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**Polyoxometalate (POM)-based, multi-functional, inorganic-organic
hybrid compounds: syntheses and molecular structures of silanol-
and/or siloxane bond-containing species grafted on mono- and
tri-lacunary Keggin POMs†**

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Synthesis of the POM precursors

K₇[α-PW₁₁O₃₉]·13H₂O. The colorless clear solution of Na₃[α-PW₁₂O₄₀]·13H₂O (20.0 g (6.29 mmol)) dissolved in 300 mL of water was adjusted to pH = 4.9 by adding a solid of Na₂CO₃ with a small portion, whereinto a solid KCl (50.0 g (0.67 mol)) was added, followed by heating with a water bath at 90 °C. The resulting colorless clear solution was cooled to room temperature and allowed to stand overnight in a refrigerator at 4 °C. White powder formed was collected on a glass filter (G 3.5) and dried *in vacuo* for 2 h. The white powder, obtained in 91.5 % yield (18.3 g scale), was soluble in water, and insoluble in methanol, ethanol, acetonitrile, acetone, dimethyl sulfoxide. TG/DTA under atmospheric conditions: a weight loss of 7.35 % was observed at below 493.8 °C with an endothermic point at 60.5 °C based on dehydration; calcd 7.35 % for x = 13 in K₇[α-PW₁₁O₃₉]·xH₂O. FTIR (KBr): 1622s, 1085s, 1041s, 950vs, 898s, 859vs, 807vs, 732vs, 592m, 509m, 433w, 410m cm⁻¹. ³¹P NMR (22.4 °C, D₂O): δ -10.77.

Na₃[α-PW₁₂O₄₀]·13H₂O. The procedure is based on the classic literature.^{S1} To the colorless clear solution of Na₂WO₄·2H₂O (100 g (0.30 mol)) dissolved in 160 mL of water was added solid Na₂HPO₄·2H₂O (50.0 g (0.28 mol)). The solution was heated in a water bath at 80 °C for 4 h. To the solution, 163 mL of 7.3 M aqueous HCl solution was slowly added, followed by stirring for 30 min in a water bath at 80 °C. The colorless solution was changed to pale yellow, and crystalline white powder was formed.

The solution was concentrated to *ca.* 200 mL of volume with a rotary evaporator at 50 °C. After cooling to room temperature, crystalline powder formed was collected on a glass filter (G 4), which was re-dissolved in 150 mL of water with a water bath at over 90 °C. The colorless clear solution was cooled to room temperature and allowed to stand overnight in a refrigerator at 4 °C. Crystalline white powder formed was collected on a glass filter (G 4) and dried in *vacuo* for 2h. Yield was 80.6 % (64.1 g scale). The white powder was soluble in water and acetone. TG/DTA under atmospheric conditions: a weight loss of 7.32 % was observed at below 492.9 °C with endothermic points at 73.4 and 212.5 °C, based on dehydration; calcd 7.37 % for $x = 13$ in $\text{Na}_3[\alpha\text{-PW}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$. FTIR (KBr): 1616m, 1080vs, 982vs, 894s, 800vs, 596m, 525s, 427w cm^{-1} . ^{31}P NMR (23.8 °C, D_2O): δ -15.04.

References

S1 A. Rosenheim and J. Jaenicke, *Z. Anorg. Allg. Chem.*, 1917, **101**, 251.

Table S1 Bond lengths (Å) and angles (°) for **1**

W-O _t (O _t : terminal oxygen)			
W(1)-O(1)	1.665(13)	W(7)-O(23)	1.676(14)
W(2)-O(3)	1.657(14)	W(8)-O(25)	1.692(12)
W(3)-O(5)	1.673(14)	W(9)-O(27)	1.666(14)
W(4)-O(17)	1.686(12)	W(10)-O(37)	1.655(13)
W(5)-O(19)	1.667(14)	W(11)-O(39)	1.648(15)
W(6)-O(21)	1.659(14)		
average = 1.668 [1.648(15)-1.692(12)]			
W-O _e (O _e : edge sharing oxygen)			
W(1)-O(2)	1.883(14)	W(5)-O(18)	1.877(14)
W(1)-O(6)	1.893(13)	W(6)-O(22)	1.942(14)
W(2)-O(2)	1.898(14)	W(7)-O(22)	1.855(15)
W(2)-O(4)	1.925(14)	W(8)-O(26)	1.882(13)
W(3)-O(4)	1.889(15)	W(9)-O(26)	1.908(13)
W(3)-O(6)	1.886(14)	W(10)-O(31)	1.891(15)
W(4)-O(18)	1.904(14)	W(11)-O(34)	1.889(13)
average = 1.894 [1.855(15)-1.942(14)]			
W-O _c (O _c : corner sharing oxygen)			
W(1)-O(8)	1.897(13)	W(7)-O(11)	1.884(14)
W(1)-O(13)	1.882(14)	W(7)-O(24)	1.894(15)
W(2)-O(9)	1.905(13)	W(7)-O(32)	1.892(13)
W(2)-O(10)	1.874(14)	W(8)-O(12)	1.877(14)
W(3)-O(11)	1.899(14)	W(8)-O(24)	1.876(15)
W(3)-O(12)	1.885(15)	W(8)-O(33)	1.882(13)
W(4)-O(8)	1.871(13)	W(9)-O(13)	1.886(13)
W(4)-O(28)	1.902(13)	W(9)-O(28)	1.901(12)
W(4)-O(29)	1.868(13)	W(9)-O(34)	1.880(13)
W(5)-O(9)	1.877(13)	W(10)-O(32)	1.886(13)
W(5)-O(20)	1.914(13)	W(10)-O(36)	1.865(13)
W(5)-O(30)	1.870(14)	W(10)-O(38)	1.851(14)
W(6)-O(10)	1.908(14)	W(11)-O(33)	1.904(12)

Table S1 continued

W(6)-O(20)	1.878(13)	W(11)-O(38)	1.885(14)
W(6)-O(31)	1.875(14)	W(11)-O(40)	1.867(13)
average = 1.885 [1.851(14)-1.914(13)]			
W-O _a (oxygen coordinating to P atom)			
W(1)-O(7A)	2.48(3)	W(1)-O(15B)	2.60(3)
W(2)-O(7A)	2.44(2)	W(2)-O(16B)	2.61(3)
W(3)-O(7A)	2.41(2)	W(3)-O(14B)	2.47(3)
W(4)-O(14A)	2.41(2)	W(4)-O(15B)	2.44(3)
W(5)-O(14A)	2.35(2)	W(5)-O(16B)	2.44(3)
W(6)-O(15A)	2.40(2)	W(6)-O(16B)	2.52(3)
W(7)-O(15A)	2.49(2)	W(7)-O(14B)	2.47(3)
W(8)-O(16A)	2.52(2)	W(8)-O(14B)	2.44(3)
W(9)-O(16A)	2.48(2)	W(9)-O(15B)	2.40(3)
W(10)-O(15A)	2.51(2)	W(10)-O(7B)	2.42(3)
W(11)-O(16A)	2.46(2)	W(11)-O(7B)	2.31(3)
average = 2.46 [2.31(3)-2.61(3)]			
P-O			
P(1)-O(7A)	1.59(2)	P(1)-O(7B)	1.60(3)
P(1)-O(14A)	1.55(2)	P(1)-O(14B)	1.56(3)
P(1)-O(15A)	1.54(2)	P(1)-O(15B)	1.53(3)
P(1)-O(16A)	1.49(2)	P(1)-O(16B)	1.45(3)
average = 1.54 [1.49(2)-1.59(2)]		average = 1.54 [1.45(3)-1.60(3)]	
O-P-O			
O(14A)-P(1)-O(7A)	106.2(12)	O(14B)-P(1)-O(7B)	105.4(15)
O(15A)-P(1)-O(7A)	104.6(12)	O(15B)-P(1)-O(7B)	105.4(15)
O(15A)-P(1)-O(14A)	109.9(12)	O(15B)-P(1)-O(14B)	108.2(14)
O(16A)-P(1)-O(7A)	108.4(12)	O(16B)-P(1)-O(7B)	110.2(15)
O(16A)-P(1)-O(14A)	112.6(12)	O(16B)-P(1)-O(14B)	112.1(16)
O(16A)-P(1)-O(15A)	114.5(12)	O(16B)-P(1)-O(15B)	115.0(16)
average = 109.4 [104.6(12)-114.5(12)]		average = 109.4 [105.4(15)-115.0(16)]	

Table S2 Bond lengths (Å) and angles (°) for **3a**

W-O _t (O _t : terminal oxygen)			
W(1)-O(1)	1.709(3)	W(3)-O(7)	1.707(4)
W(2)-O(6)	1.703(3)		
average = 1.706 [1.703(3)-1.709(3)]			
W-O _e (O _e : edge sharing oxygen)			
W(1)-O(2)	1.911(3)	W(2)-O(10) ⁱⁱ	1.940(3)
W(1)-O(2) ⁱ	1.928(3)	W(3)-O(10)	1.894(3)
average = 1.918 [1.894(3)-1.940(3)]			
W-O _c (O _c : corner sharing oxygen)			
W(1)-O(4)	1.901(3)	W(3)-O(5)	1.900(3)
W(1)-O(5)	1.918(3)	W(3)-O(9)	1.934(3)
W(2)-O(4)	1.917(3)	W(3)-O(12)	1.913(4)
W(2)-O(9)	1.871(3)		
W(2)-O(11)	1.915(3)		
average = 1.909 [1.871(3)-1.934(3)]			
W-O _a (oxygen coordinating to P atom)			
W(1)-O(3)	2.384(3)	W(3)-O(8) ⁱ	2.370(3)
W(2)-O(8)	2.344(3)		
average = 2.366 [2.344(3)-2.384(3)]			
P-O			
P(1)-O(3)	1.562(6)	P(1)-O(8)	1.527(3)
average = 1.545 [1.527(3)-1.562(6)]			
O-P-O			
O(3)-P(1)-O(8)	107.24(15)	O(8)-P(1)-O(8) ⁱ	111.60(13)
average = 109.42 [107.24(15)-111.60(13)]			

Symmetry operation: $i = -y+3/2, -z+1, x-1/2$, $ii = z+1/2, -x+3/2, -y+1$