

Electronic Supplementary Information (ESI) for

Synthesis of a phosphomolybdate possessing a tetranuclear vanadium core by installing vanadium to a lacunary template using protecting group strategy

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Materials: Acetonitrile (Kanto Chemical), acetone (Kanto Chemical), dichloromethane (Kanto Chemical), diethyl ether (Kanto Chemical), pyridine (**py**, Kanto Chemical), tetra-*n*-butyl ammonium bromide (TBABr, TCI), Vanadyl acetylacetonate (VO(acac)₂, Aldrich) were used as received. H₆PV₃Mo₉O₄₀ was obtained from Nippon Inorganic Colour & Chemical. Compound **I** was synthesized according to our previous report.^{S1}

Instruments: CSI-mass spectra were recorded on a JEOL JMS-T100CS instrument. FT-IR spectra were measured on JASCO FT/IR-4100 instrument using KCl discs. NMR spectra were recorded on a JEOL ECA-500 spectrometer (¹H, 500.16 MHz; ³¹P, 202.47 MHz, ⁵¹V, 130.23 MHz) using 5 mm tubes. Chemical shifts (δ) are reported in ppm downfield from TMS for ¹H NMR spectra, from H₃PO₄ (solvent, D₂O) for ³¹P NMR spectra, and NaVO₃ (solvent: D₂O, using NaVO₃ (−574.28 ppm) as the standard) for ⁵¹V NMR spectra respectively. UV-Vis spectra were recorded on a JASCO V-570 instrument using quartz cells with a 1.0 cm optical path length. TG-DTA was performed on a Rigaku Thermo plus TG 8120 instrument. ICP-AES analyses for P, V, and Mo were performed with Shimadzu ICPS-8100 instrument. Elemental analyses for C, H and N were performed on Elementar vario MICRO cube at the Elemental Analysis Centre of the School of Science of the University of Tokyo.

X-ray crystallography: Diffraction measurement on compound **II** was made on a Rigaku VariMax Saturn 724 diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$, 50 kV, 24 mA) at 123 K. The data were collected using CrystalClear and processed using CrysAlisPro.^{S2} Neutral scattering factors were obtained from the standard source. In the reduction of data, Lorentz and polarization corrections were made. The structural analyses were performed using WinGX.^{S3} All structures were solved by SHELXS-2013/1 (direct methods) and refined by SHELXL-2018/3.^{S4} P, Mo, V and O atoms in the POM frameworks, TBA cations were refined anisotropically. Some highly disordered TBA cations and solvent molecules were omitted by using SQUEEZE program.^{S5} The anion structure of compound **II** was a monomeric Keggin-type structure, in which a disordered 5-coordinated vanadyl cation ([VO]³⁺, **V1**) was observed on the surface of the skeleton structure. The occupancy of **V1** capping on the top and bottom surface of the skeleton was optimized to be 70% and 30%, respectively (Fig. S3c).

The other three vanadium atoms (**V2**, **V3** and **V4**) in the skeleton structure could be determined as in one of the two A- α -Keggin trivacant sites adjacent with the capping vanadyl cation, with half of the occupancy of the adjacent vanadyl cation. Importantly, ^{31}P and ^{51}V NMR studies showed that compound **II** is not a mixture but a single species with the determined positions of four vanadium atoms. The validity of the structural analysis with the disordered model was supported by ^{31}P and ^{51}V NMR, CSI-mass, DFT studies, and elemental analysis (see the main text). CCDC-2089352, contain the supplementary crystallographic data for **II**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Bond valence sum (BVS) calculations. The BVS values were calculated by the expression for the variation of the length r_{ij} of a bond between two atoms i and j in observed crystal with valence V_i using equation:

$$V_i = \sum_j \exp\left(\frac{r'_0 - r_{ij}}{B}\right)$$

Where B is a constant equal to 0.37 Å, r'_0 is bond valence parameter for a given atom pair.^{S6,S7}

Details of DFT calculations. All computational studies were performed with Gaussian 16 Revision B.01,^{S8} employing B3LYP functional. The geometries of anionic parts were optimized from the crystal structure determined in this study. In the optimizations and energy calculations, we employed 6-31+G* basis set for P and O, and LanL2DZ ECP for V and W atoms. The calculations were performed in acetonitrile and the solvent effects were included using the conductor-like polarizable continuum model (C-PCM).

Synthesis of compound II: Vanadyl acetylacetonate (199 mg, 750 μmol) was dispersed in acetone (10 mL), followed by addition of 100 μL water. **I** (366 mg, 150 μmol) was added to the solution, and the resulting solution was kept stirring at room temperature for 1h. During the procedure, green precipitate was observed. The green precipitate was collected by filtration with a membrane filter, washed with 1 mL acetone, and dried in vacuo. The collected green precipitate (260 mg, ca. 60% yield) was then dissolved in acetonitrile (20 mL), and 70 % nitric acid (60 μL) was added. After vigorously stirring at room temperature for 10 min, the color of the solution changed from green to orange. Diethyl ether was added until the solution turned muddy, followed by 3 mL additional diethyl ether. Afterwards the muddy solution was filtrated, and excess amount of diethyl ether was added to the filtrate. The resulting precipitate was collected by filtration with a membrane filter, and dried in vacuo. The orange-yellowish color powder was obtained as **II** (201 mg, ca. 80% yield). By vapor diffusion of ethyl acetate into a solution of **II** in dichloromethane, within 2 days under room temperature, red single crystals of **II** suitable

for X-ray crystallography analysis were obtained (12% based on the powder sample). Elemental analysis, calcd. (%) for $\text{TBA}_3\text{PV}_3\text{Mo}_9\text{O}_{40}(\text{V}^{\text{V}}\text{O})\cdot(\text{CH}_2\text{Cl}_2)_3\cdot(\text{CH}_3\text{CN})_{0.5}\cdot(\text{CH}_3\text{COOC}_2\text{H}_5)_{0.5}\cdot(\text{H}_2\text{O})$: C, 23.00; H, 4.34; N, 1.74; P, 1.10; Mo, 30.63; V, 7.23. Found: C, 23.08; H, 4.31; N, 1.79; P, 1.19; Mo, 30.56; V, 6.95. Positive-ion mass (ESI, acetonitrile): m/z 2725.1 (calcd. 2723.8 for $[\text{TBA}_4\text{PMo}_9\text{V}^{5+}_3\text{O}_{40}(\text{V}^{5+}\text{O})]^+$). ^{31}P NMR (202.47 MHz, acetonitrile- d_3): $\delta = -3.75$ ppm. ^{51}V NMR (130.23 MHz, acetonitrile- d_3): $\delta = -593.8, -587.8, -593.3$ ppm. IR (KBr pellet, cm^{-1}): 3411, 2962, 2934, 2874, 1636, 1483, 1469, 1379, 1102, 1073, 1048, 1010, 958, 879, 817, 794, 650, 594, 512, 381, 373.

Table S1 Crystallographic data for compound **II**.

Compound	II
Formula	C ₃₃ H ₇₄ N ₂ Cl ₂ P ₁ Mo ₉ V ₄ O ₄₁
Fw (g mol ⁻¹)	2324.03
Crystal system	monoclinic
Space group	<i>C2/c</i> (No. 15)
<i>a</i> (Å)	55.5617(14)
<i>b</i> (Å)	14.4627(2)
<i>c</i> (Å)	24.0687(6)
<i>α</i> (deg)	90
<i>β</i> (deg)	117.802(3)
<i>γ</i> (deg)	90
<i>V</i> (Å ³)	17108.3(8)
<i>Z</i>	8
<i>R</i> ₁ [<i>I</i> >2.0σ(<i>I</i>)]	0.0777
w <i>R</i> [all data]	0.1867
GOF	1.012

$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, $wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$.
Some highly disordered TBA cations and solvent molecules were omitted by using SQUEEZE program.

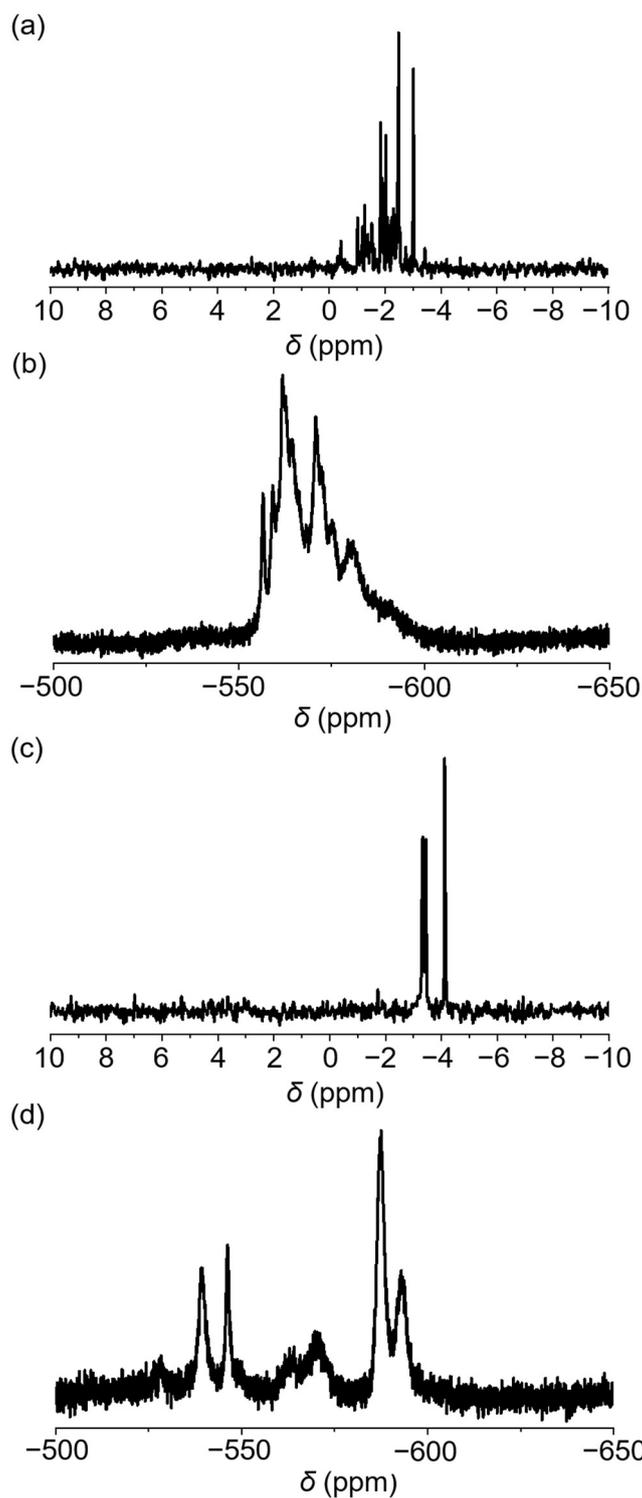


Fig. S1 (a) ^{31}P NMR and (b) ^{51}V NMR spectra of the solutions of commercially available Keggin-type vanadium-containing “mixed-addenda” phosphomolybdates $\text{H}_6[\text{PV}_3\text{Mo}_9\text{O}_{40}]$ in acetonitrile- d_3 ; (c) ^{31}P NMR and (d) ^{51}V NMR spectra of the reaction solution of $\text{TBA}_3\text{H}_6[\text{PMo}_9\text{O}_{34}]$ and $\text{VO}(\text{acac})_2$ in a mixture of acetonitrile- d_3 /water (100/1, v/v) after stirring at room temperature for 1 h, followed by addition of 70% HNO_3 and stirring at room temperature for 10 min.

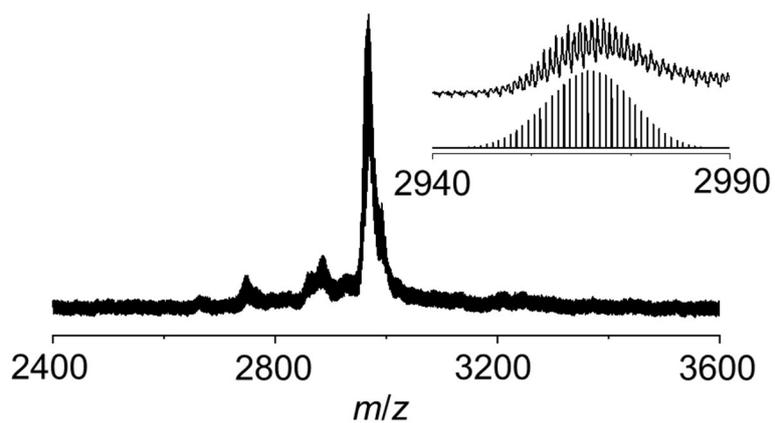


Fig. S2 Positive-ion CSI-mass spectrum of the reaction solution of **I** and VO(acac)₂ in a mixture of acetone/water (100/1, v/v) after stirring at room temperature for 1 h. Insets: a spectrum in the range of *m/z* 2940–2990, and a simulated pattern for [TBA₅PV₃V^{IV}Mo₉O₄₁]⁺ (*m/z*: 2966.7).

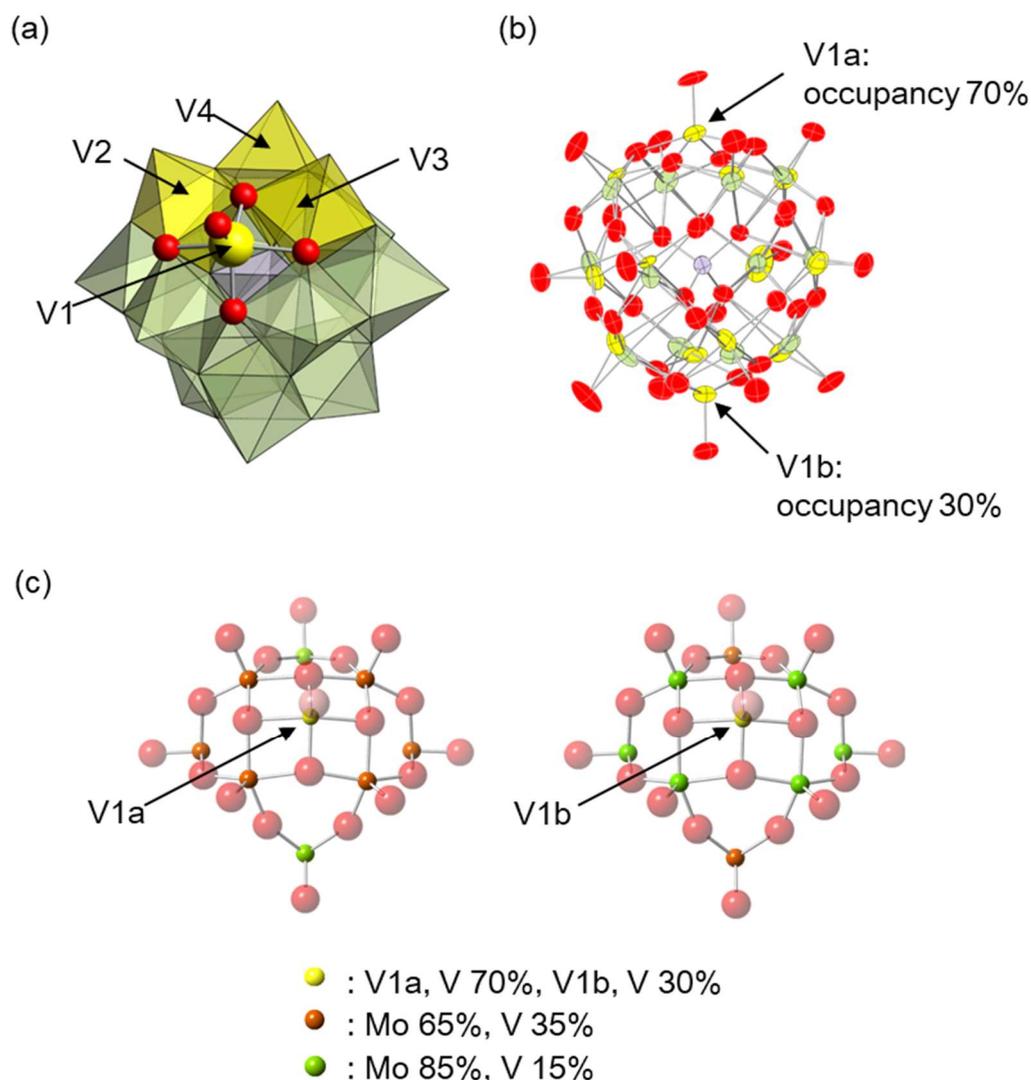


Fig. S3 (a) Polyhedral structure of the anion part of compound **II**, where the disorder is omitted for clarity. The light green, yellow, and light purple polyhedra represent $[\text{MoO}_6]$, $[\text{VO}_6]$, and $[\text{PO}_4]$, respectively. (b) Thermal ellipsoid plot representation (50% probability level) of the anion part of **II** with disordered atoms. The purple, green, yellow and red spheres represent P, Mo, V and O atoms, respectively. The 5-coordinated square pyramidal vanadyl cation **V1** was observed on the top (**V1a**, occupancy 70%) and bottom (**V1b**, occupancy 30%) surface of the POM skeleton. (c) The disorder model of the skeleton structure around the capping **V1a** and **V1b**. Two A- α -Keggin trivacant sites adjacent to the vanadyl cation accommodate three disordered 6-coordinated vanadium atoms with half of the occupancy of the center vanadyl cation.

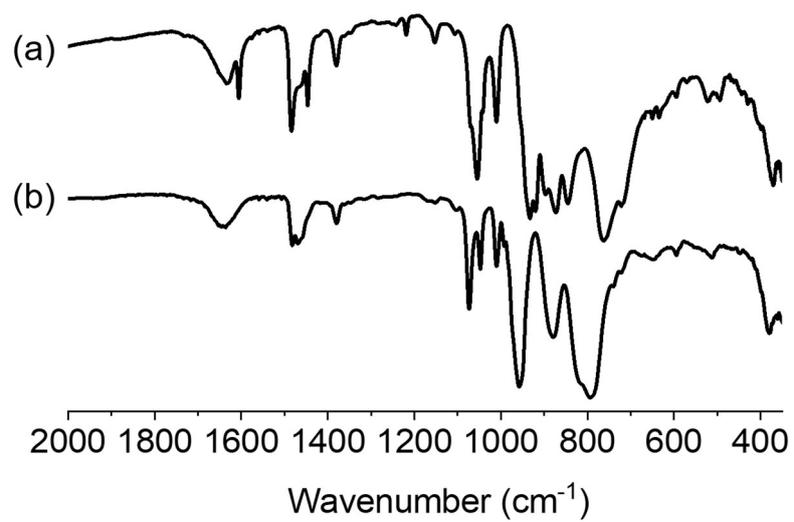


Fig. S4 IR spectra of (a) **I** (b) **II**.

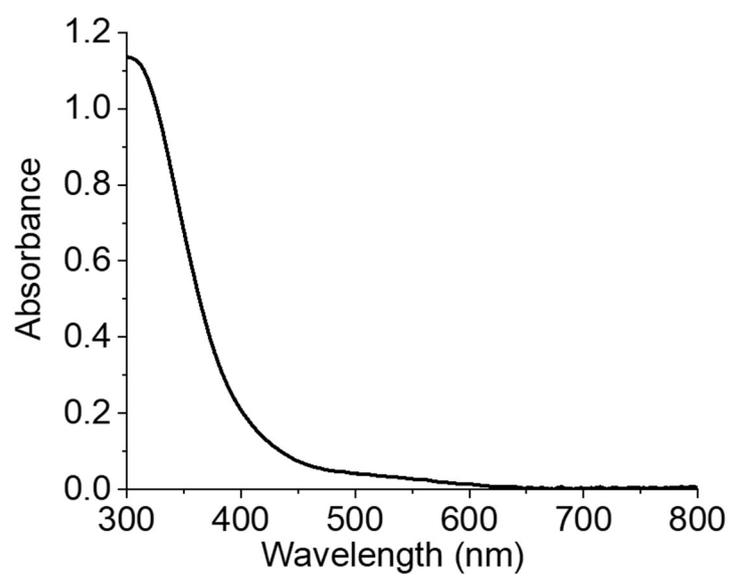


Fig. S5 UV-Vis spectrum of **II** in 1,2-dichloroethane (0.05 mM).

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