Electronic Supplementary Information (ESI) for

Ligand-directed top-down synthesis of trivacant lacunary polyoxomolybdates from plenary Keggin-type [α-$XMo_{12}O_{40}$]$^{3-}$ (X = P, As, V) in organic media

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Experimental section

Instruments: Electrospray ionization mass (ESI-mass) spectra were recorded on a Waters Xevo G2-XS QTof instrument and Shimadzu LCMS-9050 instrument. IR spectra were measured on Jasco FT/IR-4100 instrument using KBr disks. NMR spectra were recorded on a JEOL ECA-500 spectrometer (^{31}P, 202.47 MHz; ^{51}V, 130.23 MHz) using 5 mm tubes. Chemical shifts (δ) are reported in upfield from H_3PO_4 (solvent, D_2O) for ^{31}P NMR spectra and $NaVO_3$ (solvent: D_2O, using $NaVO_3$ (−574.28 ppm) as the standard), respectively. Thermogravimetric and differential thermal analyses (TG-DTA) were performed on Rigaku Thermo plus EVO2 TG-DTA 8122 instrument. Elemental analyses for P, As, V, and Mo by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were performed on Shimadzu ICPS-8100 instrument. Elemental analyses for C, H and N were performed using a MICRO CORDER JM10 at Research Infrastructure Management Center Core Facility Center of Institute of Science Tokyo.

Materials: Acetonitrile, disodium hydrogenarsenate heptahydrate, hydrochloric acid, pyridine, diethylether, ethanol and 12 molybdo(VI) phosphoric acid *n*-hydrate were purchased from Kanto Chemical. Tetrabutylammonium bromide (TBABr), 4-methoxypyridine (pyOMe), 4-cyanopyridine (pyCN), *p*-xylene and 1,3,5-tris[(1*H*-imidazole-1-yl)methyl]benzene were purchased from Tokyo Chemical Industry. Disodium molybdate(VI) dihydrate and mesitylene were purchased from FUJIFILM

Wako Pure Chemical Corporation. Ammonium vanadate(V) was purchased from Nacalai Tesque. Tetrabutylammonium hydroxide triacontahydrate was purchased from Sigma-Aldrich Japan. $TBA_3[\alpha\text{-}PMo_{12}O_{40}]$ (**PMo12**) was synthesized from 12 molybdo(VI) phosphoric acid *n*-hydrate and TBABr in ethanol and recrystallized from ethanol.

Single-crystal X-ray diffraction analysis: Diffraction measurements were performed on a Rigaku XtaLab Synergy-R diffractometer with rotating-anode Mo Kα radiation (λ = 0.71073 Å, 50 kV, 24 mA) at 93 K. The data were collected and processed using CrysAlisPro.[S1] In the reduction of data, Lorentz and polarization corrections were made. Structural analyses were performed using WinGX.[S2] All structures were solved by SHELXT-2018/2 and refined by SHELXL-2018/3.[S3] All non-hydrogen atoms were refined anisotropically. Highly disordered TBA ions and solvent molecules were omitted by using SQUEEZE program.[S4] CCDC-2408026, 2408027, 2408028, 2408029, 2408030, and 2408031 contain the supplementary crystallographic data for **I_P**, **PMo9-pyCN**, **I_{As}**, **I_V**, **II_{As}**, and **II_V**, respectively. 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: 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:

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

where B is constant equal to 0.37 Å, r'_0 is bond valence parameter for a given atom pair.[S5, S6]

Density functional theory (DFT) calculations: Computational studies were performed at Research Center for Computational Science, Okazaki, Japan. All calculations were performed with Gaussian 16 Rev B.01 package using CAM-B3LYP functional with employing the moderate-size basis set. The following basis set was used for the structure optimizations: LANL2DZ ECP for Mo; 6-31G* for P, As, V, O, C, H, N. The following basis set was used for the frequency calculations: LANL2DZ ECP for Mo; 6-31+G** for P, As, V, O, C, H, N. The solvent effects (acetonitrile) were included using the polarizable continuum model (PCM) with scaled van der Waals radii. After the geometry optimizations, the sum of electronic and thermal free energies for each component involved in the reactions (e.g., POMs, water molecule, and 4-methoxypyridine) was calculated via frequency calculations. Then, the standard Gibbs energy change of the reaction ($\Delta_r G°$) was calculated by taking the difference between the sums of these values for the reactants and the products.

Synthesis of $TBA_3[\alpha\text{-}AsMo_{12}O_{40}]$ (AsMo12): This compound was prepared according to the reported procedure.[S7] $Na_2MoO_4 \cdot 2H_2O$ (2.42 g) and $Na_2HAsO_4 \cdot 7H_2O$ (0.31 g) were dissolved in water (45 mL), and 37% hydrochloric acid (4.35 mL) were added, followed by the addition of acetonitrile (50 mL). The solution was stirred for 10 min, and then TBABr (0.8 g) was added to the solution.The precipitate formed was collected using a membrane filter, washed with water and ethanol and dried in vacuo to afford **AsMo12** as a yellow powder (85 % yield). IR (KBr pellet, cm^{-1}): 3443, 2963, 2874, 2360, 1626, 1481, 1469, 1380, 1314, 1152, 1107, 1060, 1029, 964, 895, 855, 789, 618, 501, 472, 457, 382

Synthesis of $TBA_3[\alpha\text{-}VMo_{12}O_{40}]$ (VMo12): This compound was prepared by a modification of the reported procedure.[S8] $Na_2MoO_4 \cdot 2H_2O$ (3.10 g) was dissolved in water (85 mL), and NH_4VO_3 (150 mg) dissolved in 37% hydrochloric acid (13 mL) was added, followed by the addition of acetonitrile (150 mL). The solution was stirred for 30 min, and then TBABr (2.5 g) was added. The precipitate formed was collected using a membrane filter, washed with water. The crude product was purified by recrystallization from acetonitrile to afford **VMo12** as yellow crystals (23% yield). IR (KBr pellet, cm^{-1}): 3418, 2962, 2935, 2873, 1637, 1469, 1380, 1150, 1109, 1056, 1025, 961, 888, 846, 777, 619, 455, 416, 379.

Synthesis of $TBA_3[A\text{-}\alpha\text{-}PMo_9O_{31}(pyOMe)_3]$ (I_P): To acetonitrile (4.0 mL), **PMo12** (40.0 mg, 15.7 μmol) and pyOMe (428 mg, 3.92 mmol) was added, and the resulting solution was stirred for 15 min at room temperature (~25°C), followed by filtration through a membrane filter. After the addition of diethyl ether (4.0 mL), the filtrate was kept at 25°C. The colorless crystals of $\mathbf{I_P}$ suitable for X-ray crystallographic analysis were obtained after 1 day (85% yield). Elemental analysis calcd (%) for $TBA_3[PMo_9O_{31}(C_6H_7NO)_3] \cdot 3(H_2O)$: C, 31.72; H, 5.44; N, 3.36; P, 1.24; Mo, 34.55. Found: C, 31.24; H, 5.07; N, 3.78; P, 1.16; Mo, 34.91. Negative ion MS (ESI, acetonitrile): *m/z* 1875.5 (calcd. 1875.5 for $[TBA_2(PMo_9O_{31})]^-$). IR (KBr pellet, cm^{-1}): 3439, 2962, 2936, 2875, 1630, 1606, 1484, 1447, 1381, 1220, 1152, 1060, 1011, 937, 921, 880, 817, 763, 596, 523, 501, 379.

Synthesis of $TBA_3[A\text{-}\alpha\text{-}PMo_9O_{31}(pyCN)_3]$ (PMo9-pyCN): To acetonitrile (4.0 mL), $\mathbf{I_P}$ (40.0 mg, 16.4 μmol) and pyCN (426 mg, 4.09 mmol) was added, and the resulting solution was stirred for 1 h at room temperature (~25°C), followed by filtration through a membrane filter. After the addition of diethyl ether (4.0 mL), the filtrate was kept at 25°C. The colorless crystals of **PMo9-pyCN** suitable for X-ray crystallographic analysis were obtained after 1 day (82% yield). Elemental analysis calcd (%) for $TBA_3[PMo_9O_{31}(C_6H_4N_2)_3]$: C, 32.62; H, 4,98; N, 5.19; P, 1.27; Mo, 35.54. Found: C, 32.93 H, 5.13; N, 5.30; P, 1.21; Mo, 35.78. Negative ion MS (ESI, acetonitrile): *m/z* 1875.4 (calcd. 1875.5 for $[TBA_2(PMo_9O_{31})]^-$). IR (KBr pellet, cm^{-1}): 3435, 2961, 2936, 2873, 2237, 1682, 1627, 1611, 1552, 1484, 1465, 1414, 1381, 1221, 1150, 1106, 1054, 1013, 933, 899, 876, 848, 829, 763, 726, 669, 648, 624, 596, 562, 523, 499, 429, 411, 370

Synthesis of $TBA_3[A\text{-}\alpha\text{-}AsMo_9O_{31}(pyOMe)_3]$ (I_{As}): To acetonitrile (4.0 mL), **AsMo12** (40.0 mg, 15.4 μmol) and pyOMe (421 mg, 3.86 mmol) was added, and the resulting solution was stirred for 1 h at room temperature (~25°C), followed by filtration through a membrane filter. After the addition of *p*-xylene (7.0 mL), the filtrate was kept at 25°C. The colorless crystals of $\mathbf{I_{As}}$ suitable for X-ray crystallographic analysis were obtained after 1 day (22% yield). Elemental analysis calcd (%) for

$TBA_3[AsMo_9O_{31}(C_6H_7NO)_3]\cdot 2(CH_3CN)$: C, 32.70; H, 5.29; N, 4.36; As, 2.91; Mo, 33.59. Found: C, 33.00; H, 5.25; N, 4.01; As, 2.81; Mo, 33.45. Negative ion MS (ESI, acetonitrile): *m/z* 1919.5 (calcd. 1919.5 for $[TBA_2(AsMo_9O_{31})]^-$). IR (KBr pellet, cm^{-1}): 3442, 3087, 2961, 2873, 1637, 1568, 1511, 1484, 1464, 1438, 1382, 1299, 1211, 1152, 1103, 1057, 1030, 935, 897, 876, 858, 750, 710, 660, 617, 556, 519, 429, 374.

Synthesis of $TBA_3[VMo_9O_{31}(pyOMe)_3]$ (I_V): To acetonitrile (4.0 mL), **VMo12** (40.0 mg, 15.6 μmol) and pyOMe (425 mg, 3.89 μmol) was added, and the resulting solution was stirred for 1 h at room temperature (~25°C), followed by filtration through a membrane filter. After the addition of mesitylene (8.0 mL), the filtrate was kept at 25°C. The light yellow crystals of **I_V** suitable for X-ray crystallographic analysis were obtained after 1 day (14% yield). Elemental analysis calcd (%) for $TBA_3[VMo_9O_{31}(C_6H_7NO)_3]\cdot 3(H_2O)\cdot 0.5(CH_3CN)$: C, 31.68; H, 5.42; N, 3.58; V, 2.01; Mo, 34.00. Found: C, 31.49; H, 5.19; N, 3.79; V, 1.94; Mo, 34.60. Negative ion MS (ESI, acetonitrile): *m/z* 1895.6 (calcd. 1895.5 for $[TBA_2(VMo_9O_{31})]^-$). IR (KBr pellet, cm^{-1}): 3445, 2962, 2874, 1635, 1607, 1539, 1484, 1447, 1381, 1218, 1200, 1153, 1106, 1069, 1026, 938, 879, 849, 734, 522, 371.

Synthesis of $TBA_3[AsMo_9O_{31}(C_{18}H_{18}N_6)]$ (II_{As}): To acetonitrile (4.0 mL), 1,3,5-Tris[(1*H*-imidazole-1-yl)methyl]benzene (5.12 mg, 16.1 μmol) and **I_{As}** (20.0 mg, 8.03 μmol) were added, and the resulting solution was stirred for 30 min at 80°C, followed by filtration through a membrane filter. After the addition of diethyl ether (800 μL), the filtrate was kept at 25°C. The colorless crystal of **II_{As}** suitable for X-ray crystallographic analysis were obtained after 1 day (24 % yield). Elemental analysis calcd (%) for $TBA_3[AsMo_9O_{31}(C_{18}H_{18}N_6)]\cdot 2(H_2O)$: C, 31.50; H, 5.21; N, 5.01; As, 2.98; Mo, 34.32. Found: C, 31.20; H, 5.06; N, 4.91, As, 2.94, Mo, 34.75. Positive ion MS (ESI, acetonitrile): *m/z* 2480.9 (calcd. 2480.9 for $[TBA_3H(AsMo_9O_{31})(C_{18}H_{18}N_6)]^+$) and 2723.2 (calcd. 2723.2 for $[TBA_4(AsMo_9O_{31})(C_{18}H_{18}N_6)]^+$). IR (KBr pellet, cm^{-1}): 3427, 3119, 2961, 1873, 1631, 1523, 1484, 1467, 1401, 1381, 1285, 1237, 1152, 1108, 1061, 1030, 934, 894, 868, 851, 769, 689, 657, 612, 490, 429, 376.

Synthesis of $TBA_{2.5}H_{0.5}[VMo_9O_{31}(C_{18}H_{18}N_6)]$ (II_V): To acetonitrile (4.0 mL), 1,3,5-tris[(1*H*-imidazole-1-yl)methyl]benzene (5.17 mg, 16.2 μmol) and **I_V** (20.0 mg, 8.11 μmol) were added, and the resulting solution was stirred for 30 min at 80°C, followed by filtration through a membrane filter. After the addition of mesitylene (1.0 mL), the filtrate was kept at 25°C. The light-yellow crystal of **II_V** suitable for X-ray crystallographic analysis were obtained after 1 day (11 % yield). Elemental analysis calcd (%) for $TBA_{2.5}H_{0.5}[VMo_9O_{31}(C_{18}H_{18}N_6)]\cdot(H_2O)\cdot 0.5(C_9H_{12})$: C, 31.10; H, 4.86; N, 4.93; V. 2.11; Mo, 35.78. Found: C, 30.66; H, 5.02; N, 4.67, V, 2.14, Mo, 35.56. Positive ion MS (ESI, acetonitrile): *m/z* 2457.0 (calcd. 2457.0 for $[TBA_3H(VMo_9O_{31})(C_{18}H_{18}N_6)]^+$) and 2698.2 (calcd. 2698.2 for $[TBA_4(VMo_9O_{31})(C_{18}H_{18}N_6)]^+$). IR (KBr pellet, cm^{-1}): 3445, 3118, 2961, 2936, 2872, 1633, 1523, 1483, 1380, 1284, 1235, 1153, 1108, 1063, 1030, 932, 859, 820, 742, 696, 607, 517,441, 417, 376.

Table S1 Crystallographic data of $\mathbf{I_P}$, **PMo9-pyCN**, $\mathbf{I_{As}}$, and $\mathbf{I_V}$.

	$\mathbf{I_P}$	**PMo9-pyCN**	$\mathbf{I_{As}}$	$\mathbf{I_V}$
Crystal system	Cubic	Cubic	Trigonal	Trigonal
Space group	$Pa\bar{3}$ (No. 205)	$Pa\bar{3}$ (No. 205)	$R3c$ (No. 161)	$R3c$ (No. 161)
a (Å)	27.9400(3)	27.5846(2)	19.4803(2)	37.1811(2)
b (Å)	27.9400(3)	27.5846(2)	19.4803(2)	37.1811(2)
c (Å)	27.9400(3)	27.5846(2)	51.6719(6)	52.7775(4)
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	90	120	120
Volume (Å^3)	21811.2(7)	20989.4(5)	16981.5(4)	63186.4(8)
Z	8	8	6	12
GOF	1.095	1.041	1.088	1.034
$R_1[I > 2\sigma(I)]$	0.0436	0.0491	0.0426	0.0324
wR_2	0.1301	0.1511	0.1134	0.0746

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - \mathrm{F}_c^2)]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S2 Crystallographic data of $\mathbf{II_V}$ and $\mathbf{II_{As}}$.

	$\mathbf{II_V}$	$\mathbf{II_{As}}$
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca* (No. 61)	*Pbca* (No. 61)
a (Å)	16.6755(3)	16.6642(3)
b (Å)	25.1212(5)	25.1809(4)
c (Å)	46.4027(9)	46.3159(8)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
Volume (Å^3)	19438.5(6)	19435.1(6)
Z	8	8
GOF	1.036	1.087
$R_1[I > 2\sigma(I)]$	0.0916	0.0705
wR_2	0.2548	0.1289

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S3 BVS values for $\mathbf{I_P}$, **PMo9-pyCN**, and $\mathbf{I_{As}}$.

$\mathbf{I_P}$		**PMo9-CN**		$\mathbf{I_{As}}$	
P1	4.97	P1	4.96	As1	4.99
Mo1	6.07	Mo1	6.08	Mo1	6.04
Mo2	6.03	Mo2	6.06	Mo2	5.95
Mo3	6.05	Mo3	6.07	Mo3	6.08

Table S4 BVS values for $\mathbf{I_V}$.

$\mathbf{I_V}$			
V1A	5.27	Mo7A	6.05
Mo1A	6.08	Mo8A	6.10
Mo2A	6.06	Mo9A	6.03
Mo3A	6.14	V1B_	5.20
Mo4A	5.92	Mo1B	6.17
Mo5A	6.11	Mo2B	6.10
Mo6A	5.92	Mo3B	6.10

Table S5 BVS values for $\mathbf{II}_\mathrm{V}$ and $\mathbf{II}_\mathrm{As}$.

$\mathbf{II}_\mathrm{V}$		$\mathbf{II}_\mathrm{As}$	
V1	5.19	As1	5.08
Mo1	5.99	Mo1	6.13
Mo2	5.97	Mo2	6.01
Mo3	6.01	Mo3	6.04
Mo4	5.97	Mo4	5.97
Mo5	6.14	Mo5	6.05
Mo6	5.92	Mo6	5.99
Mo7X	5.96	Mo7X	5.95
Mo8X	6.24	Mo8X	6.14
Mo9X	5.83	Mo9X	5.90
Mo7Y	5.69	Mo7Y	5.73
Mo8Y	5.64	Mo8Y	5.75
Mo9Y	5.82	Mo9Y	5.65

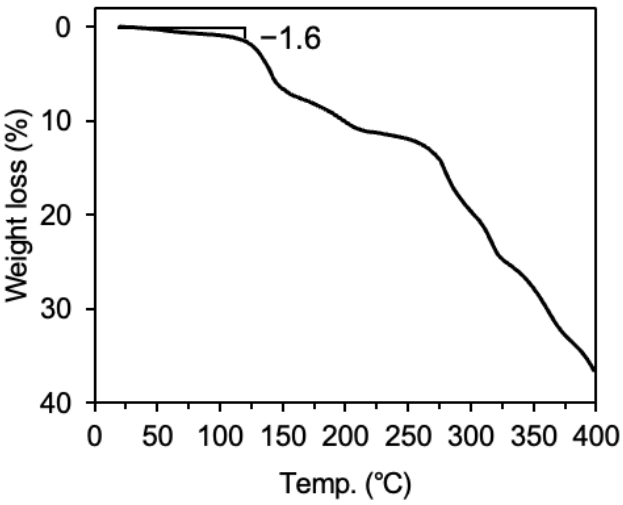

Fig. S1 TG curve of $\mathbf{I_P}$ (N_2 atmosphere).

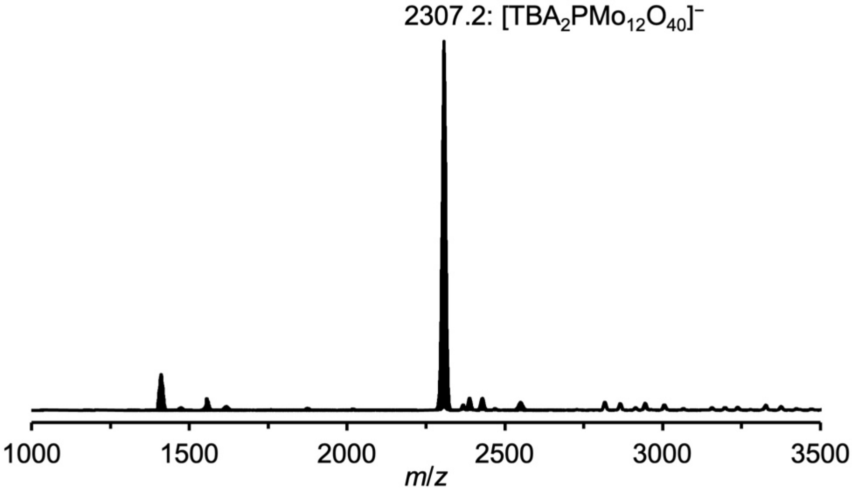

Fig. S2 ESI-mass spectrum of the reaction solution of **PMo12** and pyCN (250 equivalents with respect to **PMo12**) in acetonitrile.

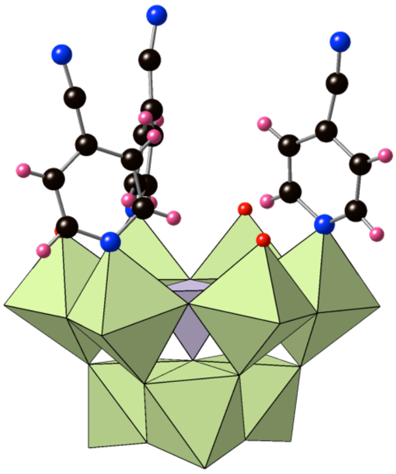

Fig. S3 Crystal structure of the anionic component of **PMo9-pyCN**. Light green octahedra and light purple tetrahedron represent [MoO_6] and [PO_4], respectively. Red, black, pink, and blue spheres denote O, C, H, and N atoms, respectively.

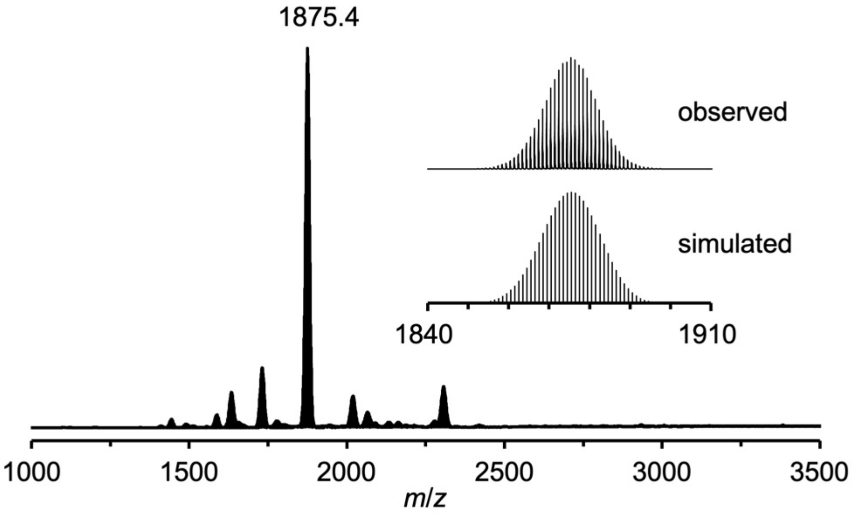

Fig. S4 ESI-mass spectrum of **PMo9-pyCN** in acetonitrile. Inset: Enlarged spectrum (top) and simulated pattern of [$TBA_2PMo_9O_{31}$]$^-$ (*m*/*z*: 1875.5, bottom).

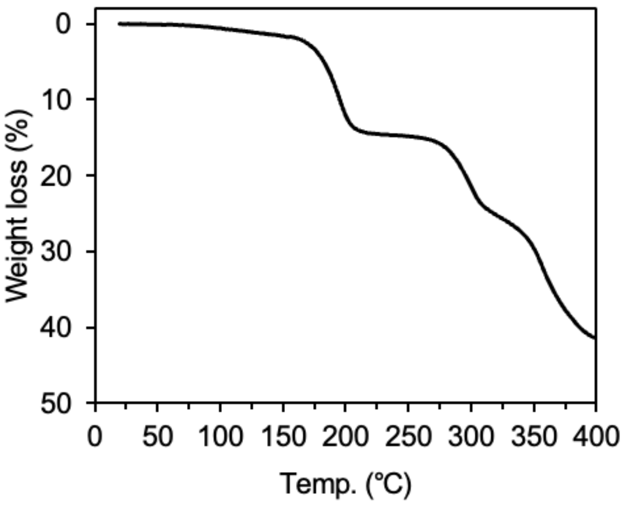

Fig. S5 TG curve of **PMo9-pyCN** (N_2 atmosphere).

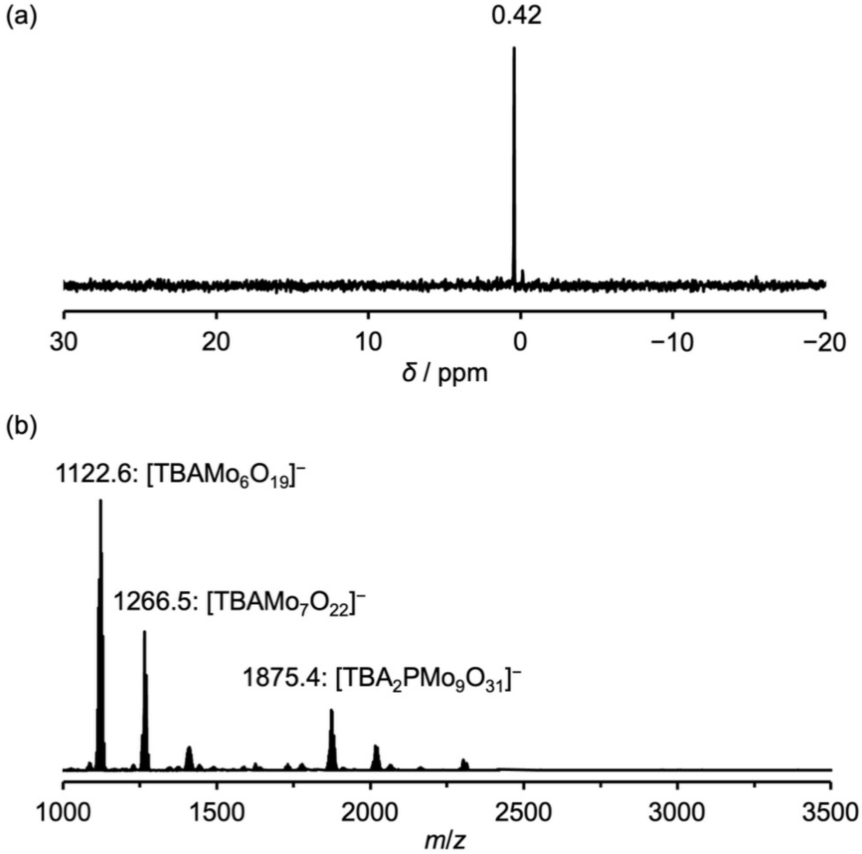

Fig. S6 (a) ^{31}P NMR and (b) ESI-mass spectra of the reaction solution of **PMo12**, pyridine (250 equivalents with respect to **PMo12**), and TBAOH (2 equivalents with respect to **PMo12**) in acetonitrile.

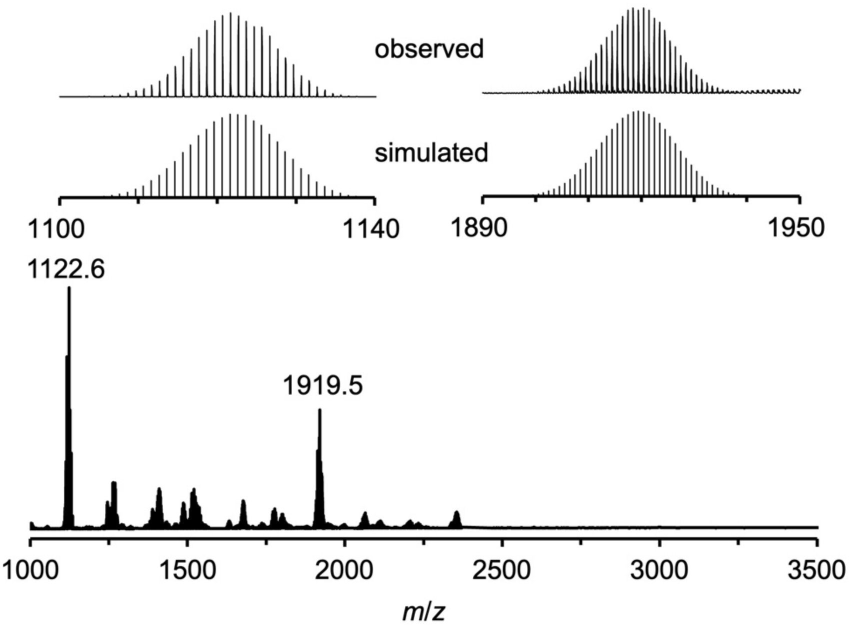

Fig. S7 ESI-mass spectrum of the reaction solution of **AsMo12** and pyOMe (250 equivalents with respect to **AsMo12**) in acetonitrile. Inset: Enlarged spectrum (top) and simulated pattern of $[\mathrm{TBAMo_6O_{19}}]^-$ (*m*/*z*: 1122.6, bottom) and $[\mathrm{TBA_2AsMo_9O_{31}}]^-$ (*m*/*z*: 1919.5, bottom).

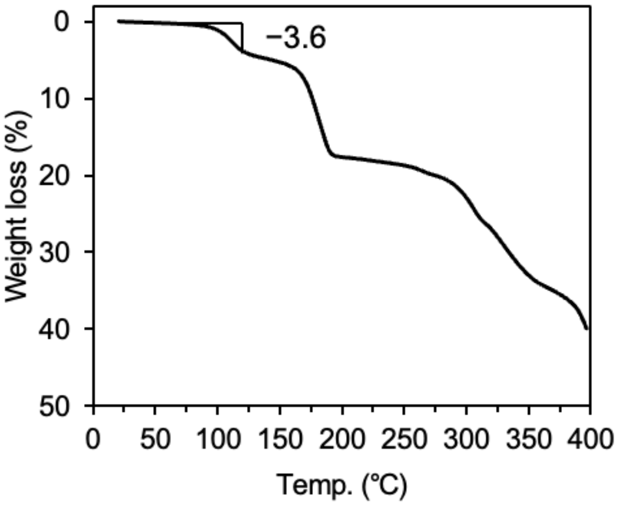

Fig. S8. TG curve of $\mathbf{I_{As}}$ (N_2 atmosphere).

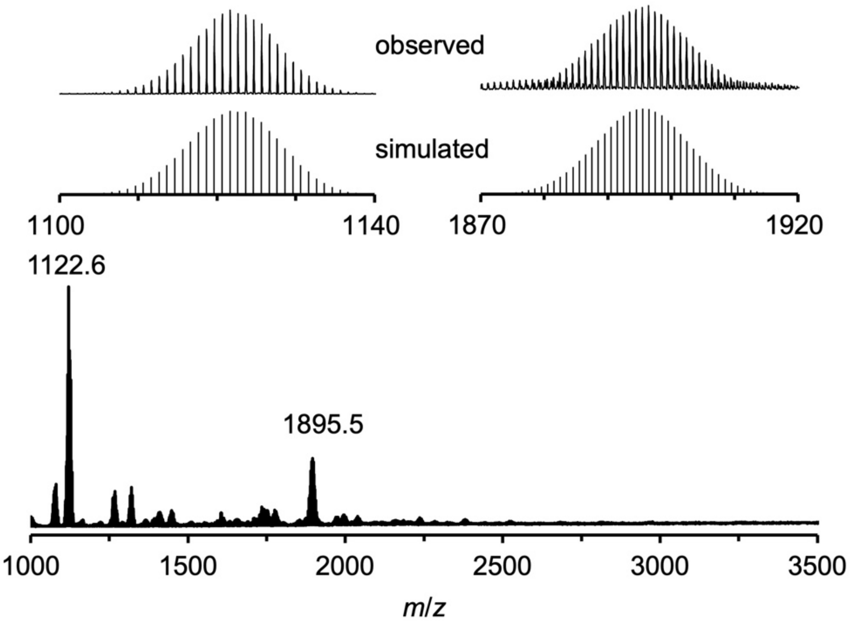

Fig. S9 ESI-mass spectrum of the reaction solution of **VMo12** and pyOMe (250 equivalents with respect to **VMo12**) in acetonitrile. Inset: Enlarged spectrum (top) and simulated pattern of $[TBAMo_6O_{19}]^-$ (*m*/*z*: 1122.6, bottom) and $[TBA_2VMo_9O_{31}]^-$ (*m*/*z*: 1895.5, bottom).

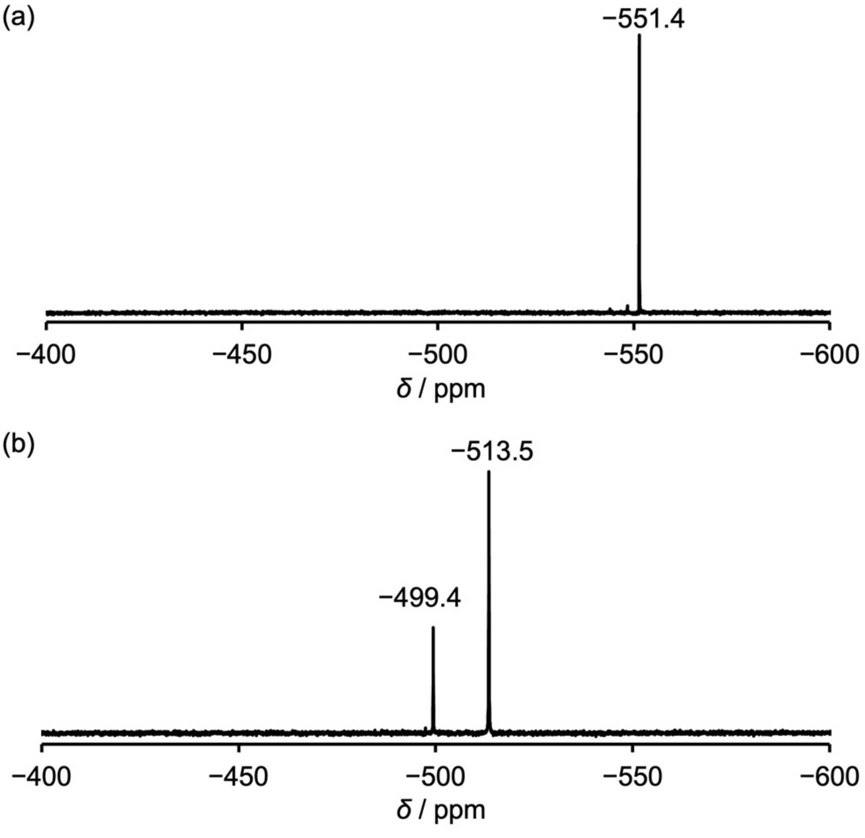

Fig. S10 ^{51}V NMR spectra of (a) **VMo12** and (b) $\mathbf{I_V}$ crystals in acetonitrile.

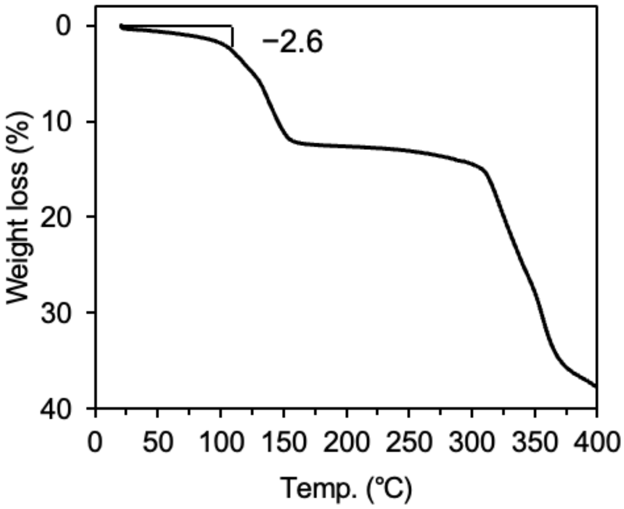

Fig. S11 TG curve of $\mathbf{I}_\mathrm{V}$ (N_2 atmosphere).

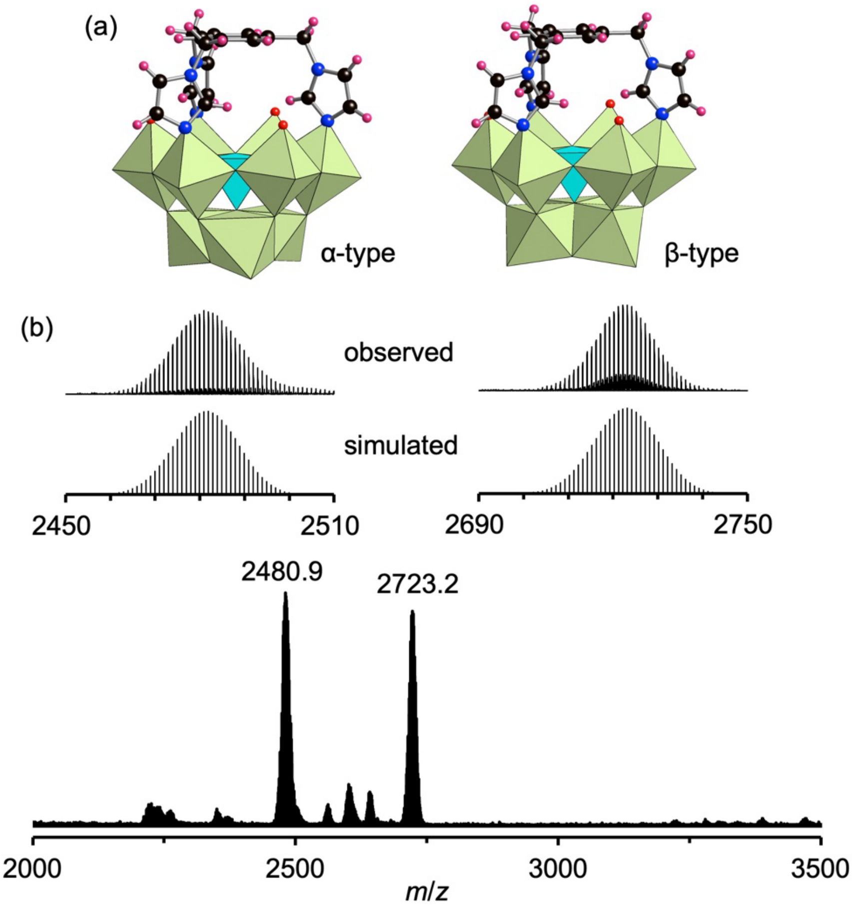

Fig. S12 (a) Crystal structure of the anionic component of $\mathbf{II}_{\mathbf{As}}$: α-type (left) and β-type (right). (b) ESI-mass spectrum of $\mathbf{II}_{\mathrm{V}}$ in acetonitrile. Inset: Enlarged spectrum (top) and simulated pattern of $[\mathrm{TBA}_3\mathrm{HAsMo}_9\mathrm{O}_{31}\mathbf{L}]^+$ (*m*/*z*: 2480.9, bottom) and $[\mathrm{TBA}_4\mathrm{AsMo}_9\mathrm{O}_{31}\mathbf{L}]^+$ (*m*/*z*: 2723.2, bottom) (**L** = $C_{18}H_{18}N_6$). Light green octahedra and light blue tetrahedron represent $[\mathrm{MoO}_6]$ and $[\mathrm{AsO}_4]$, respectively. Red, black, pink, and blue spheres denote O, C, H, and N atoms, respectively.

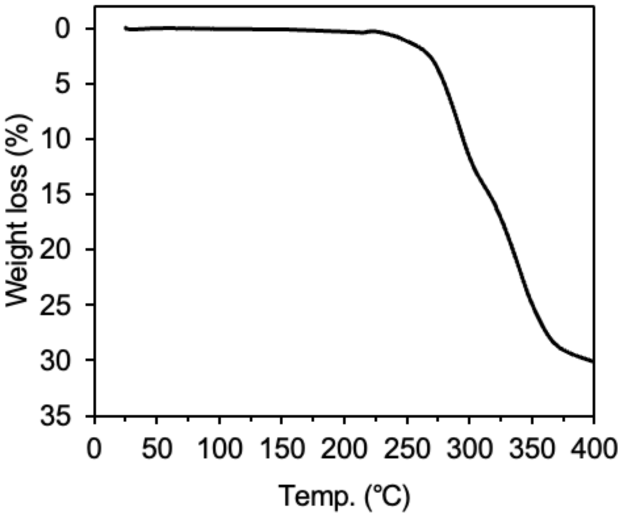

Fig. S13 TG curve of **II**$_{\mathbf{V}}$ (N_2 atmosphere).

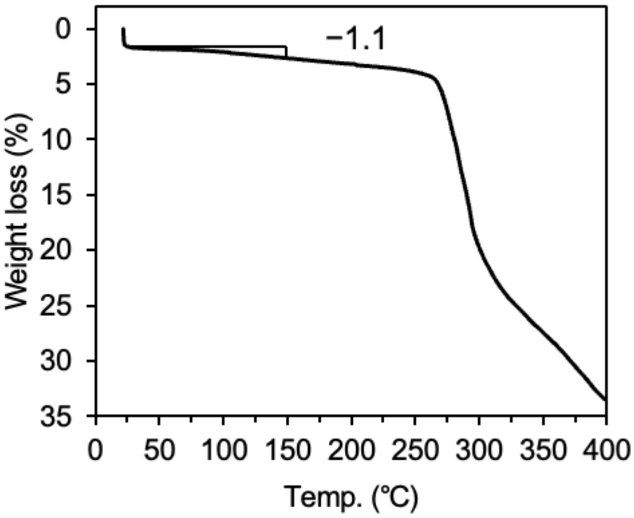

Fig. S14 TG curve of **II**$_{\mathbf{As}}$ (N_2 atmosphere).

Additional References

S1 Rigaku OD. CrysAlis PRO. Rigaku Oxford Diffraction Ltd, Yarnton, England (2018).

S2 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

S3 (a) G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112; (b) G. M. Sheldrick, *Acta Crystallogr*. *C*, 2015, **71**, 3.

S4 P. van der Sluis, A. L. Spek, *Acta Crystallogr. A*, 1990, **46**, 194

S5 N. E. Brese and M. O'Keeffe, *Acta Crystallogr. B*, 1991, **47**, 192.

S6 I. D. Brown and D. Altermatt, *Acta Crystallogr. B*, 1985, **41**, 244.

S7 S. Himeno, M. Hashimoto and T. Ueda, *Inorg. Chim. Acta*, 1999, **284**, 237.

S8 S. Himeno and A. Saito, *Inorg. Chim. Acta*, 1990, **171**, 135.