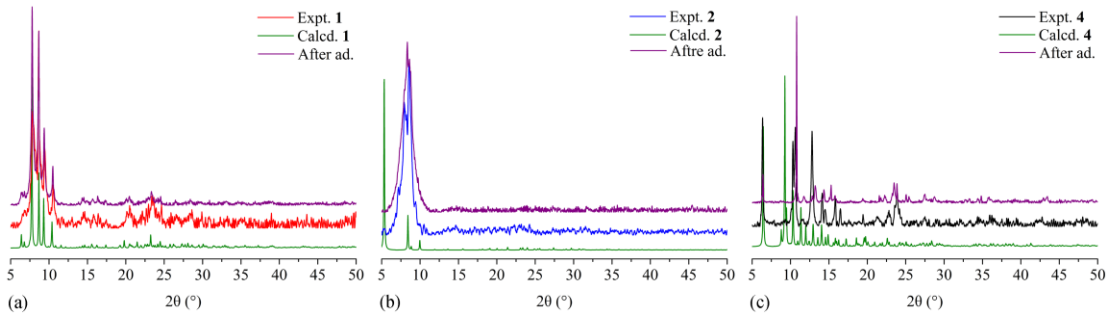


Figure S15. Powder XRD curves for $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot nH_2O$ (n = 22, **1**; n = 92, **2**) and $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]$ 62H_2O (**4**) under different circumstances respectively.

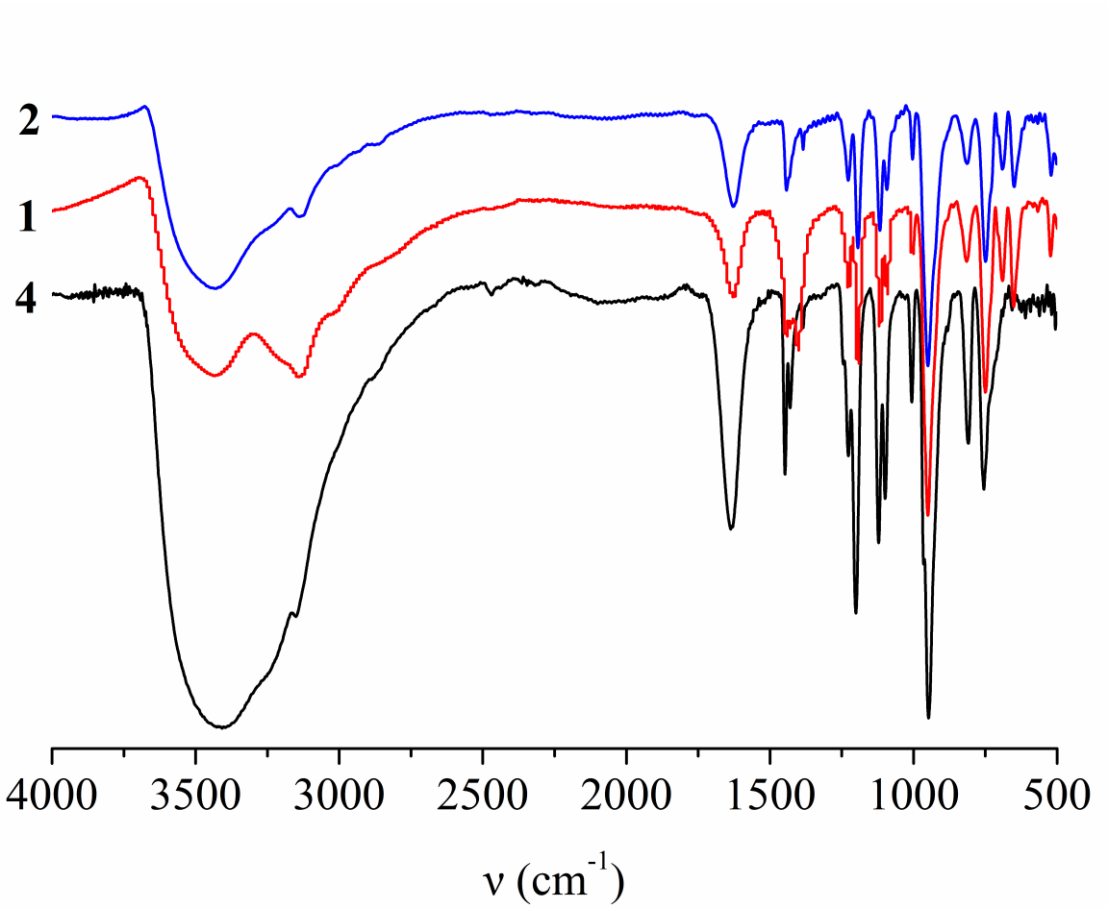


Figure S16. IR spectra of $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot nH_2O$ (n = 22, **1**; n = 92, **2**) and $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]$ $62H_2O$ (**4**) respectively.

1H-1,2,3-triazole

Molecular Formula: $C_2H_3N_3$

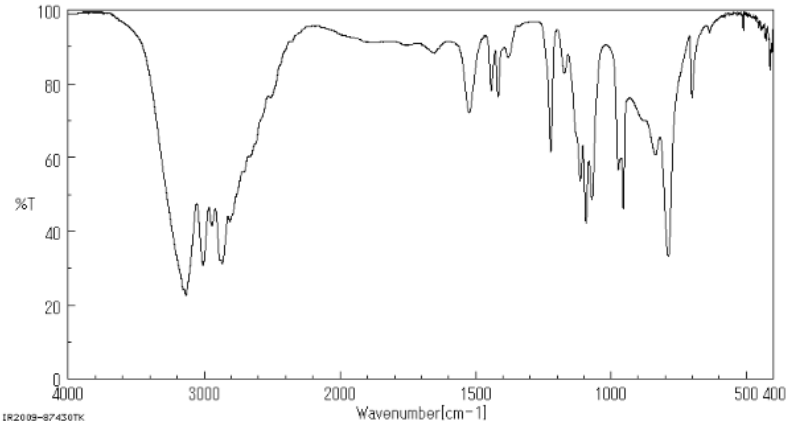
SDBS No.: 41390

Spectral Code: IR2009-87430TK

CAS Registry No: 288-36-8

IR: Liquid film

DOI:



Wave number (cm^{-1}) and Transmittance (T%)

3134 23	1524 72	1114 54	836 61
3008 31	1443 78	1092 42	788 33
2943 42	1417 77	1070 49	701 76
2865 31	1223 62	973 57	511 94
1652 88	1172 83	954 46	

Figure S17. FT-IR spectrum of 1H-1,2,3-triazole [$C_2H_3N_3$] originated from Spectral Database for Organic Compounds SDBS. URL for this compound: https://sdbs.db.aist.go.jp/sdbs/cgi-bin/landingpage?sdbsno=41390.

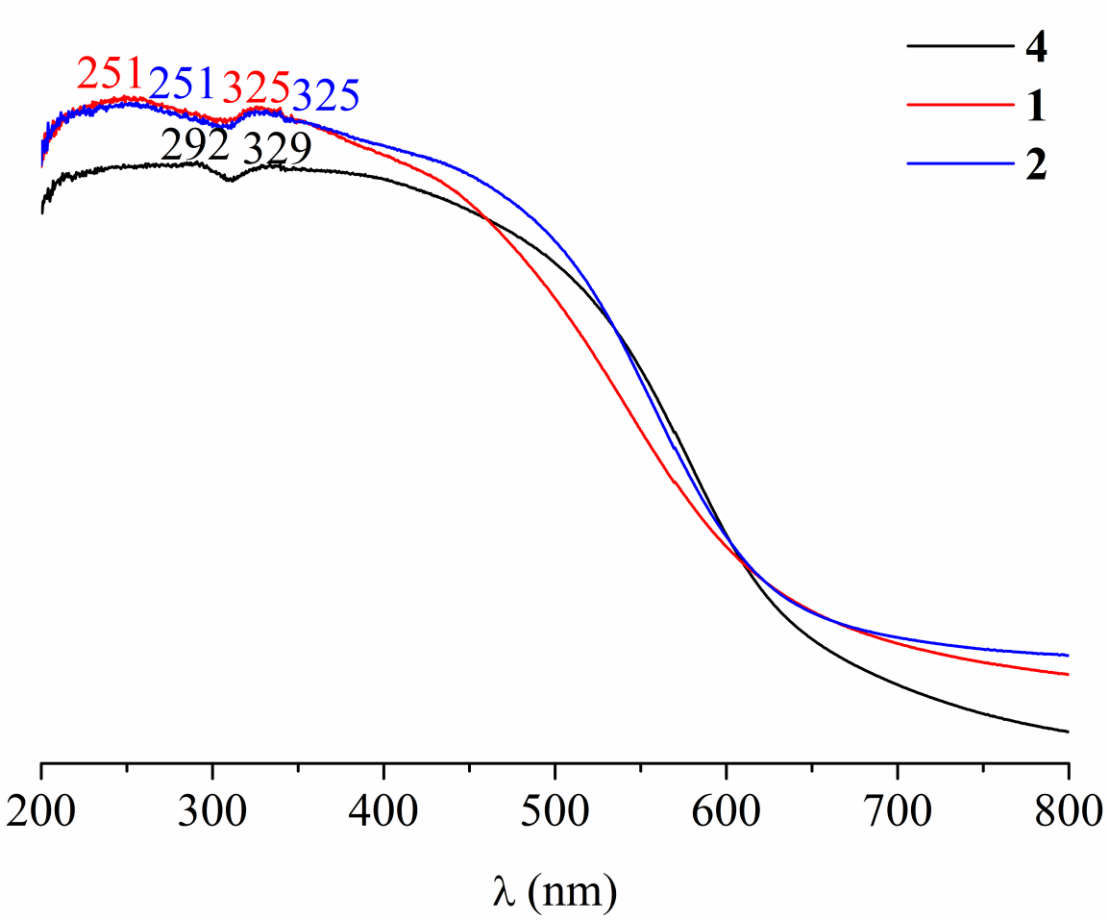


Figure S18. Diffused reflectance spectra of solid $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot nH_2O$ (n = 22, **1**; n = 92, **2**) and $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]$ $62H_2O$ (**4**) respectively.

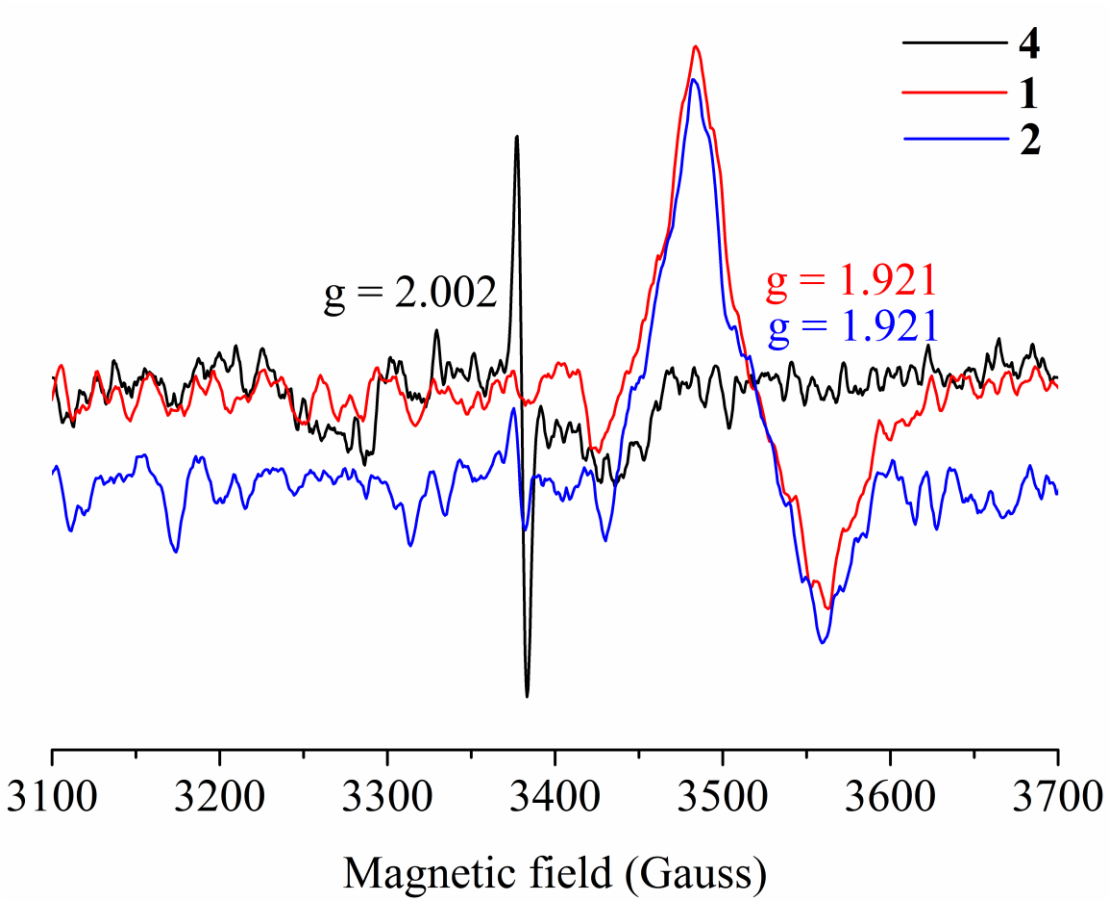


Figure S19. EPR spectra of solid **1**, **2** and **4** at 100 K respectively.

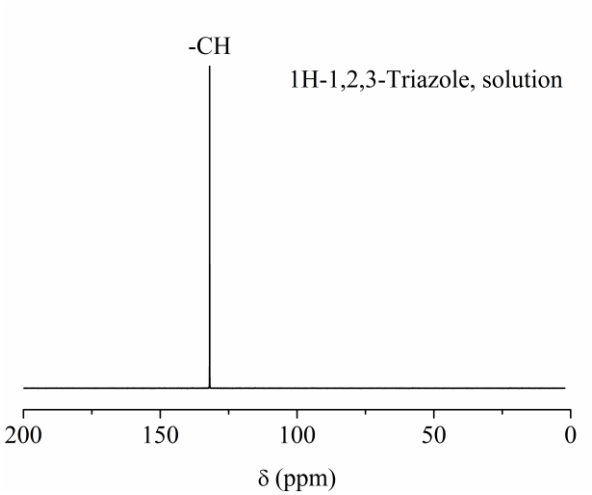


Figure S20. Solution ^{13}C NMR spectrum of pure trz.

Table S1. Crystallographic data and structural refinements for complexes $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot nH_2O$ (n = 22, **1**; n = 92, **2**), $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**) and $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\ 62H_2O$ (**4**) respectively.

Identification codes	**1**	**2**	**3**	**4**
Empirical formula	$C_{16}H_{64}Mo_{12}N_{24}O_{50}$	$C_{16}H_{204}Mo_{12}N_{24}O_{120}$	$C_{24}H_{120}Mo_{16}N_{36}O_{82}$	$C_{32}H_{172}Mo_{16}N_{48}O_{102}$
Formula weight	2544.1	3805.2	3759.9	4396.2
Temperature/K	99.8(8)	99.9(8)	150.0(1)	100.0(1)
Crystal system	monoclinic	tetragonal	triclinic	triclinic
Space group	$P\ 2_1/n$	$I\ 4_1/a$	$P\ \bar{1}$	$P\ \bar{1}$
a/Å	17.2669(2)	20.8003(2)	13.5876(1)	9.7472(1)
b/Å	20.0855(3)	20.8003(2)	19.1998(2)	18.7620(2)
c/Å	19.2031(3)	26.7130(5)	21.9901(2)	20.4530(2)
α/°	90	90	72.4920(1)	89.8000(1)
β/°	98.7530(1)	90	79.1170(1)	82.5470(1)
γ/°	90	90	85.7130(1)	83.1880(1)
Volume/Å^3	6582.35(2)	11557.4(3)	5371.62(9)	3682.33(7)
Z	4	4	2	1
ρ_{calc}g/cm^3	2.167	1.234	1.835	1.479
μ/mm^{-1}	18.797	10.705	15.398	11.324
F(000)	4048.0	4048.0	2808.0	1568.0
Crystal size/mm^3	0.3 × 0.15 × 0.1	0.4 × 0.2 × 0.1	0.3 × 0.2 × 0.1	0.1 × 0.08 × 0.02
Radiation	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/°	6.408 to 159.704	5.384 to 134.994	4.28 to 148.892	4.358 to 157.224

Index ranges	$-19 \leq h \leq 22$, $-25 \leq k \leq 22$, $-24 \leq l \leq 23$	$-18 \leq h \leq 24$, $-24 \leq k \leq 23$, $-32 \leq l \leq 32$	$-16 \leq h \leq 16$, $-23 \leq k \leq 22$, $-27 \leq l \leq 27$	$-12 \leq h \leq 12$, $-23 \leq k \leq 23$, $-25 \leq l \leq 17$
Reflections collected	50482	20237	141603	67878
Independent reflections	14046 [R_{int} = 0.0501, R_{sigma} = 0.0451]	5123 [R_{int} = 0.0413, R_{sigma} = 0.0310]	21272 [R_{int} = 0.0809, R_{sigma} = 0.0383]	15575 [R_{int} = 0.0288, R_{sigma} = 0.0208]
Data/restraints/parameters	14046/0/721	5123/0/185	21272/0/1027	15575/0/613
Goodness–of–fit on F^2	1.036	1.040	1.110	1.031
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0400, wR_2 = 0.1057	R_1 = 0.0439, wR_2 = 0.1259	R_1 = 0.0556, wR_2 = 0.1370	R_1 = 0.0501, wR_2 = 0.1393
Final R indexes [all data]	R_1 = 0.0440, wR_2 = 0.1087	R_1 = 0.0526, wR_2 = 0.1312	R_1 = 0.0617, wR_2 = 0.1424	R_1 = 0.0514, wR_2 = 0.1404
Largest diff. peak/hole/e ·Å^{-3}	1.30/-1.17	1.15/-0.85	1.57/-1.02	3.42/-1.37

Table S2. Hydrogen bond distances (Å) and angles (°) in $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**) before solvent mask.

D–H ··A	D–H(Å)	H ··A(Å)	D ··A(Å)	D–H ··A(°)
N4–H4 ··O1w	0.88	1.77	2.576(2)	150
N7–H7 ··O4wa	0.88	2.23	3.02(4)	150
N16–H16 ··O3w	0.88	2.00	2.861(2)	167
N22–H22 ··O2w	0.88	1.62	2.490(1)	168
C1–H1 ··O5wb	0.95	2.31	3.254(2)	176
C4–H4A ··O4c	0.95	2.56	3.370(1)	144
C5–H5 ··O1wd	0.95	1.65	2.557(2)	158
C7–H7A ··O2e	0.95	2.57	3.497(1)	165
C8–H8 ··O9e	0.95	2.56	3.495(1)	168
C9–H9 ··O25w	0.95	2.55	3.38(2)	146
C11–H11 ··O5we	0.95	2.22	3.17(2)	177
C14–H14 ··O11f	0.95	2.56	3.276(1)	133
C16–H16A ··O24g	0.95	2.43	3.208(1)	139

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

Table S3. Hydrogen bond distances (Å) and angles (°) in $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**) before solvent mask.

D–H ··A	D–H(Å)	H ··A(Å)	D ··A(Å)	D–H ··A(°)
N3–H3 ··O1w	1.02	2.15	3.011(2)	142
C2–H2 ··O2wa	0.95	1.90	2.80(3)	157

Symmetric codes: (a) -1/4 + *y*, 5/4 – *x*, 5/4 – *z*.

Table S4. Hydrogen bond distances (Å) and angles (°) in $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**) before solvent mask.

D–H ··A	D–H(Å)	H ··A(Å)	D ··A(Å)	D–H ··A(°)
N3–H3 ··O1w	0.86	2.23	3.07(5)	165
N6–H6A ··O2w	0.86	2.6	3.39(6)	154
N9–H9A ··O3w	0.86	2.27	3.11(2)	166
N12–H12A ··O4w	0.86	2.2	2.90(4)	139
N15–H15 ··O5w	0.86	1.71	2.544(1)	164
N21–H21 ··O6w	0.86	1.99	2.846(1)	170
N25–H25 ··O7w	0.86	2.32	3.17(2)	167
N28–H28 ··O8w	0.86	2.05	2.88(3)	163
C7–H7 ··O38a	0.93	2.53	3.453(1)	173
C8–H8 ··O9wb	0.93	2.51	3.33(5)	148
C9–H9 ··O21c	0.93	2.51	3.403(1)	162
C10–H10 ··O17c	0.93	2.57	3.490(1)	168
C10–H10 ··O36c	0.93	2.59	3.190(9)	123
C15–H15A ··O19d	0.93	2.5	3.403(1)	163
C17–H17 ··O10we	0.93	2.41	3.172(2)	139
C17–H17 ··O11we	0.93	2.4	3.25(1)	151
C21–H21A ··O12w	0.93	2.48	3.40(9)	172
C23–H23 ··O13wf	0.93	2.42	3.18(7)	139

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

Table S5. Hydrogen bond distances (Å) and angles (°) in $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\ 62H_2O$ (**4**) before solvent mask.

D–H ··A	D–H(Å)	H ··A(Å)	D ··A(Å)	D–H ··A(°)
N1–H1 ··O1w	0.88	1.86	2.732(1)	174
N4–H4 ··O2w	0.88	2.11	2.902(1)	149
N7–H7 ··O3w	0.88	2	2.867(2)	171
N10–H10 ··O4w	0.88	2.54	3.353(2)	153
N13–H13 ··O5w	0.88	2.02	2.893(1)	170
N16–H16 ··O6w	0.88	2.23	2.948(1)	138
N19–H19 ··O7w	0.88	1.95	2.783(1)	157
N22–H22 ··O8w	0.88	2.41	3.254(2)	160

Table S6. Solvent mask values are calculated based on the unit cells for compounds **1** ~ **4** respectively.

Compounds	V(Å^3)	e$^-$	V/e$^-$	V/at.	Content/Unit Cell	e$^-$
1	2161	947	2.3	24.6	88H_2O	880
2	7371	4014	1.8	20.0	368H_2O	3680
3	2224	951	2.3	25.3	88H_2O	880
4	1843	675	2.7	29.7	62H_2O	620

Table S7. Selected bond distances (Å) and angles (°) in $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**) after solvent mask and final refinements.

1			
Mo4–Mo3	2.5764(5)	Mo1–N2	2.187(5)
Mo4–O18	1.983(3)	Mo6–O26	2.118(3)
Mo4–O25	2.098(3)	Mo6–O19	1.977(4)
Mo4–O14	1.921(4)	Mo6–O27	2.187(4)
Mo4–O28	2.210(4)	Mo6–O15	1.928(4)
Mo4–O4	1.686(4)	Mo6–O6	1.698(4)
Mo4–N6	2.199(4)	Mo6–N20	2.194(5)
Mo3–O18	1.969(3)	Mo12–Mo11	2.6029(6)
Mo3–O17	2.292(3)	Mo12–O26	2.068(3)
Mo3–O22	1.983(3)	Mo12–O28	1.989(4)
Mo3–O14	1.966(4)	Mo12–O27	1.992(4)
Mo3–O3	1.694(4)	Mo12–O12	1.690(4)
Mo3–N11	2.200(5)	Mo12–N24	2.159(5)
Mo7–Mo8	2.5753(5)	Mo12–N21	2.208(5)
Mo7–O26	1.984(3)	Mo2–O21	2.100(4)
Mo7–O18	2.304(3)	Mo2–O17	1.974(3)
Mo7–O20	1.967(3)	Mo2–O13	1.924(4)
Mo7–O16	1.951(4)	Mo2–O23	2.190(4)
Mo7–O7	1.672(4)	Mo2–O2	1.691(4)
Mo7–N23	2.181(4)	Mo2–N9	2.210(5)
Mo8–O22	2.110(4)	Mo11–O25	2.070(3)
Mo8–O20	1.975(3)	Mo11–O28	1.986(4)
Mo8–O16	1.925(4)	Mo11–O27	1.977(4)
Mo8–O24	2.199(4)	Mo11–O11	1.695(4)
Mo8–O8	1.692(4)	Mo11–N5	2.199(5)
Mo8–N17	2.191(5)	Mo11–N3	2.159(5)
Mo5–Mo6	2.5784(6)	Mo10–Mo9	2.5950(6)
Mo5–O21	2.006(3)	Mo10–O22	2.077(3)
Mo5–O20	2.291(3)	Mo10–O23	1.985(4)
Mo5–O19	1.961(4)	Mo10–O24	1.979(4)
Mo5–O15	1.958(4)	Mo10–O10	1.692(4)
Mo5–O5	1.687(4)	Mo10–N12	2.162(5)
Mo5–N15	2.174(5)	Mo10–N18	2.201(5)
Mo1–Mo2	2.5843(6)	Mo9–O21	2.053(3)
Mo1–O25	1.997(3)	Mo9–O23	1.981(4)
Mo1–O17	1.965(4)	Mo9–O24	1.976(4)
Mo1–O19	2.263(4)	Mo9–O9	1.701(4)
Mo1–O13	1.969(4)	Mo9–N14	2.161(5)
Mo1–O1	1.687(5)	Mo9–N8	2.207(5)
O18–Mo4–Mo3	49.07(1)	O12–Mo12–O27	112.14(2)
O18–Mo4–O25	87.93(1)	O12–Mo12–N24	90.89(2)
O18–Mo4–O28	94.55(1)	O12–Mo12–N21	85.4(2)
O18–Mo4–N6	163.53(2)	N24–Mo12–Mo11	132.33(1)
O25–Mo4–Mo3	101.06(9)	N24–Mo12–N21	95.22(2)

O25–Mo4–O28	70.81(1)	N21–Mo12–Mo11	130.79(1)
O25–Mo4–N6	75.60(2)	O21–Mo2–Mo1	99.86(9)
O14–Mo4–Mo3	49.23(1)	O21–Mo2–O23	70.63(1)
O14–Mo4–O18	97.04(2)	O21–Mo2–N9	76.32(2)
O14–Mo4–O25	94.76(2)	O17–Mo2–Mo1	48.84(1)
O14–Mo4–O28	161.15(2)	O17–Mo2–O21	87.65(1)
O14–Mo4–N6	84.89(2)	O17–Mo2–O23	94.62(1)
O28–Mo4–Mo3	143.52(1)	O17–Mo2–N9	163.96(2)
O4–Mo4–Mo3	103.01(1)	O13–Mo2–Mo1	49.17(1)
O4–Mo4–O18	103.90(2)	O13–Mo2–O21	93.21(2)
O4–Mo4–O25	155.35(2)	O13–Mo2–O17	96.69(2)
O4–Mo4–O14	104.93(2)	O13–Mo2–O23	159.86(2)
O4–Mo4–O28	86.55(2)	O13–Mo2–N9	85.01(2)
O4–Mo4–N6	91.30(2)	O23–Mo2–Mo1	143.25(1)
N6–Mo4–Mo3	133.94(1)	O23–Mo2–N9	79.62(2)
N6–Mo4–O28	79.87(2)	O2–Mo2–Mo1	103.33(2)
O18–Mo3–Mo4	49.55(1)	O2–Mo2–O21	156.39(2)
O18–Mo3–O17	84.37(1)	O2–Mo2–O17	104.28(2)
O18–Mo3–O22	90.87(1)	O2–Mo2–O13	105.27(2)
O18–Mo3–N11	165.11(2)	O2–Mo2–O23	87.92(2)
O17–Mo3–Mo4	85.39(9)	O2–Mo2–N9	90.5(2)
O22–Mo3–Mo4	138.64(1)	N9–Mo2–Mo1	134.05(1)
O22–Mo3–O17	78.19(1)	O25–Mo11–Mo12	98.09(1)
O22–Mo3–N11	80.59(2)	O25–Mo11–N5	75.72(2)
O14–Mo3–Mo4	47.73(1)	O25–Mo11–N3	80.17(2)
O14–Mo3–O18	96.04(2)	O28–Mo11–Mo12	49.13(1)
O14–Mo3–O17	77.73(1)	O28–Mo11–O25	75.97(1)
O14–Mo3–O22	154.13(2)	O28–Mo11–N5	82.19(2)
O14–Mo3–N11	86.82(2)	O28–Mo11–N3	155.69(2)
O3–Mo3–Mo4	99.72(1)	O27–Mo11–Mo12	49.27(1)
O3–Mo3–O18	103.06(2)	O27–Mo11–O25	95.77(1)
O3–Mo3–O17	172.56(2)	O27–Mo11–O28	95.09(2)
O3–Mo3–O22	101.00(2)	O27–Mo11–N5	171.44(2)
O3–Mo3–O14	101.65(2)	O27–Mo11–N3	82.68(2)
O3–Mo3–N11	90.60(2)	O11–Mo11–Mo12	102.85(2)
N11–Mo3–Mo4	134.49(1)	O11–Mo11–O25	157.2(2)
N11–Mo3–O17	81.96(2)	O11–Mo11–O28	111.46(2)
O26–Mo7–Mo8	138.43(1)	O11–Mo11–O27	104.74(2)
O26–Mo7–O18	77.39(1)	O11–Mo11–N5	83.8(2)
O26–Mo7–N23	81.37(2)	O11–Mo11–N3	92.4(2)
O18–Mo7–Mo8	85.13(8)	N5–Mo11–Mo12	130.23(1)
O20–Mo7–Mo8	49.35(1)	N3–Mo11–Mo12	131.73(1)
O20–Mo7–O26	90.84(1)	N3–Mo11–N5	96.45(2)
O20–Mo7–O18	82.96(1)	O22–Mo10–Mo9	97.51(1)
O20–Mo7–N23	163.80(2)	O22–Mo10–N12	80.07(2)
O16–Mo7–Mo8	47.92(1)	O22–Mo10–N18	75.54(2)
O16–Mo7–O26	153.50(2)	O23–Mo10–Mo9	49.08(1)
O16–Mo7–O18	78.04(1)	O23–Mo10–O22	94.18(2)
O16–Mo7–O20	95.88(2)	O23–Mo10–N12	84.31(2)
O16–Mo7–N23	85.33(2)	O23–Mo10–N18	169.71(2)

O7–Mo7–Mo8	100.30(2)	O24–Mo10–Mo9	48.94(1)
O7–Mo7–O26	100.61(2)	O24–Mo10–O22	75.82(1)
O7–Mo7–O18	173.32(2)	O24–Mo10–O23	94.37(2)
O7–Mo7–O20	103.51(2)	O24–Mo10–N12	155.70(2)
O7–Mo7–O16	102.65(2)	O24–Mo10–N18	83.18(2)
O7–Mo7–N23	91.92(2)	O10–Mo10–Mo9	102.44(2)
N23–Mo7–Mo8	133.15(1)	O10–Mo10–O22	158.54(2)
N23–Mo7–O18	81.49(2)	O10–Mo10–O23	104.81(2)
O22–Mo8–Mo7	101.10(9)	O10–Mo10–O24	111.90(2)
O22–Mo8–O24	70.67(1)	O10–Mo10–N12	91.8(2)
O22–Mo8–N17	74.78(2)	O10–Mo10–N18	85.3(2)
O20–Mo8–Mo7	49.08(1)	N12–Mo10–Mo9	133.23(1)
O20–Mo8–O22	86.93(2)	N12–Mo10–N18	93.80(2)
O20–Mo8–O24	94.35(1)	N18–Mo10–Mo9	131.20(1)
O20–Mo8–N17	161.70(2)	O21–Mo9–Mo10	99.02(1)
O16–Mo8–Mo7	48.81(1)	O21–Mo9–N14	80.62(2)
O16–Mo8–O22	95.18(2)	O21–Mo9–N8	75.93(2)
O16–Mo8–O20	96.48(2)	O23–Mo9–Mo10	49.19(1)
O16–Mo8–O24	161.68(2)	O23–Mo9–O21	75.88(2)
O16–Mo8–N17	84.67(2)	O23–Mo9–N14	155.80(2)
O24–Mo8–Mo7	143.38(1)	O23–Mo9–N8	82.43(2)
O8–Mo8–Mo7	102.79(1)	O24–Mo9–Mo10	49.05(1)
O8–Mo8–O22	155.37(2)	O24–Mo9–O21	96.18(1)
O8–Mo8–O20	104.33(2)	O24–Mo9–O23	94.58(2)
O8–Mo8–O16	105.00(2)	O24–Mo9–N14	82.17(2)
O8–Mo8–O24	86.48(2)	O24–Mo9–N8	172.02(2)
O8–Mo8–N17	92.9(2)	O9–Mo9–Mo10	101.32(2)
N17–Mo8–Mo7	133.20(1)	O9–Mo9–O21	157.60(2)
N17–Mo8–O24	80.45(2)	O9–Mo9–O23	111.08(2)
O21–Mo5–Mo6	138.95(1)	O9–Mo9–O24	104.20(2)
O21–Mo5–O20	77.86(1)	O9–Mo9–N14	92.90(2)
O21–Mo5–N15	81.12(2)	O9–Mo9–N8	83.8(2)
O20–Mo5–Mo6	86.25(9)	N14–Mo9–Mo10	131.09(1)
O19–Mo5–Mo6	49.36(1)	N14–Mo9–N8	97.51(2)
O19–Mo5–O21	90.98(1)	N8–Mo9–Mo10	130.19(1)
O19–Mo5–O20	83.44(1)	Mo7–O26–Mo6	124.61(2)
O19–Mo5–N15	161.84(2)	Mo7–O26–Mo12	131.49(2)
O15–Mo5–Mo6	47.93(1)	Mo12–O26–Mo6	103.32(2)
O15–Mo5–O21	154.92(2)	Mo4–O18–Mo7	145.21(2)
O15–Mo5–O20	79.01(1)	Mo3–O18–Mo4	81.39(1)
O15–Mo5–O19	95.90(2)	Mo3–O18–Mo7	133.27(2)
O15–Mo5–N15	85.07(2)	Mo5–O21–Mo2	124.52(2)
O5–Mo5–Mo6	99.65(1)	Mo5–O21–Mo9	131.36(2)
O5–Mo5–O21	99.86(2)	Mo9–O21–Mo2	103.91(2)
O5–Mo5–O20	172.87(2)	Mo1–O25–Mo4	124.02(2)
O5–Mo5–O19	103.42(2)	Mo1–O25–Mo11	131.66(2)
O5–Mo5–O15	101.92(2)	Mo11–O25–Mo4	103.96(2)
O5–Mo5–N15	94.08(2)	Mo1–O17–Mo3	133.19(2)
N15–Mo5–Mo6	132.74(1)	Mo1–O17–Mo2	82.00(1)
N15–Mo5–O20	78.93(2)	Mo2–O17–Mo3	144.56(2)

O25–Mo1–Mo2	138.61(1)	Mo3–O22–Mo8	124.36(2)
O25–Mo1–O19	77.56(1)	Mo3–O22–Mo10	132.02(2)
O25–Mo1–N2	81.02(2)	Mo10–O22–Mo8	103.24(2)
O17–Mo1–Mo2	49.16(1)	Mo7–O20–Mo8	81.57(1)
O17–Mo1–O25	90.95(1)	Mo7–O20–Mo5	132.28(2)
O17–Mo1–O19	84.27(1)	Mo8–O20–Mo5	145.61(2)
O17–Mo1–O13	95.52(2)	Mo5–O19–Mo1	132.77(2)
O17–Mo1–N2	162.91(2)	Mo5–O19–Mo6	81.81(1)
O19–Mo1–Mo2	86.58(9)	Mo6–O19–Mo1	144.86(2)
O13–Mo1–Mo2	47.65(1)	Mo2–O13–Mo1	83.18(1)
O13–Mo1–O25	155.01(2)	Mo4–O14–Mo3	83.04(2)
O13–Mo1–O19	79.11(2)	Mo12–O28–Mo4	133.79(2)
O13–Mo1–N2	85.99(2)	Mo11–O28–Mo4	102.84(2)
O1–Mo1–Mo2	100.35(2)	Mo11–O28–Mo12	81.81(1)
O1–Mo1–O25	99.87(2)	Mo12–O27–Mo6	103.48(2)
O1–Mo1–O17	103.90(2)	Mo11–O27–Mo6	132.96(2)
O1–Mo1–O19	171.55(2)	Mo11–O27–Mo12	81.95(1)
O1–Mo1–O13	101.93(2)	Mo8–O16–Mo7	83.27(2)
O1–Mo1–N2	92.4(2)	Mo10–O23–Mo2	135.32(2)
N2–Mo1–Mo2	133.44(1)	Mo9–O23–Mo2	103.16(2)
N2–Mo1–O19	79.29(2)	Mo9–O23–Mo10	81.74(2)
O26–Mo6–Mo5	99.86(9)	Mo6–O15–Mo5	83.14(2)
O26–Mo6–O27	70.94(1)	Mo10–O24–Mo8	103.44(2)
O26–Mo6–N20	76.12(2)	Mo9–O24–Mo8	133.92(2)
O19–Mo6–Mo5	48.83(1)	Mo9–O24–Mo10	82.01(2)
O19–Mo6–O26	86.71(1)	N12–N11–Mo3	122.1(4)
O19–Mo6–O27	95.83(1)	N10–N11–Mo3	127.0(4)
O19–Mo6–N20	162.83(2)	N14–N15–Mo5	121.9(4)
O27–Mo6–Mo5	144.53(1)	C9–N15–Mo5	130.5(4)
O27–Mo6–N20	78.93(2)	N5–N6–Mo4	116.1(3)
O15–Mo6–Mo5	48.93(1)	C3–N6–Mo4	134.9(4)
O15–Mo6–O26	93.79(2)	N21–N20–Mo6	117.3(4)
O15–Mo6–O19	96.35(2)	N19–N20–Mo6	131.8(4)
O15–Mo6–O27	159.84(2)	N6–N5–Mo11	116.7(3)
O15–Mo6–N20	84.75(2)	N4–N5–Mo11	132.0(4)
O6–Mo6–Mo5	101.51(1)	N24–N23–Mo7	122.6(3)
O6–Mo6–O26	158.08(2)	N22–N23–Mo7	127.0(4)
O6–Mo6–O19	103.81(2)	N15–N14–Mo9	121.7(3)
O6–Mo6–O27	88.68(2)	N13–N14–Mo9	124.9(4)
O6–Mo6–O15	103.89(2)	N23–N24–Mo12	121.8(3)
O6–Mo6–N20	92.5(2)	C15–N24–Mo12	129.4(4)
N20–Mo6–Mo5	133.49(1)	N20–N21–Mo12	114.9(3)
O26–Mo12–Mo11	97.28(1)	C13–N21–Mo12	137.4(5)
O26–Mo12–N24	80.95(2)	N2–N3–Mo11	122.3(3)
O26–Mo12–N21	75.56(2)	C1–N3–Mo11	125.8(4)
O28–Mo12–Mo11	49.06(1)	N3–N2–Mo1	121.3(3)
O28–Mo12–O26	94.82(1)	N1–N2–Mo1	128.6(5)
O28–Mo12–O27	94.55(2)	N11–N12–Mo10	121.9(3)
O28–Mo12–N24	83.43(2)	C7–N12–Mo10	128.7(4)
O28–Mo12–N21	170.38(2)	N8–N9–Mo2	115.7(4)

O27–Mo12–Mo11	48.78(1)	C5–N9–Mo2	134.4(5)
O27–Mo12–O26	75.93(1)	N9–N8–Mo9	116.4(3)
O27–Mo12–N24	156.56(2)	N7–N8–Mo9	134.5(5)
O27–Mo12–N21	82.87(2)	N18–N17–Mo8	117.3(4)
O12–Mo12–Mo11	102.90(2)	N16–N17–Mo8	132.9(4)
O12–Mo12–O26	158.42(2)	N17–N18–Mo10	115.7(3)
O12–Mo12–O28	104.11(2)	C11–N18–Mo10	135.3(5)

Table S8. Selected bond distances (Å) and angles (°) in $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**) after solvent mask and final refinements.

2			
Mo2–Mo1	2.5718(6)	Mo1–O2	1.927(4)
Mo2–O3	1.965(4)	Mo1–O1	1.692(4)
Mo2–O3^{1}	2.291(4)	Mo1–N4^{1}	2.215(5)
Mo2–O5	1.996(3)	Mo3–Mo3^{3}	2.5972(9)
Mo2–O2	1.959(4)	Mo3–O5	2.062(4)
Mo2–O4	1.689(4)	Mo3–O6^{3}	1.987(4)
Mo2–N1	2.172(5)	Mo3–O6	1.977(4)
Mo1–O3	1.963(4)	Mo3–O7	1.692(4)
Mo1–O5^{1}	2.101(4)	Mo3–N2	2.158(5)
Mo1–O6^{2}	2.181(4)	Mo3–N5	2.211(5)
O3–Mo2–Mo1	49.07(1)	N4^{1}–Mo1–Mo2	134.34(1)
O3^{1}–Mo2–Mo1	86.75(9)	O5–Mo3–Mo3^{3}	98.58(1)
O3–Mo2–O3^{1}	83.98(2)	O5–Mo3–N2	80.62(2)
O3–Mo2–O5	91.48(2)	O5–Mo3–N5	75.99(2)
O3–Mo2–N1	163.61(2)	O6^{3}–Mo3–Mo3^{3}	48.91(1)
O5–Mo2–Mo1	139.28(1)	O6–Mo3–Mo3^{3}	49.23(1)
O5–Mo2–O3^{1}	78.16(1)	O6–Mo3–O5	95.37(2)
O5–Mo2–N1	81.30(2)	O6^{3}–Mo3–O5	75.59(2)
O2–Mo2–Mo1	48.03(1)	O6–Mo3–O6^{3}	94.28(2)
O2–Mo2–O3	95.73(2)	O6^{3}–Mo3–N2	155.67(2)
O2–Mo2–O3^{1}	79.24(1)	O6–Mo3–N2	82.85(2)
O2–Mo2–O5	155.39(2)	O6–Mo3–N5	171.28(2)
O2–Mo2–N1	85.38(2)	O6^{3}–Mo3–N5	82.50(2)
O4–Mo2–Mo1	98.62(1)	O7–Mo3–Mo3^{3}	101.90(2)
O4–Mo2–O3	102.49(2)	O7–Mo3–O5	157.77(2)
O4–Mo2–O3^{1}	173.35(2)	O7–Mo3–O6	104.5(2)
O4–Mo2–O5	99.94(2)	O7–Mo3–O6^{3}	112.1(2)
O4–Mo2–O2	101.40(2)	O7–Mo3–N2	91.9(2)
O4–Mo2–N1	93.28(2)	O7–Mo3–N5	84.2(2)
N1–Mo2–Mo1	133.28(1)	N2–Mo3–Mo3^{3}	131.98(1)
N1–Mo2–O3^{1}	80.16(2)	N2–Mo3–N5	96.72(2)
O3–Mo1–Mo2	49.12(1)	N5–Mo3–Mo3^{3}	130.02(1)
O3–Mo1–O5^{1}	87.22(1)	Mo2–O3–Mo2^{2}	131.79(2)
O3–Mo1–O6^{2}	93.62(2)	Mo1–O3–Mo2^{2}	145.97(2)
O3–Mo1–N4^{1}	163.45(2)	Mo1–O3–Mo2	81.81(1)
O5^{1}–Mo1–Mo2	100.18(1)	Mo2–O5–Mo1^{2}	124.88(2)
O5^{1}–Mo1–O6^{2}	70.82(1)	Mo2–O5–Mo3	131.36(2)
O5^{1}–Mo1–N4^{1}	76.27(2)	Mo3–O5–Mo1^{2}	103.62(2)
O6^{2}–Mo1–Mo2	142.62(1)	Mo3^{3}–O6–Mo1^{1}	103.36(2)
O6^{2}–Mo1–N4^{1}	80.16(2)	Mo3–O6–Mo1^{1}	135.4(2)
O2–Mo1–Mo2	49.11(1)	Mo3–O6–Mo3^{3}	81.86(15)
O2–Mo1–O3	96.84(2)	Mo1–O2–Mo2	82.86(15)
O2–Mo1–O5^{1}	93.68(2)	N2–N1–Mo2	122.0(3)
O2–Mo1–O6^{2}	160.86(2)	C2–N1–Mo2	130.1(4)

O2–Mo1–N4[1]	85.37(2)	N1–N2–Mo3	121.4(3)
O1–Mo1–Mo2	102.62(2)	N3–N2–Mo3	127.5(4)
O1–Mo1–O3	104.56(2)	N5–N4–Mo1[2]	115.5(3)
O1–Mo1–O5[1]	156.81(2)	C4–N4–Mo1[2]	136.0(5)
O1–Mo1–O6[2]	88.29(2)	N4–N5–Mo3	116.5(3)
O1–Mo1–O2	104.42(2)	N6–N5–Mo3	131.4(5)
O1–Mo1–N4[1]	90.7(2)		

Symmetric codes: [1] -1/4 + *y*, 5/4 – *x*, 5/4 – *z*; [2] 5/4 – *y*, 1/4 + *x*, 5/4 – *z*; 1 – *x*, 3/2 – *y*, +*z*.

Table S9. Selected bond distances (Å) and angles (°) in $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**) after solvent mask and final refinements.

3			
Mo5–Mo6	2.5801(7)	Mo9–N27	2.184(6)
Mo5–O34	1.998(4)	Mo12–O30	1.961(5)
Mo5–O30	2.323(5)	Mo12–O29	2.281(5)
Mo5–O27	1.953(5)	Mo12–O31	1.990(5)
Mo5–O23	1.948(5)	Mo12–O26	1.961(5)
Mo5–O11	1.687(5)	Mo12–O18	1.679(6)
Mo5–N14	2.179(6)	Mo12–N35	2.192(7)
Mo16–Mo15	2.5937(8)	Mo13–Mo14	2.5964(1)
Mo16–O34	2.057(4)	Mo13–O32	1.973(5)
Mo16–O35	1.983(5)	Mo13–O31	2.064(5)
Mo16–O36	1.967(5)	Mo13–O38	1.969(6)
Mo16–O22	1.685(5)	Mo13–O19	1.694(6)
Mo16–N20	2.213(6)	Mo13–N16	2.219(9)
Mo16–N13	2.160(6)	Mo13–N36	2.165(7)
Mo7–Mo8	2.5728(7)	Mo14–O33	2.067(5)
Mo7–O28	1.969(5)	Mo14–O32	1.960(6)
Mo7–O34	2.125(5)	Mo14–O38	1.980(6)
Mo7–O35	2.194(4)	Mo14–O20	1.688(6)
Mo7–O24	1.925(5)	Mo14–N22	2.152(7)
Mo7–O13	1.677(5)	Mo14–N29	2.178(8)
Mo7–N19	2.206(6)	Mo10–O33	2.107(5)
Mo15–O35	1.962(5)	Mo10–O29	1.976(5)
Mo15–O36	1.975(5)	Mo10–O38	2.192(6)
Mo15–O37	2.060(5)	Mo10–O25	1.918(6)
Mo15–O21	1.686(5)	Mo10–O16	1.685(6)
Mo15–N32	2.204(6)	Mo10–N30	2.212(7)
Mo15–N26	2.159(6)	Mo3–Mo4	2.5424(1)
Mo6–O27	1.970(5)	Mo3–O7	2.153(6)
Mo6–O23	1.914(5)	Mo3–O9	1.942(8)
Mo6–O32	2.206(5)	Mo3–O8	1.925(6)
Mo6–O31	2.122(5)	Mo3–O3	1.711(7)
Mo6–O12	1.687(5)	Mo3–N7	2.213(7)
Mo6–N17	2.212(6)	Mo3–N4	2.203(1)
Mo8–O28	1.960(5)	Mo4–O10	2.168(6)
Mo8–O24	1.961(5)	Mo4–O9	1.947(6)
Mo8–O27	2.301(5)	Mo4–O8	1.920(8)
Mo8–O33	1.997(5)	Mo4–N11	2.202(7)
Mo8–O14	1.689(5)	Mo4–N1[1]	2.183(9)
Mo8–N23	2.170(6)	Mo4–O4	1.698(6)
Mo11–Mo12	2.5776(8)	Mo1–Mo2	2.5533(1)
Mo11–O36	2.191(5)	Mo1–O10[1]	2.161(6)
Mo11–O30	1.962(5)	Mo1–O6	1.938(6)
Mo11–O37	2.120(5)	Mo1–O5	1.934(8)
Mo11–O26	1.922(5)	Mo1–O1	1.679(7)
Mo11–O17	1.694(6)	Mo1–N2	2.207(9)

Mo11–N33	2.202(7)	Mo1–N10[1]	2.208(9)
Mo9–Mo10	2.5776(8)	Mo2–O6	1.940(7)
Mo9–O28	2.309(5)	Mo2–O7	2.153(6)
Mo9–O37	1.996(5)	Mo2–O5	1.923(7)
Mo9–O29	1.962(5)	Mo2–O2	1.683(7)
Mo9–O25	1.957(6)	Mo2–N8	2.220(7)
Mo9–O15	1.673(6)	Mo2–N5	2.205(1)
O34–Mo5–Mo6	138.65(1)	O32–Mo14–O38	94.5(2)
O34–Mo5–O30	78.03(2)	O32–Mo14–N22	82.9(2)
O34–Mo5–N14	81.2(2)	O32–Mo14–N29	170.4(2)
O30–Mo5–Mo6	86.01(1)	O38–Mo14–Mo13	48.70(2)
O27–Mo5–Mo6	49.17(1)	O38–Mo14–O33	75.6(2)
O27–Mo5–O34	90.99(2)	O38–Mo14–N22	156.4(2)
O27–Mo5–O30	83.98(2)	O38–Mo14–N29	83.5(3)
O27–Mo5–N14	164.2(2)	O20–Mo14–Mo13	102.5(2)
O23–Mo5–Mo6	47.52(2)	O20–Mo14–O33	157.9(3)
O23–Mo5–O34	153.98(2)	O20–Mo14–O32	105.1(3)
O23–Mo5–O30	77.51(2)	O20–Mo14–O38	110.2(3)
O23–Mo5–O27	95.2(2)	O20–Mo14–N22	93.0(3)
O23–Mo5–N14	86.4(2)	O20–Mo14–N29	84.4(3)
O11–Mo5–Mo6	99.15(2)	N22–Mo14–Mo13	131.59(2)
O11–Mo5–O34	101.1(2)	N22–Mo14–N29	95.2(3)
O11–Mo5–O30	172.6(2)	N29–Mo14–Mo13	131.5(2)
O11–Mo5–O27	103.4(2)	O33–Mo10–Mo9	100.16(1)
O11–Mo5–O23	102.0(2)	O33–Mo10–O38	70.44(2)
O11–Mo5–N14	91.6(2)	O33–Mo10–N30	75.3(2)
N14–Mo5–Mo6	133.84(2)	O29–Mo10–Mo9	48.88(2)
N14–Mo5–O30	80.9(2)	O29–Mo10–O33	86.7(2)
O34–Mo16–Mo15	98.93(1)	O29–Mo10–O38	94.6(2)
O34–Mo16–N20	75.89(2)	O29–Mo10–N30	162.0(2)
O34–Mo16–N13	80.6(2)	O38–Mo10–Mo9	143.34(2)
O35–Mo16–Mo15	48.53(1)	O38–Mo10–N30	79.9(3)
O35–Mo16–O34	76.45(2)	O25–Mo10–Mo9	48.95(2)
O35–Mo16–N20	82.4(2)	O25–Mo10–O33	94.2(2)
O35–Mo16–N13	156.5(2)	O25–Mo10–O29	96.4(2)
O36–Mo16–Mo15	48.99(1)	O25–Mo10–O38	160.6(2)
O36–Mo16–O34	96.31(2)	O25–Mo10–N30	84.8(3)
O36–Mo16–O35	94.10(2)	O16–Mo10–Mo9	103.1(2)
O36–Mo16–N20	172.0(2)	O16–Mo10–O33	156.2(2)
O36–Mo16–N13	83.4(2)	O16–Mo10–O29	104.7(3)
O22–Mo16–Mo15	102.2(2)	O16–Mo10–O38	87.6(3)
O22–Mo16–O34	157.1(2)	O16–Mo10–O25	104.9(3)
O22–Mo16–O35	111.7(2)	O16–Mo10–N30	92.2(3)
O22–Mo16–O36	104.1(2)	N30–Mo10–Mo9	133.5(2)
O22–Mo16–N20	83.9(2)	O7–Mo3–Mo4	106.00(2)
O22–Mo16–N13	91.5(3)	O7–Mo3–N7	74.7(2)
N20–Mo16–Mo15	129.62(2)	O7–Mo3–N4	75.3(3)
N13–Mo16–Mo15	132.21(2)	O9–Mo3–Mo4	49.27(2)
N13–Mo16–N20	97.0(2)	O9–Mo3–O7	89.0(3)

O28–Mo7–Mo8	48.94(1)	O9–Mo3–N7	86.8(3)
O28–Mo7–O34	87.03(2)	O9–Mo3–N4	164.3(3)
O28–Mo7–O35	94.03(2)	O8–Mo3–Mo4	48.5(2)
O28–Mo7–N19	163.8(2)	O8–Mo3–O7	90.9(3)
O34–Mo7–Mo8	99.49(1)	O8–Mo3–O9	93.6(3)
O34–Mo7–O35	70.72(2)	O8–Mo3–N7	165.5(3)
O34–Mo7–N19	76.84(2)	O8–Mo3–N4	86.5(3)
O35–Mo7–Mo8	142.77(1)	O3–Mo3–Mo4	99.1(3)
O35–Mo7–N19	79.90(2)	O3–Mo3–O7	154.9(3)
O24–Mo7–Mo8	49.13(1)	O3–Mo3–O9	107.0(4)
O24–Mo7–O28	96.5(2)	O3–Mo3–O8	106.9(3)
O24–Mo7–O34	92.25(2)	O3–Mo3–N7	86.7(3)
O24–Mo7–O35	159.48(2)	O3–Mo3–N4	87.9(4)
O24–Mo7–N19	85.2(2)	N7–Mo3–Mo4	135.6(2)
O13–Mo7–Mo8	102.13(2)	N4–Mo3–Mo4	134.7(2)
O13–Mo7–O28	103.4(2)	N4–Mo3–N7	89.2(3)
O13–Mo7–O34	157.8(2)	O10–Mo4–Mo3	106.42(2)
O13–Mo7–O35	88.8(2)	O10–Mo4–N11	74.8(3)
O13–Mo7–O24	105.7(2)	O10–Mo4–N1^{1}	75.3(3)
O13–Mo7–N19	91.5(2)	O9–Mo4–Mo3	49.1(2)
N19–Mo7–Mo8	134.26(1)	O9–Mo4–O10	91.6(2)
O35–Mo15–Mo16	49.26(1)	O9–Mo4–N11	166.4(3)
O35–Mo15–O36	94.55(2)	O9–Mo4–N1^{1}	85.3(3)
O35–Mo15–O37	96.13(2)	O8–Mo4–Mo3	48.69(2)
O35–Mo15–N32	172.3(2)	O8–Mo4–O10	88.8(3)
O35–Mo15–N26	84.2(2)	O8–Mo4–O9	93.6(3)
O36–Mo15–Mo16	48.74(1)	O8–Mo4–N11	87.5(3)
O36–Mo15–O37	76.46(2)	O8–Mo4–N1^{1}	164.0(3)
O36–Mo15–N32	82.3(2)	N1^{1}–Mo4–Mo3	135.6(2)
O36–Mo15–N26	156.7(2)	N1^{1}–Mo4–Mo3	134.1(2)
O37–Mo15–Mo16	98.90(1)	N1^{1}–Mo4–N11	89.8(3)
O37–Mo15–N32	76.3(2)	O4–Mo4–Mo3	98.8(3)
O37–Mo15–N26	80.6(2)	O4–Mo4–O10	154.8(3)
O21–Mo15–Mo16	101.65(2)	O4–Mo4–O9	106.1(3)
O21–Mo15–O35	103.7(2)	O4–Mo4–O8	107.3(4)
O21–Mo15–O36	111.4(2)	O4–Mo4–N11	86.4(3)
O21–Mo15–O37	157.8(2)	O4–Mo4–N1^{1}	88.2(4)
O21–Mo15–N32	84.0(2)	O10^{1}–Mo1–Mo2	105.02(2)
O21–Mo15–N26	91.4(3)	O10^{1}–Mo1–N2	75.0(3)
N32–Mo15–Mo16	129.62(2)	O10^{1}–Mo1–N10^{1}	74.9(2)
N26–Mo15–Mo16	133.33(2)	O6–Mo1–Mo2	48.9(2)
N26–Mo15–N32	95.9(2)	O6–Mo1–O10^{1}	88.7(2)
O27–Mo6–Mo5	48.60(1)	O6–Mo1–N2	163.6(3)
O27–Mo6–O32	95.00(2)	O6–Mo1–N10^{1}	87.3(3)
O27–Mo6–O31	87.24(2)	O5–Mo1–Mo2	48.4(2)
O27–Mo6–N17	163.1(2)	O5–Mo1–O10^{1}	90.4(3)
O23–Mo6–Mo5	48.65(1)	O5–Mo1–O6	93.3(3)
O23–Mo6–O27	95.7(2)	O5–Mo1–N2	84.7(3)
O23–Mo6–O32	160.1(2)	O5–Mo1–N10^{1}	165.3(3)
O23–Mo6–O31	93.4(2)	O1–Mo1–Mo2	98.7(3)

O23–Mo6–N17	86.1(2)	O1–Mo1–O10[1]	156.3(3)
O32–Mo6–Mo5	143.46(1)	O1–Mo1–O6	106.3(3)
O32–Mo6–N17	78.9(2)	O1–Mo1–O5	106.5(4)
O31–Mo6–Mo5	100.42(1)	O1–Mo1–N2	89.8(3)
O31–Mo6–O32	70.38(2)	O1–Mo1–N10[1]	87.3(4)
O31–Mo6–N17	75.9(2)	N2–Mo1–Mo2	132.9(2)
O12–Mo6–Mo5	102.92(2)	N2–Mo1–N10[1]	90.6(3)
O12–Mo6–O27	104.9(2)	N10[1]–Mo1–Mo2	135.8(2)
O12–Mo6–O23	105.4(3)	O6–Mo2–Mo1	48.78(2)
O12–Mo6–O32	88.0(2)	O6–Mo2–O7	88.6(2)
O12–Mo6–O31	156.2(2)	O6–Mo2–N8	88.3(3)
O12–Mo6–N17	90.8(3)	O6–Mo2–N5	164.0(3)
N17–Mo6–Mo5	134.65(2)	O7–Mo2–Mo1	103.90(2)
O28–Mo8–Mo7	49.25(1)	O7–Mo2–N8	75.4(2)
O28–Mo8–O24	95.67(2)	O7–Mo2–N5	75.4(3)
O28–Mo8–O27	83.88(2)	O5–Mo2–Mo1	48.7(2)
O28–Mo8–O33	90.4(2)	O5–Mo2–O6	93.5(3)
O28–Mo8–N23	161.9(2)	O5–Mo2–O7	88.9(3)
O24–Mo8–Mo7	47.96(1)	O5–Mo2–N8	164.2(3)
O24–Mo8–O27	78.78(2)	O5–Mo2–N5	86.0(3)
O24–Mo8–O33	154.4(2)	O2–Mo2–Mo1	99.8(3)
O24–Mo8–N23	85.6(2)	O2–Mo2–O6	107.3(4)
O27–Mo8–Mo7	86.88(1)	O2–Mo2–O7	156.3(3)
O33–Mo8–Mo7	138.28(2)	O2–Mo2–O5	107.0(4)
O33–Mo8–O27	77.20(2)	O2–Mo2–N8	87.3(4)
O33–Mo8–N23	81.2(2)	O2–Mo2–N5	88.1(4)
O14–Mo8–Mo7	99.83(2)	N8–Mo2–Mo1	136.8(2)
O14–Mo8–O28	104.8(2)	N5–Mo2–Mo1	134.5(2)
O14–Mo8–O24	101.5(2)	N5–Mo2–N8	87.9(3)
O14–Mo8–O27	171.2(2)	Mo7–O28–Mo9	144.9(2)
O14–Mo8–O33	100.9(2)	Mo8–O28–Mo7	81.81(2)
O14–Mo8–N23	92.6(3)	Mo8–O28–Mo9	132.9(2)
N23–Mo8–Mo7	133.39(2)	Mo5–O34–Mo16	131.5(2)
N23–Mo8–O27	78.7(2)	Mo5–O34–Mo7	125.3(2)
O36–Mo11–Mo12	142.83(1)	Mo16–O34–Mo7	103.09(2)
O36–Mo11–N33	79.3(2)	Mo16–O35–Mo7	103.1(2)
O30–Mo11–Mo12	48.92(1)	Mo15–O35–Mo16	82.21(18)
O30–Mo11–O36	94.19(2)	Mo15–O35–Mo7	135.3(2)
O30–Mo11–O37	87.3(2)	Mo7–O24–Mo8	82.91(19)
O30–Mo11–N33	163.9(2)	Mo16–O36–Mo15	82.28(2)
O37–Mo11–Mo12	98.97(1)	Mo16–O36–Mo11	134.8(2)
O37–Mo11–O36	70.80(2)	Mo15–O36–Mo11	103.4(2)
O37–Mo11–N33	76.7(2)	Mo11–O30–Mo5	145.3(2)
O26–Mo11–Mo12	49.06(2)	Mo12–O30–Mo5	132.3(2)
O26–Mo11–O36	158.9(2)	Mo12–O30–Mo11	82.13(2)
O26–Mo11–O30	96.5(2)	Mo15–O37–Mo11	103.0(2)
O26–Mo11–O37	91.6(2)	Mo9–O37–Mo15	131.3(3)
O26–Mo11–N33	85.6(2)	Mo9–O37–Mo11	125.6(2)
O17–Mo11–Mo12	102.88(2)	Mo5–O27–Mo6	82.23(2)
O17–Mo11–O36	89.6(2)	Mo5–O27–Mo8	132.4(2)

O17–Mo11–O30	104.6(2)	Mo6–O27–Mo8	145.0(2)
O17–Mo11–O37	157.9(2)	Mo6–O23–Mo5	83.8(2)
O17–Mo11–O26	105.2(3)	Mo8–O33–Mo14	130.9(3)
O17–Mo11–N33	90.1(3)	Mo8–O33–Mo10	124.8(3)
N33–Mo11–Mo12	134.55(2)	Mo14–O33–Mo10	103.7(2)
O28–Mo9–Mo10	85.71(1)	Mo13–O32–Mo6	103.7(2)
O37–Mo9–Mo10	139.30(2)	Mo14–O32–Mo6	133.8(2)
O37–Mo9–O28	78.59(2)	Mo14–O32–Mo13	82.6(2)
O37–Mo9–N27	80.8(2)	Mo9–O29–Mo12	131.7(2)
O29–Mo9–Mo10	49.36(2)	Mo9–O29–Mo10	81.8(2)
O29–Mo9–O28	84.01(2)	Mo10–O29–Mo12	146.3(2)
O29–Mo9–O37	91.5(2)	Mo12–O31–Mo6	124.8(2)
O29–Mo9–N27	164.4(2)	Mo12–O31–Mo13	131.5(3)
O25–Mo9–Mo10	47.65(2)	Mo13–O31–Mo6	103.6(2)
O25–Mo9–O28	77.8(2)	Mo11–O26–Mo12	83.2(2)
O25–Mo9–O37	154.5(2)	Mo13–O38–Mo14	82.2(2)
O25–Mo9–O29	95.6(2)	Mo13–O38–Mo10	133.4(3)
O25–Mo9–N27	86.1(2)	Mo14–O38–Mo10	103.7(2)
O15–Mo9–Mo10	99.6(2)	Mo10–O25–Mo9	83.4(2)
O15–Mo9–O28	172.8(2)	$Mo1^{1}$–O10–Mo4	120.2(2)
O15–Mo9–O37	100.0(3)	Mo1–O6–Mo2	82.4(3)
O15–Mo9–O29	103.1(3)	N20–N19–Mo7	115.2(4)
O15–Mo9–O25	102.2(3)	C14–N19–Mo7	136.9(5)
O15–Mo9–N27	91.7(3)	N19–N20–Mo16	116.8(4)
N27–Mo9–Mo10	133.68(2)	N21–N20–Mo16	131.7(5)
N27–Mo9–O28	81.2(2)	Mo3–O7–Mo2	121.1(3)
O30–Mo12–Mo11	48.95(1)	N22–N23–Mo8	123.0(5)
O30–Mo12–O29	85.08(2)	N24–N23–Mo8	127.0(5)
O30–Mo12–O31	91.52(2)	Mo3–O9–Mo4	81.6(3)
O30–Mo12–N35	163.6(3)	Mo4–O8–Mo3	82.8(3)
O29–Mo12–Mo11	87.67(1)	N33–N32–Mo15	116.2(4)
O31–Mo12–Mo11	139.17(1)	N31–N32–Mo15	132.7(5)
O31–Mo12–O29	77.7(2)	N13–N14–Mo5	122.3(4)
O31–Mo12–N35	81.4(2)	N15–N14–Mo5	127.2(5)
O26–Mo12–Mo11	47.76(2)	N27–N26–Mo15	121.1(4)
O26–Mo12–O30	95.3(2)	N25–N26–Mo15	128.1(6)
O26–Mo12–O29	79.0(2)	N26–N27–Mo9	122.4(5)
O26–Mo12–O31	155.0(2)	C17–N27–Mo9	127.7(6)
O26–Mo12–N35	85.5(2)	N16–N17–Mo6	116.7(6)
O18–Mo12–Mo11	100.0(2)	N18–N17–Mo6	131.3(6)
O18–Mo12–O30	104.3(3)	N14–N13–Mo16	121.9(4)
O18–Mo12–O29	170.4(2)	C10–N13–Mo16	129.5(5)
O18–Mo12–O31	99.8(3)	N32–N33–Mo11	115.8(4)
O18–Mo12–O26	101.8(3)	C21–N33–Mo11	134.5(6)
O18–Mo12–N35	91.5(3)	N23–N22–Mo14	120.7(4)
N35–Mo12–Mo11	133.15(2)	C16–N22–Mo14	129.0(5)
N35–Mo12–O29	79.0(3)	N17–N16–Mo13	115.8(5)
O32–Mo13–Mo14	48.48(2)	C12–N16–Mo13	136.7(7)
O32–Mo13–O31	76.32(2)	Mo2–O5–Mo1	82.9(3)
O32–Mo13–N16	82.1(2)	N35–N36–Mo13	121.9(5)

O32–Mo13–N36	156.6(2)	C23–N36–Mo13	126.0(6)
O31–Mo13–Mo14	98.37(1)	N29–N30–Mo10	115.4(6)
O31–Mo13–N16	75.9(2)	C19–N30–Mo10	134.4(7)
O31–Mo13–N36	81.1(2)	N7–N8–Mo2	122.3(5)
O38–Mo13–Mo14	49.07(2)	N9–N8–Mo2	126.9(7)
O38–Mo13–O32	94.4(2)	N36–N35–Mo12	122.2(5)
O38–Mo13–O31	96.5(2)	N34–N35–Mo12	128.1(7)
O38–Mo13–N16	172.2(2)	N10–N11–Mo4	123.8(6)
O38–Mo13–N36	82.0(3)	N12–N11–Mo4	126.5(7)
O19–Mo13–Mo14	102.3(2)	N8–N7–Mo3	124.7(6)
O19–Mo13–O32	110.8(3)	C6–N7–Mo3	126.9(6)
O19–Mo13–O31	157.2(3)	N2–N1–Mo4[1]	124.3(6)
O19–Mo13–O38	104.3(3)	C2–N1–Mo4[1]	128.4(9)
O19–Mo13–N16	83.5(3)	N1–N2–Mo1	122.7(6)
O19–Mo13–N36	92.5(3)	N3–N2–Mo1	124.7(9)
N16–Mo13–Mo14	129.43(2)	N4–N5–Mo2	124.0(7)
N36–Mo13–Mo14	130.9(2)	N6–N5–Mo2	127.5(1)
N36–Mo13–N16	98.4(3)	N30–N29–Mo14	117.1(5)
O33–Mo14–Mo13	97.13(1)	N28–N29–Mo14	134.9(7)
O33–Mo14–N22	81.4(2)	N11–N10–Mo1[1]	123.0(6)
O33–Mo14–N29	74.9(2)	C8–N10–Mo1[1]	128.8(8)
O32–Mo14–Mo13	48.90(2)	N5–N4–Mo3	122.7(7)
O32–Mo14–O33	95.4(2)	C4–N4–Mo3	127.7(1)

Symmetric codes: [1]1 – *x*, 2 – *y*, -*z*.

Table S10. Selected bond distances (Å) and angles (°) in $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\cdot 62H_2O$ (**4**) after solvent mask and final refinements.

4			
Mo4–Mo3	2.5550(5)	Mo3–N5	2.211(4)
Mo4–O9	1.948(3)	Mo8–O11^2	2.154(4)
Mo4–O8	1.943(4)	Mo8–O19	1.940(3)
Mo4–O2^1	2.147(3)	Mo8–O18	1.948(4)
Mo4–O10	1.688(4)	Mo8–O20	1.699(4)
Mo4–N8	2.193(4)	Mo8–N24	2.194(5)
Mo4–N12	2.197(4)	Mo8–N15^2	2.206(4)
Mo7–Mo8	2.5499(6)	Mo2–O6	2.141(3)
Mo7–O16	2.136(3)	Mo2–O3	1.941(4)
Mo7–O19	1.936(4)	Mo2–O4	1.937(4)
Mo7–O18	1.938(4)	Mo2–N2	2.183(5)
Mo7–O17	1.688(4)	Mo2–N6	2.223(4)
Mo7–N20	2.191(4)	Mo2–O5	1.691(4)
Mo7–N17	2.214(4)	Mo5–Mo6	2.5468(6)
Mo1–Mo2	2.5471(6)	Mo5–O14	1.934(4)
Mo1–O3	1.943(4)	Mo5–O11	2.146(3)
Mo1–O4	1.934(4)	Mo5–O13	1.940(4)
Mo1–O2	2.156(3)	Mo5–N14	2.207(4)
Mo1–O1	1.696(4)	Mo5–N23^2	2.205(5)
Mo1–N9^1	2.202(4)	Mo5–O12	1.692(4)
Mo1–N11^1	2.208(5)	Mo6–O16	2.151(3)
Mo3–O6	2.152(3)	Mo6–O14	1.948(4)
Mo3–O9	1.943(3)	Mo6–O13	1.937(4)
Mo3–O8	1.944(4)	Mo6–N18	2.206(4)
Mo3–O7	1.691(4)	Mo6–N21	2.195(5)
Mo3–N3	2.196(4)	Mo6–O15	1.684(4)
O9–Mo4–Mo3	48.86(1)	O6–Mo2–N2	74.88(1)
O9–Mo4–O2^1	88.71(1)	O6–Mo2–N6	75.17(1)
O9–Mo4–N8	163.43(2)	O3–Mo2–Mo1	49.06(1)
O9–Mo4–N12	86.87(2)	O3–Mo2–O6	89.15(1)
O8–Mo4–Mo3	48.93(1)	O3–Mo2–N2	163.97(2)
O8–Mo4–O9	94.02(1)	O3–Mo2–N6	87.50(2)
O8–Mo4–O2^1	90.15(2)	O4–Mo2–Mo1	48.81(1)
O8–Mo4–N8	86.47(2)	O4–Mo2–O6	90.90(1)
O8–Mo4–N12	165.34(2)	O4–Mo2–O3	93.67(2)
O2^1–Mo4–Mo3	104.54(9)	O4–Mo2–N2	85.45(2)
O2^1–Mo4–N8	74.72(2)	O4–Mo2–N6	166.00(2)
O2^1–Mo4–N12	75.23(2)	N2–Mo2–Mo1	133.96(1)
O10–Mo4–Mo3	99.29(1)	N2–Mo2–N6	89.59(2)
O10–Mo4–O9	106.21(2)	N6–Mo2–Mo1	135.99(1)
O10–Mo4–O8	106.85(2)	O5–Mo2–Mo1	98.77(2)
O10–Mo4–O2^1	156.13(2)	O5–Mo2–O6	154.98(2)
O10–Mo4–N8	89.41(2)	O5–Mo2–O3	107.07(2)
O10–Mo4–N12	86.86(2)	O5–Mo2–O4	106.51(2)

N8–Mo4–Mo3	135.25(1)	O5–Mo2–N2	88.46(2)
N8–Mo4–N12	88.56(2)	O5–Mo2–N6	86.39(2)
N12–Mo4–Mo3	135.39(1)	O14–Mo5–Mo6	49.24(1)
O16–Mo7–Mo8	105.50(8)	O14–Mo5–O11	88.74(1)
O16–Mo7–N20	75.18(2)	O14–Mo5–O13	94.01(2)
O16–Mo7–N17	75.10(1)	O14–Mo5–N14	85.73(2)
O19–Mo7–Mo8	48.94(1)	O14–Mo5–N23^{2}	163.64(2)
O19–Mo7–O16	90.87(1)	O11–Mo5–Mo6	106.12(1)
O19–Mo7–O18	94.15(2)	O11–Mo5–N14	75.27(2)
O19–Mo7–N20	86.02(2)	O11–Mo5–N23^{2}	74.90(2)
O19–Mo7–N17	165.80(2)	O13–Mo5–Mo6	48.89(1)
O18–Mo7–Mo8	49.14(1)	O13–Mo5–O11	91.29(2)
O18–Mo7–O16	88.79(1)	O13–Mo5–N14	166.57(2)
O18–Mo7–N20	163.97(2)	O13–Mo5–N23^{2}	86.36(2)
O18–Mo7–N17	87.91(2)	N14–Mo5–Mo6	134.38(1)
O17–Mo7–Mo8	98.88(2)	N23^{2}–Mo5–Mo6	135.00(1)
O17–Mo7–O16	155.57(2)	N23^{2}–Mo5–N14	90.14(2)
O17–Mo7–O19	106.60(2)	O12–Mo5–Mo6	98.85(2)
O17–Mo7–O18	106.38(2)	O12–Mo5–O14	106.9(2)
O17–Mo7–N20	88.86(2)	O12–Mo5–O11	155.0(2)
O17–Mo7–N17	86.2(2)	O12–Mo5–O13	106.52(2)
N20–Mo7–Mo8	134.73(1)	O12–Mo5–N14	86.33(2)
N20–Mo7–N17	88.16(2)	O12–Mo5–N23^{2}	88.6(2)
N17–Mo7–Mo8	136.58(1)	O16–Mo6–Mo5	105.02(9)
O3–Mo1–Mo2	48.99(1)	O16–Mo6–N18	75.41(2)
O3–Mo1–O2	89.94(1)	O16–Mo6–N21	74.98(1)
O3–Mo1–N9^{1}	164.40(2)	O14–Mo6–Mo5	48.77(1)
O3–Mo1–N11^{1}	86.46(2)	O14–Mo6–O16	91.23(1)
O4–Mo1–Mo2	48.91(1)	O14–Mo6–N18	166.52(2)
O4–Mo1–O3	93.70(2)	O14–Mo6–N21	86.57(2)
O4–Mo1–O2	91.15(1)	O13–Mo6–Mo5	48.98(1)
O4–Mo1–N9^{1}	85.03(2)	O13–Mo6–O16	87.46(1)
O4–Mo1–N11^{1}	166.00(2)	O13–Mo6–O14	93.66(2)
O2–Mo1–Mo2	107.02(9)	O13–Mo6–N18	87.64(2)
O2–Mo1–N9^{1}	74.56(1)	O13–Mo6–N21	162.43(2)
O2–Mo1–N11^{1}	74.85(1)	N18–Mo6–Mo5	136.01(1)
O1–Mo1–Mo2	99.22(2)	N21–Mo6–Mo5	135.20(1)
O1–Mo1–O3	107.16(2)	N21–Mo6–N18	88.18(2)
O1–Mo1–O4	107.02(2)	O15–Mo6–Mo5	98.95(2)
O1–Mo1–O2	153.75(2)	O15–Mo6–O16	155.95(2)
O1–Mo1–N9^{1}	88.02(2)	O15–Mo6–O14	106.26(2)
O1–Mo1–N11^{1}	86.23(2)	O15–Mo6–O13	107.3(2)
N9^{1}–Mo1–Mo2	133.60(1)	O15–Mo6–N18	86.08(2)
N9^{1}–Mo1–N11^{1}	91.05(2)	O15–Mo6–N21	89.4(2)
N11^{1}–Mo1–Mo2	134.90(1)	Mo2–O6–Mo3	121.68(2)
O6–Mo3–Mo4	105.05(8)	Mo7–O16–Mo6	121.95(2)
O6–Mo3–N3	75.10(1)	Mo5–O14–Mo6	81.98(1)
O6–Mo3–N5	75.69(2)	Mo3–O9–Mo4	82.10(1)
O9–Mo3–Mo4	49.04(1)	Mo2–O3–Mo1	81.95(1)
O9–Mo3–O6	91.34(1)	Mo4–O8–Mo3	82.17(1)

O9–Mo3–O8	94.16(1)	Mo5–O11–Mo8[2]	120.82(2)
O9–Mo3–N3	86.65(2)	Mo7–O19–Mo8	82.25(1)
O9–Mo3–N5	166.94(2)	Mo1–O4–Mo2	82.27(1)
O8–Mo3–Mo4	48.90(1)	Mo4[1]–O2–Mo1	121.23(2)
O8–Mo3–O6	88.18(1)	Mo7–O18–Mo8	82.02(1)
O8–Mo3–N3	163.28(2)	Mo6–O13–Mo5	82.14(2)
O8–Mo3–N5	87.07(2)	N2–N3–Mo3	122.1(3)
O7–Mo3–Mo4	99.52(1)	C1–N3–Mo3	129.7(4)
O7–Mo3–O6	155.39(2)	N17–N18–Mo6	123.4(3)
O7–Mo3–O9	106.12(2)	C11–N18–Mo6	126.9(4)
O7–Mo3–O8	107.25(2)	N20–N21–Mo6	122.9(3)
O7–Mo3–N3	88.48(2)	C13–N21–Mo6	129.0(5)
O7–Mo3–N5	85.84(2)	N8–N9–Mo1[1]	123.3(3)
N3–Mo3–Mo4	135.55(1)	C5–N9–Mo1[1]	128.3(4)
N3–Mo3–N5	88.49(2)	N6–N5–Mo3	123.6(3)
N5–Mo3–Mo4	135.42(1)	N4–N5–Mo3	126.8(4)
O11[2]–Mo8–Mo7	106.07(9)	N15–N14–Mo5	124.3(3)
O11[2]–Mo8–N24	75.11(2)	N13–N14–Mo5	126.7(4)
O11[2]–Mo8–N15[2]	75.58(2)	N12–N11–Mo1[1]	121.4(3)
O19–Mo8–Mo7	48.81(1)	N10–N11–Mo1[1]	128.5(4)
O19–Mo8–O11[2]	90.26(1)	N21–N20–Mo7	124.2(3)
O19–Mo8–O18	93.73(2)	N19–N20–Mo7	125.9(4)
O19–Mo8–N24	84.84(2)	N3–N2–Mo2	124.7(3)
O19–Mo8–N15[2]	165.73(2)	N1–N2–Mo2	125.6(4)
O18–Mo8–Mo7	48.83(1)	N18–N17–Mo7	122.8(3)
O18–Mo8–O11[2]	90.33(1)	N16–N17–Mo7	128.5(4)
O18–Mo8–N24	165.35(2)	N23–N24–Mo8	124.4(4)
O18–Mo8–N15[2]	88.21(2)	C15–N24–Mo8	126.9(5)
O20–Mo8–Mo7	99.18(2)	N5–N6–Mo2	121.9(3)
O20–Mo8–O11[2]	154.75(2)	C3–N6–Mo2	129.3(4)
O20–Mo8–O19	106.47(2)	N14–N15–Mo8[2]	121.8(3)
O20–Mo8–O18	106.88(2)	C9–N15–Mo8[2]	130.0(4)
O20–Mo8–N24	87.4(2)	N9–N8–Mo4	123.5(3)
O20–Mo8–N15[2]	86.40(2)	N7–N8–Mo4	126.8(4)
N24–Mo8–Mo7	133.28(1)	N11–N12–Mo4	125.0(3)
N24–Mo8–N15[2]	89.72(2)	C7–N12–Mo4	126.3(4)
N15[2]–Mo8–Mo7	136.60(1)	N24–N23–Mo5[2]	122.1(3)
O6–Mo2–Mo1	106.24(9)	N22–N23–Mo5[2]	128.5(5)

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

Table S11. Detail calibrated adsorption data of O_2, N_2, H_2, CO_2 and CH_4 for $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**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
	0.900	1.5813	1.890	9.0025	0.900	0.9257	1.890	1.7564	0.940	0.7972
	1.890	1.9301	3.900	13.5607	1.900	1.2820	3.900	1.6592	1.900	0.8505
	3.900	2.6979	5.899	16.6295	3.892	1.7251	5.891	1.8107	3.910	1.0087
	5.900	3.4002	7.894	18.5663	5.900	2.0589	7.894	1.8859	5.920	1.1248
	7.892	4.0917	9.895	21.1311	7.891	2.5872	9.893	1.5630	7.903	1.2074
	9.896	4.8177	11.892	21.3441	9.897	3.0075	11.894	1.5258	9.908	1.2834
	11.897	5.4820	13.894	22.7225	11.896	3.2776	13.897	1.5629	11.898	1.2871
	13.894	6.1824	15.894	24.6018	13.897	3.5745	15.897	1.3655	13.900	1.2602
	15.896	6.8405	17.891	24.2306	15.894	3.8736	17.895	1.8172	15.904	1.4452
	17.893	7.5693	19.891	24.9869	17.897	4.0393	19.898	1.3034	17.903	1.3809
	19.894	8.2260	21.890	25.4241	19.893	4.3574	21.894	1.0864	19.905	1.4030
	21.894	8.9479	23.893	26.4310	21.897	4.6019	23.895	0.9024	21.903	1.3629
	23.897	9.7688	25.891	27.3056	23.895	4.8638	25.893	0.1680	23.905	1.3439
	25.894	10.2773	27.891	27.4578	25.894	5.0127	27.894	0.2313	25.899	1.4795
	27.895	10.8506	29.890	26.9080	27.895	5.5375	29.897	0.5958	27.902	1.3596
	29.894	11.3417			29.894	5.5375			29.901	1.4205

Table S12. Detail calibrated adsorption data of O_2, N_2, H_2, CO_2 and CH_4 for $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**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
	0.900	1.4501	0.900	3.2546	0.890	1.3226	1.900	1.8467	0.950	0.5587
	1.900	1.7079	1.898	5.0015	1.900	1.7825	3.892	1.9404	1.900	0.5563
	3.890	2.2177	3.895	7.5216	3.900	1.9703	5.895	2.0959	3.900	0.8015
	5.900	2.8717	5.890	9.4914	5.892	2.1854	7.899	2.3314	5.920	0.8594
	7.899	3.3792	7.899	11.4860	7.900	2.4001	9.892	2.5248	7.901	0.8961
	9.894	4.0212	9.893	12.7996	9.896	2.5265	11.897	2.5403	9.902	0.8909
	11.900	4.7719	11.893	14.3160	11.895	2.7388	13.897	2.3445	11.899	0.9466
	13.899	5.3626	13.898	15.6131	13.897	2.8865	15.897	2.2223	13.903	0.9576
	15.895	5.8832	15.896	16.3529	15.895	3.1307	17.894	2.2450	15.904	0.9958
	17.895	6.2592	17.893	17.3741	17.898	3.2823	19.894	2.2363	17.906	1.0091
	19.895	6.8636	19.894	18.4949	19.898	3.4875	21.896	2.2363	19.902	1.0193
	21.893	7.4717	21.892	19.4329	21.896	3.8252	23.893	2.1959	21.904	0.9880
	23.894	7.9572	23.891	20.5326	23.899	4.0227	25.894	2.0587	23.902	1.0013
	25.895	8.4706	25.891	21.8976	25.897	4.0868	27.896	2.1265	25.901	1.0066
	27.893	9.0386	27.890	22.3821	27.898	3.8209	29.896	2.0240	27.905	1.0055
	29.894	9.5352	29.892	22.3821	29.895	4.1120			29.905	0.9363

Table S13. Detail calibrated adsorption data of O_2, N_2, H_2, CO_2 and CH_4 for $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\cdot 62H_2O$ (**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
	1.890	1.9801	1.900	4.3777	1.900	1.6147	1.900	1.4938	0.900	0.9765
	3.900	2.7500	3.895	5.5027	3.890	1.8450	3.900	1.4683	1.910	1.2171
	5.900	3.3188	5.900	6.4341	5.895	2.2571	5.897	1.2941	3.940	1.5123
	7.893	4.0136	7.891	6.5935	7.895	2.5051	7.890	1.4545	5.900	1.6228
	9.897	4.8157	9.893	7.0682	9.898	2.8680	9.896	1.3581	7.900	1.6403
	11.896	5.4713	11.897	7.8248	11.898	3.0938	11.895	1.5277	9.899	1.7455
	13.900	6.2334	13.891	7.5977	13.897	3.3608	13.895	1.2208	11.901	1.8427
	15.894	6.9517	15.891	7.8816	15.896	3.7361	15.895	1.1456	13.903	1.8760
	17.895	7.6225	17.894	7.7419	17.897	3.7925	17.895	0.7756	15.905	1.9831
	19.894	8.4193	19.892	7.4837	19.897	3.9513	19.895	0.8226	17.902	1.9784
	21.896	9.0010	21.892	7.3727	21.894	4.5598	21.896	1.0951	19.904	1.9884
	23.894	9.5698	23.895	7.6885	23.895	4.6446	23.895	0.6176	21.904	2.0333
	25.895	10.4327	25.893	7.4434	25.895	4.8430	25.894	0.4748	23.905	2.0177
	27.895	10.8618	27.890	7.5405	27.896	5.4442	27.892	0.6507	25.905	1.9880
	29.894	11.5437	29.892	7.7903	29.893	5.4442	29.891	0.0657	27.907	2.0204
									29.903	2.0466

Table S14. Bond valence calculations for complexes $[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot nH_2O$ (n = 22, **1**; n = 92, **2**), $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**) and $[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\ 62H_2O$ (**4**) respectively.

Complexes	Atoms	N	$\sum S_{ij}$	Δ
$[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 22H_2O$ (**1**)	Mo1	5+	5.299	0.299
	Mo2	5+	5.223	0.223
	Mo3	5+	5.248	0.248
	Mo4	5+	5.234	0.234
	Mo5	5+	5.303	0.303
	Mo6	5+	5.173	0.173
	Mo7	5+	5.411	0.411
	Mo8	5+	5.210	0.210
	Mo9	5+	5.323	0.323
	Mo10	5+	5.310	0.310
	Mo11	5+	5.315	0.315
	Mo12	5+	5.285	0.285
		5+	**5.278_{av}**	**0.278_{av}**
$[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 92H_2O$ (**2**)	Mo1	5+	5.233	0.233
	Mo2	5+	5.303	0.303
	Mo3	5+	5.326	0.326
		5+	**5.287_{av}**	**0.287_{av}**
$[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]_{½}\cdot[Mo_{12}O_{12}(\mu_2\text{-}O)_4(\mu_3\text{-}O)_{12}(Htrz)_4(trz)_4]\cdot 44H_2O$ (**3**)	Mo1	5+	5.376	0.376
	Mo2	5+	5.377	0.377
	Mo3	5+	5.244	0.244
	Mo4	5+	5.333	0.333
	Mo5	5+	5.321	0.321
	Mo6	5+	5.222	0.222
	Mo7	5+	5.256	0.256
	Mo8	5+	5.314	0.314
	Mo9	5+	5.365	0.365
	Mo10	5+	5.245	0.245
	Mo11	5+	5.217	0.217
	Mo12	5+	5.346	0.346
	Mo13	5+	5.342	0.342
	Mo14	5+	5.453	0.453
	Mo15	5+	5.432	0.432
	Mo16	5+	5.392	0.392
		5+	**5.327_{av}**	**0.327_{av}**

$[Mo_8O_8(\mu_2\text{-}O)_{12}(Htrz)_8]\ 62H_2O$ (**4**)	Mo1	5+	5.292	0.292
	Mo2	5+	5.346	0.346
	Mo3	5+	5.306	0.306
	Mo4	5+	5.349	0.349
	Mo5	5+	5.330	0.330
	Mo6	5+	5.352	0.352
	Mo7	5+	5.379	0.379
	Mo8	5+	5.271	0.271
		5+	**5.328_{av}**	**0.328_{av}**