# Supporting information

# Successive constructions of regular tetra-, hexa- and octanuclear microporous polyoxovanadates(III) for gas adsorptions

Zhen-Lang Xie, Dong-Li An, Wei-Zheng Weng, Zhao-Hui Zhou*

*State Key Laboratory of Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China, Tel: + 86-592-2184531; Fax: + 86-592-2183047*
zhzhou@xmu.edu.cn

**Figures and Table Options**

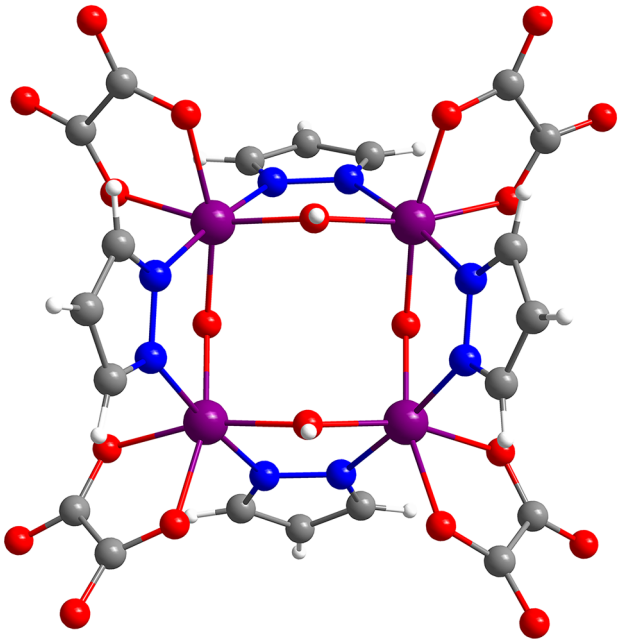

Figure S1. Ball-and-stick models of polyanionic cluster $[V_4(\mu_2\text{-}OH)_4(ox)_4(pz)_4]^{4-}$ (**1**).

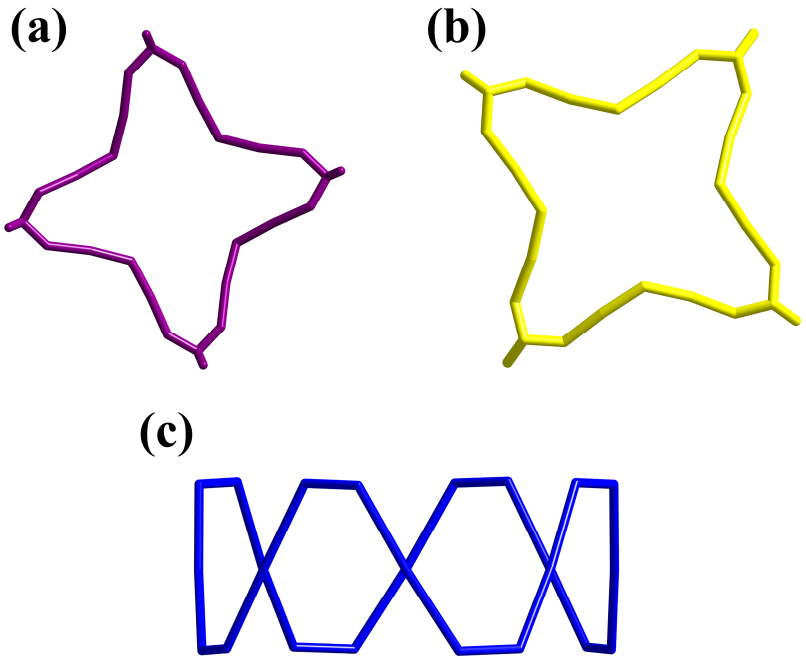


Figure S2. (a) “Violet” and (b) “yellow”: cosine-like "V–O–S–O–V–O" rings of **4**. (c): sinusoid-like "V–N–N–V" ring.

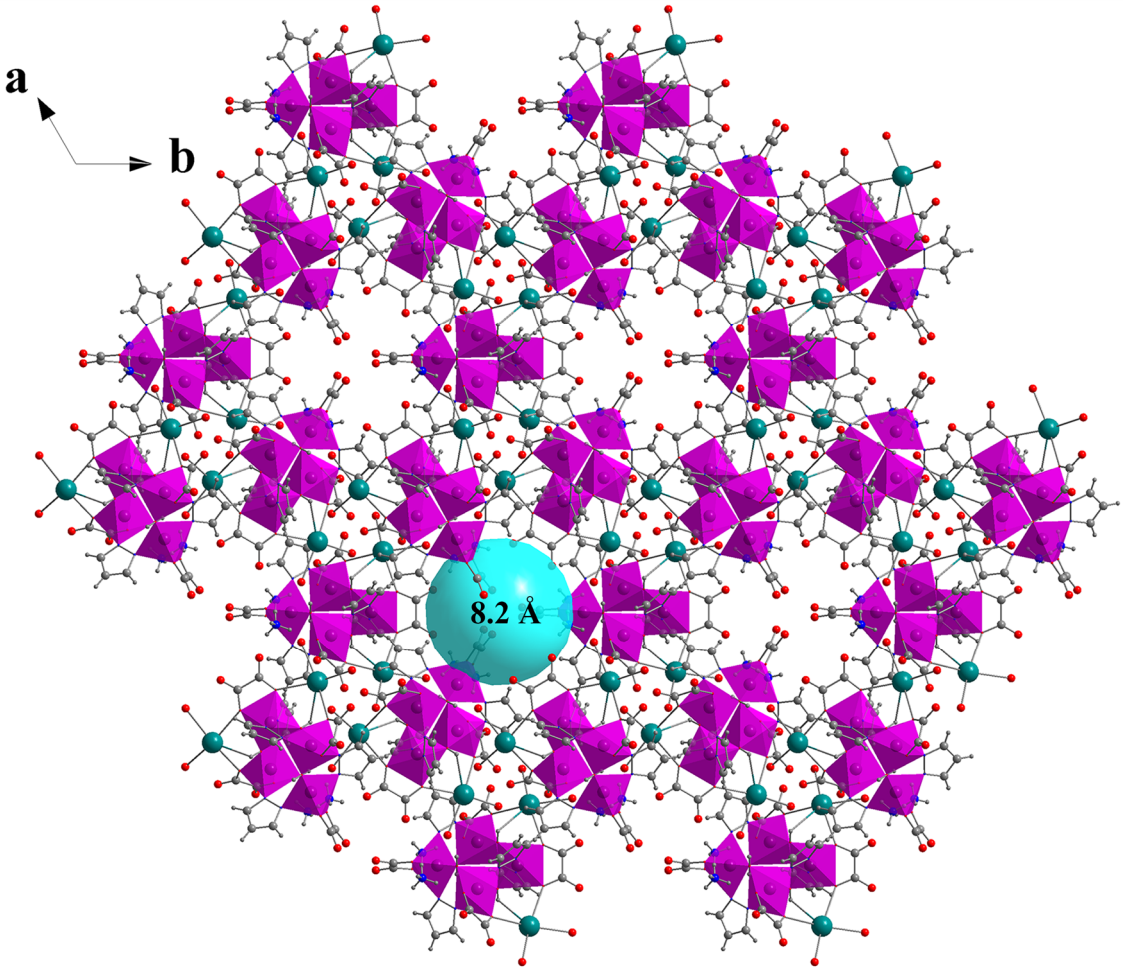


Figure S3. 2D packing diagram of **1** observed along the *c* axis.

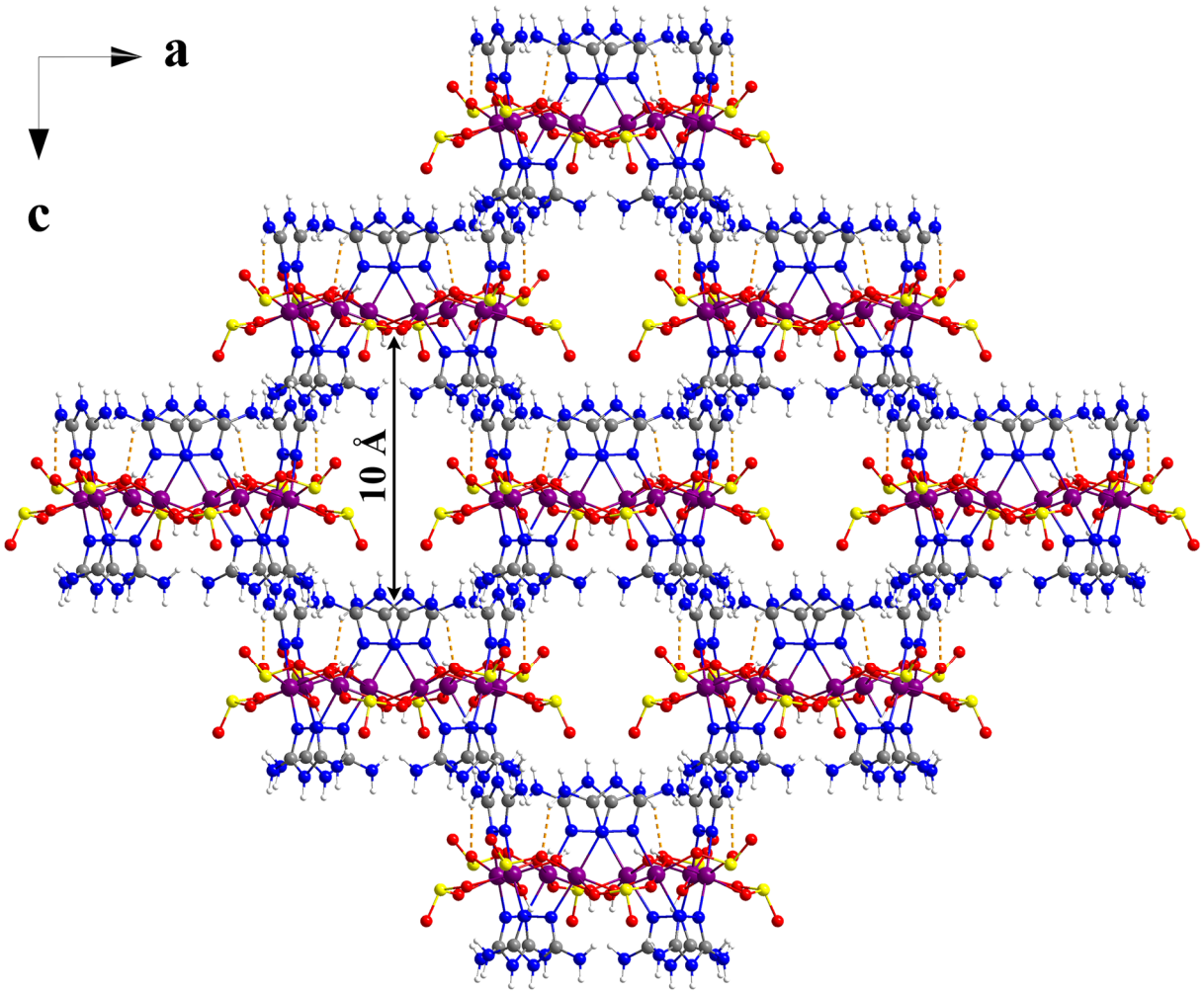


Figure S4. Channels in **4** viewed along *b* axis.

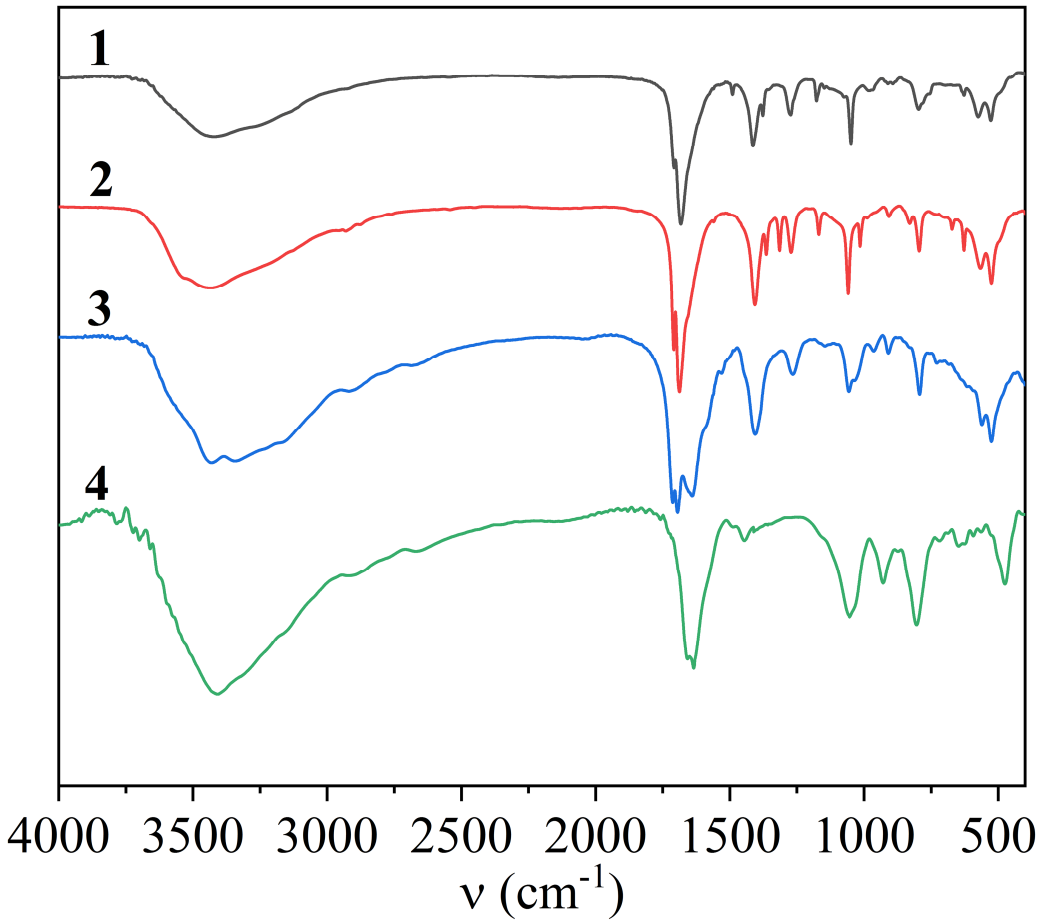


Figure S5. Fourier transform infrared (FT-IR) spectra of $(NH_4)_2K_2[V_4(\mu_2\text{-}OH)_4(ox)_4(pz)_4]\cdot 9H_2O$ (**1**), $(NH_4)_2Na_2[V_4(\mu_2\text{-}OH)_4(ox)_4(4\text{-}mpz)_4]\cdot 7H_2O$ (**2**), $K_2[V_6(\mu_2\text{-}OH)_6(ox)_6(Hdatrz)_6]Cl_2\cdot 29.5H_2O$ (**3**) and $[V_8(\mu_2\text{-}OH)_8(SO_3)_8(Hdatrz)_8]\cdot 38H_2O$ (**4**).

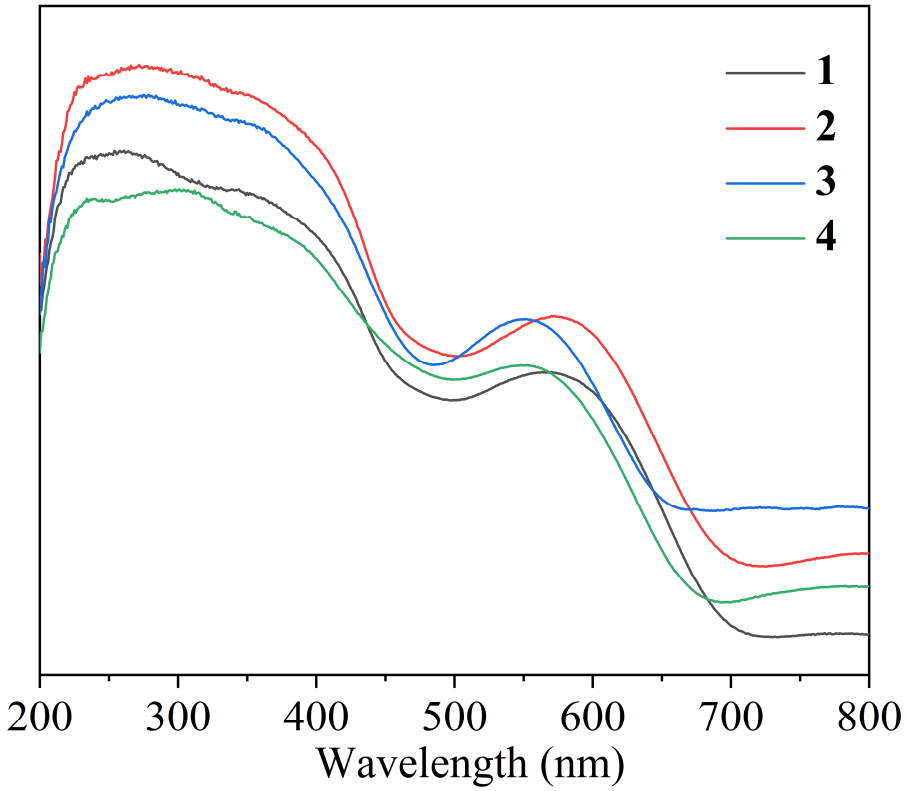


Figure S6. Solid-state UV-vis spectra of $(NH_4)_2K_2[V_4(\mu_2\text{-}OH)_4(ox)_4(pz)_4]\cdot 9H_2O$ (**1**), $(NH_4)_2Na_2[V_4(\mu_2\text{-}OH)_4(ox)_4(4\text{-}mpz)_4]\cdot 7H_2O$ (**2**), $K_2[V_6(\mu_2\text{-}OH)_6(ox)_6(Hdatrz)_6]Cl_2\cdot 29.5H_2O$ (**3**) and $[V_8(\mu_2\text{-}OH)_8(SO_3)_8(Hdatrz)_8]\cdot 38H_2O$ (**4**).

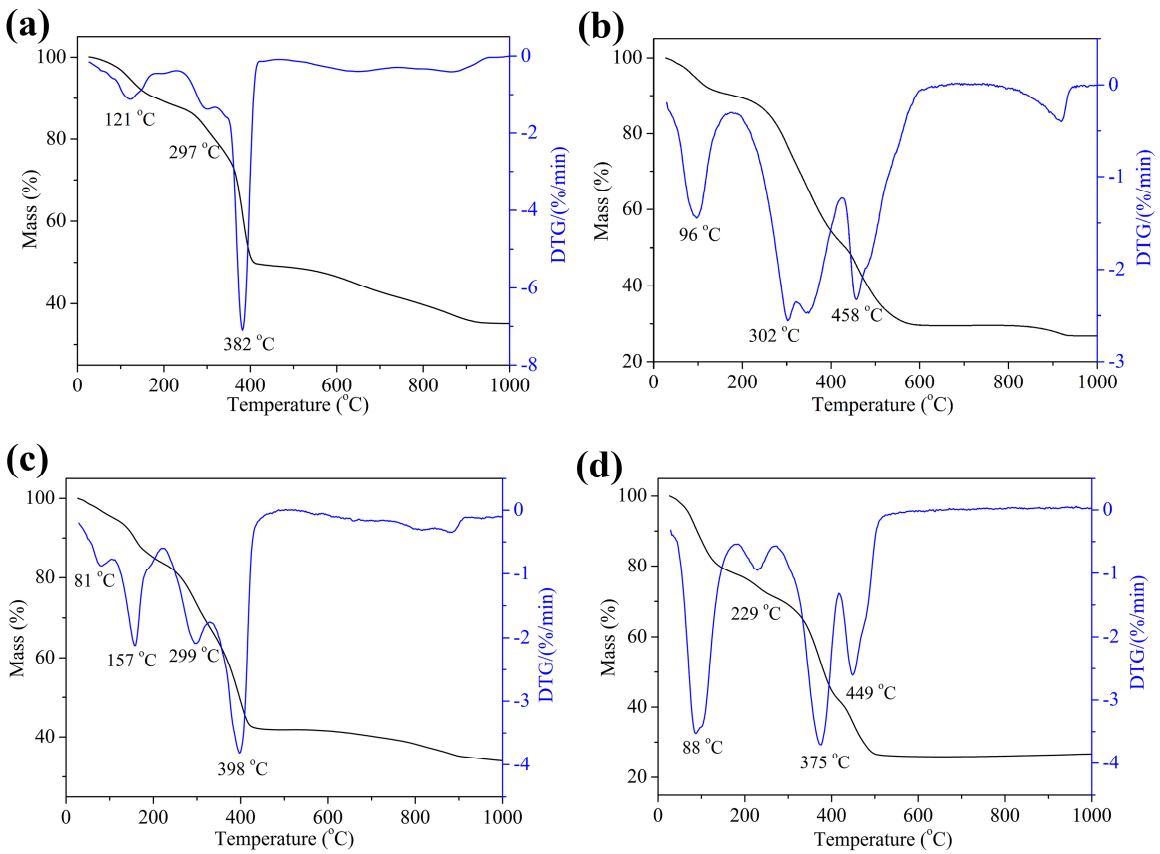


Figure S7. TGA curves of solid samples $(NH_4)_2K_2[V_4(\mu_2\text{-}OH)_4(ox)_4(pz)_4]\cdot 9H_2O$ (**1**, a), $(NH_4)_2Na_2[V_4(\mu_2\text{-}OH)_4(ox)_4(4\text{-}mpz)_4]\cdot 7H_2O$ (**2**, b), $K_2[V_6(\mu_2\text{-}OH)_6(ox)_6(Hdatrz)_6]Cl_2\cdot 29.5H_2O$ (**3**, c) and $[V_8(\mu_2\text{-}OH)_8(SO_3)_8(Hdatrz)_8]\cdot 38H_2O$ (**4**, d).

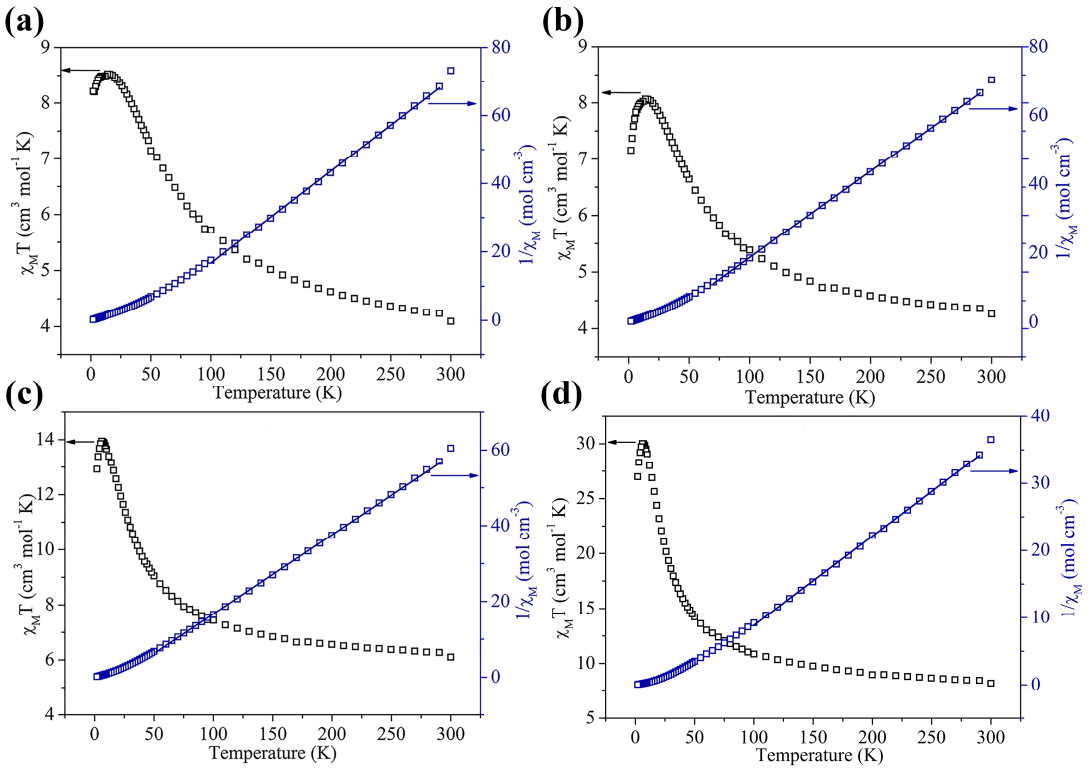


Figure S8. Temperature dependence of magnetic susceptibilities of $(NH_4)_2K_2[V_4(\mu_2\text{-}OH)_4(ox)_4(pz)_4]\cdot 9H_2O$ (**1**, a), $(NH_4)_2Na_2[V_4(\mu_2\text{-}OH)_4(ox)_4(4\text{-}mpz)_4]\cdot 7H_2O$ (**2**, b), $K_2[V_6(\mu_2\text{-}OH)_6(ox)_6(Hdatrz)_6]Cl_2\cdot 29.5H_2O$ (**3**, c) and $[V_8(\mu_2\text{-}OH)_8(SO_3)_8(Hdatrz)_8]\cdot 38H_2O$ (**4**, d) under 0.1 T applied field between 300 and 2 K. Blue lines correspond to the best fitting results.

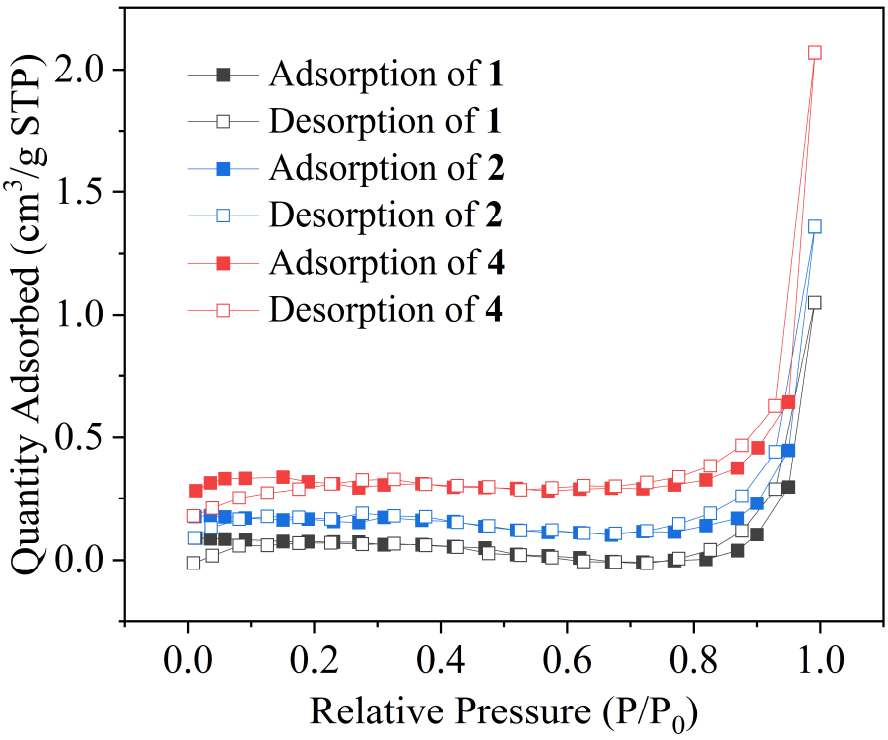


Figure S9. $N_2$ adsorption-desorption isotherms of $(NH_4)_2K_2[V_4(\mu_2\text{-}OH)_4(ox)_4(pz)_4]\cdot 9H_2O$ (**1**), $(NH_4)_2Na_2[V_4(\mu_2\text{-}OH)_4(ox)_4(4\text{-}mpz)_4]\cdot 7H_2O$ (**2**) and $[V_8(\mu_2\text{-}OH)_8(SO_3)_8(Hdatrz)_8]\cdot 38H_2O$ (**4**) at 77K.

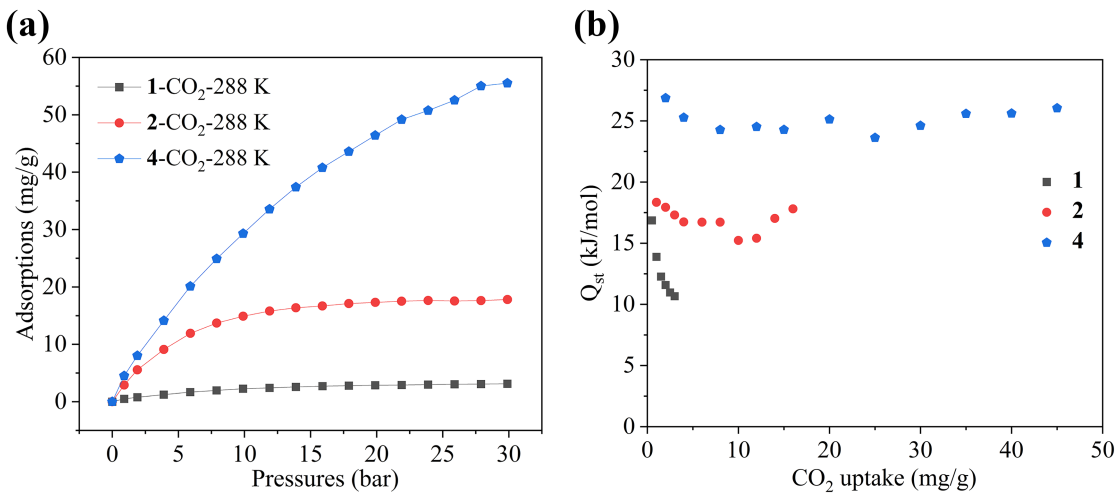


Figure S10. (a) $CO_2$ adsorption isotherms for **1**, **2** and **4** at 288 K; (b) Isosteric heat of adsorption ($Q_{st}$) plotted against $CO_2$ uptake for **1**, **2** and **4**.

**Isosteric heat of adsorption was calculated using Clausius–Clapeyron equation:**

$Q_{st} = RT_1T_2\ln(P_2/P_1)/(T_2-T_1)$;

$R = 8.314 \times 10^{-3}$ kJ/(mol·K$^{-1}$), $T_1 = 288$ K, $T_2 = 298$ K.

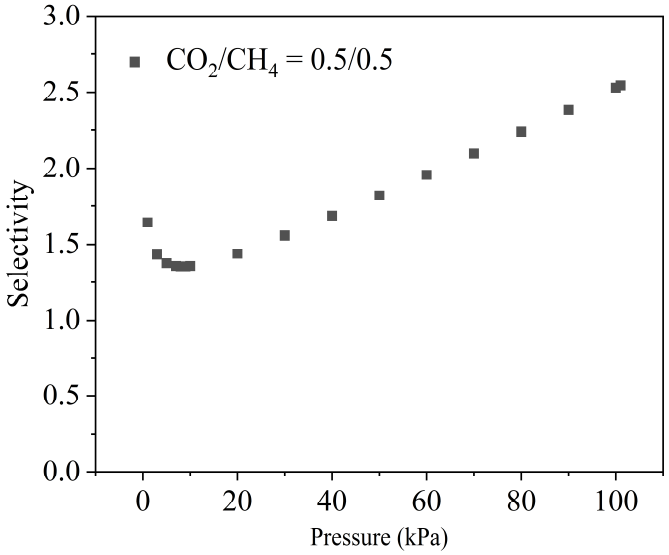


Figure S11. IAST selectivity of equimolar $CO_2/CH_4$ = 0.5/0.5 mixture for **4**.

**Calculation of $CO_2/CH_4$ selectivity**

The ideal adsorbed solution theory (IAST) developed by Myers and Praunitz was used to quantify the $CO_2/CH_4$ (50/50) selectivities for **4**. Pure component isotherm of $CO_2$ and $CH_4$ at 298 K were fitted to the single-site Langmuir-Freundlich (LF) model:

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

where *a* represents the saturation adsorption capacities; *b* is the affinity constants; *p* is the pressure of the bulk gas at equilibrium with the adsorbed phase; *c* is the deviations from an ideal homogeneous surface. The fitting parameters of LF equation as well as the correlation coefficients ($R^2$) were listed below:

| Adsorbates | *a* | *b* | *c* | $R^2$ |
|---|---|---|---|---|
| $CO_2$ | 3.13 | 0.02678 | 0.87785 | 0.9995 |
| $CH_4$ | 1.04 | 0.06081 | 1.04342 | 0.9990 |

The adsorption selectivity is defined as

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

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

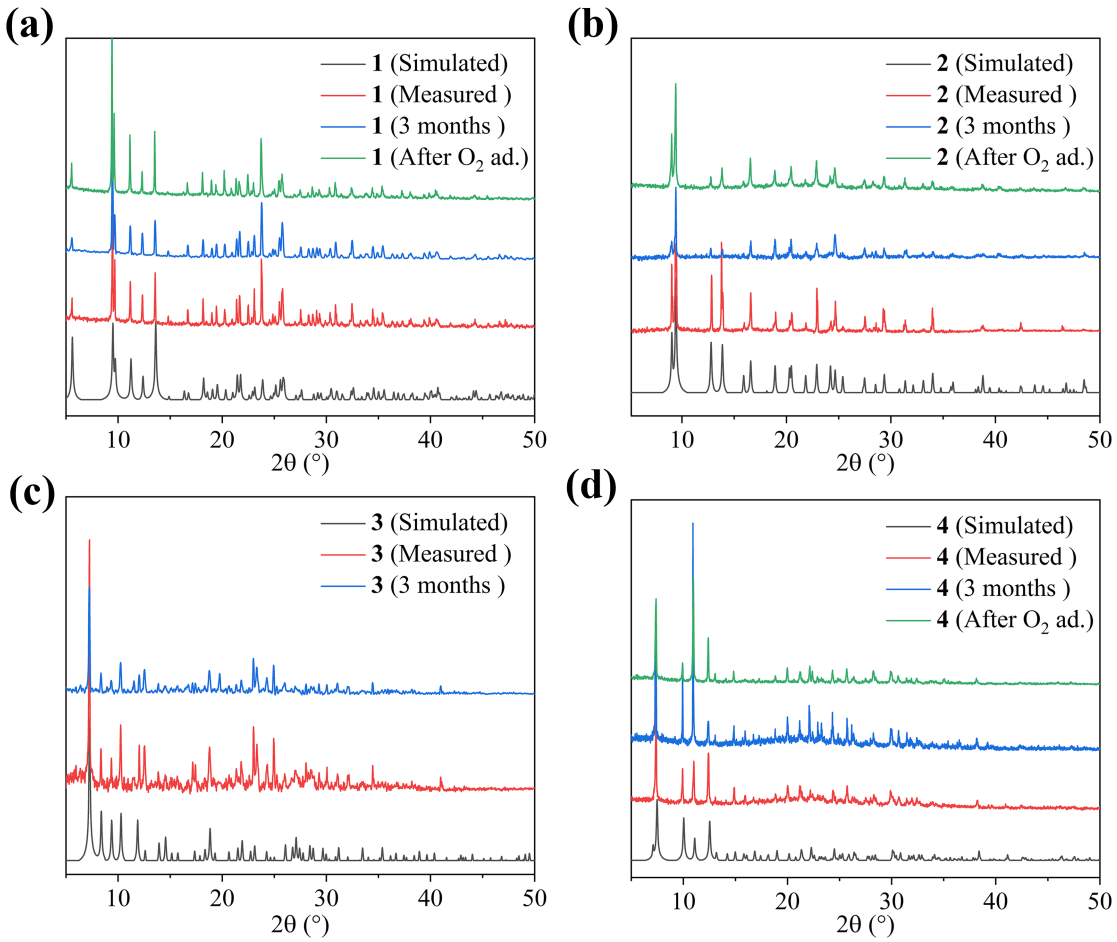


Figure S12. Comparison of the observed PXRD (red) with the simulated patterns (black) calculated from the SXRD data for $(NH_4)_2K_2[V_4(\mu_2\text{-}OH)_4(ox)_4(pz)_4]\cdot 9H_2O$ (**1**, a), $(NH_4)_2Na_2[V_4(\mu_2\text{-}OH)_4(ox)_4(4\text{-}mpz)_4]\cdot 7H_2O$ (**2**, b), $K_2[V_6(\mu_2\text{-}OH)_6(ox)_6(Hdatrz)_6]Cl_2\cdot 29.5H_2O$ (**3**, c) and $[V_8(\mu_2\text{-}OH)_8(SO_3)_8(Hdatrz)_8]\cdot 38H_2O$ (**4**, d), respectively.

Table S1. Crystallographic data and structural refinement details for $(NH_4)_2K_2[V_4(\mu_2\text{-}OH)_4(ox)_4(pz)_4]\cdot 9H_2O$ (**1**), $(NH_4)_2Na_2[V_4(\mu_2\text{-}OH)_4(ox)_4(4\text{-}mpz)_4]\cdot 7H_2O$ (**2**), $K_2[V_6(\mu_2\text{-}OH)_6(ox)_6(Hdatrz)_6]Cl_2\cdot 29.5H_2O$ (**3**) and $[V_8(\mu_2\text{-}OH)_8(SO_3)_8(Hdatrz)_8]\cdot 38H_2O$ (**4**), respectively.

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Empirical formula | $C_{20}H_{34}K_2N_{10}O_{29}V_4$ | $C_{24}H_{40}N_{10}Na_2O_{27}V_4$ | $C_{24}Cl_2H_{88.5}K_2N_{30}O_{59.5}V_6$ | $C_{16}H_{124}N_{40}O_{70}S_8V_8$ |
| Formula weight | 1160.53 | 1150.40 | 2204.48 | 2661.54 |
| Temperature/K | 100(1) | 100(1) | 100(1) | 100(1) |
| Crystal system | Trigonal | Orthorhombic | Cubic | Tetragonal |
| Space group | *P* $3_221$ | *C* $222_1$ | *P a*-3 | *P* 4*nc* |
| a/Å | 18.1163(1) | 12.6075(5) | 21.0340(1) | 17.5495(8) |
| b/Å | 18.1163(1) | 19.6716(6) | 21.0340(1) | 17.5495(8) |
| c/Å | 11.4282(6) | 19.2268(6) | 21.0340(1) | 15.9061(1) |
| $\alpha$/° | 90 | 90 | 90 | 90 |
| $\beta$/° | 90 | 90 | 90 | 90 |
| $\gamma$/° | 120 | 90 | 90 | 90 |
| Volume/Å$^3$ | 3248.24(4) | 4768.40(3) | 9306.06(1) | 4898.84(6) |
| *Z* | 3 | 4 | 4 | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.780 | 1.602 | 1.573 | 1.804 |
| $\mu$/mm$^{-1}$ | 9.713 | 7.416 | 7.211 | 8.879 |
| *F*(000) | 1758.0 | 2336.0 | 4514.0 | 2774.0 |
| Crystal size/mm$^3$ | 0.10 × 0.05 × 0.05 | 0.10 × 0.05 × 0.05 | 0.1 × 0.1 × 0.05 | 0.1 × 0.05 × 0.05 |

| | | | | |
|---|---|---|---|---|
| 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/° | 5.632 to 153.962 | 8.330 to 133.978 | 7.280 to 153.388 | 7.124 to 154.232 |
| Reflections collected | 48980 | 9530 | 12070 | 69024 |
| Independent reflections | 4498 | 4005 | 3071 | 5037 |
| $R_{int}$ | 0.0454 | 0.0542 | 0.0259 | 0.0379 |
| Data/restraints/parameters | 4498/2/263 | 4005/12/291 | 3071/1/166 | 5037/6/244 |
| Goodness of fit on $F^2$ | 1.040 | 1.042 | 1.069 | 1.039 |
| Final $R$ indexes [$I$>=2σ(I)] | $R_1$ = 0.0472, w$R_2$ = 0.1253 | $R_1$ = 0.0736, w$R_2$ = 0.2013 | $R_1$ = 0.0524, w$R_2$ = 0.1577 | $R_1$ = 0.0477, w$R_2$ = 0.1279 |
| Final $R$ indexes [all data] | $R_1$ = 0.0477, w$R_2$ = 0.1258 | $R_1$ = 0.0787, w$R_2$ = 0.2087 | $R_1$ = 0.0545, w$R_2$ = 0.1597 | $R_1$ = 0.0487, w$R_2$ = 0.1292 |
| Largest diff. peak and hole / eÅ$^{-3}$ | 1.33/-1.07 | 1.72/-0.50 | 0.99/-0.32 | 0.42/-0.58 |

Table S2. Selected bond distances (Å) and angles (°) for $(NH_4)_2K_2[V_4(\mu_2\text{-}OH)_4(ox)_4(pz)_4]\cdot 9H_2O$ (**1**), $(NH_4)_2Na_2[V_4(\mu_2\text{-}OH)_4(ox)_4(4\text{-}mpz)_4]\cdot 7H_2O$ (**2**), $K_2[V_6(\mu_2\text{-}OH)_6(ox)_6(Hdatrz)_6]Cl_2\cdot 29.5H_2O$ (**3**) and $[V_8(\mu_2\text{-}OH)_8(SO_3)_8(Hdatrz)_8]\cdot 38H_2O$ (**4**), respectively.

| | | | |
|---|---|---|---|
| **1** | | | |
| V1–O5 | 1.948(4) | V3–O9 | 2.041(4) |
| V1–O6 | 1.934(4) | V3–N2[a] | 2.081(4) |
| V1–O1 | 2.049(4) | V3–N2 | 2.081(4) |
| V1–O2 | 2.043(4) | V2–O6[a] | 1.945(4) |
| V1–N3 | 2.105(4) | V2–O6 | 1.946(4) |
| V1–N1 | 2.085(5) | V2–O7[a] | 2.041(7) |
| V3–O5[a] | 1.947(4) | V2–O7 | 2.041(7) |
| V3–O5 | 1.947(4) | V2–N4 | 2.097(5) |
| V3–O9[a] | 2.041(4) | V2–N4[a] | 2.097(5) |
| | | | |
| O5–V1–O1 | 88.46(2) | O6[a]–V2–O6 | 103.3(2) |
| O5–V1–O2 | 163.16(2) | O6–V2–O7 | 89.5(3) |
| O5–V1–N3 | 92.64(2) | O6–V2–O7[a] | 165.5(3) |
| O5–V1–N1 | 84.53(2) | O6[a]–V2–O7 | 165.5(3) |
| O6–V1–O5 | 105.36(2) | O7[a]–V2–N4[a] | 95.6(3) |
| O6–V1–O1 | 164.04(2) | O7–V2–N4[a] | 88.4(3) |
| O6–V1–O2 | 90.14(2) | O7[a]–V2–N4 | 88.4(3) |
| O6–V1–N3 | 84.21(2) | O7–V2–N4 | 95.6(3) |
| O6–V1–N1 | 91.85(2) | N4–V2–N4[a] | 174.9(3) |
| O1–V1–N3 | 87.28(2) | O5–V3–O9 | 91.34(2) |
| O1–V1–N1 | 97.47(2) | O5[a]–V3–O9[a] | 91.34(2) |
| O2–V1–O1 | 77.24(2) | O5–V3–O9[a] | 167.24(2) |
| O2–V1–N3 | 95.48(2) | O5–V3–N2[a] | 90.99(2) |
| O2–V1–N1 | 88.52(2) | O5–V3–N2 | 84.78(2) |
| N1–V1–N3 | 174.38(2) | O5[a]–V3–N2 | 91.00(2) |
| O5[a]–V3–O5 | 100.3(2) | O5[a]–V3–N2[a] | 84.78(2) |
| O5–V3–O9[a] | 167.24(2) | O9[a]–V3–O9 | 77.6(2) |
| O6[a]–V2–O7[a] | 89.5(3) | O9–V3–N2 | 95.33(2) |
| O6–V2–N4 | 84.23(2) | O9[a]–V3–N2 | 89.81(2) |
| O6–V2–N4[a] | 92.59(2) | O9–V3–N2[a] | 89.81(2) |
| O6[a]–V2–N4[a] | 84.23(2) | O9[a]–V3–N2[a] | 95.33(2) |
| O6[a]–V2–N4 | 92.59(2) | N2[a]–V3–N2 | 173.4(3) |
| O7–V2–O7[a] | 78.8(6) | | |

Symmetric codes: (a) $-y + x, -y, 4/3 - z$

**2**

| | | | |
|---|---|---|---|
| V1–O10[a] | 1.953(6) | V2–O10 | 1.955(6) |
| V1–O5 | 1.931(6) | V2–O5 | 1.955(6) |
| V1–O2 | 2.036(6) | V2–O7 | 2.026(6) |
| V1–O1 | 2.048(7) | V2–O6 | 2.061(6) |
| V1–N4[a] | 2.094(7) | V2–N1 | 2.100(7) |
| V1–N2 | 2.096(7) | V2–N3 | 2.099(7) |
| | | | |
| O10[a]–V1–O2 | 166.7(3) | O10–V2–O7 | 89.8(3) |
| O10[a]–V1–O1 | 91.4(3) | O10–V2–O6 | 165.0(3) |
| O10[a]–V1–N4[a] | 85.3(3) | O10–V2–N1 | 92.0(3) |
| O10[a]–V1–N2 | 91.2(3) | O10–V2–N3 | 85.1(3) |
| O5–V1–O10[a] | 101.6(3) | O5–V2–O10 | 102.0(3) |
| O5–V1–O2 | 90.5(3) | O5–V2–O7 | 166.5(3) |
| O5–V1–O1 | 165.5(3) | O5–V2–O6 | 91.7(3) |
| O5–V1–N4[a] | 93.0(3) | O5–V2–N1 | 84.6(3) |
| O5–V1–N2 | 85.0(3) | O5–V2–N3 | 92.1(3) |
| O2–V1–O1 | 77.2(3) | O7–V2–O6 | 77.4(3) |
| O2–V1–N4[a] | 88.7(3) | O7–V2–N1 | 88.5(3) |
| O2–V1–N2 | 95.30(3) | O7–V2–N3 | 95.6(3) |
| O1–V1–N4[a] | 94.4(3) | O6–V2–N1 | 95.4(3) |
| O1–V1–N2 | 88.4(3) | O6–V2–N3 | 88.3(3) |
| N4[a]–V1–N2 | 175.6(3) | N3–V2–N1 | 175.0(3) |

Symmetric codes: (a) $x$, $1 - y$, $1 - z$

**3**

| | | | |
|---|---|---|---|
| V1–O5 | 1.934(2) | V1–O1 | 2.032(2) |
| V1–O5[a] | 1.938(2) | V1–N2[a] | 2.096(2) |
| V1–O2 | 2.038(2) | V1–N1 | 2.098(2) |
| | | | |
| O5–V1–O5[a] | 99.66(1) | O5[a]–V1–N1 | 89.29(9) |
| O5[a]–V1–O2 | 167.91(8) | O2–V1–N2[a] | 90.78(9) |
| O5–V1–O2 | 92.28(8) | O2–V1–N1 | 93.23(9) |
| O5–V1–O1 | 170.18(8) | O1–V1–O2 | 78.26(9) |
| O5[a]–V1–O1 | 89.90(8) | O1–V1–N2[a] | 92.84(1) |
| O5[a]–V1–N2[a] | 87.35(9) | O1–V1–N1 | 90.69(9) |
| O5–V1–N2[a] | 89.87(9) | N2[a]–V1–N1 | 175.12(1) |
| O5–V1–N1 | 87.20(9) | | |

Symmetric codes: (a) ½ – y, -½ + $z$, $x$

**4**

| | | | |
|---|---|---|---|
| V1–O1 | 1.944(4) | V2–O1[a] | 1.963(4) |
| V1–O2 | 1.969(4) | V2–O2 | 1.983(4) |
| V1–O3 | 2.033(4) | V2–O6 | 1.986(4) |

| | | | |
|---|---|---|---|
| V1–N1 | 2.056(5) | V2–O4 | 2.030(4) |
| V1–O8[b] | 2.012(4) | V2–N7[a] | 2.159(5) |
| V1–N6 | 2.123(5) | V2–N2 | 2.071(5) |
| | | | |
| O1–V1–O2 | 97.84(2) | O1[a]–V2–O2 | 91.93(2) |
| O1–V1–O3 | 170.21(2) | O1[a]–V2–O6 | 90.47(2) |
| O1–V1–N1 | 94.61(2) | O1[a]–V2–O4 | 172.59(2) |
| O1–V1–O8[b] | 90.10(2) | O1[a]–V2–N7[a] | 86.47(2) |
| O1–V1–N6 | 84.55(2) | O1[a]–V2–N2 | 94.32(2) |
| O2–V1–O3 | 87.81(2) | O2–V2–O6 | 174.50(2) |
| O2–V1–N1 | 86.29(2) | O2–V2–O4 | 89.98(2) |
| O2–V1–O8[b] | 172.05(2) | O2–V2–N7[a] | 90.95(2) |
| O2–V1–N6 | 89.40(2) | O2–V2–N2 | 85.21(2) |
| O3–V1–N1 | 93.70(2) | O6–V2–O4 | 88.26(2) |
| O3–V1–N6 | 87.50(2) | O6–V2–N7[a] | 94.1(2) |
| N1–V1–N6 | 175.40(2) | O6–V2–N2 | 89.7(2) |
| O8[b]–V1–O3 | 84.34(2) | O4–V2–N7[a] | 86.35(2) |
| O8[b]–V1–N1 | 93.00(2) | O4–V2–N2 | 92.96(2) |
| O8[b]–V1–N6 | 91.50(2) | N2–V2–N7[a] | 176.10(2) |

Symmetric codes: (a) 1 – *y*, *x*, *z*; (b) *y*,1-*x*, *z*

Table S3. Hydrogen bonds observed in $(NH_4)_2K_2[V_4(\mu_2\text{-}OH)_4(ox)_4(pz)_4]\cdot 9H_2O$ (**1**), $(NH_4)_2Na_2[V_4(\mu_2\text{-}OH)_4(ox)_4(4\text{-}mpz)_4]\cdot 7H_2O$ (**2**), $K_2[V_6(\mu_2\text{-}OH)_6(ox)_6(Hdatrz)_6]Cl_2\cdot 29.5H_2O$ (**3**) and $[V_8(\mu_2\text{-}OH)_8(SO_3)_8(Hdatrz)_8]\cdot 38H_2O$ (**4**).

| D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | D–H···A(°) |
|---|---|---|---|---|
| **1** | | | | |
| O5–H5···O2w[a] | 0.86 | 1.85 | 2.710(6) | 176 |
| N5–H5B···O7 | 0.91 | 2.25 | 2.095(1) | 122 |
| N5–H5D···O2 | 0.91 | 1.83 | 2.738(1) | 179 |
| O6–H6···O1w[b] | 0.83 | 1.97 | 2.773(6) | 164 |
| Symmetric codes: (a) $1 - x + y$, $1 - x$, $1/3 + z$; (b) $y$, $-1 + x$, $1 - z$ | | | | |
| **2** | | | | |
| O5–H5···N5 | 0.85(2) | 1.87(2) | 2.710(1) | 170(2) |
| N5–H5A···O8[a] | 0.91 | 2.03 | 2.889(2) | 156 |
| N5–H5B···O3[b] | 0.91 | 2.42 | 3.206(2) | 145 |
| O10–H10···O1w | 0.84(4) | 1.88(4) | 2.689(2) | 161(6) |
| Symmetric codes: (a) $-x$, $y$, $½ - z$; (b) $-½ + x$, $½ - y$, $1 - z$ | | | | |
| **3** | | | | |
| N3–H3···O3[a] | 0.88 | 2.18 | 2.824(4) | 129 |
| N3–H3···O4[a] | 0.88 | 2.14 | 2.880(4) | 141 |
| N4–H4A···O1 | 0.88 | 2.22 | 2.946(4) | 140 |
| N4–H4B···O3[a] | 0.88 | 2.34 | 2.985(4) | 130 |
| O5–H5···Cl1 | 0.85(3) | 2.31(4) | 3.150(2) | 169(4) |

| | | | | |
|---|---|---|---|---|
| N5–H5A···O2 | 0.88 | 2.32 | 3.022(4) | 137 |
| N5–H5B···O4[a] | 0.88 | 2.37 | 3.089(4) | 140 |

Symmetric codes: (a) $1 - y$, $1 - z$, $1 - x$

**4**

| | | | | |
|---|---|---|---|---|
| N3–H3···O5[a] | 0.88 | 1.85 | 2.694(7) | 160 |
| N4–H4A···O7[b] | 0.88 | 2.39 | 3.192(9) | 152 |
| N4–H4A···O8[b] | 0.88 | 2.34 | 3.048(9) | 137 |
| N5–H5B···O6 | 0.89 | 2.12 | 2.938(8) | 152 |
| N9–H9A···O3 | 0.88 | 2.57 | 3.119(9) | 121 |
| N10–H10A···O4[b] | 0.88 | 2.19 | 2.919(8) | 140 |

Symmetric codes: (a) $-\frac{1}{2} + y$, $\frac{1}{2} + x$, $\frac{1}{2} + z$; (b) $y$, $1 - x$, $z$

Table S4. Comparisons of V–O distances (Å) in **1** ~ **4** and a series of tetra-, hexa- and octanuclear vanadium(III/IV/V) clusters with bridging μ2-hydroxy/μ2-oxygen groups.

| Complexes | V–μ2-OH | V–μ2-O |
|---|---|---|
| **{$V^{V}_{4}O_{12}$}** | | |
| $[Co_2(phen)_4V_4O_{12}]$ $C_6H_{11}OH·H_2O$[1] | | 1.791(3) |
| $[Mn_2(phen)_4V_4O_{12}]$ $C_6H_{11}OH·H_2O$[1] | | 1.788(4) |
| $[Ni_2(phen)_4V_4O_{12}]$ $C_6H_{11}OH·H_2O$[1] | | 1.794(4) |
| $[\{Ni(quaterpy)(H_2O)\}_2V_4O_{12}]$ $10H_2O$[2] | | 1.778(4) |
| Average | | 1.788(4) |
| **{$V^{V}_{4}O_{8}$}** | | |
| $Na_4[V_4O_8(rac\text{-tart})_2]$ $12H_2O$[3] | | 1.826(2) |
| $(NEt_4)_4[V_4O_8((R,R)\text{-tart})_2]$ $6H_2O$[3] | | 1.832(2) |
| $(C_{24}H_{20}P)[V_4O_8(C_2H_3O_2)_4(NO_3)]$[4] | | 1.811(2) |
| Average | | 1.823(2) |
| **{$V^{V}_{6}O_{13}$}** | | |
| $(Bu_4N)_2[V_6O_{13}\{(OCH_2)_3CCH_2OOCC_6H_4Br\text{-}p\}_2]$[5] | | 1.835(3) |
| $(Bu_4N)_2[V_6O_{13}\{(OCH_2)_3CCH_2OOCC_6H_4NO_2\text{-}m\}_2]$[5] | | 1.841(5) |
| $(Bu_4N)_2[V_6O_{13}\{(OCH_2)_3CCH_2OOCC_4H_3S\}_2]$[5] | | 1.843(2) |
| Average | | 1.840(5) |
| **{$V^{IV}_{4}O_{4}$}** | | |
| $[Cp^*VCl(\mu\text{-}O)]_4$[6] | | 1.800(2) |
| **{$V^{III}_{4}(OH)_{4}$}** | | |
| $(NH_4)_2K_2[V_4(\mu_2\text{-}OH)_4(ox)_4(pz)_4]·9H_2O$ (**1**) | 1.942(5) | |
| $(NH_4)_2Na_2[V_4(\mu_2\text{-}OH)_4(ox)_4(4\text{-}mpz)_4]·7H_2O$ (**2**) | 1.939(5) | |
| $[V_4(\mu\text{-}OOCCH_3)_4(\mu\text{-}OH)_4(OH_2)_8]Cl_4·3H_2O$[7] | 1.939(1) | |
| $[V_4(\mu\text{-}OH)_4(\mu\text{-}OOCCF_3)_4(OH_2)_8]Cl_4·7.5H_2O$[8] | 1.939(3) | |
| $[V_4(\mu\text{-}OH)_4(\mu\text{-}OOCCH_3)_4(OH_2)_8]Cl_4·CH_3COOH·12H_2O$[8] | 1.939(1) | |
| $[V_4(\mu\text{-}OH)_4(\mu\text{-}OOCCH_3)_4(OH_2)_8]Cl_4·3H_2O$[8] | 1.940(4) | |
| Average | 1.940(5) | |
| **{$V^{III}_{4}O_{2}$}** | | |

| | | |
|---|---|---|
| [{V(μ-hpnbpda)$_2$}{μ-(C$_6$H$_5$O)$_2$PO$_2$}$_2$(μ-O)$_2$]·6CH$_3$OH[9] | | 1.897(5) |
| **{V$^{III}_6$(OH)$_6$}** | | |
| K$_2$[V$_6$(μ$_2$-OH)$_6$(ox)$_6$(Hdatrz)$_6$]Cl$_2$·29.5H$_2$O (**3**) | 1.936(2) | |
| **{V$^{III}_8$(OH)$_8$}** | | |
| [V$_8$(μ$_2$-OH)$_8$(SO$_3$)$_8$(Hdatrz)$_8$]·38H$_2$O (**4**) | 1.965(4) | |
| D-[H$_2$N(CH$_3$)$_2$]$_{12.5}$(H$_3$N(CH$_2$)$_2$NH$_3$)(H$_3$O)$_{1.5}$(Vμ$_2$-OH)$_8$(SO$_4$)$_{16}$·2H$_2$O[10] | 1.957(3) | |
| L-[H$_2$N(CH$_3$)$_2$]$_{12.5}$(H$_3$N(CH$_2$)$_2$NH$_3$)(H$_3$O)$_{1.5}$(Vμ$_2$-OH)$_8$(SO$_4$)$_{16}$·2H$_2$O[10] | 1.966(5) | |
| [(CH$_3$)$_2$NH$_2$]$_{17.4}$[V$_8$(μ$_2$-OH)$_8$(μ$_2$-SO$_4$)$_{16}$][SO$_4$]$_{0.7}$[11] | 1.949(2) | |
| [V$_8$(μ-OH)$_4$(μ-OEt)$_8$(μ-CH$_3$COO)$_{12}$)][12] | 1.967(7) | |
| Average | 1.961(7) | |

Table S5. Bond valence sum calculations for $(NH_4)_2K_2[V_4(\mu_2\text{-}OH)_4(ox)_4(pz)_4]\cdot 9H_2O$ (**1**), $(NH_4)_2Na_2[V_4(\mu_2\text{-}OH)_4(ox)_4(4\text{-}mpz)_4]\cdot 7H_2O$ (**2**), $K_2[V_6(\mu_2\text{-}OH)_6(ox)_6(Hdatrz)_6]Cl_2\cdot 29.5H_2O$ (**3**) and $[V_8(\mu_2\text{-}OH)_8(SO_3)_8(Hdatrz)_8]\cdot 38H_2O$ (**4**), respectively.

| Complexes | Atoms | n | s | \|d\| | Assignment |
|---|---|---|---|---|---|
| **1** | V(1) | 3 | 2.986 | 0.014 | |
| | V(2) | 3 | 2.982 | 0.018 | |
| | V(3) | 3 | 3.017 | 0.017 | |
| | **average** | **3** | **2.995** | **0.005** | **V(III)** |
| | O(5) | 1 | 1.194 | 0.194 | $\mu_2$-$OH^-$ |
| | O(6) | 1 | 1.170 | 0.170 | $\mu_2$-$OH^-$ |
| **2** | V(1) | 3 | 2.994 | 0.006 | |
| | V(2) | 3 | 2.937 | 0.063 | |
| | **average** | **3** | **2.966** | **0.034** | **V(III)** |
| | O(5) | 1 | 1.184 | 0.184 | $\mu_2$-$OH^-$ |
| | O(10) | 1 | 1.149 | 0.149 | $\mu_2$-$OH^-$ |
| **3** | V(1) | **3** | **3.025** | **0.025** | **V(III)** |
| | O(5) | 1 | 1.208 | 0.208 | $\mu_2$-$OH^-$ |
| **4** | V(1) | 3 | 3.015 | 0.015 | |
| | V(2) | 3 | 2.941 | 0.059 | |
| | **average** | **3** | **2.978** | **0.022** | **V(III)** |
| | O(3) | 1 | 1.151 | 0.151 | $\mu_2$-$OH^-$ |
| | O(4) | 1 | 1.083 | 0.083 | $\mu_2$-$OH^-$ |

Table S6. Comparisons of $CO_2$ adsorption data for **1**, **2** and **4** with other porous polyoxometalates at 298 K.

| Adsorbents | Amount ($mmol \cdot g^{-1}$) | Pressure (bar) |
|---|---|---|
| **1** | 0.006 | 1 |
| **2** | 0.053 | 1 |
| **4** | 0.089 | 1 |
| | 1.080 | 30 |
| $[Mo^{V}_{8}O_{8}(\mu_2\text{-}O)_{12}(Htrz)_{8}]\cdot 62H_2O$ **13** | 0.052 | 1 |
| $Na_3[Mo^{V}_{6}O_{6}(\mu_2\text{-}O)_{9}(Htrz)_{3}(trz)_{3}]\cdot 7.5H_2O$ **14** | 0.020 | 1 |
| COMOC-2 **15** | 1.230 | 1 |
| $SO_2$-COMOC-2 **15** | 2.130 | 1 |
| MFM-300($V^{III}$) **16** | 6.000 | 1 |
| MFM-300($V^{IV}$) **16** | 3.540 | 1 |
| $NH_2$-MIL-47 **17** | 5.800 | 29 |
| V-MIL-100 **18** | 14.2 | 1 |

Abbreviations: Htrz = 1H-1,2,3-triazole; $SO_2$-COMOC-2 = $[V^{III}(O)V^{IV}(OH)(C_{14}H_6SO_6)_2]\text{-}(DMF)_{0.3}(H_2O)_{0.7}(CH_3OH)_{1.15}$; MFM-300($V^{III}$) = $V^{III}_2(OH)_2$(biphenyl-3,3',5,5'-tetracarboxylate); MFM-300($V^{IV}$) = $V^{IV}_2O_2$(biphenyl-3,3',5,5'-tetracarboxylate).

Table S7. V–$\mu_2$-O distances (Å) for $(NH_4)_2K_2[V_4(\mu_2\text{-}OH)_4(ox)_4(pz)_4]\cdot 9H_2O$ (**1**), $(NH_4)_2Na_2[V_4(\mu_2\text{-}OH)_4(ox)_4(4\text{-}mpz)_4]\cdot 7H_2O$ (**2**) and $[V_8(\mu_2\text{-}OH)_8(SO_3)_8(Hdatrz)_8]\cdot 38H_2O$ (**4**) before and after $O_2$ adsorption.

| Before $O_2$ adsorption | | | After $O_2$ adsorption | | |
|---|---|---|---|---|---|
| **1** | V1–O5 | 1.948(4) | **1** | V1–O5 | 1.940(5) |
| | V1–O6 | 1.934(4) | | V1–O6 | 1.932(5) |
| | V2–O6 | 1.946(4) | | V2–O6 | 1.947(5) |
| | V3–O5 | 1.947(4) | | V3–O5 | 1.949(5) |
| **2** | V1–O5 | 1.931(6) | **2** | V1–O5 | 1.926(2) |
| | V2–O5 | 1.955(6) | | V2–O5 | 1.949(2) |
| | V2–O10 | 1.955(6) | | V2–O10 | 1.941(2) |
| **4** | V1–O1 | 1.944(4) | **4** | V1–O1 | 1.939(4) |
| | V1–O2 | 1.969(4) | | V1–O2 | 1.951(4) |
| | V2–O2 | 1.983(4) | | V2–O2 | 1.980(4) |

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