Supporting Information for

Control of Polymorphisms and Functions in All-Inorganic Ionic Crystals based on Polyaluminum Hydroxide and Polyoxometalates

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Supporting Information

Table S1. Selected bond distances and angles for **POM6-*N***

Table S2. Selected bond distances and angles for **POM6-*P***

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Figure S4. Thermogravimetry.

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Figure S8. Calibration curves of (a) Na (λ = 589 nm) and (b) K (λ = 766.5 nm) in AAS.

Figure S9. Crystal structure of **Al_{13}-sulfate**.

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Figure S11. Powder XRD patterns of **POM6-*N*** and **POM6-*P*** before and after evacuation.

Figure S12. N_2 adsorption isotherms (77 K).

Figure S13. SEM images.

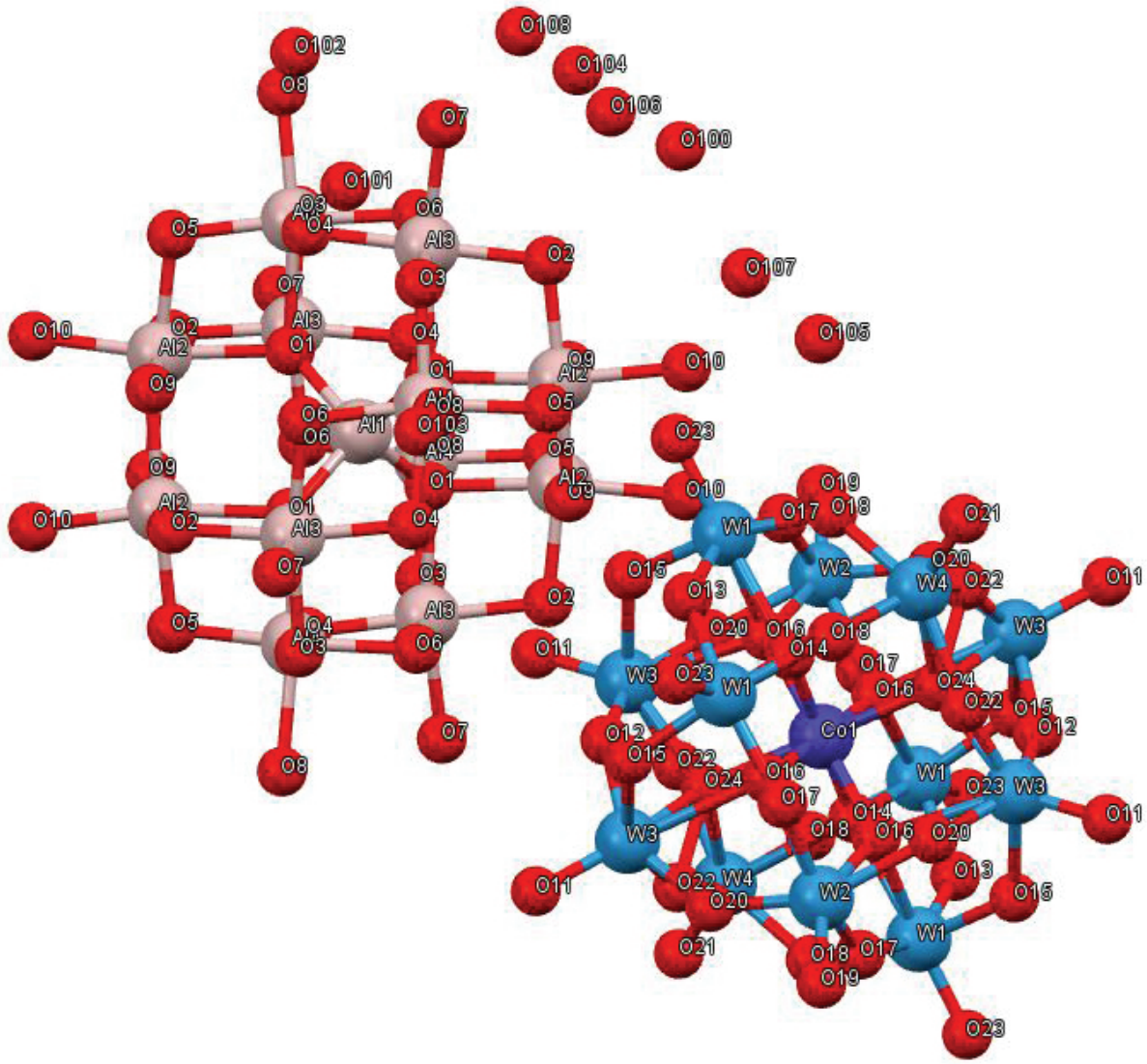
Figure S14. Effects of anions of additives.

Figure S15. Effects of cations of additives.

Table S1. Selected bond distances (Å) and angles (°) for **POM6-*N*** (refer to the atom numbering schemes)

POM6-*N*							
W1-O13	1.85(3)	Al3-O6	1.83(2)	O19-W2-O20	106	O2-Al2-O5	93.8(8)
W1-O14	2.19(3)	Al3-O7	1.96(2)	O20-W2-O20#	147	O2-Al2-O9	172.3(8)
W1-O15	1.87(3)	Al3-O4	1.85(2)	O11-W3-O12	111(2)	O2-Al2-O10	88.9(8)
W1-O16	2.12(3)	Al4-O1	2.03(2)	O11-W3-O15	95(1)	O5-Al2-O10	89.4(8)
W1-O18	1.89(3)	Al4-O3	1.85(2)	O11-W3-O16	148.6(9)	O5-Al2-O9	173.0(8)
W1-O23	1.64(3)	Al4-O4	1.86(2)	O11-W3-O20	104(1)	O9-Al2-O10	93.5(8)
W1-O17	1.90(3)	Al4-O5	1.87(2)	O11-W3-O22	113(1)	O9-Al2-O9#	79.6(7)
W2-O16	2.22	Al4-O8	1.97(2)	O11-W3-O24	146(1)	O1-Al3-O2	81.8(7)
W2-O17	1.78	Al4-O6	1.89(2)	O12-W3-O15	83(2)	O1-Al3-O3	82.5(7)
W2-O19	1.839	O13-W1-O14	59(1)	O12-W3-O16	88(2)	O1-Al3-O6	95.9(7)
W2-O20	1.93	O13-W1-O15	91(1)	O12-W3-O20	145(2)	O1-Al3-O7	169.6(8)
W3-O11	1.65(2)	O13-W1-O16	101(1)	O12-W3-O22	94(2)	O1-Al3-O4	97.4(7)
W3-O12	1.81(6)	O13-W1-O18	89(1)	O12-W3-O24	54(2)	O2-Al3-O3	94.2(8)
W3-O15	2.03(4)	O13-W1-O23	103(2)	O15-W3-O16	62(1)	O2-Al3-O6	93.5(8)
W3-O20	1.76(4)	O13-W1-O17	155(1)	O15-W3-O20	91(2)	O2-Al3-O7	90.5(8)
W3-O22	1.66(3)	O14-W1-O15	102(1)	O15-W3-O22	151(2)	O2-Al3-O4	171.7(9)
W3-O24	2.17(3)	O14-W1-O16	53(1)	O15-W3-O24	110(1)	O3-Al3-O6	171.8(8)
W4-O21	1.66(3)	O14-W1-O18	67(1)	O16-W3-O20	59(1)	O3-Al3-O7	91.1(8)
W4-O22	1.94(3)	O14-W1-O23	156(1)	O16-W3-O22	89(1)	O3-Al3-O4	93.8(8)
W4-O24	2.12(3)	O14-W1-O17	97(1)	O16-W3-O24	65(1)	O6-Al3-O7	91.6(8)
W4-O18	1.90(3)	O15-W1-O16	71(1)	O20-W3-O22	75(2)	O1-Al4-O3	82.6(7)
Co1-O14	1.82	O15-W1-O18	168(1)	O20-W3-O24	97(1)	O1-Al4-O4	96.6(7)
Co1-O16	1.86	O15-W1-O23	91(2)	O22-W3-O24	48(1)	O1-Al4-O5	82.1(7)
Co1-O24	2.06	O15-W1-O17	87(1)	O21-W4-O22	115(1)	O1-Al4-O8	169.4(9)
Al1-O1	1.83	O16-W1-O18	98(1)	O21-W4-O24	148(1)	O1-Al4-O6	95.5(7)
Al2-O1	1.99(2)	O16-W1-O23	150(1)	O22-W4-O24	47(1)	O3-Al4-O4	170.8(9)
Al2-O2	1.85(2)	O16-W1-O17	54(1)	O22-W4-O22#	85(1)	O3-Al4-O5	95.3(8)
Al2-O5	1.87(2)	O18-W1-O23	100(1)	O14-W4-O18	62(1)	O3-Al4-O8	89.3(9)
Al2-O6	1.88(2)	O16-W2-O17	101	O18-W4-O18#	89(1)	O3-Al4-O6	94.3(8)
Al2-O10	1.95(2)	O16-W2-O19	151.7	O1-Al1-O1#	109.2	O4-Al4-O5	93.6(8)
Al2-O9	1.86(2)	O16-W2-O20	62	O1-Al2-O2	82.8(7)	O4-Al4-O8	92.5(9)
Al3-O1	2.01(2)	O16-W2-O16	57	O1-Al2-O5	83.2(7)	O4-Al4-O6	76.6(8)
Al3-O2	1.86(2)	O17-W2-O17#	153	O1-Al2-O9	95.8(7)	O5-Al4-O8	91.8(9)
Al3-O3	1.87(2)	O17-W2-O20	89	O1-Al2-O10	168.5(8)	O5-Al4-O6	169.7(8)

Symmetry Codes: (1) +x, +y, +z, (2) 1/2-x, +y, 1/2+z, (3) +x, 1/2-y, 1/2+z, (4) 1/2-x, 1/2-y, z, (5) +y, +x, +z, (6) 1/2+y, -x, 1/2-z, (7) -y, 1/2+x, 1/2-z, (8) 1/2+y, 1/2+x, -z, (9) -x, -y, -z, (10) -1/2+x, -y, -1/2-z, (11) -x, -1/2+y, -1/2-z, (12) -1/2+x, -1/2+y, -z, (13) -y, -x, -z, (14) -1/2-y, +x, -1/2+z, (15) +y, -1/2-x, -1/2+z, (16) -1/2-y, -1/2-x, +z



Atom numbering scheme for **POM6-*N***

Table S2. Selected bond distances (Å) and angles (°) for **POM6-*P*** (refer to the atom numbering schemes)

POM6-*P*							
W1-O41	1.64	Al1-O9	1.83(2)	Al10-O5	1.91(2)	O55-W2-O61	61(2)
W1-O42	2.24	Al1-O10	1.95(3)	Al10-O6	2.00(3)	O55-W2-O63	95(2)
W1-O58	1.95	Al1-O18	2.00(2)	Al10-O16	1.99(2)	O61-W2-O63	54(1)
W1-O59	1.8	Al1-O32	1.86(2)	Al10-O28	1.85(3)	O45-W3-O49	113(1)
W2-O43	1.70(4)	Al1-O38	1.88(2)	Al10-O39	1.82(2)	O45-W3-O53	148(1)
W2-O49	1.81(3)	Al2-O7	1.90(2)	Al10-O40	1.83(2)	O45-W3-O57	104(2)
W2-O52	1.67(2)	Al2-O35	1.81(2)	Al11-O8	1.92(3)	O45-W3-O58	100(2)
W2-O53	2.30(4)	Al2-O36	2.03(2)	Al11-O9	1.89(2)	O45-W3-O62	111(2)
W2-O55	1.88(4)	Al2-O37	1.88(2)	Al11-O18	2.06(2)	O45-W3-O42	150(1)
W2-O61	2.36(4)	Al2-O39	1.86(2)	Al11-O26	1.87(2)	O49-W3-O53	56(1)
W2-O63	1.74(4)	Al2-O40	1.87(2)	Al11-O27	1.86(2)	O49-W3-O57	74(2)
W3-O45	1.67(2)	Al3-O1	1.95(3)	Al11-O31	1.83(2)	O49-W3-O58	147(2)
W3-O49	1.80(3)	Al3-O2	1.87(2)	Al12-O12	1.88(3)	O49-W3-O62	93(2)
W3-O53	2.23(4)	Al3-O3	1.86(2)	Al12-O19	1.85(2)	O49-W3-O42	87(1)
W3-O57	1.67(4)	Al3-O12	1.84(3)	Al12-O23	1.93(3)	O53-W3-O57	102(2)
W3-O58	1.83(5)	Al3-O25	2.07(2)	Al12-O24	1.86(2)	O53-W3-O58	96(2)
W3-O62	1.76(4)	Al3-O38	1.88(2)	Al12-O25	2.07(2)	O53-W3-O62	47(2)
W3-O42	2.38(4)	Al4-O20	1.82(2)	Al12-O34	1.86(2)	O53-W3-O42	62(1)
W4-O47	1.92(3)	Al4-O21	1.92(2)	Al13-O3	1.86(2)	O57-W3-O58	97(2)
W4-O48	1.58(3)	Al4-O29	1.85(2)	Al13-O4	1.96(3)	O57-W3-O62	145(2)
W4-O54	1.80(4)	Al4-O30	1.85(2)	Al13-O17	1.83(2)	O57-W3-O42	59(2)
W4-O56	1.92(4)	Al4-O36	2.05(2)	Al13-O24	1.83(2)	O58-W3-O62	76(2)
W4-O60	2.22(4)	Al4-O37	1.89(2)	Al13-O25	2.00(2)	O58-W3-O42	62(2)
W4-O61	2.04(3)	Al5-O16	1.83(2)	Al13-O33	1.86(2)	O62-W3-O42	89(2)
W4-O63	1.94(4)	Al5-O18	1.81(2)	O41-W1-O42	153	O47-W4-O48	99(2)
W5-O46	1.65	Al5-O25	1.80(2)	O41-W1-O58	103	O47-W4 O54	87(2)
W5-O54	1.87	Al5-O36	1.84(2)	O41-W1-O59	103	O47-W4-O56	89(2)
W5-O55	1.85	Al6-O18	2.01(2)	O42-W1-O58	91	O47-W4-O60	66(1)
W5-O61	2.28	Al6-O22	1.94(2)	O42-W1-O59	99	O47-W4-O61	101(1)
W5-O54	1.87	Al6-O29	1.86(2)	O42-W1-O42#	54	O47-W4-O63	156(1)
W5-O55	1.85	Al6-O30	1.88(2)	O58-W1-O59	93	O48-W4-O54	102(2)
W5-O61	2.28	Al6-O31	1.83(2)	O58-W1-O58#	153	O48-W4-O56	106(2)
W6-O47	1.90(3)	Al6-O32	1.91(2)	O59-W1-O59#	153	O48-W4-O60	157(2)
W6-O50	1.67(3)	Al7-O5	1.85(3)	O43-W2-O49	92(2)	O48-W4-O61	148(2)
W6-O51	1.95(4)	Al7-O14	1.82(2)	O43-W2-O52	109(2)	O48-W4-O63	105(2)
W6-O60	2.33(4)	Al7-O15	1.94(2)	O43-W2-O53	49(2)	O54-W4-O56	152(2)
W6-O43	1.92(4)	Al7-O16	2.04(2)	O43-W2-O55	78(2)	O54-W4-O60	95(2)
W6-O53	2.07(4)	Al7-O17	1.84(2)	O43-W2-O61	96(2)	O54-W4-O61	55(2)
W6-O62	1.86(4)	Al7-O33	1.83(2)	O43-W2-O63	147(2)	O54-W4-O63	89(2)
W7-O44	1.65(4)	Al8-O11	1.97(3)	O49-W2-O52	114(1)	O56-W4-O60	59(2)
W7-O51	1.88(4)	Al8-O19	1.88(2)	O49-W2-O53	55(1)	O56-W4-O61	99(2)
W7-O56	1.80(4)	Al8-O20	1.84(2)	O49-W2-O55	143(2)	O56-W4-O63	83(2)
W7-O57	2.02(4)	Al8-O34	1.87(2)	O49-W2-O61	86(1)	O60-W4-O61	55(1)
W7-O59	1.91(4)	Al8-O35	1.87(2)	O49-W2-O63	75(2)	O60-W4-O63	91(1)
W7-O60	2.22(4)	Al8-O36	2.01(2)	O52-W2-O53	149(1)	O61-W4-O63	58(1)
W7-O42	2.16(4)	Al9-O13	1.96(3)	O52-W2-O55	103(2)	O46-W5-O54	107
Co1-O42	1.84	Al9-O14	1.87(2)	O52-W2-O61	147(1)	O46-W5-O55	105
Co1-O53	1.97	Al9-O16	1.99(2)	O52-W2-O63	104(1)	O46-W5-O61	150
Co1-O60	1.84	Al9-O26	1.89(2)	O53-W2-O55	94(2)	O46-W5-O54	107
Co1-O61	1.91	Al9-O27	1.82(2)	O53-W2-O61	65(1)	O46-W5-O55	105
Al1-O2	1.88(2)	Al9-O28	1.87(3)	O53-W2-O63	100(2)	O46-W5-O61	150

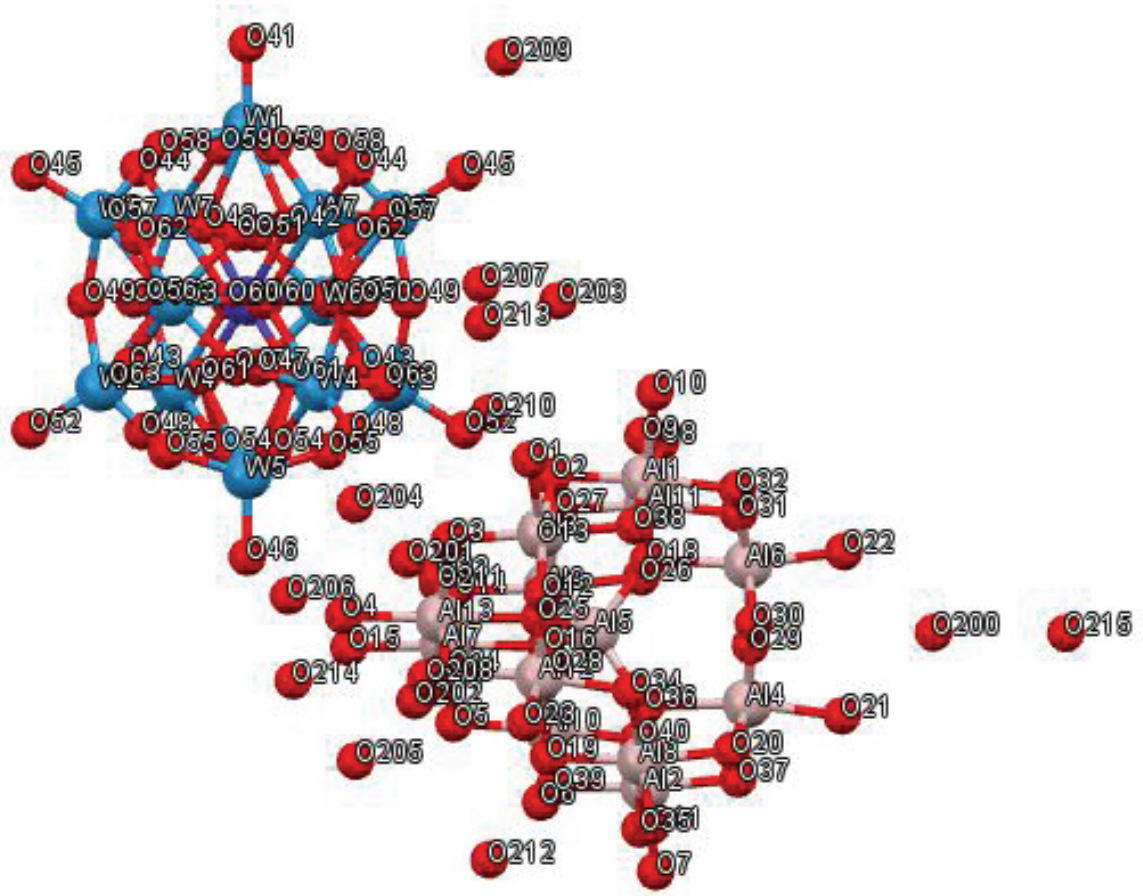
Table S2. Continued (1)

POM6-*P*							
O54-W5-O55	92	O56-W7-O59	156(2)	O12-Al3-O25	83(1)	O16-Al7-O17	96(1)
O54-W5-O61	50	O56-W7-O60	60(2)	O12-Al3-O38	93(1)	O16-Al7-O33	95(1)
O54-W5-O54#	146	O56-W7-O42	101(2)	O25-Al3-O38	94.4(9)	O17-Al7-O33	76(1)
O54-W5-O55	79	O57-W7-O59	88(2)	O20-Al4-O21	93.9(9)	O11-Al8-O19	93(1)
O54-W5-O61	98	O57-W7-O60	92(2)	O20-Al4-O29	169(1)	O11-Al8-O20	91(1)
O55-W5-O61	63	O57-W7-O42	59(2)	O20-Al4-O30	93.3(9)	O11-Al8-O34	92(1)
O55-W5-O55	150	O59-W7-O60	97(2)	O20-Al4-O36	80.0(8)	O11-Al8-O35	91(1)
O55-W5-O61	90	O59-W7-O42	56(2)	O20-Al4-O37	93.0(9)	O11-Al8-O36	168(1)
O61-W5-O55	90	O60-W7-O42	55(1)	O21-Al4-O29	94.6(9)	O19-Al8-O20	171(1)
O61-W5-O61#	61	O2-Al1-O9	92.4(9)	O21-Al4-O30	91.6(9)	O19-Al8-O34	77.9(9)
O54-W5-O55	92	O2-Al1-O10	92(1)	O21-Al4-O36	171.1(9)	O19-Al8-O35	95.0(9)
O54-W5-O61	50	O2-Al1-O18	96.0(9)	O21-Al4-O37	91.2(9)	O19-Al8-O36	96.4(9)
O55-W5-O61	63	O2-Al1-O32	173(1)	O29-Al4-O30	80.1(9)	O20-Al8-O34	94.2(9)
O47-W6-O50	99(1)	O2-Al1-O38	79.6(9)	O29-Al4-O36	92.2(9)	O20-Al8-O35	92.7(9)
O47-W6-O51	89(2)	O9-Al1-O10	88(1)	O29-Al4-O37	93.2(9)	O20-Al8-O36	80.5(9)
O47-W6-O60	64(1)	O9-Al1-O18	83.2(9)	O30-Al4-O36	95.1(9)	O34-Al8-O35	172(1)
O47-W6-O43	86(2)	O9-Al1-O32	95(1)	O30-Al4-O37	173(1)	O34-Al8-O36	97.4(9)
O47-W6-O53	104(1)	O9-Al1-O38	172(1)	O36-Al4-O37	82.7(8)	O35-Al8-O36	80.7(8)
O47-W6-O62	148(2)	O10-Al1-O18	169(1)	O16-Al5-O18	110(1)	O13-Al9-O14	90(1)
O50-W6-O51	98(2)	O10-Al1-O32	90(1)	O16-Al5-O25	109(1)	O13-Al9-O16	171(1)
O50-W6-O60	152(1)	O10-Al1-O38	95(1)	O16-Al5-O36	108(1)	O13-Al9-O26	93(1)
O50-W6-O43	112(2)	O18-Al1-O32	82.9(9)	O18-Al5-O25	110.0(9)	O13-Al9-O27	91(1)
O50-W6-O53	150(1)	O18-Al1-O38	94.7(9)	O18-Al5-O36	109.2(9)	O13-Al9-O28	92(1)
O50-W6-O62	112(2)	O32-Al1-O38	93(1)	O25-Al5-O36	109.9(9)	O14-Al9-O16	83(1)
O51-W6-O60	62(2)	O7-Al2-O35	89(1)	O18-Al6-O22	170(1)	O14-Al9-O26	173(1)
O51-W6-O43	150(2)	O7-Al2-O36	168(1)	O18-Al6-O29	93.6(9)	O14-Al9-O27	95(1)
O51-W6-O53	100(2)	O7-Al2-O37	89.8(9)	O18-Al6-O30	94.7(9)	O14-Al9-O28	93(1)
O51-W6-O62	82(2)	O7-Al2-O39	92(1)	O18-Al6-O31	82.6(9)	O16-Al9-O26	95(1)
O60-W6-O43	89(2)	O7-Al2-O40	95(1)	O18-Al6-O32	81.4(9)	O16-Al9-O27	96(1)
O60-W6-O53	57(1)	O35-Al2-O36	81.6(9)	O22Al6-O29	95(1)	O16-Al9-O28	83(1)
O60-W6-O62	86(2)	O35-Al2-O37	92.7(9)	O22-Al6-O30	92(1)	O26-Al9-O27	78(1)
O43-W6-O53	52(2)	O35-Al2-O39	95.8(9)	O22-Al6-O31	92(1)	O26-Al9-O28	94(1)
O43-W6-O62	87(2)	O35-Al2-O40	172(1)	O22-Al6-O32	91(1)	O27-Al9-O28	172(1)
O53-W6-O62	49(2)	O36-Al2-O37	83.6(8)	O29-Al6-O30	79.0(9)	O5-Al10-O6	91(1)
O44-W7-O51	101(2)	O36-Al2-O39	96.1(9)	O29-Al6-O31	95.8(9)	O5-Al10-O16	84(1)
O44-W7-O56	104(2)	O36-Al2-O40	95.2(9)	O29-Al6-O32	170(1)	O5-Al10-O28	93(1)
O43-W6-O53	52(2)	O37-Al2-O39	171(1)	O30-Al6-O31	174(1)	O5-Al10-O39	93(1)
O43-W6-O62	87(2)	O37-Al2-O40	94.6(9)	O30-Al6-O32	92(1)	O5-Al10-O40	172(1)
O53-W6-O62	49(2)	O39-Al2-O40	76.9(9)	O31-Al6-O32	92(1)	O6-Al10-O16	169(1)
O44-W7-O51	101(2)	O1-Al3-O2	93(1)	O5-Al7-O14	95(1)	O6-Al10-O28	88(1)
O44-W7-O56	104(2)	O1-Al3-O3	92(1)	O5-Al7-O15	91(1)	O6-Al10-O39	92(1)
O44-W7-O57	103(2)	O1-Al3-O12	92(1)	O5-Al7-O16	83(1)	O6-Al10-O40	92(1)
O44-W7-O59	100(2)	O1-Al3-O25	170(1)	O5-Al7-O17	95(1)	O16-Al10-O28	83(1)
O44-W7-O60	158(2)	O1-Al3-O38	94(1)	O5-Al7-O33	171(1)	O16-Al10-O39	97(1)
O44-W7-O42	148(2)	O2-Al3-O3	93(1)	O14-Al7-O15	92(1)	O16-Al10-O40	95(1)
O51-W7-O56	90(2)	O2-Al3-O12	172(1)	O14-Al7-O16	83(1)	O28-Al10-O39	174(1)
O51-W7-O57	156(2)	O2-Al3-O25	93.7(9)	O14-Al7-O17	170(1)	O28-Al10-O40	95(1)
O51-W7-O59	87(2)	O2-Al3-O38	80.0(9)	O14-Al7-O33	94(1)	O39-Al10-O40	79.1(9)
O51-W7-O60	65(2)	O3-Al3-O12	94(1)	O15-Al7-O16	172(1)	O8-Al11-O9	92(1)
O51-W7-O42	99(2)	O3-Al3-O25	81.0(9)	O15-Al7-O17	91(1)	O8-Al11-O18	169(1)
O56-W7-O57	85(2)	O3-Al3-O38	172(1)	O15-Al7-O33	91(1)	O8-Al11-O26	93(1)

Table S2. Continued (2)

POM6-*P*							
O8-Al11-O27	93(1)	O27-Al11-O31	171(1)	O23-Al12-O25	169(1)	O4-Al13-O17	92(1)
O8-Al11-O31	92(1)	O12-Al12-O19	172(1)	O23-Al12-O34	92(1)	O4-Al13-O24	91(1)
O9-Al11-O18	80.1(9)	O12-Al12-O23	92(1)	O24-Al12-O25	81.0(9)	O4-Al13-O25	172(1)
O9-Al11-O26	171(1)	O12-Al12-O24	92(1)	O24-Al12-O34	174(1)	O4-Al13-O33	93(1)
O9-Al11-O27	95(1)	O12-Al12-O25	82(1)	O25-Al12-O34	97.6(9)	O17-Al13-O24	96(1)
O9-Al11-O31	93.0(9)	O12-Al12-O34	94(1)	O3-Al13-O4	92(1)	O17-Al13-O25	94(1)
O18-Al11-O26	95.9(9)	O19-Al12-O23	92(1)	O3-Al13-O17	170(1)	O17-Al13-O33	76(1)
O18-Al11-O27	94.8(9)	O19-Al12-O24	95(1)	O3-Al13-O24	93(1)	O24-Al13-O25	84(1)
O18-Al11-O31	81.3(8)	O19-Al12-O25	95.7(9)	O3-Al13-O25	83.0(9)	O24-Al13-O33	171(1)
O26-Al11-O27	77(1)	O19-Al12-O34	78.7(9)	O3-Al13-O33	95(1)	O25-Al13-O33	93.1(9)
O26-Al11-O31	95(1)	O23-Al12-O24	90(1)				

Symmetry Codes: (1) x, y, z, (2) x, -y, -z+1/2, (3) -x+1/2, y, -z, (4) -x, -y+1/2, z, (5) x+1/2, y+1/2, z+1/2, (6) x+1/2, -y+1/2, -z+1, (7) -x+1, y+1/2, -z+1/2, (8) -x+1/2, -y+1, z+1/2, (9) -x, -y, -z, (10) -x, y, z-1/2, (11) x-1/2, -y, z, (12) x, y-1/2, -z, (13) -x+1/2, -y+1/2, -z+1/2, (14) -x+1/2, y+1/2, z, (15) x, -y+1/2, z+1/2, (16) x+1/2, y, -z+1/2



Atom numbering scheme for **POM6-*P*** (disordered POM is omitted for the clarity)

Table S3. Possible hydrogen bonds (O-O < 3.0 Å) and their distances (Å) in **POM6-*N*** and **POM6-*P*.** Ot and Ob stands for the terminal and bridging oxygen, respectively, of the POM.

POM6-*N*		**POM6-*P***	
Between POM and Al_{13}		Between POM and Al_{13}	
O10(POM, Ot)-O19(Al_{13}, OH_2) × 4	2.833	O46(POM, Ot)-O4(Al_{13}, OH_2) × 1	2.828
O11(POM, Ot)-O4(Al_{13}, OH) × 4	2.818	O41(POM, Ot)-O15(Al_{13}, OH_2) × 1	2.869
O11(POM, Ot)-O6(Al_{13}, OH) × 4	2.793	O45(POM, Ot)-O39(Al_{13}, OH) × 1	2.749
		O45(POM, Ot)-O19(Al_{13}, OH) × 1	2.804
		O52(POM, Ot)-O2(Al_{13}, OH) × 1	2.782
		O52(POM, Ot)-O27(Al_{13}, OH) × 1	2.835
		Between Al_{13} and Al_{13}	
		O32(Al_{13}, OH)-O22(Al_{13}, OH_2) × 2	2.660
		O37(Al_{13}, OH)-O21(Al_{13}, OH_2) × 2	2.691
		Between disordered POM and Al_{13}	
		O28(Al_{13}, OH)-O68(POM, Ot) × 1	2.863
		O28(Al_{13}, OH)-O70(POM, Ob) × 1	2.790
		O31(Al_{13}, OH)-O76(POM, Ot) × 1	2.731
		O29(Al_{13},OH)-O78(POM, Ob)× 1	2.794
		O13(Al_{13}, OH_2)-O85(POM, Ot) × 1	2.832
		O37(Al_{13}, OH)-O89(POM, Ot) × 1	2.643
		O6(Al_{13}, OH_2)-O93(POM, Ot) × 1	2.963
		O7(Al_{13}, OH_2)-O94(POM, Ob) × 1	2.815
		O20(Al_{13}, OH)-O88(POM, Ot) × 2	2.771

Table S4. Pinacol to pinacolone rearrangement over various solid catalysts and conditions

Catalyst	Temp [K]	Solvent	Time [h]	Conv. [%]	Selec.[a] [%]	Reference
H-ZSM-5	393	-	4	80	90	1
Ca-HY	393	-	4	70	88	1
La-HY	393	-	4	68	82	1
Nafion-H	448	-	0.6	92	75	2
Fe-AlPO	383	Toluene	3	69	81	3
Ni-AlPO	383	Toluene	3	50	80	3
Cu-AlPO	383	Toluene	3	54	80	3
Fe-ZSM-5	383	Toluene	6	0	-	4
Fe-MCM-41	383	Toluene	6	33	64	4
MCM-41	383	Toluene	6	13	14	4
Phosphonate-polysilsesquioxane	413	-	12	-	80[d]	5
Fe-Na-montmorillonite[b]	398	-	1	34	100	6
Al_{13}-montmorillonite[b]	398	-	1	100	100	6
Fe-Al_{13}-montmorillonite[b]	398	-	1	100	100	6
None	573-723	scH_2O	-	100	100	8
$H_4SiMo_{12}O_{40}$	423	-	1	100	44[c]	9
$H_3PMo_{12}O_{40}$	423	-	1	100	43[c]	9
$H_4SiW_{12}O_{40}$	423	-	1	100	71	9
$H_3PW_{12}O_{40}$	423	-	1	100	78	9
$[Cr_3O(OOCPh)_6(H_2O)]_4[SiW_{12}O_{40}]$	373	Toluene	12	100	79	10
$[Fe_3O(OOCPh)_6(H_2O)]_4[SiW_{12}O_{40}]$	373	Toluene	6	100	80	10
Al_2O_3	473	-	1	62	44	11
Aluminum phosphate	473	-	1	62	46	11
SiO_2	473	-	1	34	42	11
ZrO_2	473	-	1	31	44	11

a: by-product is 2,3-dimethyl-1,3-butadiene. b: catalyst : reactant = 5 : 1. c: by-product is acetone.

(1) *J. Mol. Catal.* **1994**, *87*, 39. (2) *Tetrahedron* **1994**, *50*, 8195. (3) *Microporous Mesoporous Mater*. **1998**, *21*, 505. (4) *J. Mol. Catal. A: Chemical* **2002**, *181*, 189. (5) *Chem. Commun.* **2001**, 67. (6) *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 1591. (7) *J. Am. Chem. Soc.* **2002**, *124*, 5962. (8) *J. Am. Chem. Soc.* **2000**, *122*, 1908. (9) *J. Mol. Catal. A: Chemical* **1996**, *107*, 305. (10) *Inorg. Chem.* **2012**, *51*, 775. (11) *Indian J. Chem. Technol.* **2005**, *12*, 447.

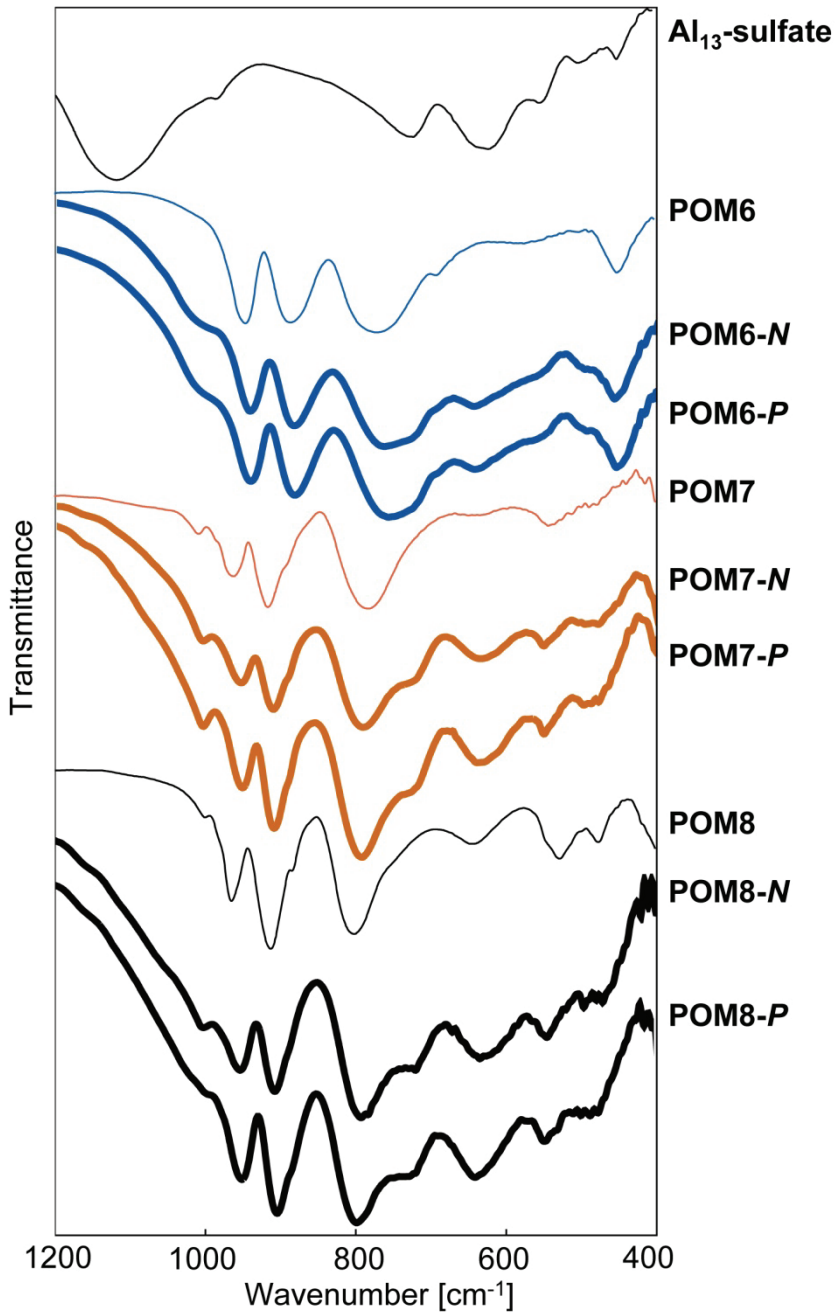


Figure S1. IR spectra of **Al_{13}-POMs** and the raw materials. **POM6-*N***: 941 ν(W=O), 882 ν(W-Oc-W), 760 ν(W-Oe-W, 641 ν(Al-OH_{Oh}), 553 ν(Al-OH_{Oh}), 492 ν(Al-OH_{2Oh}). **POM6-*P***: 940 ν(W=O), 881 ν(W-Oc-W), 755 ν(W-Oe-W), 640 ν(Al-OH_{Oh}), 540 ν(Al-OH_{Oh}), 491 ν(Al-OH_{2Oh}). **POM7-*N***: 948 ν(W=O), 904 ν(Si-O), 788 ν(W-Oe-W), 632 ν(Al-OH_{Oh}), 548 ν(Al-OH_{Oh}), 493 ν(Al-OH_{2Oh}). **POM7-*P***: 952 ν(W=O), 909 ν(Si-O), 792 ν(W-Oe-W), 637 ν(Al-OH_{Oh}), 548 ν(Al-OH_{Oh}), 494 ν(Al-OH_{2Oh}). **POM8-*N***: 954 ν(W=O), 907 ν(Si-O), 791 ν(W-Oe-W), 634 ν(Al-OH_{Oh}), 544 ν(Al-OH_{Oh}), 495 ν(Al-OH_{2Oh}). **POM8-*P***: 950 ν(W=O), 903 ν(Si-O), 796 ν(W-Oe-W), 637 ν(Al-OH_{Oh}), 544 ν(Al-OH_{Oh}), 496 ν(Al-OH_{2Oh}).

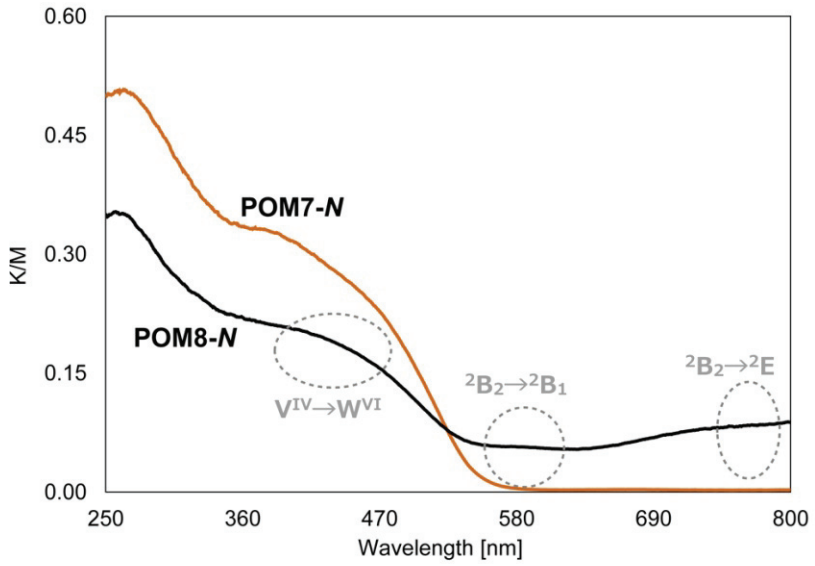


Figure S2. Diffuse-reflectance UV-*vis* spectra of **POM7-*N*** and **POM8-*N***.

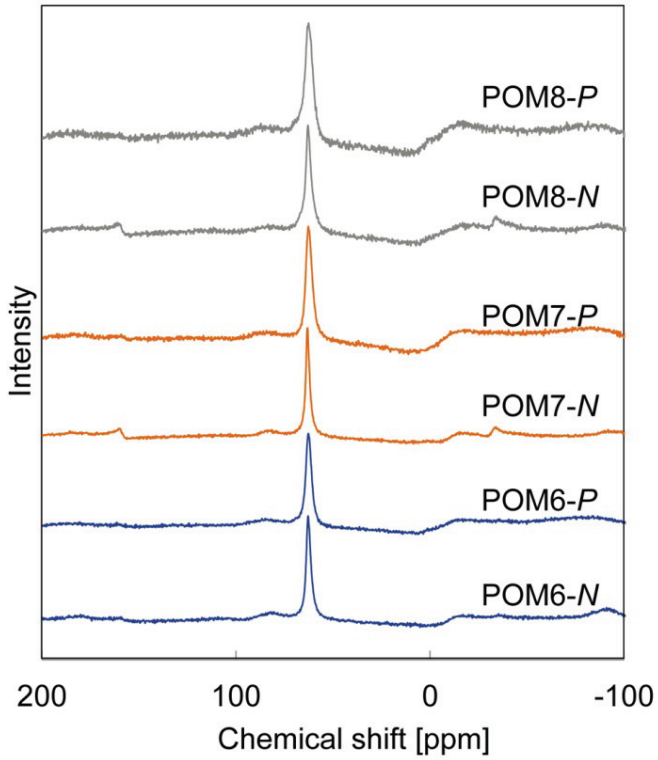


Figure S3. Solid state ^{27}Al-MASNMR spectra of **Al_{13}-POMs**. The signal at 63 ppm can be reasonably assigned to [AlO_4] of **Al_{13}**.[S1] The signal for [AlO_6] is broadened beyond detection due to the distortion of the octahedra.[S1]

(S1) S. M. Bradley, R. A. Kydd, C. A. Fyfe, *Inorg. Chem.* **1992**, *31*, 1181-1185.

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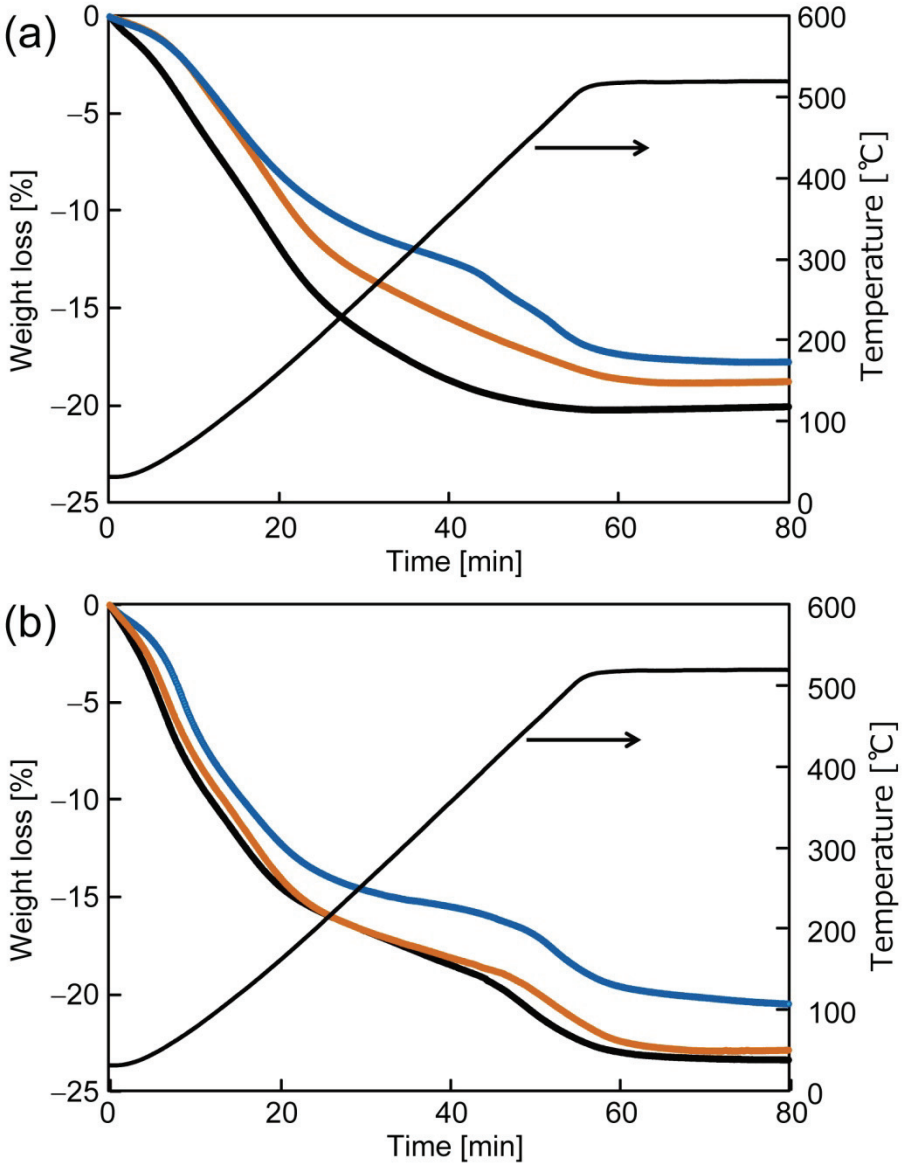

Figure S4. Thermogravimetry of (a) needle-type and (b) plate-type crystals under dry N_2 flow (100 mL min^{-1}) in the temperature range of rt to 500 °C (10 °C min^{-1}). Blue, orange, and black lines show the data for **POM6-N** and ***P***, **POM7-*N*** and ***P***, and **POM8-*N*** and ***P***, respectively. The weight losses after the measurements were 17.7% (**POM6-*N***), 18.8% (**POM7-*N***), 20.0% (**POM8-*N***), 20.5% (**POM6-*P***), 22.8% (**POM7-*P***), and 23.4% (**POM8-*P***). Assuming that the water of crystallization and water molecules coordinated to $\mathbf{Al_{13}}$ are lost after the measurements, the amounts of water of crystallization were determined as $34H_2O$ (**POM6-*N***), $32H_2O$ (**POM7-*N***), $35H_2O$ (**POM8-*N***), $42H_2O$ (**POM6-*P***), $43H_2O$ (**POM7-*P***), and $45H_2O$ (**POM8-*P***).

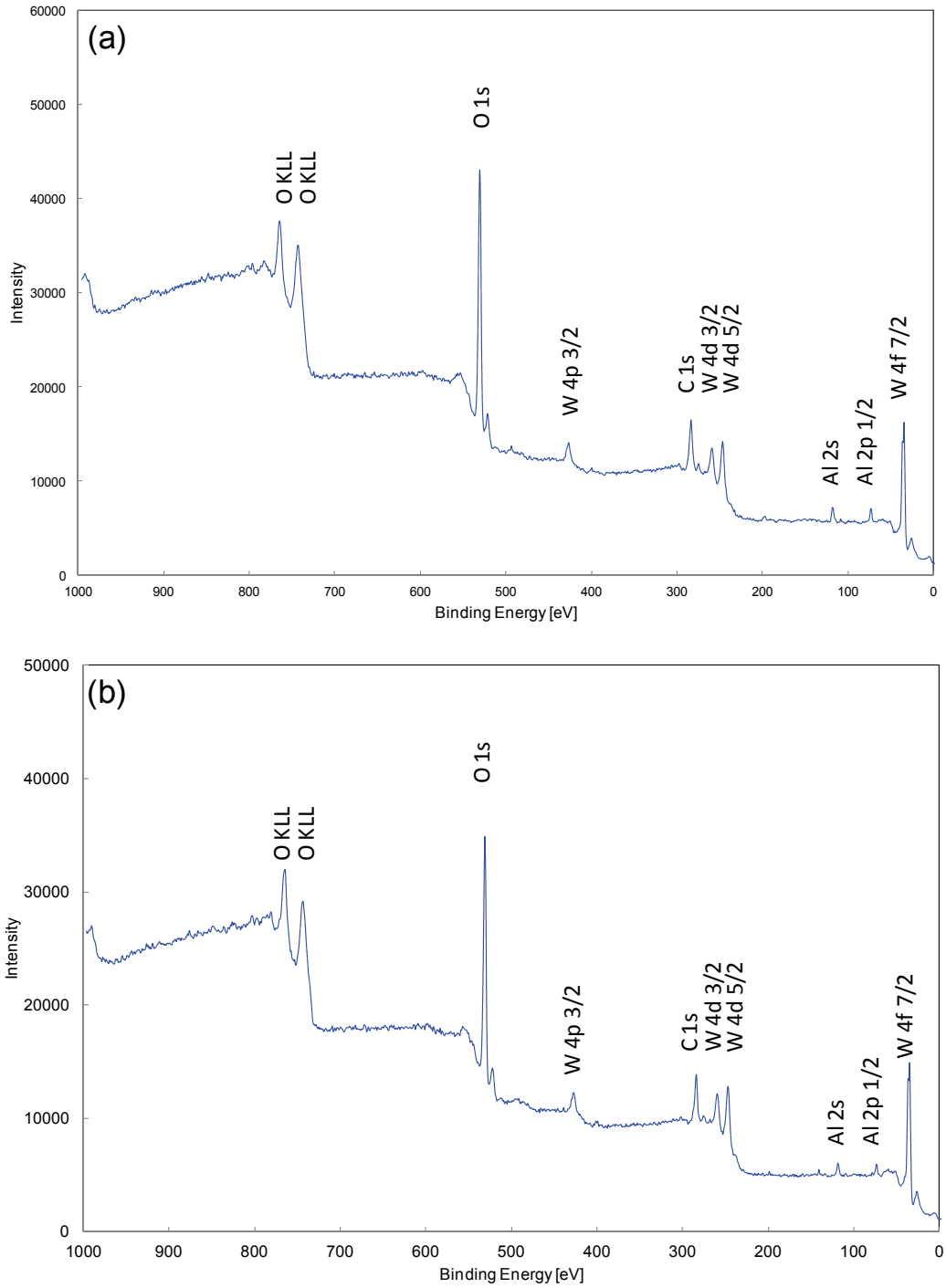

Figure S5. Wide scan XPS spectra of (a) **POM6-*N*** and (b) **POM6-*P***. Note that Cl 2p signals (around 200 eV) are absent in the spectra suggesting that Cl^- does not exist in the compounds to compensate the surplus cation charge. In addition, ion-exchange (IonPac® AS12A anion-exchange column) chromatography measurements (Thermo Fisher Scientific) showed that the amount of Cl in **POM6-*N*** and **POM6-*P*** were less than 0.05 wt%.

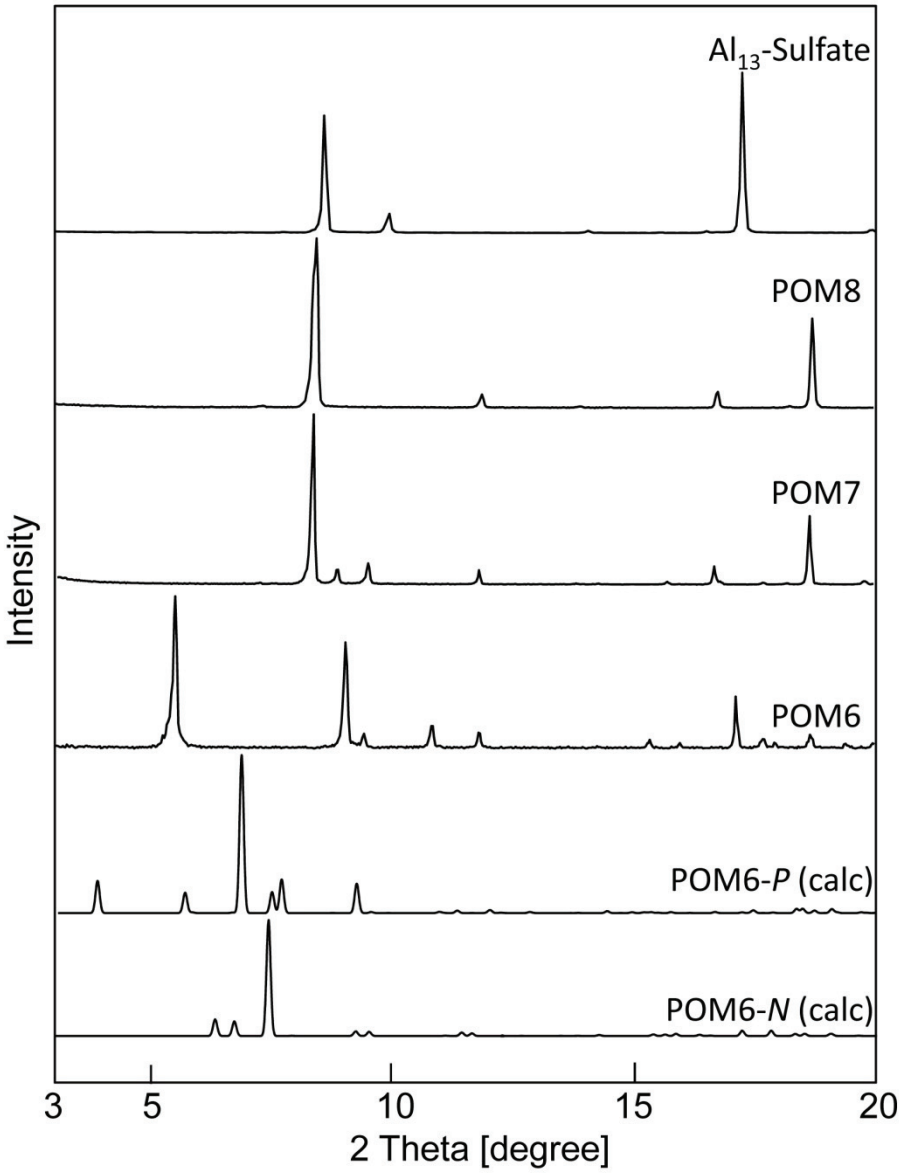

Figure S6. Powder XRD patterns of **Al_{13}-POMs** (**POM6-*P*** and **POM6-*N***) and the raw materials.

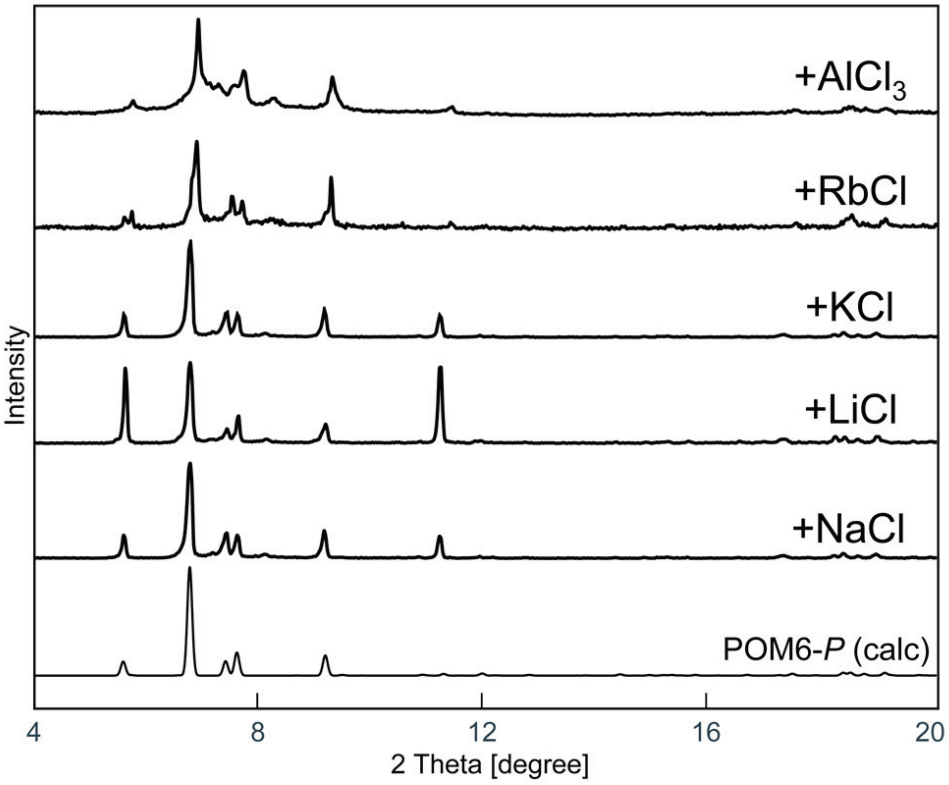

Figure S7. Powder XRD patterns of **POM6-*P*** synthesized with additives other than NaCl.

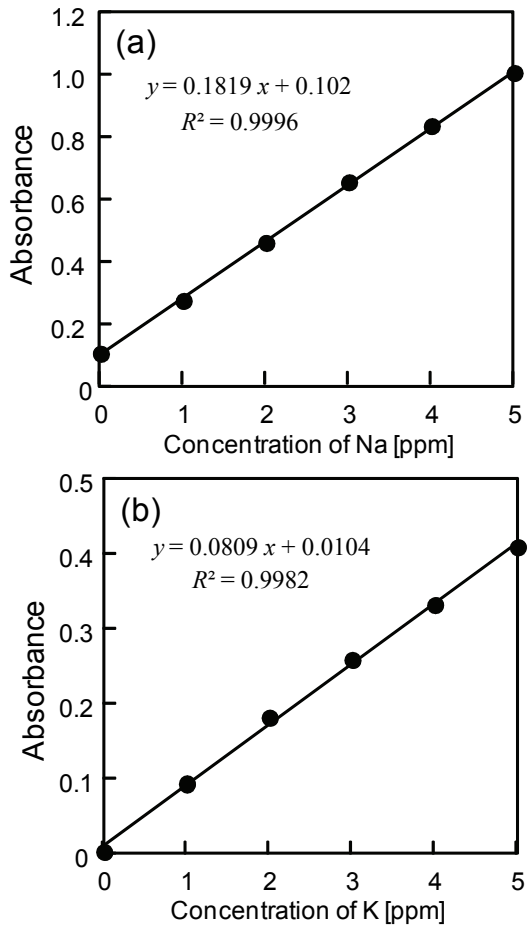

Figure S8. Calibration curves of (a) Na (λ = 589 nm) and (b) K (λ = 766.5 nm) in AAS. Absorbance values at λ = 589 nm were 0.0301 (**POM6-*N***), 0.0295 (**POM6-*P***), 0.0586 (**POM7-*N***), 0.0836 (**POM7-*P***), 0.0831 (**POM8-*N***), and 0.0829 (**POM8-*P***). Absorbance values at λ = 766.5 nm were 0.0038 (**POM6-*N***), 0.0078 (**POM6-*P***), 0.0076 (**POM7-*N***), 0.0005 (**POM7-*P***), 0.0029 (**POM8-*N***), and 0.0036 (**POM8-*P***). If one Na^+ or K^+ instead of proton (H^+) were contained in **POM8-*N*** or **POM8-*P***, the concentration of Na or K would be 0.5 ppm and detectable. These results show that the ionic crystals do not contain these elements.

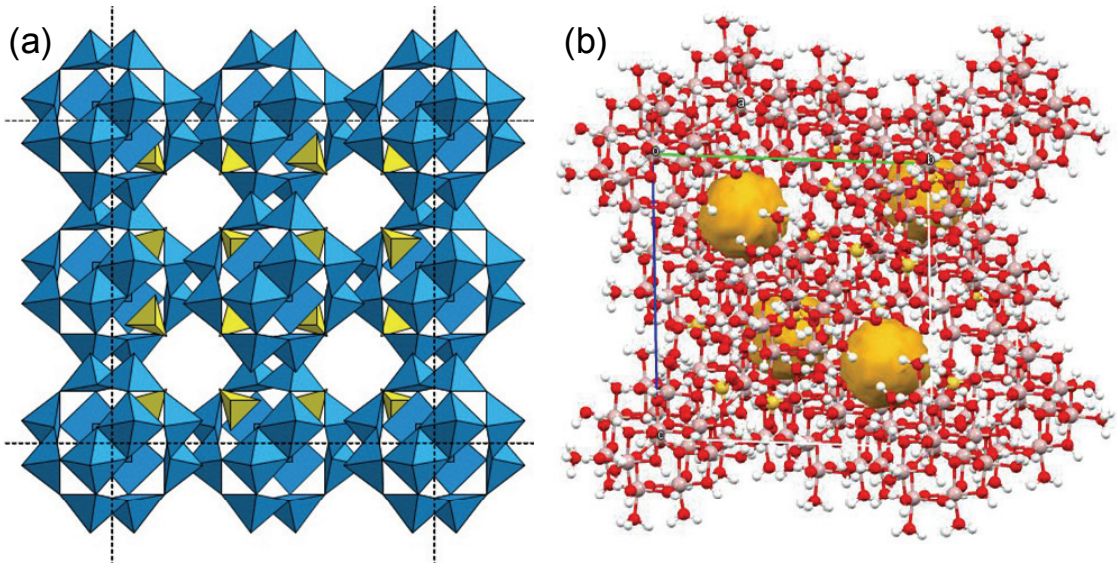

Figure S9. Crystal structure of **Al_{13}-sulfate** (cubic *F*23 (#196), *a* = 17.7686(19)) (a) Polyhedral representation and (b) void analysis (probe diameter 4 Å, grid spacing 0.5 Å) of the unit cell. Light blue and yellow polyhedra show the [AlO_6] and [SO_4] units, respectively. *Note that the voids are closed.*

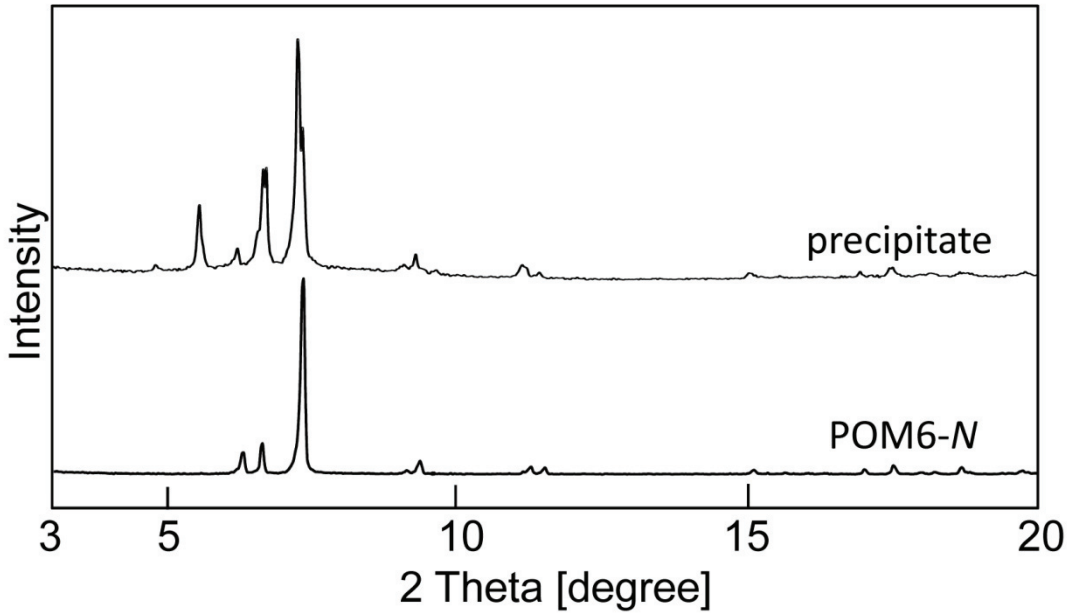

Figure S10. Powder XRD patterns of the precipitate and the needle crystal (**POM6-*N***). The precipitate was collected immediately (< 1 min) from the aqueous solution after mixing the solution of $\mathbf{Al_{13}}$ with POM.

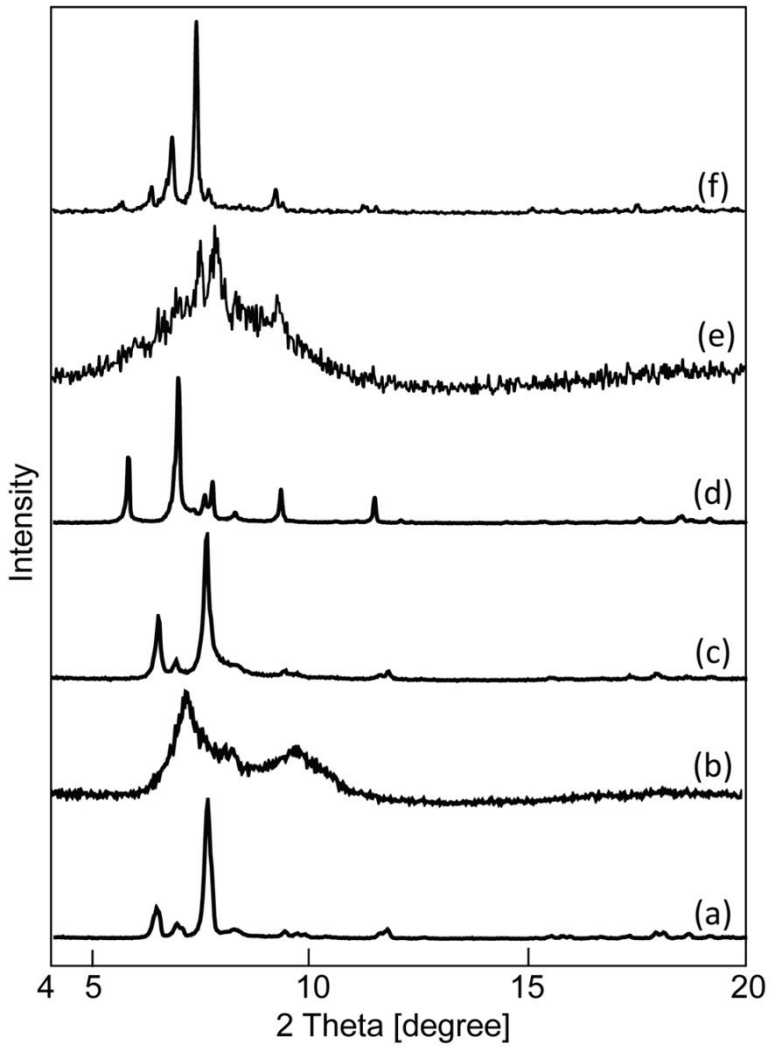

Figure S11. Powder XRD patterns of **POM6-*N*** (a) as synthesized, (b) after evacuation at rt, and (c) after exposure of (b) to water vapor. Powder XRD patterns of **POM6-*P*** (d) as synthesized, (e) after evacuation at rt, and (f) after exposure of (e) to water vapor. Note that the crystal structures can be restored by exposure to water vapor.

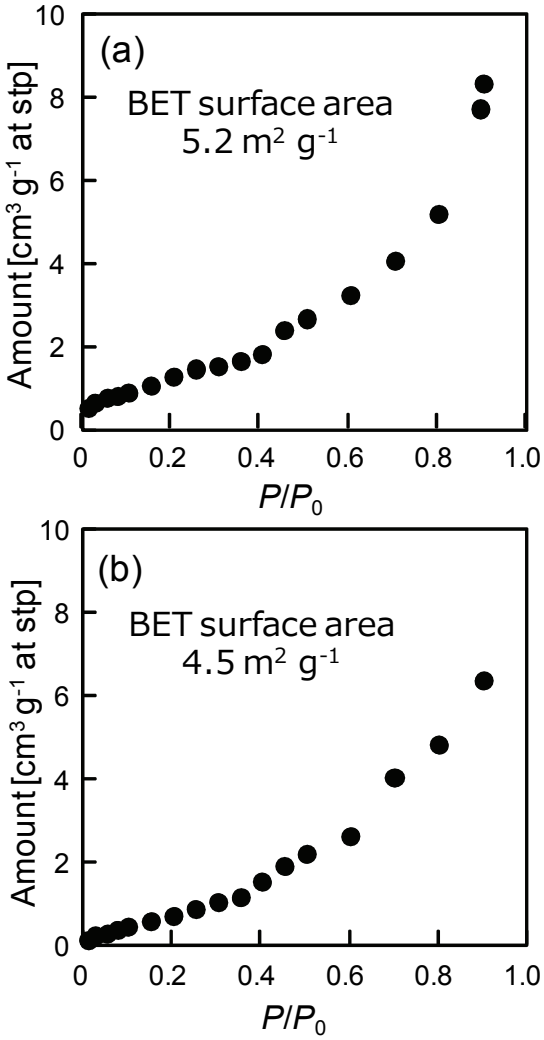

Figure S12. N_2 adsorption isotherms (77 K) of (a) **POM6-*N*** and (b) **POM6-*P*** (pretreatment: evacuation at 298 K for 3 h).

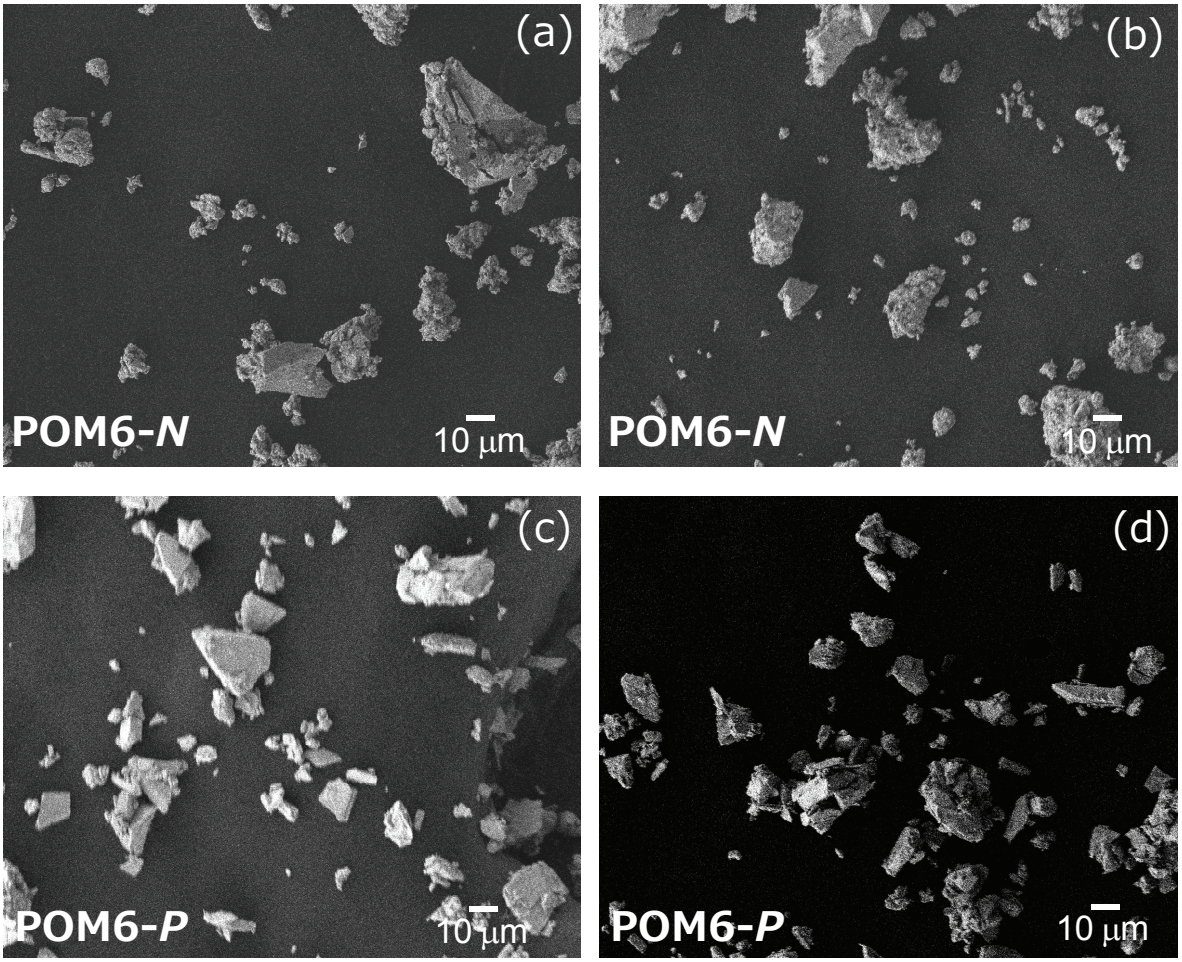

Figure S13. SEM images of (a) **POM6-*N***, (b) **POM6-*N*** (after reaction), (c) **POM6-*P***, (d) **POM6-*P*** (after reaction). Note that the particle sizes and morphologies are similar.

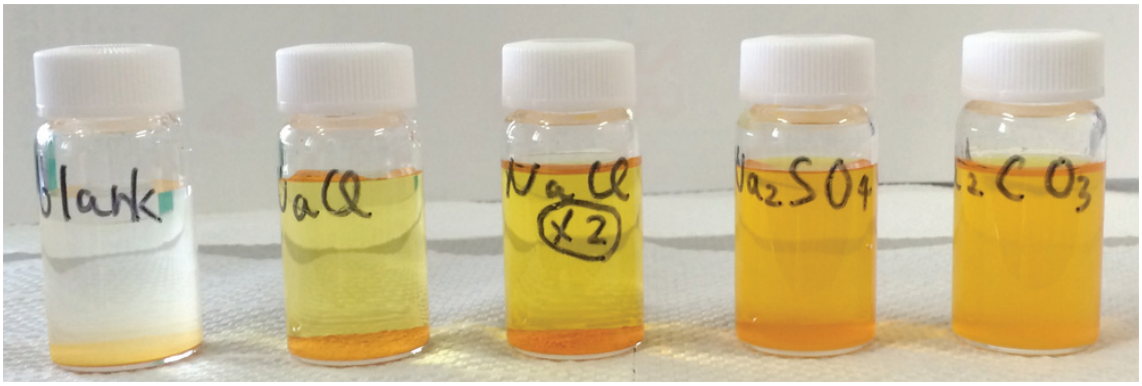

Figure S14. Effects of anions: Photo images of **POM7-*N*** in water after 150 min with no additives (blank), NaCl, $NaSO_4$, or Na_2CO_3. Conditions: 0.1 g of **POM7-*N***, 15 mL of water, and 20 mmol of NaCl, Na_2SO_4, or Na_2CO_3. 40 mmol of NaCl is added for the bottle labeled "NaCl×2".

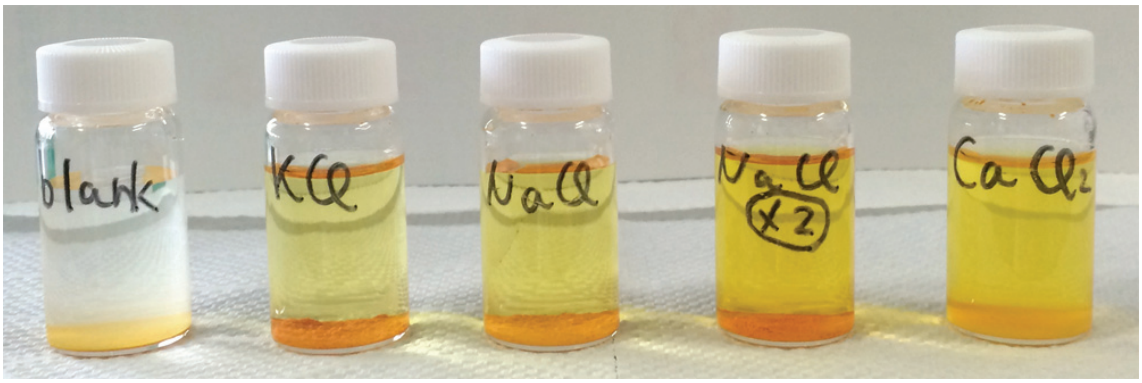

Figure S15. Effects of cations: Photo images of **POM7-*N*** in water after 150 min with no additives (blank), KCl, NaCl, or $CaCl_2$. Conditions: 0.1 g of **POM7-*N***, 15 mL of water, and 20 mmol of KCl, NaCl, or $CaCl_2$. 40 mmol of NaCl is added for the bottle labeled "NaCl×2".