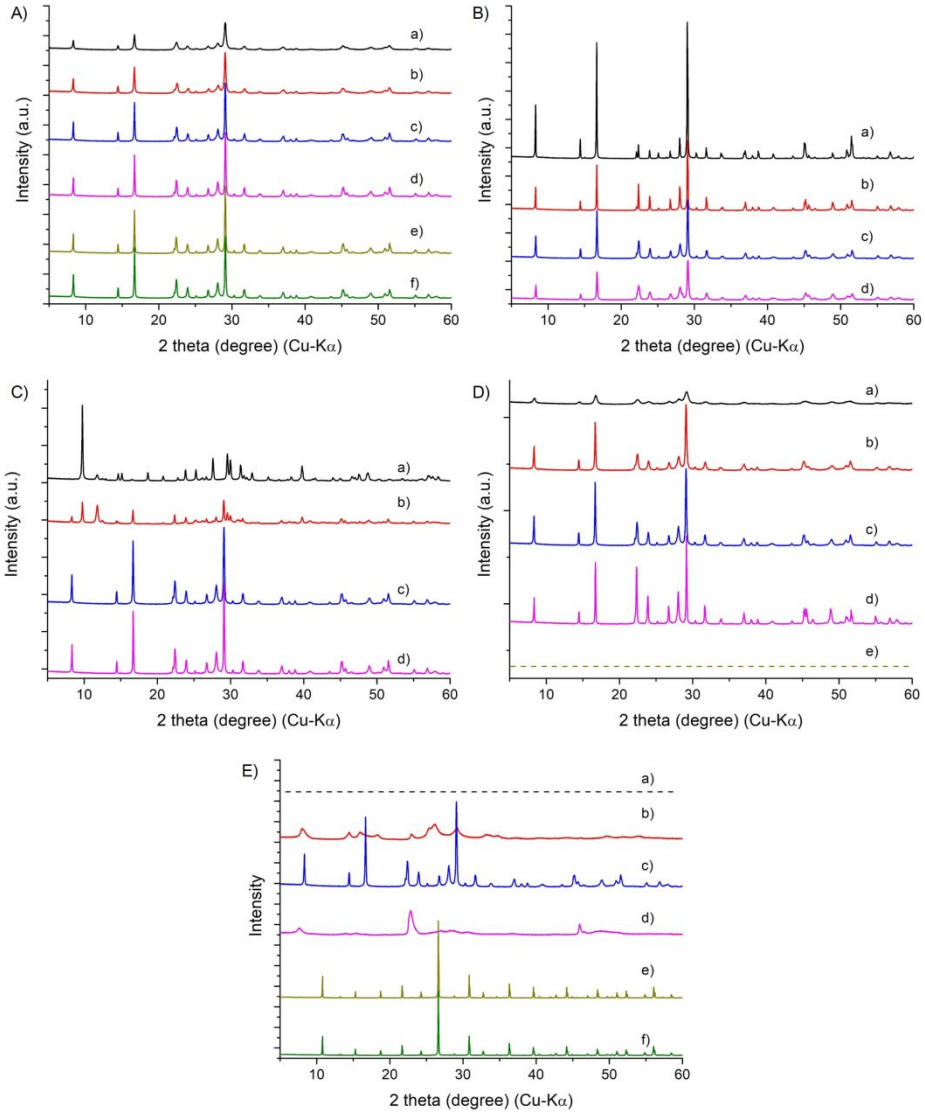

Figure S1. A) reaction time effects, a) 0 h (Table S1, entry 2), b) 1 h (entry 3), c) 2 h (entry 4), d) 4 h (entry 5), e) 6 h (entry 6), and f) 8 h (entry 1); B) concentration effect, a) 0.25c (entry 7), b) 0.5c (entry 8), c) 1c (entry 1), and d) 2c (entry 9); C) acidity effect, a) 0.5 mL (entry 10), b) 1 mL (entry 11), c) 1.5 mL (entry 1), and d) 3 mL of concentrated HCl (entry 12); D) temperature effect, a) 25 ^{o}C (entry 13), b) 60 ^{o}C (entry 14), c) 100 ^{o}C (entry 1), d) 135 ^{o}C (entry 15), and e) 175 ^{o}C (entry 16); E) starting material effect, a) Li_2MoO_4 (entry 17), b) Na_2MoO_4 (entry 18), c) K_2MoO_4 (entry 1), d) $CaMoO_4$ (entry 19), e) H_3PO_4 (entry 20), and f) $Na_4P_2O_7$ (entry 21). Standard reaction condition: MoO_3 (10.33 mmol) was dissolved in KOH solution (0.52 M, 40 mL), followed by addition of H_3PO_4 (1.7 mmol) and HCl solution (ca. 36 %, 1.5 mL). The solution was heated at 100 ^{o}C for 6 hours.

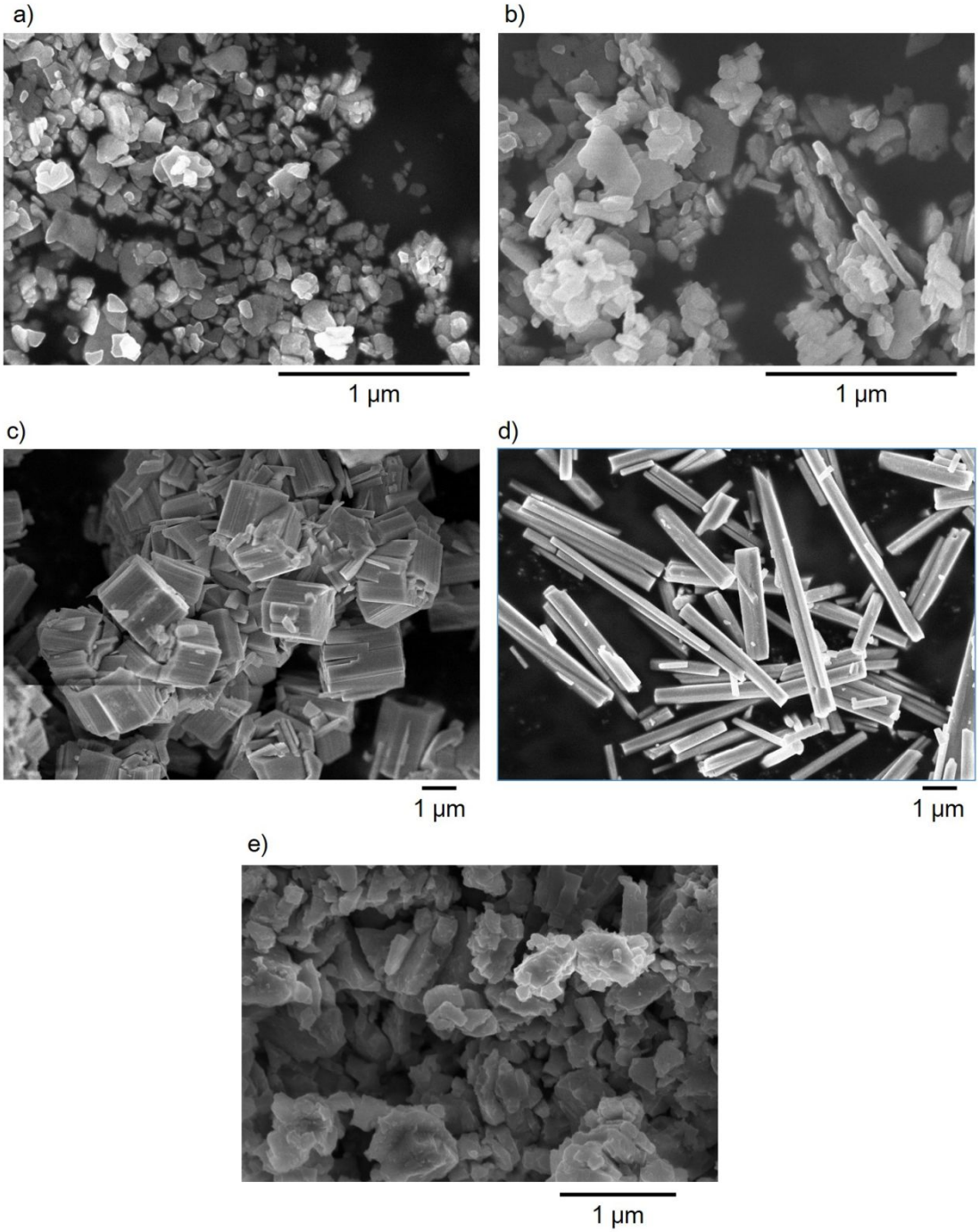

Figure S2. SEM images of molybdophosphites prepared under the conditions in Table S1 a) entry 8, b) entry 1 (**MoP^{III}O**), c) entry 7, d) entry 6, and e) **MoP^{V}O**.

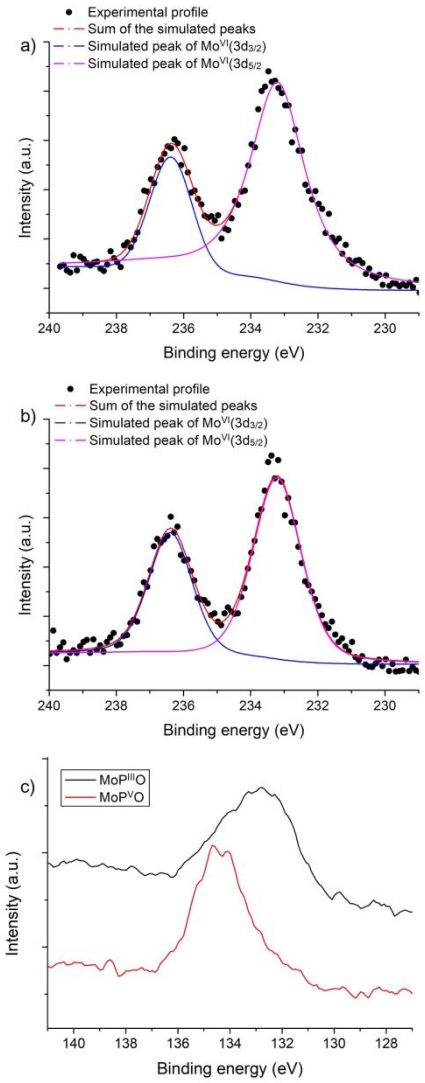

Figure S3. XPS profiles of a) Mo in **MoP^{III}O**, b) Mo in **MoP^{V}O**, and c) P in **MoP^{III}O** and **MoP^{V}O**.

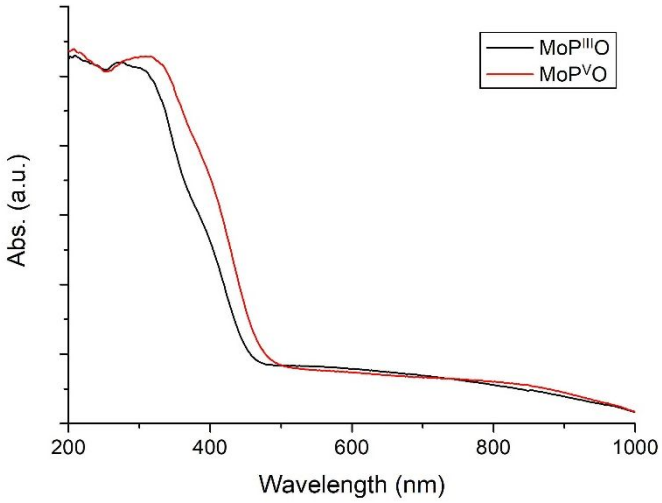

Figure S4. DR-UV-vis spectra of the **MoP^{III}O** and **MoP^{V}O**.

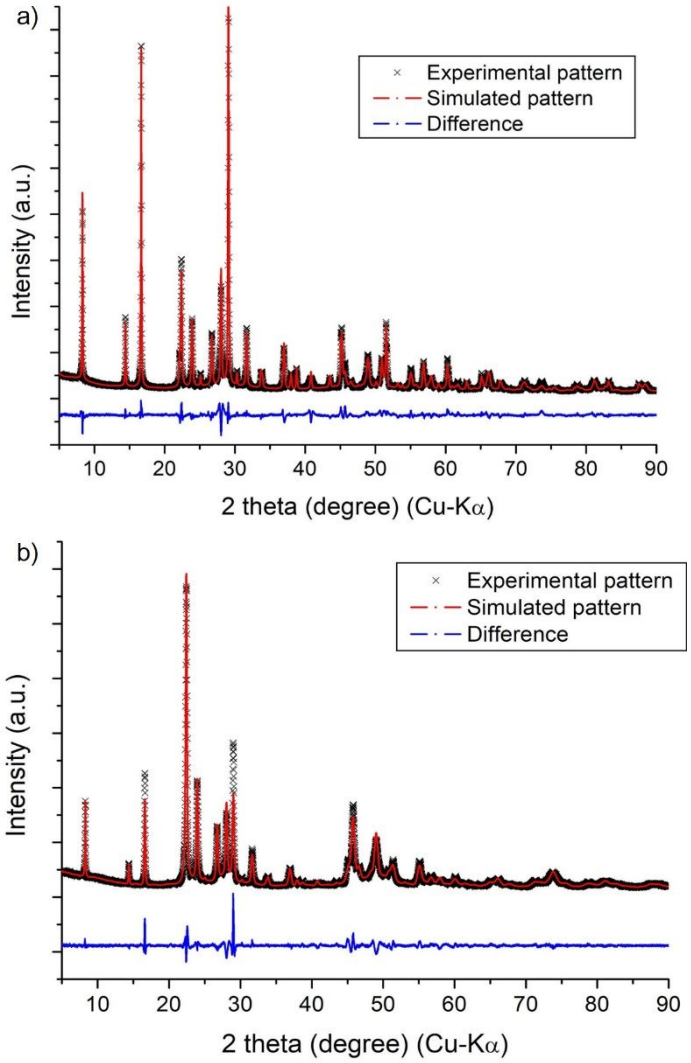

Figure S5. Comparison of simulated XRD pattern from Rietveld refinement with the experimental pattern a) **MoP^{III}O** and b) **MoP^{V}O**.

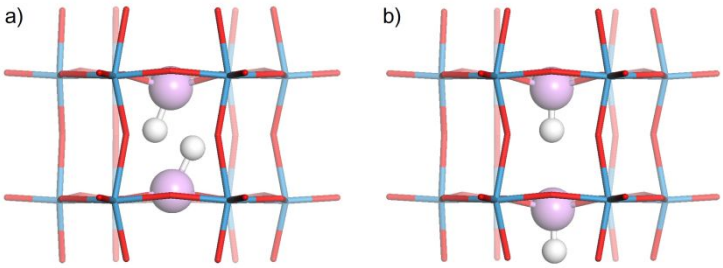

Figure S6. Structure models of **MoP^{III}O** in a) the “face to face” manner and b) the “face to end” manner, Mo (blue), O (red), P (purple), H (white).

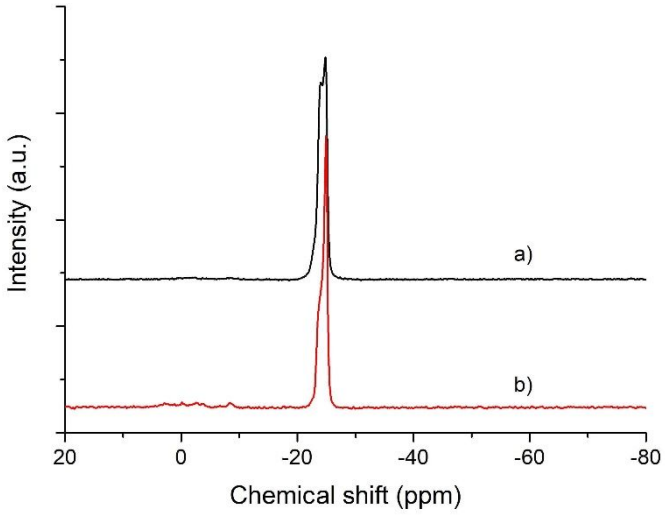

Figure S 7. Solid state ^{31}P MAS NMR with H-coupling mode of a) **MoP^{V}O** without heating and b) **MoP^{V}O** heated at 350 ^{o}C in air for 2 h.

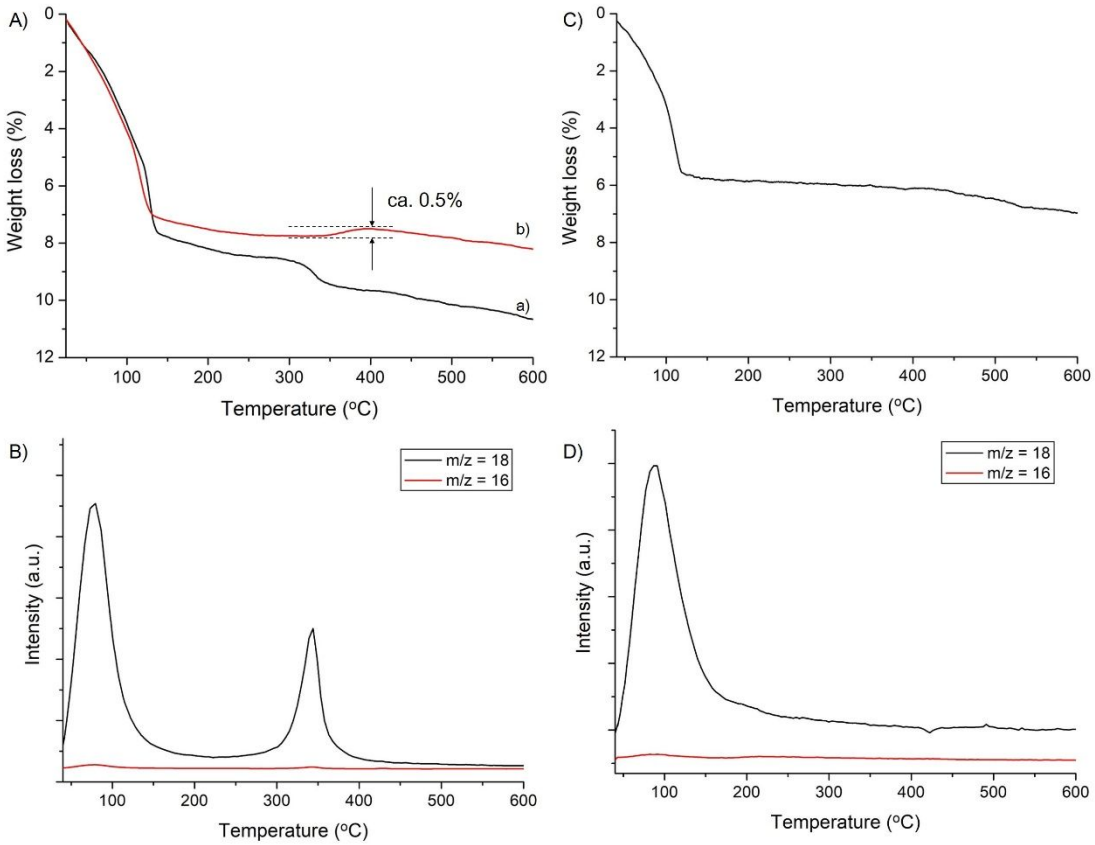

Figure S8. A) TG-DTA profiles of a) **MoP^{III}O** under O_2 and b) under N_2, B) TPD-MS of **MoP^{III}O** under N_2, C) A) TG-DTA profiles of **MoP^{V}O** under N_2, and D) TPD-MS of **MoP^{V}O** under N_2,

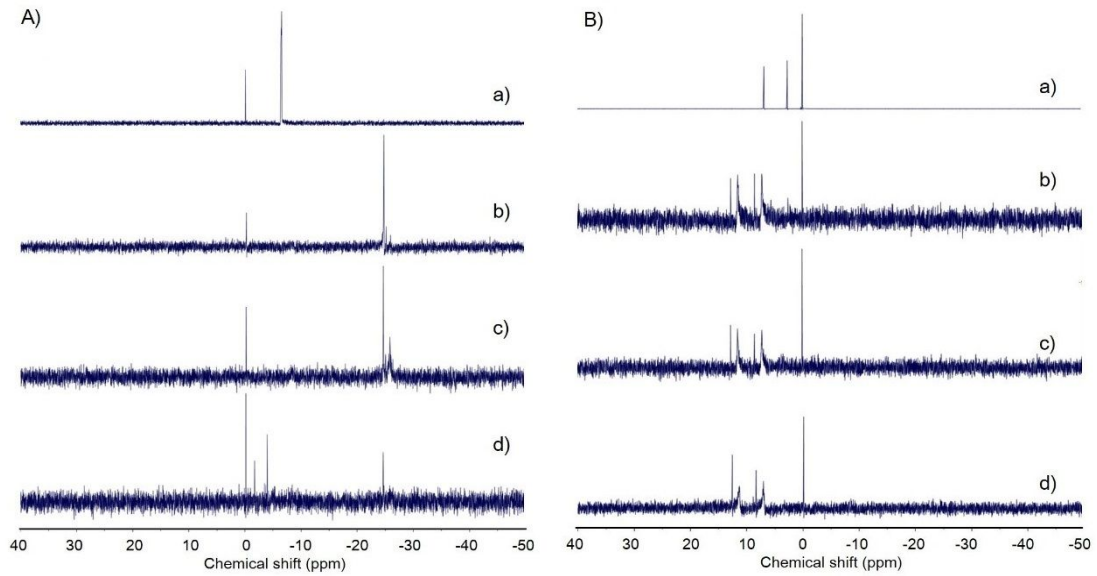

Figure S9. A) ^{31}P NMR of a) $Na_4P^V_2O_7$ in D_2O solution; ^{31}P NMR was measured after b) 0 h, c) 1 h, and d) 24 h after addition of 6 equivalent of Na_2MoO_4 to the $Na_4P^V_2O_7$ solution. B) ^{31}P NMR (non-decoupling mode) of a) $H_3P^{III}O_3$ in D_2O; ^{31}P NMR (non-decoupling mode) was measured after b) 0 h, c) 1 h, and d) 24 h after addition of 6 equivalent of Na_2MoO_4 to the $H_3P^{III}O_3$ solution. Water diluted H_3PO_4 in a sealed glass tube was added as an internal standard, the chemical shift of which was 0 ppm.

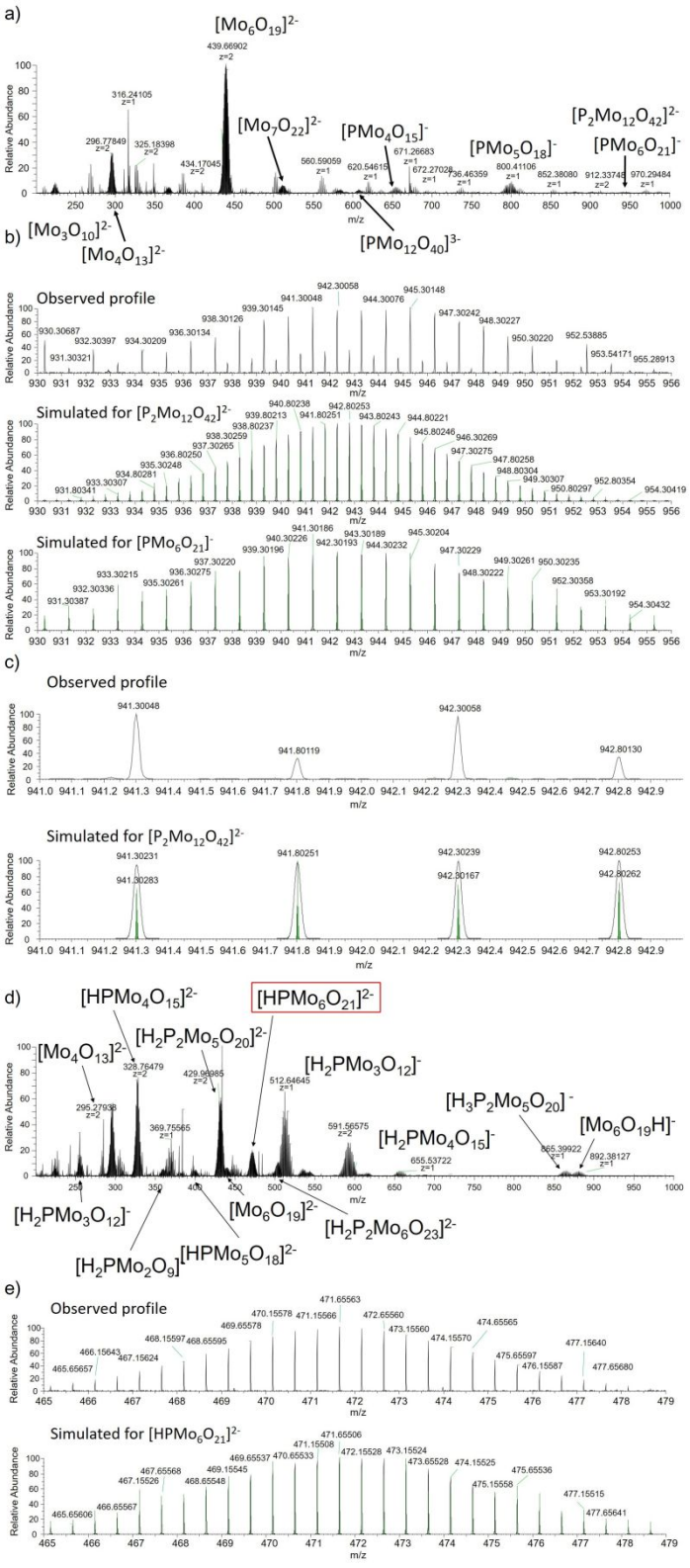

Figure S10. ESI-MS of a) reaction solution for **MoP^{V}O** ($Na_2P_2O_7$, Na_2MoO_4, HCl, and water) dissolved in CH_3CN, b) enlarged profile together with simulated profile for $[P_2Mo_{12}O_{42}]^{2-}$ and $[PMo_6O_{21}]^{-}$, and c) further enlarged profile together with simulated profile for $[P_2Mo_{12}O_{42}]^{2-}$. ESI-MS of d) reaction solution for **MoP^{III}O** (H_3PO_3, Na_2MoO_4, HCl, and water) dissolved in CH_3CN and e) enlarged profile together with simulated profile for $[HPMo_6O_{21}]^{2-}$.

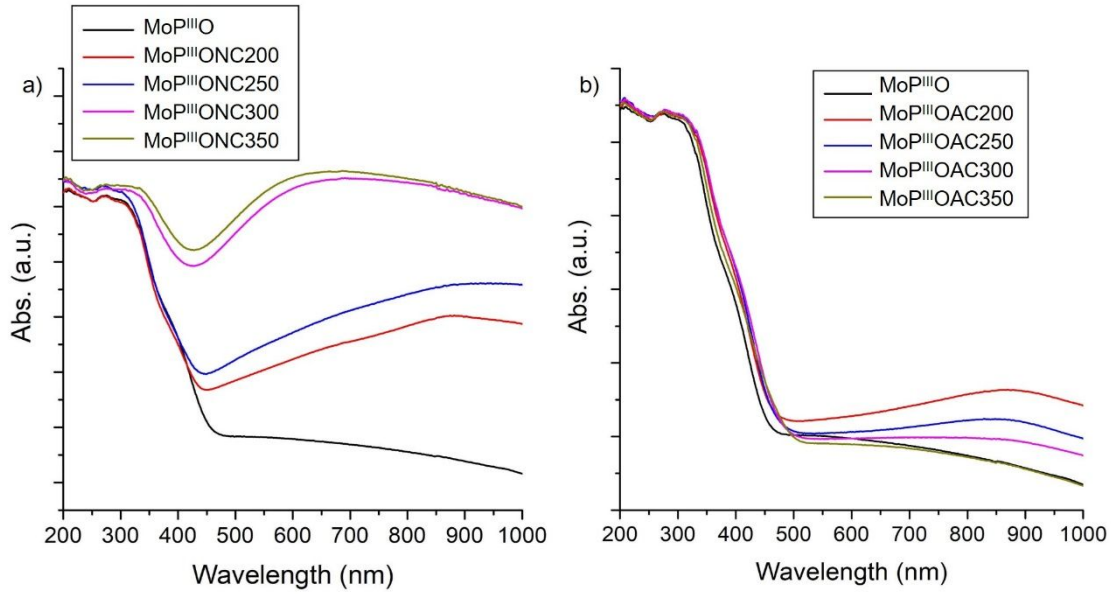

Figure S11. DR-UV-vis spectra of a) **MoP^{III}O** calcined under N_2 and b) **MoP^{III}O** calcined under air.

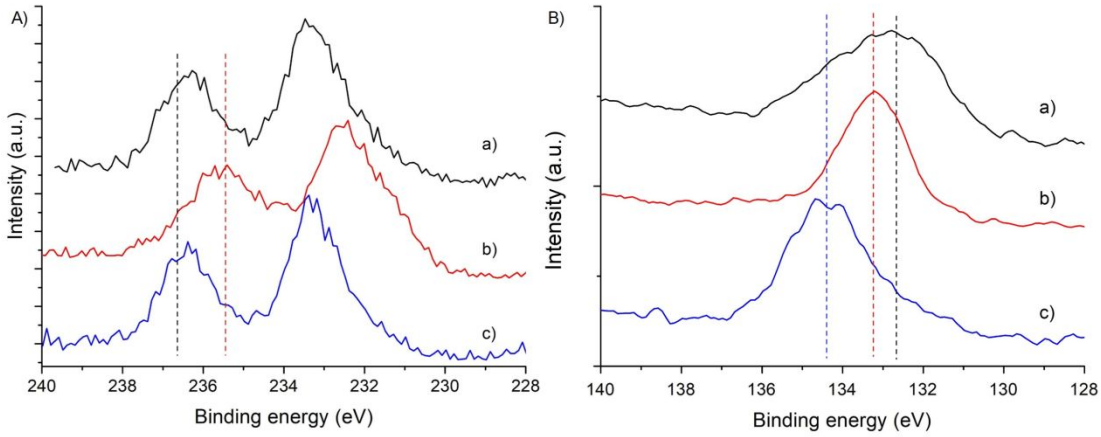

Figure S12. XPS profiles of A) Mo and B) P, a) **MoP^{III}O**, b) **MoP^{III}ONC350**, and c) **MoP^{V}O**.

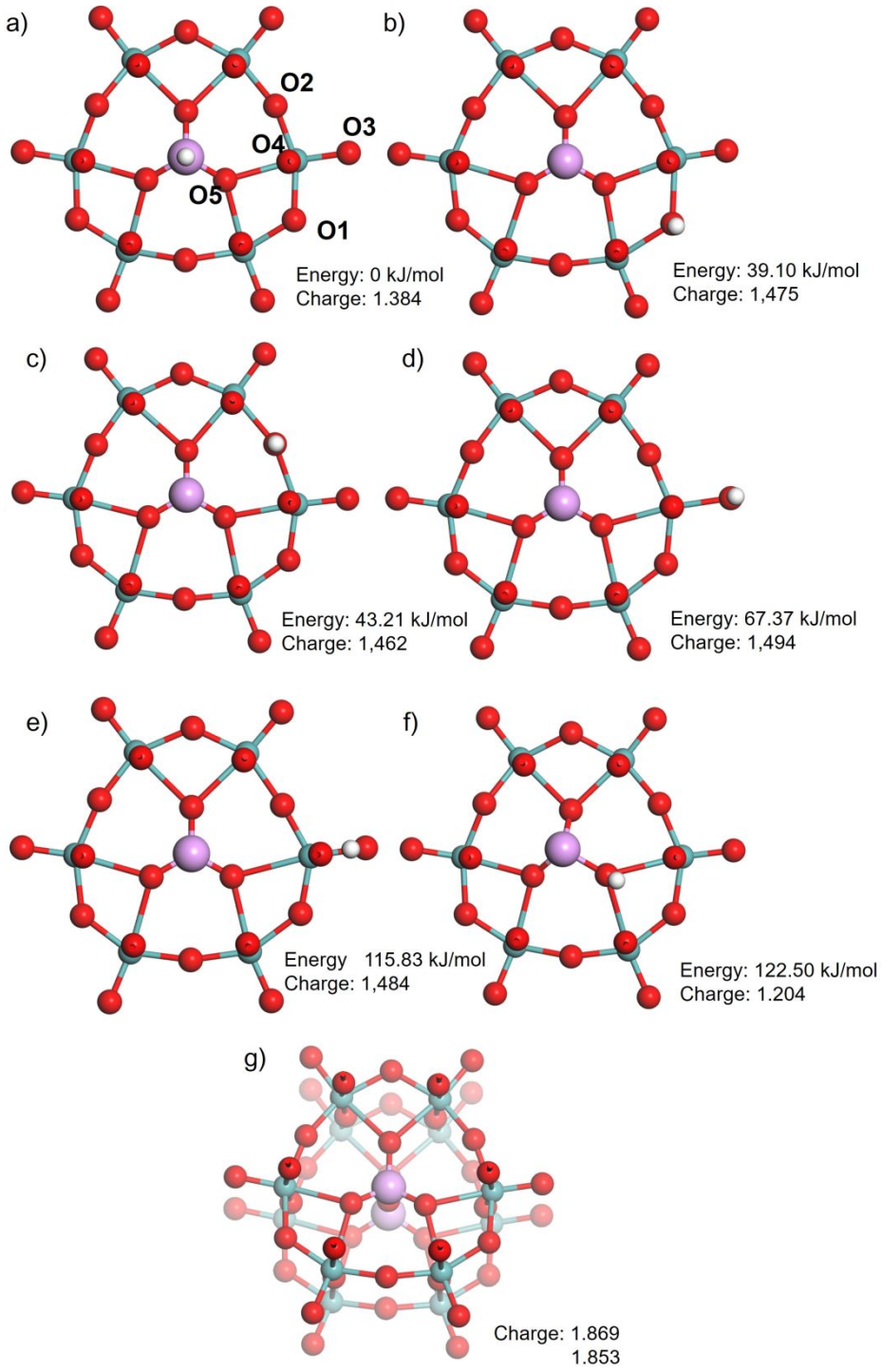

Figure S13. Structure models of a) **MoP^{III}O**, the material with protonated b) O1, c) O2, d) O3, e) O4, and f) O5, and g) **MoP^{V}O,** Mo (blue), O (red), P (purple), H (white).

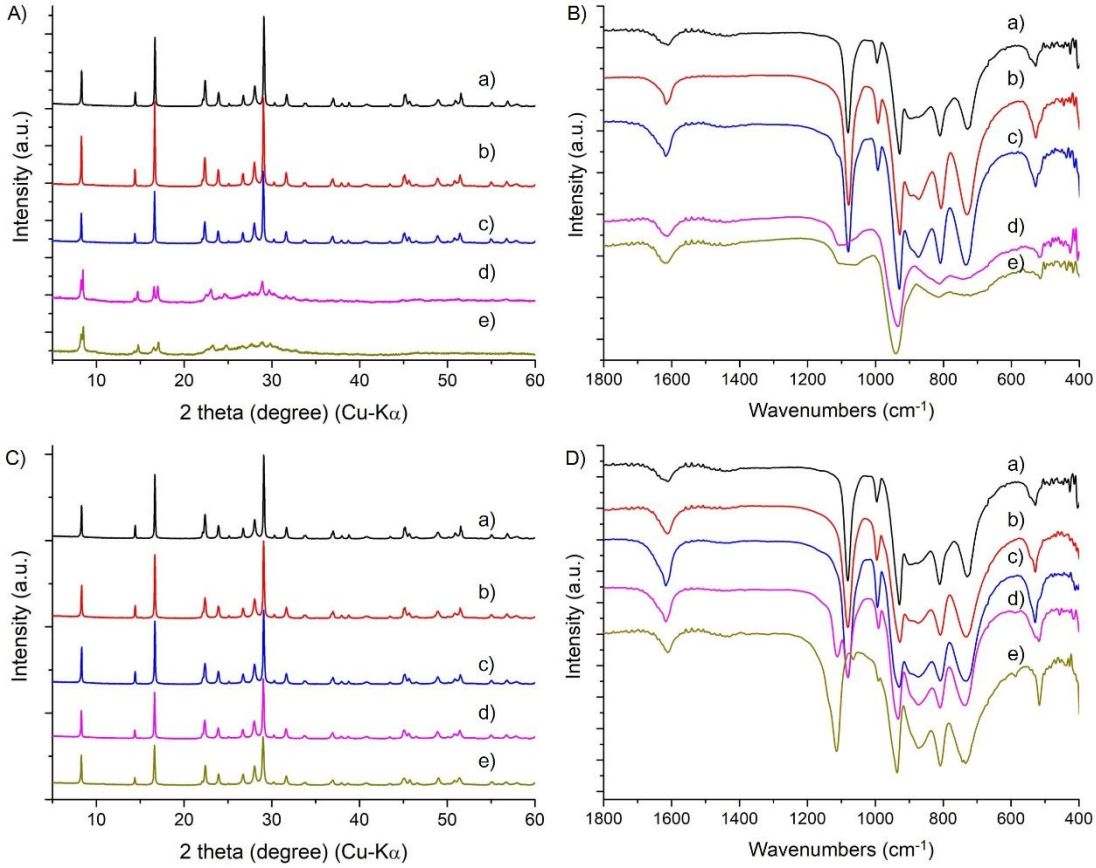

Figure S14. A) XRD patterns and B) FTIR spectra of a) **MoP^{III}O**, b) **MoP^{III}ONC200**, c) **MoP^{III}ONC250**, d) **MoP^{III}ONC300**, and e) **MoP^{III}ONC350.** C) XRD patterns and D) FTIR spectra of a) **MoP^{III}O**, b) **MoP^{III}OAC200**, c) **MoP^{III}OAC250**, d) **MoP^{III}OAC300**, and e) **MoP^{III}OAC350**,

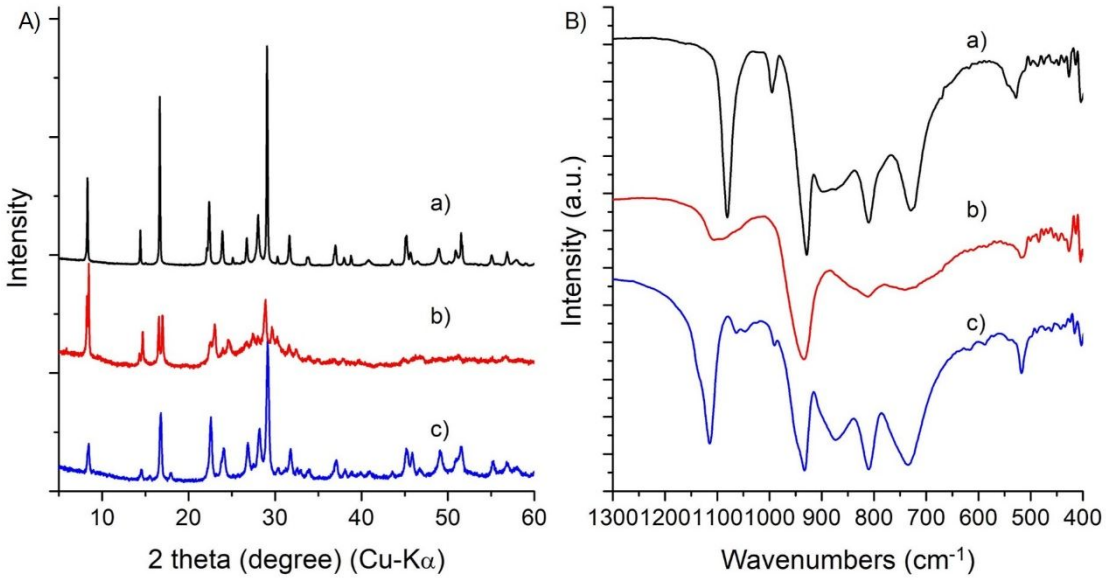

Figure S15. A) XRD patterns and B) FTIR spectra of a) **MoP^{III}O**, b) **MoP^{III}ONC300**, and c) **MoP^{III}ONC300** calcined at 350 ^{o}C in air.

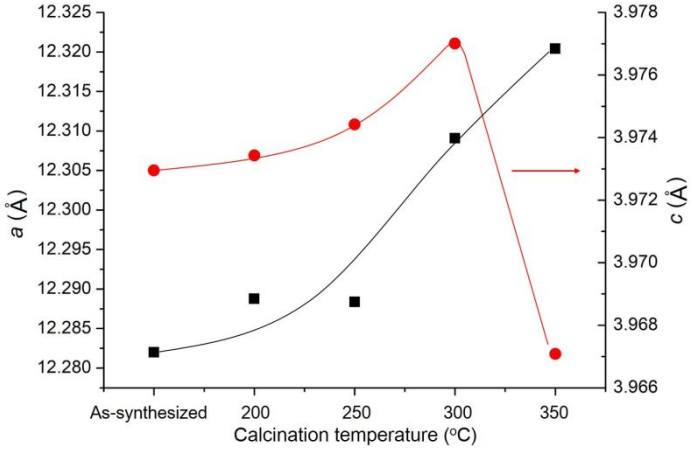

Figure S16. Lattice parameter change of **MoP^{III}O** after calcination in air.

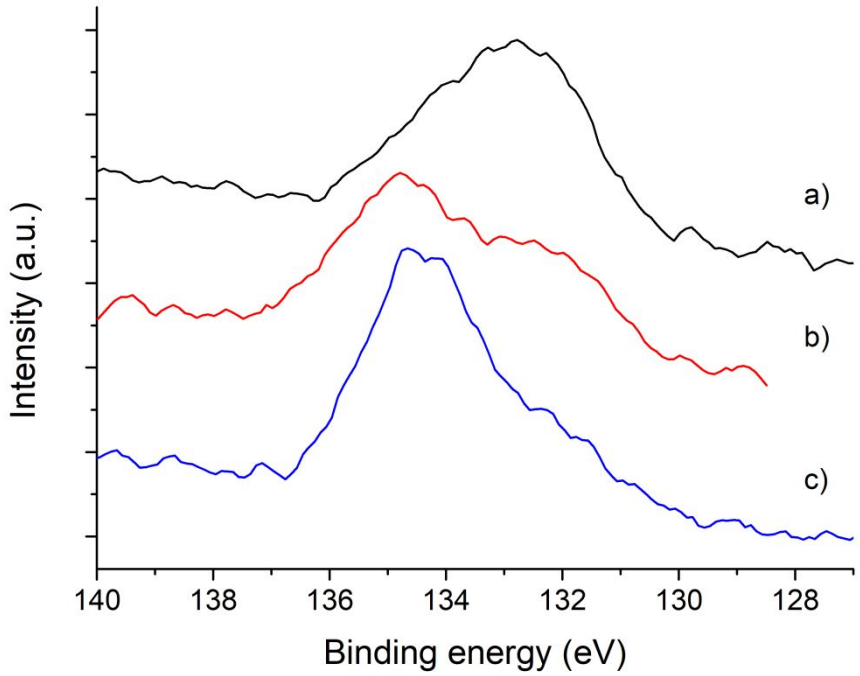

Figure S17. XPS spectra of P for a) **MoP^{III}O**, b) **MoP^{III}OAC300**, and c) **MoP^{III}OAC350**.

Table S1. Synthetic conditions of molecular wires based on Mo and P.

Entry	Mo (M)	P (M)	HCl (c) volume (mL)	Temp. (°C)	Time (h)	**$MoP^{III}O$** [a]	Other phases
	$KOH+MoO_3$	H_3PO_3					
1	0.258	0.0423	1.5	100	8	Y	N
2	0.258	0.0423	1.5	100	0	Y	N
3	0.258	0.0423	1.5	100	1	Y	N
4	0.258	0.0423	1.5	100	2	Y	N
5	0.258	0.0423	1.5	100	4	Y	N
6	0.258	0.0423	1.5	100	6	Y	N
7	0.0645	0.0106	0.375	100	8	Y	N
8	0.129	0.0211	0.75	100	8	Y	N
9	0.516	0.0846	3	100	8	Y	N
10	0.258	0.0423	0.5	100	8	N	N
11	0.258	0.0423	1	100	8	N	N
12	0.258	0.0423	3	100	8	Y	N
13	0.258	0.0423	1.5	25	8	Y	N
14	0.258	0.0423	1.5	60	8	N	Y
15	0.258	0.0423	1.5	135	8	Y	Y
16	0.258	0.0423	1.5	175	8	N	Y
17	Li_2MoO_4	H_3PO_3					
	0.258	0.0423	1.5	100	8	N	N
18	Na_2MoO_4	H_3PO_3					
	0.258	0.0423	1.5	100	8	Y	N
19	$CaMoO_4$	H_3PO_3					
	0.258	0.0423	1.5	100	8	Y	N
20	$KOH+MoO_3$	H_3PO_4					
	0.258	0.0423	1.5	100	8	N	Y
21	$KOH+MoO_3$	$Na_4P_2O_7$					
	0.258	0.0423	1.5	100	8	N	Y

Standard reaction condition: MoO_3 (10.33 mmol) was dissolved in KOH solution (0.52 M, 40 mL), followed by addition of H_3PO_4 (1.7 mmol) and HCl solution (ca. 36 %, 1.5 mL). The solution was heated at 100 °C for 6 hours. [a] Y indicates that the desired **$MoP^{III}O$** was obtained and N indicate that no **$MoP^{III}O$** was not obtained.

Table S2. Crystallographic information and Rietveld refinement parameters for the materials obtained from powder XRD.

	$MoP^{III}O$	**$MoP^{V}O$**
crystal system	trigonal	trigonal
space group	*P*3	*P*3
$a = b$ (Å)	12.27993	12.31228
c (Å)	3.97228	3.96386
agreement factors		
R_{wp}	7.77%	6.88%
$R_{wp(w/o\ bck)}$	15.87%	16.33%
R_p	5.72%	4.99%
pattern parameter		
peak shape function	Pseudo-Voigt	Pseudo-Voigt
FWHM	U = 0.01099, V = -0.00822, W = 0.00156	U = 1.62685, V = -0.14427, W = 0.00930
profile parameter	N_A = 0.81685, N_B = -0.00120	N_A = 1.04393, N_B = -0.01154
line shift		
instrument geometry	Bragg-Brentano	Bragg-Brentano
zero point	-0.03232	-0.12700
shift#1	0.02020	0.10181
shift#2	0.02845	0.05932
correction:		
method	Berar-Baldinozzi	Berar-Baldinozzi
parameter	P1 = -0.05685, P2 = 0.01856, P3 = -0.01826, P4 = -0.06162	P1 = -0.02933, P2 = 0.04043, P3 = 0.01519, P4 = -0.09442
background coefficients	polynomial = 20	polynomial = 100
preferred orientation		
function	March-Dollase	March-Dollase
	R0 = 0.96513	R0 = 0.56710

Table S3. Initial structure of **MoP^{III}O** from charge flipping

X	Y	Z	Intensity	Assignment
0.6667	0.3334	0.5462	26.69	cation
0.8307	0.1605	0.0509	26.15	Mo
0.1714	0.3263	0.0488	18.8	Mo
0.3333	0.6667	0.0444	12.07	cation
0	0	0.8187	13.5	P
0	0	0.2798	11.02	P
0.7363	0.0015	0.0375	4.22	O
0.1435	0.2998	0.5562	3.67	O
0.2615	0.4646	0.0259	3.42	O
0.3333	0.6666	0.7244	4.42	cation
0.3333	0.6667	0.3652	4.3	cation
0.1152	0.0137	0.0472	2.12	O
0.7882	0.1081	0.4111	2.78	O

Table S4. Initial structure of **MoP^{V}O** from charge flipping

X	Y	Z	Intensity	Assignment
0.3409	0.1692	0.1194	15.11	Mo
0.4972	0.0041	0.1196	11.73	Mo
0.3334	0.6667	0.6306	8.78	cation
0	0	0.6104	6.97	cation
0.3334	0.6667	0.1788	6.4	cation
0.4163	0.0861	0.1083	5.89	O
0.6667	0.3333	0.8828	7.29	P
0.6667	0.3333	0.3462	7.05	O
0.6662	0.0911	0.1135	3.28	O
0.1943	0.3884	0.6187	3.72	cation
0.3389	0.3942	0.1282	1.81	O
0.8434	0.0603	0.17	2.02	O
0.3409	0.1692	0.1194	15.11	Mo

Table S5. The structure of **MoP^{III}O** after Rietveld refinement.

Atom	X	Y	Z	U_{iso}	Occupancy
Mo1	-0.15798	-0.32732	0.18113	0.01	1
Mo2	0.16298	-0.17032	0.31253	0.01	1
O3	0.16041	-0.15046	0.79941	0.06	1
O4	-0.16219	-0.31906	0.68048	0.06	1
O5	-0.00111	-0.29964	0.23894	0.06	1
O6	0.30931	-1.7E-4	0.26123	0.06	1
O7	0.24553	-0.25184	0.27017	0.06	1
O8	-0.22973	-0.50574	0.19353	0.06	1
O9	0.13803	-3.9E-4	1.26125	0.06	1
O10	0.53067	-0.00604	0.40613	0.06	0.64
O11	0.33333	0.66667	0.78608	0.06	0.95
O12	0.33333	0.66667	0.7715	0.06	0.65
K13	0.57416	0.50182	0.80877	0.06	0.41
O14	0.50214	0.51696	0.85789	0.06	0.93
P15	0	0	0.38845	0.081	1
O16	0.33333	-0.33333	-0.71331	0.06	0.8
O17	-0.33333	-0.66667	-0.12432	0.06	1

Table S6. The structure of **MoP^{V}O** after Rietveld refinement.

Atom	X	Y	Z	U_{iso}	Occupancy
Mo1	-0.16114	-0.3286	0.21419	0.01	1
Mo2	0.16888	-0.16799	0.34211	0.01	1
O3	0.15999	-0.15287	0.82926	0.06	1
O4	-0.12541	-0.26433	0.72937	0.06	1
O5	-0.00692	-0.31486	0.30534	0.06	1
O6	0.31316	0.00757	0.33426	0.06	1
O7	0.25372	-0.24362	0.2775	0.06	1
O8	-0.22109	-0.50514	0.20086	0.06	1
O9	0.14082	0.00506	1.23494	0.06	1
O10	0.49855	-0.00304	0.32402	0.06	1
K11	0.31377	0.68166	0.7804	0.06	0.92
O12	0.46356	0.50408	0.77143	0.06	0.99
O13	0.29997	0.18343	0.79244	0.06	0.98
O14	0.55896	0.51386	0.94344	0.06	1
O15	0.4209	0.31387	0.80044	0.06	0.89
P16	0	0	1.2437	0.06	1
O17	0	0	0.75724	0.06	0.5
O18	0.33333	-0.33333	-0.85002	0.06	0.76
O19	-0.33333	-0.66667	-0.31071	0.06	1

Table S 7. Bond length and BVS of **$MoP^{III}O$**

Atom 1	Atom 2	Bond length (Å)
Mo1	O6	2.006
Mo1	O9	2.237
Mo1	O4	1.993
Mo1	O4	1.988
Mo1	O8	1.910
Mo1	O5	1.796
	BVS:	5.225
Mo2	O7	1.753
Mo2	O5	1.862
Mo2	O6	1.97
Mo2	O3	1.952
Mo2	O3	2.055
Mo2	O9	2.265
	BVS:	5.543
P15	O9	1.771
	BVS:	R0 was not available

Table S 8. Bond length and BVS of **MoP^{V}O**

Atom 1	Atom 2	Bond length (Å)
Mo1	O6	1.940
Mo1	O9	2.174
Mo1	O4	2.154
Mo1	O4	2.041
Mo1	O8	1.915
Mo1	O5	1.865
	BVS:	4.811
Mo2	O6	1.997
Mo2	O9	2.361
Mo2	O3	2.049
Mo2	O3	1.948
Mo2	O7	1.731
Mo2	O5	2.015
	BVS:	5.119
P16	O9	1.704
P16	O17	2.036
P16	O17	1.928
	BVS:	2.748