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A fully reduced $\{V^{IV}_{18}O_{42}\}$ host and VO_4^{3-}, Cl^- as guest anions: synthesis, characterization and proton conductivity

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Electronic Supporting Information (ESI)

Section S1. Powder X-ray diffraction analysis of compounds 1 and 2

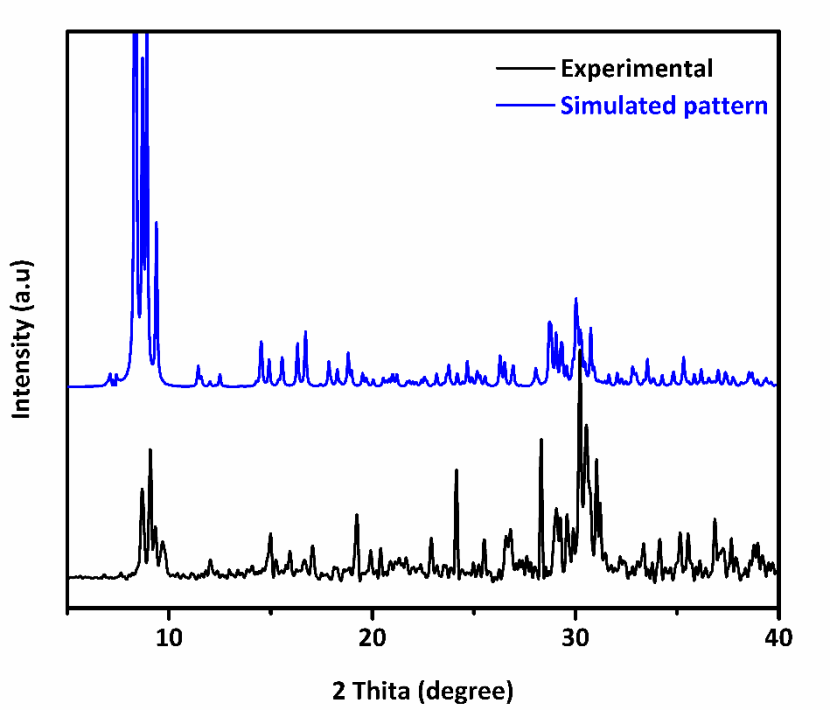


Fig. S1 Powder X-ray diffraction analysis of compound **1**.

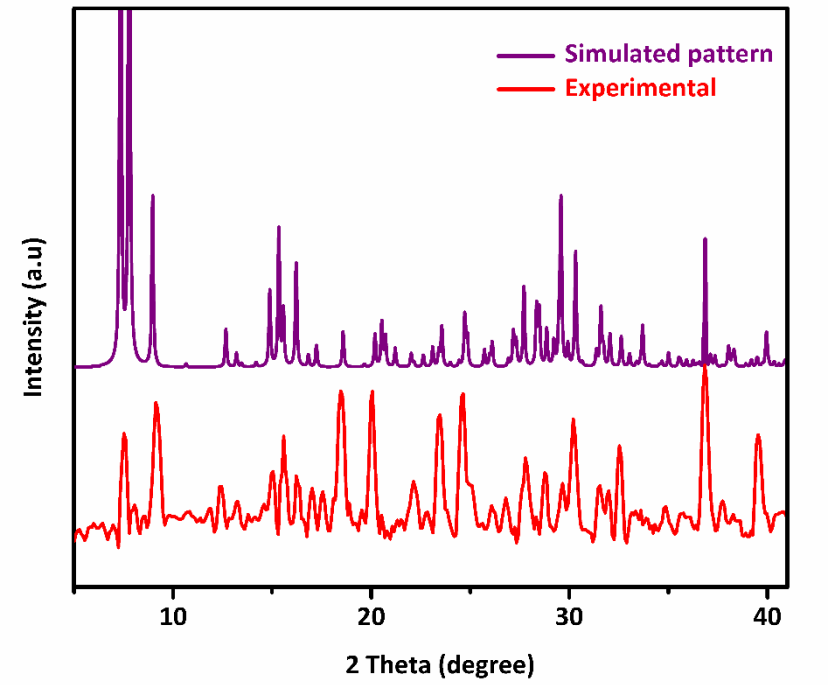


Fig. S2 Powder X-ray diffraction analysis of compound **2**.

Section S2. Single crystal X-ray crystallography of compounds 1 and 2

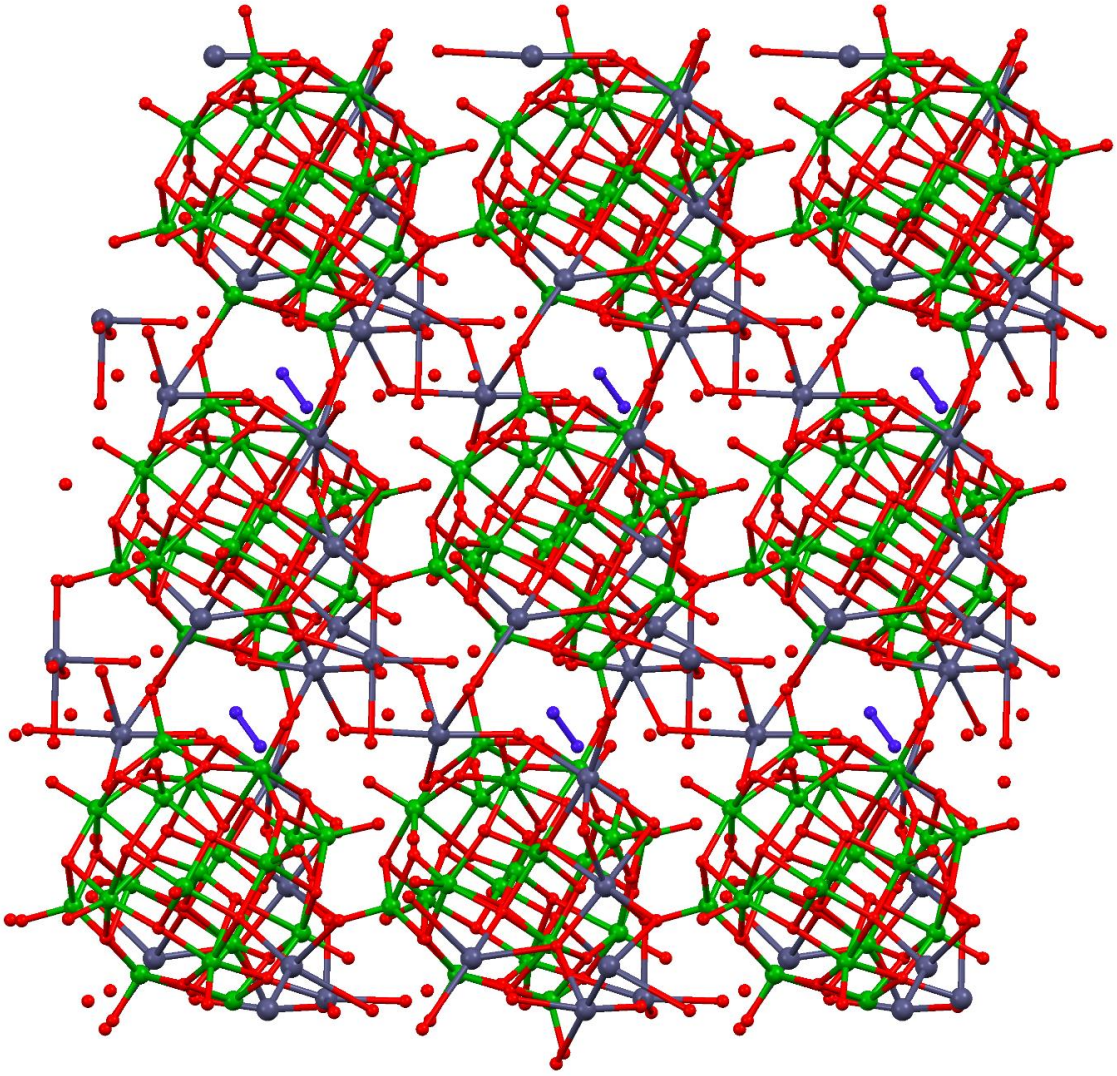


Fig. S3 Molecular packing, found in the crystal structure of compound **1**, viewed down to the crystallographic *b*-axis.

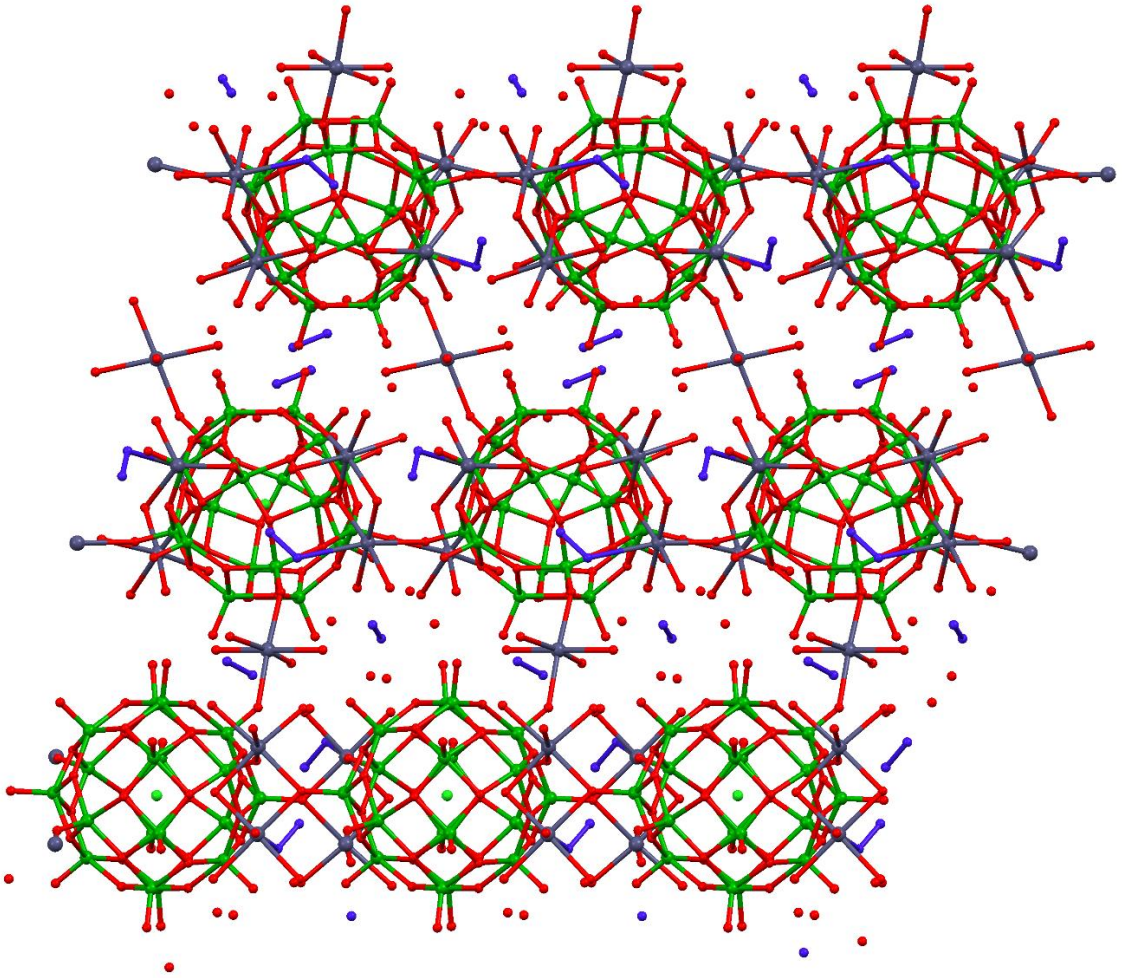


Fig. S4 Molecular packing, found in the crystal structure of compound **2**, viewed down to the crystallographic *b*-axis.

Table S1. Bond distances (Å) and angles (°) for compound **1**

V(1)-O(2)	1.689(8)	V(11)-O(41)	1.632(8)
V(1)-O(4)	1.698(7)	V(11)-O(16)	1.932(8)
V(1)-O(1)	1.711(7)	V(11)-O(39)	1.974(7)
V(1)-O(3)	1.731(7)	V(11)-O(43)	1.989(7)
V(15)-O(46)	1.625(7)	V(11)-O(38)	2.044(8)
V(15)-O(8)	1.936(7)	V(11)-O(2)	2.403(8)
V(15)-O(34)	1.958(7)	V(8)-O(27)	1.612(8)
V(15)-O(9)	2.021(7)	V(8)-O(29)	1.944(8)
V(15)-O(32)	2.059(7)	V(8)-O(28)	1.985(8)
V(15)-O(4)	2.368(7)	V(8)-O(25)	1.985(8)
V(9)-O(30)	1.625(7)	V(8)-O(23)	2.078(7)
V(9)-O(25)	1.940(7)	V(8)-O(3)	2.431(7)
V(9)-O(31)	1.975(7)	V(17)-O(36)	1.620(8)
V(9)-O(21)	1.987(8)	V(17)-O(31)	1.926(7)
V(9)-O(32)	2.057(7)	V(17)-O(29)	1.966(8)
V(9)-O(4)	2.439(7)	V(17)-O(35)	1.978(7)
V(16)-O(45)	1.620(7)	V(17)-O(38)	2.082(8)
V(16)-O(44)	1.930(7)	V(17)-O(2)	2.355(7)
V(16)-O(35)	1.970(7)	V(4)-O(13)	1.634(8)
V(16)-O(34)	1.977(7)	V(4)-O(14)	1.926(7)
V(16)-O(43)	1.977(8)	V(4)-O(16)	1.945(7)
V(10)-O(33)	1.659(8)	V(4)-O(11)	1.963(8)
V(10)-O(34)	1.892(7)	V(4)-O(15)	2.050(7)
V(10)-O(31)	1.894(7)	V(3)-O(10)	1.630(8)
V(10)-O(35)	1.950(8)	V(3)-O(12)	1.952(8)
V(10)-O(32)	2.103(8)	V(3)-O(7)	1.962(7)
V(6)-O(19)	1.622(8)	V(3)-O(11)	2.000(7)
V(6)-O(20)	1.953(7)	V(3)-O(6)	2.029(7)
V(6)-O(21)	1.964(7)	V(3)-O(1)	2.413(8)
V(6)-O(7)	1.970(7)	V(19)-O(26)	1.651(8)
V(6)-O(9)	2.026(7)	V(19)-O(12)	1.903(8)
V(18)-O(47)	1.622(8)	V(19)-O(20)	1.936(8)
V(18)-O(8)	1.949(8)	V(19)-O(23)	2.058(7)
V(18)-O(44)	1.955(7)	V(19)-O(18)	2.073(8)
V(18)-O(6)	2.000(8)	V(19)-O(3)	2.198(8)
V(18)-O(15)	2.059(7)	V(14)-O(42)	1.670(9)
V(18)-O(1)	2.357(7)	V(14)-O(16)	1.866(7)

V(14)-O(44)	1.903(8)	O(46)-V(15)-O(9)	97.1(4)
V(14)-O(43)	1.936(8)	O(8)-V(15)-O(9)	81.7(3)
V(14)-O(15)	2.111(8)	O(34)-V(15)-O(9)	159.2(3)
V(7)-O(22)	1.641(8)	O(46)-V(15)-O(32)	97.4(4)
V(7)-O(25)	1.873(7)	O(8)-V(15)-O(32)	159.2(3)
V(7)-O(20)	1.886(7)	O(34)-V(15)-O(32)	81.4(3)
V(7)-O(21)	1.960(8)	O(9)-V(15)-O(32)	98.0(3)
V(7)-O(23)	2.129(8)	O(46)-V(15)-O(4)	164.0(3)
V(13)-O(40)	1.625(8)	O(8)-V(15)-O(4)	88.5(3)
V(13)-O(39)	1.928(8)	O(34)-V(15)-O(4)	86.5(3)
V(13)-O(28)	1.953(8)	O(9)-V(15)-O(4)	73.7(3)
V(13)-O(14)	1.970(8)	O(32)-V(15)-O(4)	71.7(3)
V(13)-O(18)	2.071(8)	O(30)-V(9)-O(25)	104.3(4)
V(2)-O(5)	1.632(9)	O(30)-V(9)-O(31)	102.8(4)
V(2)-O(7)	1.870(7)	O(25)-V(9)-O(31)	90.9(3)
V(2)-O(8)	1.902(7)	O(30)-V(9)-O(21)	101.1(4)
V(2)-O(9)	2.024(8)	O(25)-V(9)-O(21)	84.0(3)
V(2)-O(6)	2.026(8)	O(31)-V(9)-O(21)	156.1(3)
V(12)-O(37)	1.647(9)	O(30)-V(9)-O(32)	98.0(4)
V(12)-O(39)	1.873(8)	O(25)-V(9)-O(32)	157.3(3)
V(12)-O(29)	1.884(8)	O(31)-V(9)-O(32)	79.9(3)
V(12)-O(28)	1.970(8)	O(21)-V(9)-O(32)	96.1(3)
V(12)-O(38)	2.106(8)	O(30)-V(9)-O(4)	165.0(4)
V(5)-O(17)	1.634(9)	O(25)-V(9)-O(4)	88.4(3)
V(5)-O(14)	1.856(8)	O(31)-V(9)-O(4)	84.6(3)
V(5)-O(12)	1.895(8)	O(21)-V(9)-O(4)	72.0(3)
V(5)-O(11)	1.960(7)	O(32)-V(9)-O(4)	70.2(3)
V(5)-O(18)	2.129(8)	O(45)-V(16)-O(44)	105.3(4)
		O(45)-V(16)-O(35)	102.2(4)
O(2)-V(1)-O(4)	109.0(4)	O(44)-V(16)-O(35)	152.4(3)
O(2)-V(1)-O(1)	109.4(4)	O(45)-V(16)-O(34)	103.5(4)
O(4)-V(1)-O(1)	108.8(4)	O(44)-V(16)-O(34)	91.1(3)
O(2)-V(1)-O(3)	108.9(4)	O(35)-V(16)-O(34)	80.7(3)
O(4)-V(1)-O(3)	110.5(4)	O(45)-V(16)-O(43)	101.9(4)
O(1)-V(1)-O(3)	110.2(4)	O(44)-V(16)-O(43)	80.2(3)
O(46)-V(15)-O(8)	103.4(4)	O(35)-V(16)-O(43)	96.0(3)
O(46)-V(15)-O(34)	103.6(3)	O(34)-V(16)-O(43)	154.5(3)
O(8)-V(15)-O(34)	91.5(3)	O(33)-V(10)-O(34)	118.3(4)

O(33)-V(10)-O(31)	118.9(4)	O(16)-V(11)-O(43)	84.5(3)
O(34)-V(10)-O(31)	122.7(3)	O(39)-V(11)-O(43)	156.0(3)
O(33)-V(10)-O(35)	105.7(4)	O(41)-V(11)-O(38)	98.0(4)
O(34)-V(10)-O(35)	83.4(3)	O(16)-V(11)-O(38)	156.0(3)
O(31)-V(10)-O(35)	85.3(3)	O(39)-V(11)-O(38)	79.3(3)
O(33)-V(10)-O(32)	104.7(4)	O(43)-V(11)-O(38)	96.9(3)
O(34)-V(10)-O(32)	81.8(3)	O(41)-V(11)-O(2)	166.2(4)
O(31)-V(10)-O(32)	80.5(3)	O(16)-V(11)-O(2)	87.9(3)
O(35)-V(10)-O(32)	149.6(3)	O(39)-V(11)-O(2)	83.3(3)
O(19)-V(6)-O(20)	103.9(4)	O(43)-V(11)-O(2)	73.2(3)
O(19)-V(6)-O(21)	100.9(4)	O(38)-V(11)-O(2)	69.8(3)
O(20)-V(6)-O(21)	83.3(3)	O(27)-V(8)-O(29)	104.4(4)
O(19)-V(6)-O(7)	104.0(4)	O(27)-V(8)-O(28)	100.5(4)
O(20)-V(6)-O(7)	88.5(3)	O(29)-V(8)-O(28)	83.1(3)
O(21)-V(6)-O(7)	155.0(3)	O(27)-V(8)-O(25)	102.5(4)
O(19)-V(6)-O(9)	99.9(4)	O(29)-V(8)-O(25)	91.6(3)
O(20)-V(6)-O(9)	155.8(3)	O(28)-V(8)-O(25)	157.1(3)
O(21)-V(6)-O(9)	96.5(3)	O(27)-V(8)-O(23)	96.5(4)
O(7)-V(6)-O(9)	81.5(3)	O(29)-V(8)-O(23)	158.5(3)
O(47)-V(18)-O(8)	102.3(4)	O(28)-V(8)-O(23)	98.2(3)
O(47)-V(18)-O(44)	102.3(4)	O(25)-V(8)-O(23)	78.8(3)
O(8)-V(18)-O(44)	92.8(3)	O(27)-V(8)-O(3)	162.4(4)
O(47)-V(18)-O(6)	98.8(4)	O(29)-V(8)-O(3)	90.9(3)
O(8)-V(18)-O(6)	81.9(3)	O(28)-V(8)-O(3)	72.6(3)
O(44)-V(18)-O(6)	159.0(3)	O(25)-V(8)-O(3)	85.3(3)
O(47)-V(18)-O(15)	97.8(4)	O(23)-V(8)-O(3)	69.3(3)
O(8)-V(18)-O(15)	159.8(3)	O(36)-V(17)-O(31)	103.0(4)
O(44)-V(18)-O(15)	81.2(3)	O(36)-V(17)-O(29)	101.7(4)
O(6)-V(18)-O(15)	96.9(3)	O(31)-V(17)-O(29)	91.9(3)
O(47)-V(18)-O(1)	164.5(4)	O(36)-V(17)-O(35)	100.5(4)
O(8)-V(18)-O(1)	89.4(3)	O(31)-V(17)-O(35)	83.7(3)
O(44)-V(18)-O(1)	87.1(3)	O(29)-V(17)-O(35)	157.8(3)
O(6)-V(18)-O(1)	72.5(3)	O(36)-V(17)-O(38)	96.9(4)
O(15)-V(18)-O(1)	71.2(3)	O(31)-V(17)-O(38)	159.6(3)
O(41)-V(11)-O(16)	105.1(4)	O(29)-V(17)-O(38)	79.5(3)
O(41)-V(11)-O(39)	101.2(4)	O(35)-V(17)-O(38)	97.2(3)
O(16)-V(11)-O(39)	89.7(3)	O(36)-V(17)-O(2)	164.8(4)
O(41)-V(11)-O(43)	102.8(4)	O(31)-V(17)-O(2)	90.6(3)

O(29)-V(17)-O(2)	84.3(3)	O(26)-V(19)-O(3)	163.8(4)
O(35)-V(17)-O(2)	74.1(3)	O(12)-V(19)-O(3)	89.6(3)
O(38)-V(17)-O(2)	70.3(3)	O(20)-V(19)-O(3)	89.0(3)
O(13)-V(4)-O(14)	105.9(4)	O(23)-V(19)-O(3)	74.5(3)
O(13)-V(4)-O(16)	102.0(4)	O(18)-V(19)-O(3)	75.4(3)
O(14)-V(4)-O(16)	90.2(3)	O(42)-V(14)-O(16)	117.3(4)
O(13)-V(4)-O(11)	102.9(4)	O(42)-V(14)-O(44)	120.9(4)
O(14)-V(4)-O(11)	84.1(3)	O(16)-V(14)-O(44)	121.0(3)
O(16)-V(4)-O(11)	155.1(3)	O(42)-V(14)-O(43)	109.7(4)
O(13)-V(4)-O(15)	97.8(4)	O(16)-V(14)-O(43)	87.8(3)
O(14)-V(4)-O(15)	155.6(3)	O(44)-V(14)-O(43)	81.9(3)
O(16)-V(4)-O(15)	79.4(3)	O(42)-V(14)-O(15)	100.7(4)
O(11)-V(4)-O(15)	96.0(3)	O(16)-V(14)-O(15)	79.7(3)
O(10)-V(3)-O(12)	101.6(4)	O(44)-V(14)-O(15)	81.0(3)
O(10)-V(3)-O(7)	102.0(4)	O(43)-V(14)-O(15)	149.6(3)
O(12)-V(3)-O(7)	92.0(3)	O(22)-V(7)-O(25)	120.2(4)
O(10)-V(3)-O(11)	99.3(4)	O(22)-V(7)-O(20)	117.9(4)
O(12)-V(3)-O(11)	80.6(3)	O(25)-V(7)-O(20)	121.2(3)
O(7)-V(3)-O(11)	158.5(3)	O(22)-V(7)-O(21)	106.3(4)
O(10)-V(3)-O(6)	100.4(4)	O(25)-V(7)-O(21)	86.5(3)
O(12)-V(3)-O(6)	157.9(3)	O(20)-V(7)-O(21)	85.2(3)
O(7)-V(3)-O(6)	81.1(3)	O(22)-V(7)-O(23)	101.9(4)
O(11)-V(3)-O(6)	98.1(3)	O(25)-V(7)-O(23)	80.0(3)
O(10)-V(3)-O(1)	166.4(4)	O(20)-V(7)-O(23)	80.9(3)
O(12)-V(3)-O(1)	87.9(3)	O(21)-V(7)-O(23)	151.8(3)
O(7)-V(3)-O(1)	87.2(3)	O(40)-V(13)-O(39)	103.3(4)
O(11)-V(3)-O(1)	72.4(3)	O(40)-V(13)-O(28)	102.4(4)
O(6)-V(3)-O(1)	70.8(3)	O(39)-V(13)-O(28)	84.1(3)
O(26)-V(19)-O(12)	101.3(4)	O(40)-V(13)-O(14)	102.3(4)
O(26)-V(19)-O(20)	102.0(4)	O(39)-V(13)-O(14)	91.1(3)
O(12)-V(19)-O(20)	94.1(3)	O(28)-V(13)-O(14)	155.3(3)
O(26)-V(19)-O(23)	95.1(4)	O(40)-V(13)-O(18)	99.4(4)
O(12)-V(19)-O(23)	163.6(3)	O(39)-V(13)-O(18)	156.7(3)
O(20)-V(19)-O(23)	81.6(3)	O(28)-V(13)-O(18)	96.1(3)
O(26)-V(19)-O(18)	94.3(4)	O(14)-V(13)-O(18)	79.0(3)
O(12)-V(19)-O(18)	81.2(3)	O(5)-V(2)-O(7)	119.1(4)
O(20)-V(19)-O(18)	163.7(3)	O(5)-V(2)-O(8)	118.7(4)
O(23)-V(19)-O(18)	98.6(3)	O(7)-V(2)-O(8)	122.2(3)

O(5)-V(2)-O(9)	104.5(4)	O(39)-V(12)-O(38)	80.0(3)
O(7)-V(2)-O(9)	84.0(3)	O(29)-V(12)-O(38)	80.8(3)
O(8)-V(2)-O(9)	82.5(3)	O(28)-V(12)-O(38)	149.8(3)
O(5)-V(2)-O(6)	104.4(4)	O(17)-V(5)-O(14)	120.0(6)
O(7)-V(2)-O(6)	83.5(3)	O(17)-V(5)-O(12)	120.6(6)
O(8)-V(2)-O(6)	82.4(3)	O(14)-V(5)-O(12)	118.8(3)
O(9)-V(2)-O(6)	151.1(3)	O(17)-V(5)-O(11)	108.2(5)
O(37)-V(12)-O(39)	118.5(5)	O(14)-V(5)-O(11)	86.0(3)
O(37)-V(12)-O(29)	119.1(5)	O(12)-V(5)-O(11)	83.0(3)
O(39)-V(12)-O(29)	121.7(3)	O(17)-V(5)-O(18)	102.6(5)
O(37)-V(12)-O(28)	108.8(5)	O(14)-V(5)-O(18)	80.0(3)
O(39)-V(12)-O(28)	85.1(3)	O(12)-V(5)-O(18)	79.9(3)
O(29)-V(12)-O(28)	85.0(3)	O(11)-V(5)-O(18)	149.2(3)
O(37)-V(12)-O(38)	101.4(4)		

Symmetry transformations used to generate equivalent atoms: #1 x,-y+2,z+1/2 #2 x,-y+2,z-1/2 #3 x+1/2,y+1/2,z #4 x+1/2,-y+3/2,z-1/2 #5 x,-y+1,z-1/2 #6 x-1/2,-y+3/2,z-1/2 #7 x,-y+1,z+1/2 #8 x-1/2,y+1/2,z #9 x-1/2,-y+3/2,z+1/2 #10 x-1/2,y-1/2,z #11 x+1/2,-y+3/2,z+1/2 #12 x+1/2,y-1/2,z

Table S2. Bond distances (Å) and angles (°) for compound **2**

V(1)-O(1)	1.626(4)	V(9)-O(15)	1.945(4)
V(1)-O(2)	1.933(4)	V(9)-O(14)	1.946(4)
V(1)-O(4)	1.940(4)	V(9)-O(10)#1	1.955(4)
V(1)-O(5)	1.943(4)	V(5)-O(21)	1.633(4)
V(1)-O(3)	1.960(4)	V(5)-O(8)	1.920(4)
V(3)-O(7)	1.614(4)	V(5)-O(5)	1.924(4)
V(3)-O(8)	1.953(4)	V(5)-O(13)	1.954(4)
V(3)-O(4)	1.956(4)	V(5)-O(19)	1.960(4)
V(3)-O(17)#1	1.957(4)	V(6)-O(20)	1.613(4)
V(3)-O(9)	1.958(4)	V(6)-O(3)#1	1.883(4)
V(7)-O(18)	1.624(4)	V(6)-O(19)	1.893(4)
V(7)-O(15)	1.940(4)	V(6)-O(5)	1.931(4)
V(7)-O(2)#1	1.951(4)	V(6)-O(3)	1.952(4)
V(7)-O(13)	1.951(4)	V(2)-O(6)	1.636(4)
V(7)-O(19)	1.957(4)	V(2)-O(2)	1.917(4)
V(9)-O(16)	1.624(4)	V(2)-O(15)#1	1.935(4)
V(9)-O(17)	1.939(4)	V(2)-O(17)#1	1.940(4)

V(2)-O(4)	1.948(4)	O(18)-V(7)-O(19)	104.84(19)
V(4)-O(12)	1.626(4)	O(15)-V(7)-O(19)	149.89(16)
V(4)-O(14)	1.918(4)	O(2)#1-V(7)-O(19)	90.35(15)
V(4)-O(13)	1.941(4)	O(13)-V(7)-O(19)	79.41(15)
V(4)-O(9)	1.946(4)	O(16)-V(9)-O(17)	104.09(19)
V(4)-O(8)	1.948(4)	O(16)-V(9)-O(15)	107.23(19)
V(8)-O(11)	1.606(4)	O(17)-V(9)-O(15)	80.97(15)
V(8)-O(9)	1.875(4)	O(16)-V(9)-O(14)	108.80(19)
V(8)-O(10)	1.881(4)	O(17)-V(9)-O(14)	147.09(16)
V(8)-O(14)	1.912(4)	O(15)-V(9)-O(14)	90.25(16)
V(8)-O(10)#1	1.952(4)	O(16)-V(9)-O(10)#1	105.61(19)
		O(17)-V(9)-O(10)#1	91.74(15)
O(1)-V(1)-O(2)	104.98(18)	O(15)-V(9)-O(10)#1	147.16(16)
O(1)-V(1)-O(4)	105.52(19)	O(14)-V(9)-O(10)#1	78.61(16)
O(2)-V(1)-O(4)	83.39(15)	O(21)-V(5)-O(8)	106.29(19)
O(1)-V(1)-O(5)	107.60(18)	O(21)-V(5)-O(5)	107.8(2)
O(2)-V(1)-O(5)	147.25(16)	O(8)-V(5)-O(5)	94.54(16)
O(4)-V(1)-O(5)	91.03(16)	O(21)-V(5)-O(13)	110.20(19)
O(1)-V(1)-O(3)	105.56(19)	O(8)-V(5)-O(13)	82.17(16)
O(2)-V(1)-O(3)	88.70(15)	O(5)-V(5)-O(13)	141.24(16)
O(4)-V(1)-O(3)	148.92(16)	O(21)-V(5)-O(19)	110.31(19)
O(5)-V(1)-O(3)	79.59(15)	O(8)-V(5)-O(19)	142.79(16)
O(7)-V(3)-O(8)	106.75(18)	O(5)-V(5)-O(19)	80.70(15)
O(7)-V(3)-O(4)	104.63(19)	O(13)-V(5)-O(19)	79.28(15)
O(8)-V(3)-O(4)	92.30(16)	O(20)-V(6)-O(3)#1	105.9(2)
O(7)-V(3)-O(17)#1	103.55(18)	O(20)-V(6)-O(19)	106.0(2)
O(8)-V(3)-O(17)#1	149.69(16)	O(3)#1-V(6)-O(19)	96.41(16)
O(4)-V(3)-O(17)#1	80.49(15)	O(20)-V(6)-O(5)	108.6(2)
O(7)-V(3)-O(9)	106.77(19)	O(3)#1-V(6)-O(5)	144.44(16)
O(8)-V(3)-O(9)	79.65(16)	O(19)-V(6)-O(5)	82.25(16)
O(4)-V(3)-O(9)	148.59(16)	O(20)-V(6)-O(3)	107.3(2)
O(17)#1-V(3)-O(9)	91.26(15)	O(3)#1-V(6)-O(3)	81.76(17)
O(18)-V(7)-O(15)	105.25(19)	O(19)-V(6)-O(3)	145.75(16)
O(18)-V(7)-O(2)#1	105.73(18)	O(5)-V(6)-O(3)	80.08(15)
O(15)-V(7)-O(2)#1	82.51(15)	O(6)-V(2)-O(2)	111.8(2)
O(18)-V(7)-O(13)	104.29(18)	O(6)-V(2)-O(15)#1	110.44(18)
O(15)-V(7)-O(13)	92.23(16)	O(2)-V(2)-O(15)#1	83.53(15)
O(2)#1-V(7)-O(13)	149.86(15)	O(6)-V(2)-O(17)#1	111.8(2)

O(2)-V(2)-O(17)#1	136.45(16)	O(13)-V(4)-O(8)	81.78(15)
O(15)#1-V(2)-O(17)#1	81.18(16)	O(9)-V(4)-O(8)	80.06(16)
O(6)-V(2)-O(4)	111.57(18)	O(11)-V(8)-O(9)	107.8(2)
O(2)-V(2)-O(4)	83.60(15)	O(11)-V(8)-O(10)	106.7(2)
O(15)#1-V(2)-O(4)	137.90(16)	O(9)-V(8)-O(10)	93.30(17)
O(17)#1-V(2)-O(4)	81.12(15)	O(11)-V(8)-O(14)	109.2(2)
O(12)-V(4)-O(14)	106.7(2)	O(9)-V(8)-O(14)	83.47(17)
O(12)-V(4)-O(13)	105.84(19)	O(10)-V(8)-O(14)	143.20(17)
O(14)-V(4)-O(13)	94.13(16)	O(11)-V(8)-O(10)#1	107.8(2)
O(12)-V(4)-O(9)	110.7(2)	O(9)-V(8)-O(10)#1	143.92(17)
O(14)-V(4)-O(9)	81.46(17)	O(10)-V(8)-O(10)#1	82.13(17)
O(13)-V(4)-O(9)	142.94(16)	O(14)-V(8)-O(10)#1	79.48(16)
O(12)-V(4)-O(8)	110.2(2)	O(30)-Na(3)-O(22)#1	89.5(2)
O(14)-V(4)-O(8)	142.58(16)	O(28)-Na(3)-O(6)#1	89.80(18)

Symmetry transformations used to generate equivalent atoms: #1 y,x,-z+1 #2 x-1,y,z #3 x-y,-y,-z+2/3 #4 x+1,y,z

Section S3. Thermogravimetric analyses (TGA) of compounds 1 and 2

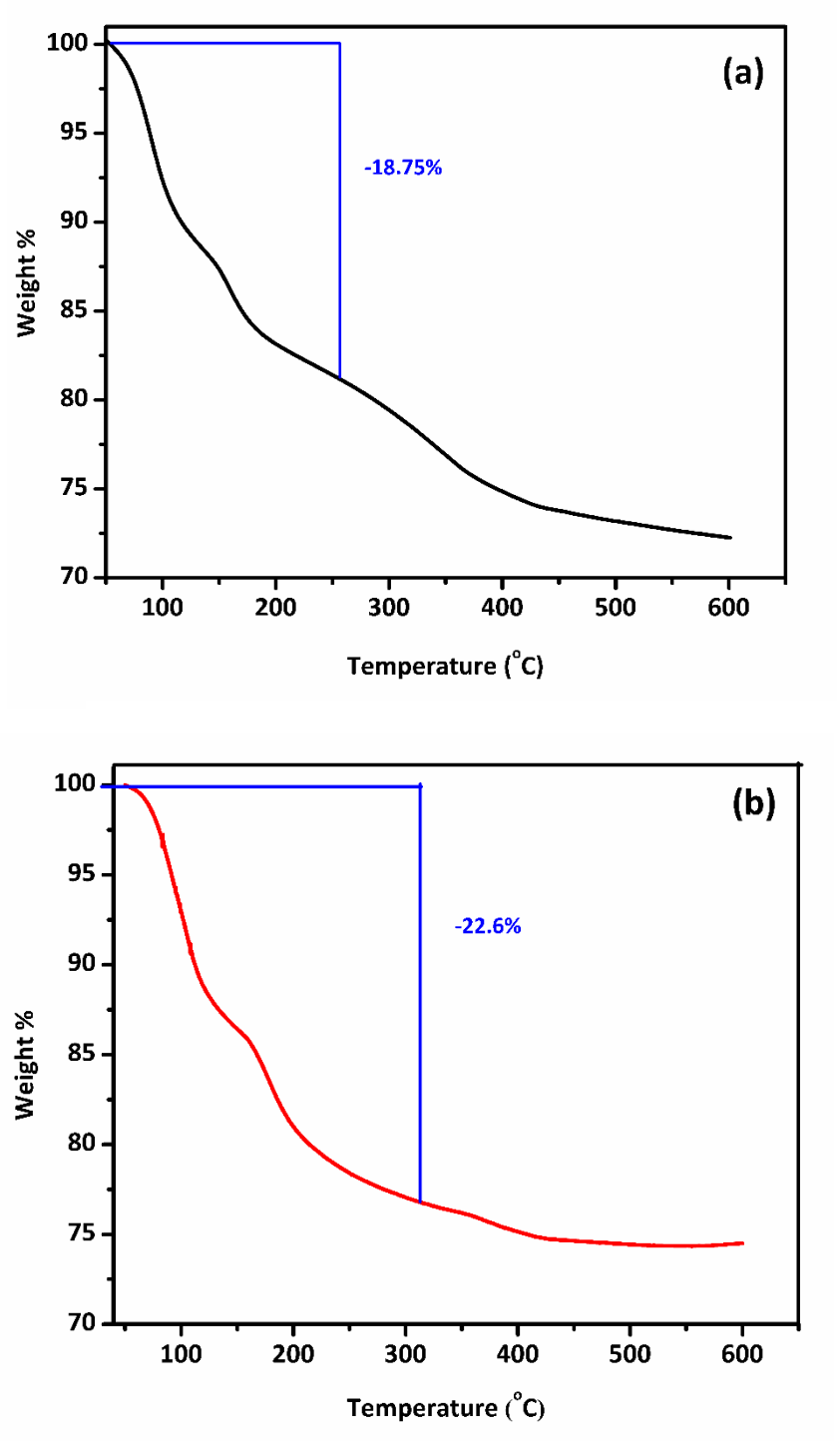


Fig. S5 Thermogravimetric profiles of compound **1**(Fig. **a**) and compound **2** (Fig. **b**).

Section S4. Bond valance sum calculations on the crystal structures of compounds 1 and 2

Compound 1

Bond valence calculation. Numbers in brackets after atom symbols are at.no., r and c - see *O"Keeffe and Brese, J.A.C.S. 1991, 113, 3226*.

```
......V1O6

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.63  1.47
                     -O  ( 8,  .63, 3.15) 1.77  2.00   .54
                     -O  ( 8,  .63, 3.15) 1.77  1.96   .61
                     -O  ( 8,  .63, 3.15) 1.77  1.97   .59
                     -O  ( 8,  .63, 3.15) 1.77  2.02   .51
                     -O  ( 8,  .63, 3.15) 1.77  2.40   .18

  Bond valence sum for V   3.90

......V2O6

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.61  1.54
                     -O  ( 8,  .63, 3.15) 1.77  1.98   .57
                     -O  ( 8,  .63, 3.15) 1.77  2.06   .46
                     -O  ( 8,  .63, 3.15) 1.77  1.94   .64
                     -O  ( 8,  .63, 3.15) 1.77  1.94   .64
                     -O  ( 8,  .63, 3.15) 1.77  2.39   .19

  Bond valence sum for V   4.04

......V3O6

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.62  1.51
                     -O  ( 8,  .63, 3.15) 1.77  1.99   .55
                     -O  ( 8,  .63, 3.15) 1.77  2.06   .46
                     -O  ( 8,  .63, 3.15) 1.77  1.94   .64
                     -O  ( 8,  .63, 3.15) 1.77  1.93   .66
                     -O  ( 8,  .63, 3.15) 1.77  2.46   .16

  Bond valence sum for V   3.98

......V4O5

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.64  1.43
                     -O  ( 8,  .63, 3.15) 1.77  2.08   .43
                     -O  ( 8,  .63, 3.15) 1.77  1.86   .79
```

```
                    -O  ( 8,  .63, 3.15) 1.77  1.95   .62
                    -O  ( 8,  .63, 3.15) 1.77  1.90   .70

  Bond valence sum for V   3.98

.......V5O6

  V  (23, 1.21, 1.45)                      Rij   Dij   Vij
                    -O  ( 8,  .63, 3.15) 1.77  1.63  1.48
                    -O  ( 8,  .63, 3.15) 1.77  1.93   .65
                    -O  ( 8,  .63, 3.15) 1.77  2.00   .55
                    -O  ( 8,  .63, 3.15) 1.77  2.05   .48
                    -O  ( 8,  .63, 3.15) 1.77  1.96   .61
                    -O  ( 8,  .63, 3.15) 1.77  2.45   .16

  Bond valence sum for V   3.92

.......V6O6

  V  (23, 1.21, 1.45)                      Rij   Dij   Vij
                    -O  ( 8,  .63, 3.15) 1.77  1.63  1.46
                    -O  ( 8,  .63, 3.15) 1.77  2.06   .46
                    -O  ( 8,  .63, 3.15) 1.77  1.96   .60
                    -O  ( 8,  .63, 3.15) 1.77  1.93   .65
                    -O  ( 8,  .63, 3.15) 1.77  1.99   .56
                    -O  ( 8,  .63, 3.15) 1.77  2.33   .22

  Bond valence sum for V   3.96

.......V7O5

  V  (23, 1.21, 1.45)                      Rij   Dij   Vij
                    -O  ( 8,  .63, 3.15) 1.77  1.62  1.51
                    -O  ( 8,  .63, 3.15) 1.77  2.00   .55
                    -O  ( 8,  .63, 3.15) 1.77  1.94   .64
                    -O  ( 8,  .63, 3.15) 1.77  1.99   .56
                    -O  ( 8,  .63, 3.15) 1.77  1.98   .57

  Bond valence sum for V   3.84

.......V8O5

  V  (23, 1.21, 1.45)                      Rij   Dij   Vij
                    -O  ( 8,  .63, 3.15) 1.77  1.63  1.46
                    -O  ( 8,  .63, 3.15) 1.77  1.88   .75
                    -O  ( 8,  .63, 3.15) 1.77  2.00   .55
                    -O  ( 8,  .63, 3.15) 1.77  1.89   .72
                    -O  ( 8,  .63, 3.15) 1.77  2.08   .44
```

```
  Bond valence sum for V   3.92

......V9O6

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.63  1.49
                     -O  ( 8,  .63, 3.15) 1.77  1.96   .60
                     -O  ( 8,  .63, 3.15) 1.77  2.07   .45
                     -O  ( 8,  .63, 3.15) 1.77  1.94   .64
                     -O  ( 8,  .63, 3.15) 1.77  1.98   .57
                     -O  ( 8,  .63, 3.15) 1.77  2.45   .16

  Bond valence sum for V   3.91

......V10O6

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.62  1.50
                     -O  ( 8,  .63, 3.15) 1.77  1.95   .62
                     -O  ( 8,  .63, 3.15) 1.77  1.95   .62
                     -O  ( 8,  .63, 3.15) 1.77  2.06   .47
                     -O  ( 8,  .63, 3.15) 1.77  2.05   .47
                     -O  ( 8,  .63, 3.15) 1.77  2.33   .22

  Bond valence sum for V   3.90

......V11O5

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.61  1.54
                     -O  ( 8,  .63, 3.15) 1.77  1.96   .61
                     -O  ( 8,  .63, 3.15) 1.77  2.05   .48
                     -O  ( 8,  .63, 3.15) 1.77  1.96   .60
                     -O  ( 8,  .63, 3.15) 1.77  1.95   .62

  Bond valence sum for V   3.85

......V12O6

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.62  1.52
                     -O  ( 8,  .63, 3.15) 1.77  1.93   .65
                     -O  ( 8,  .63, 3.15) 1.77  1.99   .56
                     -O  ( 8,  .63, 3.15) 1.77  2.09   .43
                     -O  ( 8,  .63, 3.15) 1.77  1.98   .57
                     -O  ( 8,  .63, 3.15) 1.77  2.42   .17
```

```
  Bond valence sum for V   3.91

......V13O5

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.65  1.40
                     -O  ( 8,  .63, 3.15) 1.77  2.14   .37
                     -O  ( 8,  .63, 3.15) 1.77  1.89   .74
                     -O  ( 8,  .63, 3.15) 1.77  1.96   .61
                     -O  ( 8,  .63, 3.15) 1.77  1.89   .73

  Bond valence sum for V   3.85

......V14O6

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.67  1.33
                     -O  ( 8,  .63, 3.15) 1.77  1.91   .70
                     -O  ( 8,  .63, 3.15) 1.77  1.93   .65
                     -O  ( 8,  .63, 3.15) 1.77  2.05   .48
                     -O  ( 8,  .63, 3.15) 1.77  2.08   .43
                     -O  ( 8,  .63, 3.15) 1.77  2.19   .32

  Bond valence sum for V   3.92

......V15O5

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.62  1.54
                     -O  ( 8,  .63, 3.15) 1.77  1.96   .61
                     -O  ( 8,  .63, 3.15) 1.77  1.93   .66
                     -O  ( 8,  .63, 3.15) 1.77  1.96   .61
                     -O  ( 8,  .63, 3.15) 1.77  2.06   .46

  Bond valence sum for V   3.88

......V16O5

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.64  1.43
                     -O  ( 8,  .63, 3.15) 1.77  1.89   .73
                     -O  ( 8,  .63, 3.15) 1.77  2.02   .51
                     -O  ( 8,  .63, 3.15) 1.77  1.88   .74
                     -O  ( 8,  .63, 3.15) 1.77  2.12   .40

  Bond valence sum for V   3.81

......V17O5
```

```
  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.65  1.39
                     -O  ( 8,  .63, 3.15) 1.77  2.10   .41
                     -O  ( 8,  .63, 3.15) 1.77  1.88   .75
                     -O  ( 8,  .63, 3.15) 1.77  1.88   .75
                     -O  ( 8,  .63, 3.15) 1.77  1.95   .61

  Bond valence sum for V   3.91

......V18O5

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.64  1.43
                     -O  ( 8,  .63, 3.15) 1.77  1.99   .56
                     -O  ( 8,  .63, 3.15) 1.77  1.88   .76
                     -O  ( 8,  .63, 3.15) 1.77  1.90   .71
                     -O  ( 8,  .63, 3.15) 1.77  2.11   .40

  Bond valence sum for V   3.87

......V19O4

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.70  1.21
                     -O  ( 8,  .63, 3.15) 1.77  1.70  1.22
                     -O  ( 8,  .63, 3.15) 1.77  1.73  1.13
                     -O  ( 8,  .63, 3.15) 1.77  1.72  1.16

  Bond valence sum for V   4.72
```

Compound 2

```
Bond valence calculation. Numbers in brackets after atom symbols are
at.no., r and c - see O"Keeffe and Brese, J.A.C.S. 1991, 113, 3226

......V1

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.96   .61
                     -O  ( 8,  .63, 3.15) 1.77  1.97   .59
                     -O  ( 8,  .63, 3.15) 1.77  1.95   .62
                     -O  ( 8,  .63, 3.15) 1.77  1.94   .63
                     -O  ( 8,  .63, 3.15) 1.77  1.63  1.49

  Bond valence sum for V   3.93
```

```
......V2

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.96   .61
                     -O  ( 8,  .63, 3.15) 1.77  1.97   .60
                     -O  ( 8,  .63, 3.15) 1.77  1.96   .61
                     -O  ( 8,  .63, 3.15) 1.77  1.96   .61
                     -O  ( 8,  .63, 3.15) 1.77  1.62  1.52

  Bond valence sum for V   3.94

......V3

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.94   .63
                     -O  ( 8,  .63, 3.15) 1.77  1.95   .61
                     -O  ( 8,  .63, 3.15) 1.77  1.95   .61
                     -O  ( 8,  .63, 3.15) 1.77  1.92   .67
                     -O  ( 8,  .63, 3.15) 1.77  1.63  1.48

  Bond valence sum for V   4.01

......V4

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.96   .61
                     -O  ( 8,  .63, 3.15) 1.77  1.90   .71
                     -O  ( 8,  .63, 3.15) 1.77  1.88   .75
                     -O  ( 8,  .63, 3.15) 1.77  1.94   .64
                     -O  ( 8,  .63, 3.15) 1.77  1.61  1.55

  Bond valence sum for V   4.26

......V5

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
                     -O  ( 8,  .63, 3.15) 1.77  1.96   .60
                     -O  ( 8,  .63, 3.15) 1.77  1.89   .72
                     -O  ( 8,  .63, 3.15) 1.77  1.92   .68
                     -O  ( 8,  .63, 3.15) 1.77  1.89   .73
                     -O  ( 8,  .63, 3.15) 1.77  1.60  1.58

  Bond valence sum for V   4.32

......V6

  V  (23, 1.21, 1.45)                          Rij   Dij   Vij
```

```
                    -O  ( 8,  .63, 3.15) 1.77  1.94   .64
                    -O  ( 8,  .63, 3.15) 1.77  1.96   .61
                    -O  ( 8,  .63, 3.15) 1.77  1.95   .62
                    -O  ( 8,  .63, 3.15) 1.77  1.95   .62
                    -O  ( 8,  .63, 3.15) 1.77  1.62  1.51

  Bond valence sum for V   3.99

......V7

  V  (23, 1.21, 1.45)                        Rij   Dij   Vij
                    -O  ( 8,  .63, 3.15) 1.77  1.93   .65
                    -O  ( 8,  .63, 3.15) 1.77  1.95   .62
                    -O  ( 8,  .63, 3.15) 1.77  1.95   .63
                    -O  ( 8,  .63, 3.15) 1.77  1.98   .58
                    -O  ( 8,  .63, 3.15) 1.77  1.62  1.51

  Bond valence sum for V   3.98

......V8

  V  (23, 1.21, 1.45)                        Rij   Dij   Vij
                    -O  ( 8,  .63, 3.15) 1.77  1.92   .67
                    -O  ( 8,  .63, 3.15) 1.77  1.97   .59
                    -O  ( 8,  .63, 3.15) 1.77  1.96   .60
                    -O  ( 8,  .63, 3.15) 1.77  1.92   .67
                    -O  ( 8,  .63, 3.15) 1.77  1.64  1.43

  Bond valence sum for V   3.96

......V9

  V  (23, 1.21, 1.45)                        Rij   Dij   Vij
                    -O  ( 8,  .63, 3.15) 1.77  1.95   .63
                    -O  ( 8,  .63, 3.15) 1.77  1.92   .67
                    -O  ( 8,  .63, 3.15) 1.77  1.93   .65
                    -O  ( 8,  .63, 3.15) 1.77  1.94   .63
                    -O  ( 8,  .63, 3.15) 1.77  1.64  1.45

  Bond valence sum for V   4.03
```

Section S5. X-ray photoelectron spectra for compounds 1 and 2

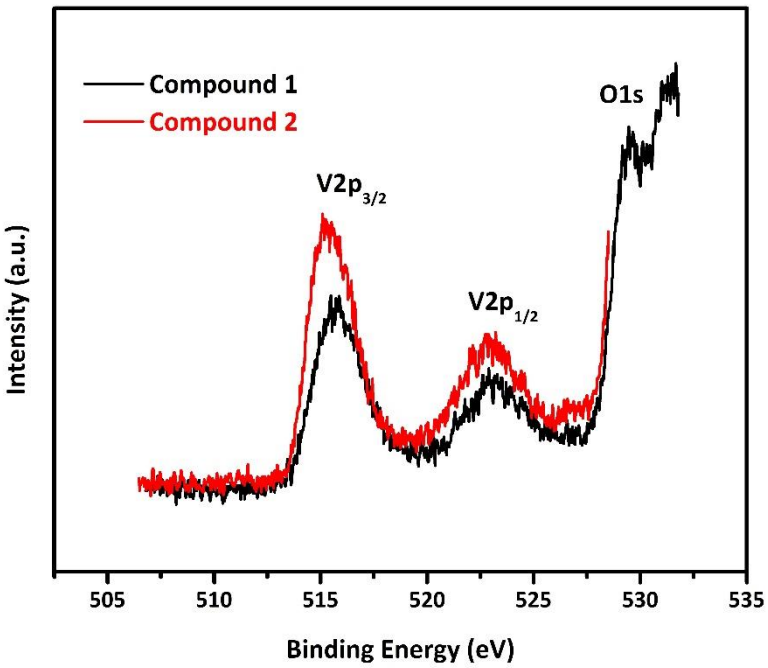


Fig. S6 Vanadium core level XPS spectra of compounds **1** and **2**.

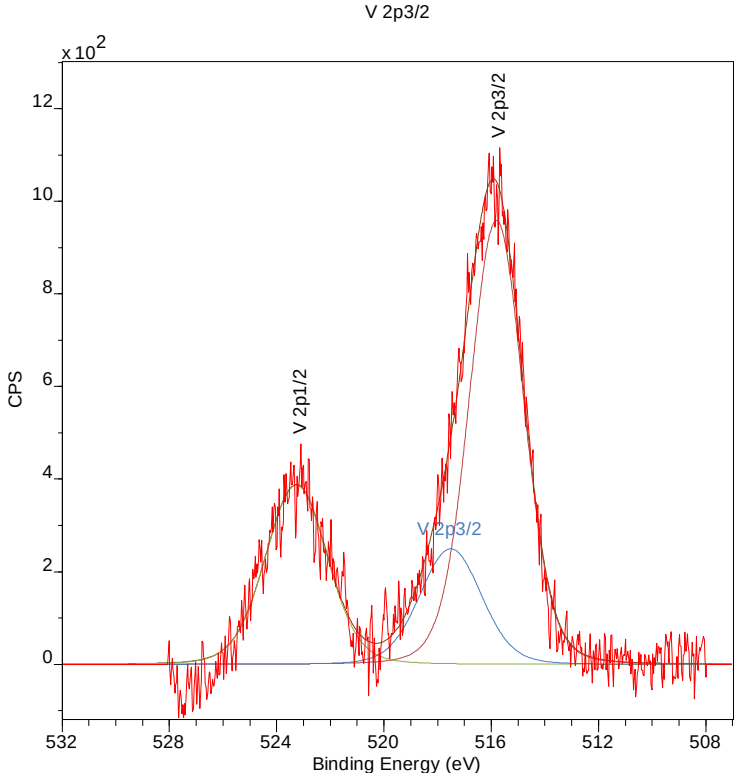


Fig. S7 Deconvoluted XPS spectrum of compound **1**.

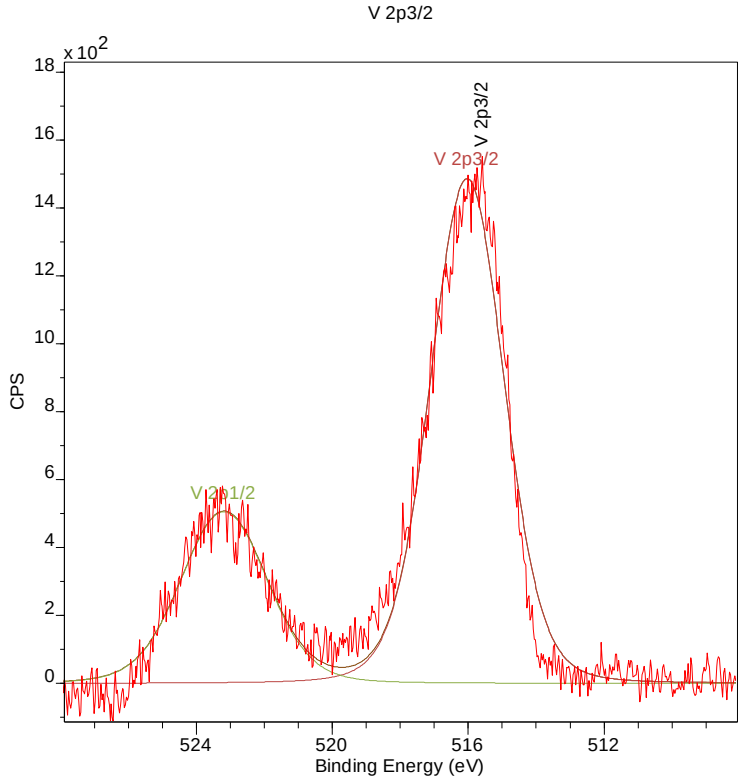


Fig. S8 Deconvoluted XPS spectrum of compound **2**.

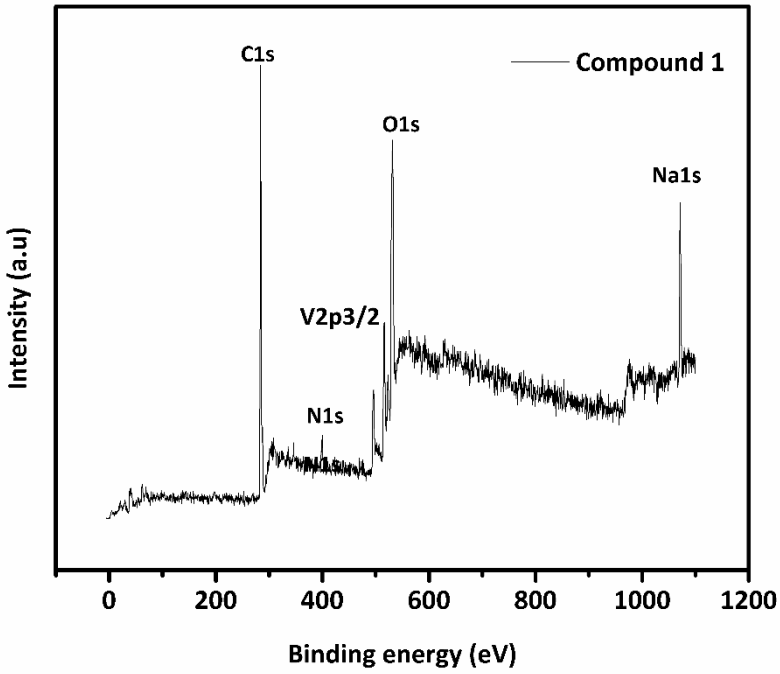


Fig. S9 Survey scan XPS spectrum of compound **1**.

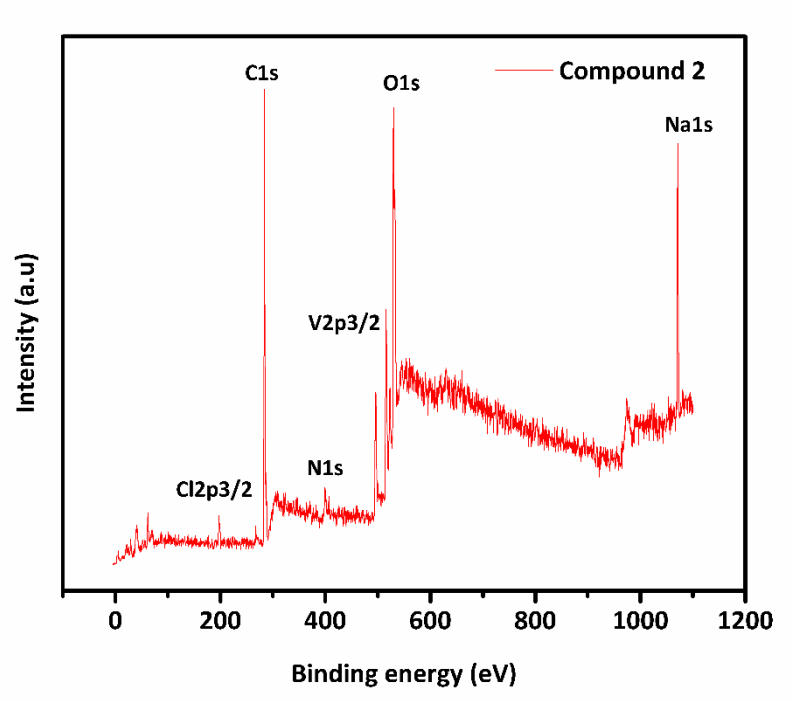
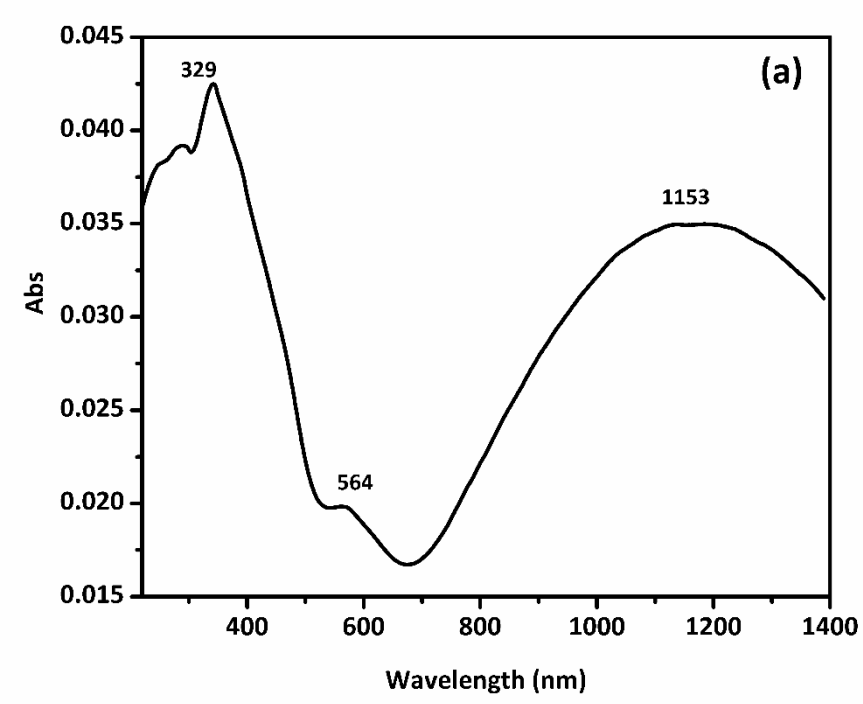


Fig. S10 Survey scan XPS spectrum of compound **2**.

Section S6. UV-Vis absorption spectra for compounds 1 and 2



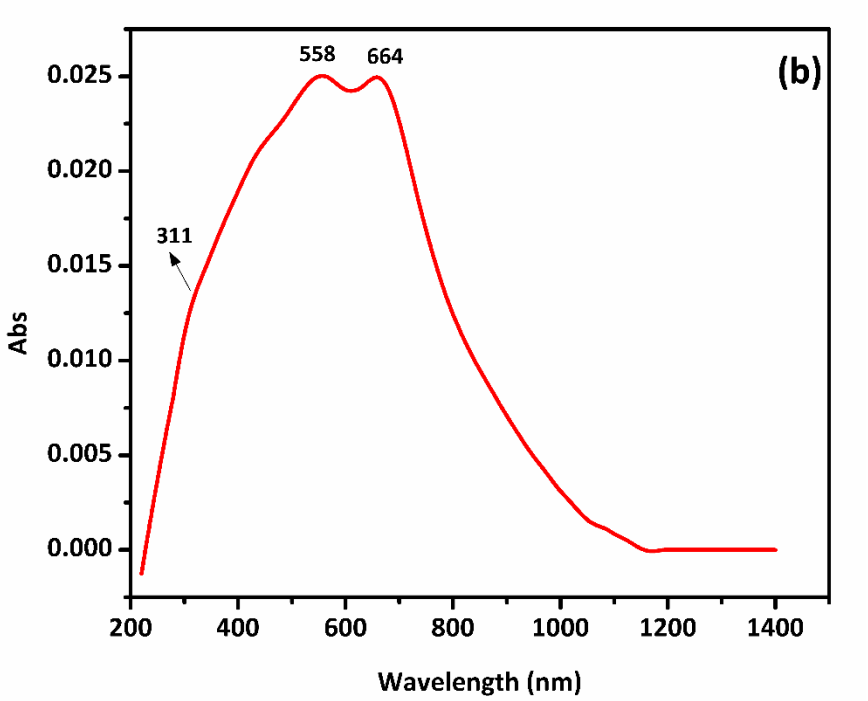


Fig. S11 UV-visible spectra of compound **1**(Fig. **a**) and compound **2**(Fig. **b**).

Section S7. ICP-OES and CHN analysis reports of compounds 1 and 2

PBMDJFKBPCKEIH
KBPEOBJF
PMLFAFCEJJCJGD
IPFMGADF
PKCAFALEBHHGNB
CJFKGHBF

Issued to:
Dr.Sathish Kumar Kurapati
C/o Prof.Samar K Das, School of Chemistry,
University of Hyderabad, Hyderabad-500046.

Kind Attn.:Mr.Sateesh.M, 9908652965

Report No. : LLPL/18-19/001890
Issue Date : 08/06/2018
Customer Ref. : TRF
Ref.Date : 31/05/2018

Sample Particulars : NaV19O46

Qty. Received : 1No Vial

Test Parameters : Vanadium as V,Sodium as Na

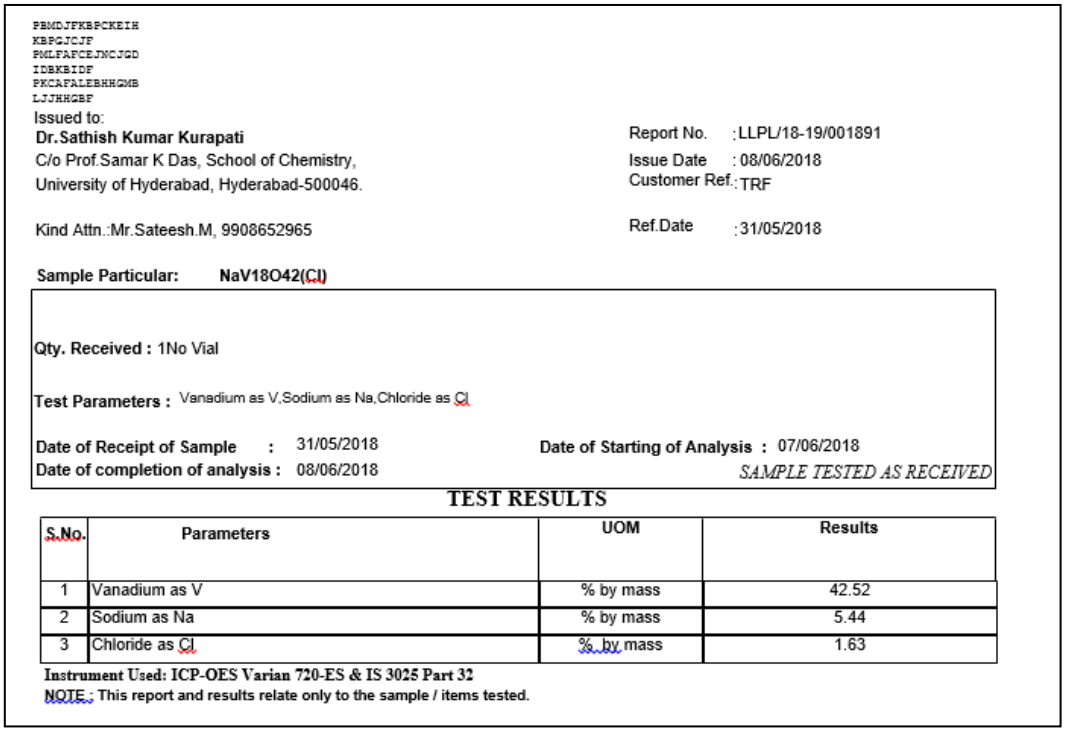
Date of Receipt of Sample : 31/05/2018
Date of completion of analysis : 08/06/2018
Date of Starting of Analysis : 07/06/2018
SAMPLE TESTED AS RECEIVED

TEST RESULTS

S.No.	Parameters	UOM	Results
1	Vanadium as V	% by mass	42.33
2	Sodium as Na	% by mass	7.20

Instrument Used: ICP-OES Varian 720-ES
NOTE : This report and results relate only to the sample / items tested.

Fig. S12 ICP-OES analysis of compound **1**.



PBMDJFKBPCKEIH
KBPGJCJF
PMLFAFCEJNCJGD
IDBKBIDF
PKCAPALEBHHGMB
LJJHHGBF

Issued to:
Dr.Sathish Kumar Kurapati
C/o Prof.Samar K Das, School of Chemistry,
University of Hyderabad, Hyderabad-500046.

Kind Attn.:Mr.Sateesh.M, 9908652965

Report No. : LLPL/18-19/001891
Issue Date : 08/06/2018
Customer Ref.: TRF

Ref.Date : 31/05/2018

Sample Particular: **NaV18O42(Cl)**

Qty. Received : 1No Vial

Test Parameters : Vanadium as V,Sodium as Na,Chloride as Cl

Date of Receipt of Sample : 31/05/2018
Date of completion of analysis : 08/06/2018

Date of Starting of Analysis : 07/06/2018

SAMPLE TESTED AS RECEIVED

TEST RESULTS

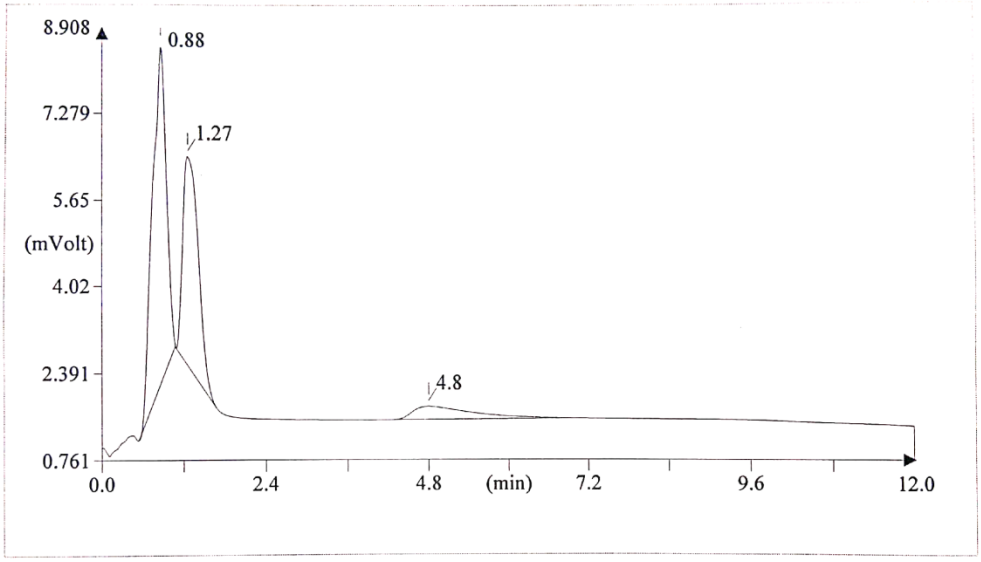
S.No.	Parameters	UOM	Results
1	Vanadium as V	% by mass	42.52
2	Sodium as Na	% by mass	5.44
3	Chloride as Cl	% by mass	1.63

Instrument Used: ICP-OES Varian 720-ES & IS 3025 Part 32
NOTE : This report and results relate only to the sample / items tested.

Fig. S13 ICP-OES analysis of compound **2**.

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	NA-V19 (# 31)
Analysis type:	UnkNown
Chromatogram filename:	UNK-01042019-1.dat
Sample weight:	1.048



Element Name	Element %	Ret. Time
Nitrogen	1. 28	0. 88
Carbon	0. 09	1. 27
Hydrogen	2. 42	4. 80

Fig. S14 CHN analysis report of compound **1**.

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
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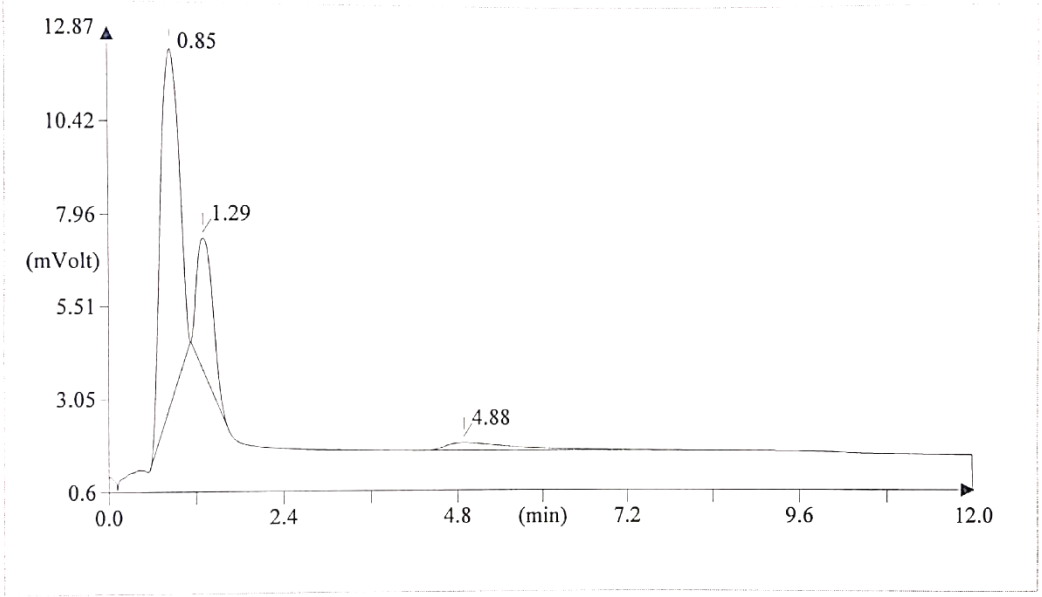
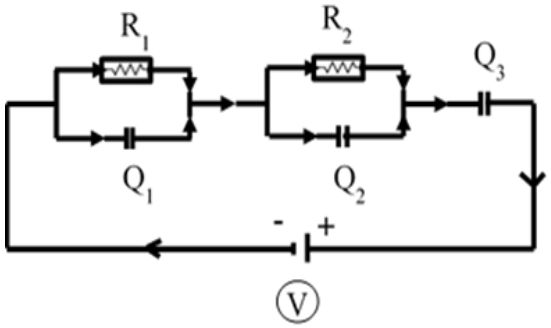


Element Name	Element %	Ret. Time
Nitrogen	4. 86	0. 85
Carbon	0. 12	1. 29
Hydrogen	3. 23	4. 88

Fig. S15 CHN analysis report of compound **2**.

Section S8. Electrochemical Impedance spectra analysis of compounds 1 and 2 and controlled experiments

a) Calculation of proton conductivity from Impedance spectra by fitting with equivalent circuit as described below:



Impedance data of compounds **1** and **2** were fitted with the equivalent circuit **{(R_1/Q_1)+(R_2/Q_2)+Q_3}** that consists of three main components, connected in a series. The first component (Z_1) contains (R_1/Q_1) contributing to electrolyte impedance/resistance. The second component (Z_2) represents (R_2/Q_2) contributing to resistance of electrolyte-electrode interface. The third one (Q_3) is a constant phase element contributing to lower region frequency of the Nyquist plot. However, the electrolyte resistance R_1 is considered to calculate the conductivity of electrolyte. Here, the tables, given below, provide the R_1 values obtained by fitting of experimental impedance data for compounds **1** and **2**.

Table S3. Fitting parameters used to calculate proton conductivity for compound **1** at various temperatures and 70% relative humidity (RH).

Temp. (^{o}C)	R_1(Ω)	Conductivity (Scm^{-1})
50	82.71	3.01×10^{-3}
40	226.3	1.10×10^{-3}
30	433.2	5.74×10^{-4}
20	587.2	4.24×10^{-4}

Table S4. Fitting parameters used to calculate proton conductivity for compound **2** at various temperatures and 70% relative humidity (RH).

Temp. (^{o}C)	R_1(Ω)	Conductivity (Scm^{-1})
50	1228	1.97×10^{-4}
40	1818	1.33×10^{-4}
30	3137	7.73×10^{-5}
20	4319	5.61×10^{-5}

Calculation of proton conductivity for compound 1 from R_1 value at 50 ^oC using the formula, described below:

$$R = \rho \times \frac{l}{a} \quad \ldots\ldots\ldots\ldots\ldots \textit{Eqn (1)}$$

Here we know that,
R = resistance of the electrolyte (R1)
ρ = specific resistance of the electrolyte
l = thickness of the pallet (cm)
a = cross section area of pellet (cm^2)
Therefore, $x = \frac{l}{a}$
Than the *Eqn (1)* can be written as,

$$\rho = \frac{R}{x} \ldots\ldots\ldots\ldots\ldots \textit{Eqn (2)}$$

R_1 = 82.71 (**Ω**)
l = 0.286 cm
a = 1.1455 cm^2
Therefore, x = 0.249 cm^{-1} (~ 0.25)
Specific resistance of the electrolyte (ρ) = 332.16 **Ω** cm
We calculated specific resistance from *Eqn (2),*
Than we know that, the conductance is inversely proportion to the resistance.

$$\sigma = \frac{1}{\rho} \ldots\ldots\ldots\ldots\ldots \textit{Eqn (3)}$$

By putting the specific resistance value in *Eqn (3),* we get the specific conductivity of compound **1** at 50 ^oC.
Thus, the proton conductivity of compound **1**, $(\boldsymbol{\sigma})_{50\ ^oC}$ = **3.01×10^{-3} Scm^{-1}**.

* *Note:* Similar data fitting and calculation procedures were used to calculate proton conductivity values for **1** and **2** at various experimental conditions.

Calculation of activation energy (*Ea*) for compounds 1 and 2:
Activation energy of compounds **1** and **2** for their proton conductivity was calculated from their variable temperature conductivity values. The derived plot was constructed as **ln(σT)** *vs* **1000/T** (refer to main text). The slope value of the plot was used in Arrhenius equation to calculate the activation energies for compounds **1** and **2**.

From Arrhenius equation,

$$\boldsymbol{\sigma T = A.e^{\left(-\frac{Ea}{RT}\right)}} \ldots\ldots\ldots\ldots\ldots \textit{Eqn (4)}$$

Here, $\boldsymbol{\sigma}$ = conductivity of electrolyte, *i.e.,* proton conductivity;
-Ea **=** activation energy for proton conduction;
R = Ideal gas constant; ***T*** = temperature in Kelvins (K) scale.

Eqn (4) can be written as,

$$\boldsymbol{ln(\sigma T) = lnA - \left(\frac{Ea}{RT}\right)} \text{..... } \textit{Eqn (5)}$$

Eqn (5) can be rewritten as,

$$\boldsymbol{ln(\sigma T) = lnA - \left(\frac{Ea}{R\times 1000}\right) \times \left(\frac{1000}{T}\right)} \text{ ..... } \textit{Eqn (6)}$$

Eqn (6) represent the straight line between **ln(σT)** and **1000/T**.

Thus, value of slope **(m)** = $-\left(\frac{\boldsymbol{Ea}}{\boldsymbol{R\times 1000}}\right)$

For compound **1 s**lope (**m**) = **-**2.813 S cm^{-1} K^2.
And compound **2** slope (**m**) = **-**2.194 S cm^{-1} K^2.

Therefore, the activation energy for compound **1**, ***Ea*** **= 0.24 eV (23.3 kJ/mol),**
Whereas for compound **2**, ***Ea*** **= 0.19 eV (18.4 kJ/mol)**

b) Detailed calculations of standard deviation of proton conductivity values for compounds 1 and 2:

The following equation (**1**) was used to calculate the standard deviation of compounds **1** and **2**. For this calculation, four proton conductivity measurements were recorded in 24 hours with 6 hours regular time intervals at a particular temperature and relative humidity (i.e., 50 ^oC and 70% RH). The obtained four proton conductivity values were used to calculate the standard deviation for compounds **1** and **2**.

$$S^2 = \frac{\sum(xi-xa)^2}{n-1} \text{ ..... equation (1)}$$

Hence here,

xi = Proton conductivity value,

xa = Mean value of total number of proton conductivity values, here is four data points,

n = Number of data points,

S = Standard deviation.

For compound **1**:

Cycle number	xi	xa	$(xi - xa)$	$(xi - xa)^2$
1st	3.01×10^{-3}	3.62×10^{-3}	6.1×10^{-4}	3.72×10^{-7}
2nd	2.99×10^{-3}		6.3×10^{-4}	3.96×10^{-7}
3rd	3.68×10^{-3}		6.0×10^{-5}	3.6×10^{-9}
4th	4.83×10^{-3}		1.2×10^{-3}	1.46×10^{-6}

Note: the sign is taken as positive in the calculation of $(xi - xa)$ and$(xi - xa)$.

$$xa = \frac{sum\ of all\ xi\ values}{number\ of\ data\ points} \ldots\ldots\ldots\ldots\ldots\ldots \text{equation (2)}$$

$$xa = \frac{\{(3.01 \times 10\text{^}(-3)) + (2.99 \times 10\text{^}(-3)) + (3.68 \times 10\text{^}(-3)) + (4.83 \times 10\text{^}(-3))\}}{4}$$

$$xa = 3.627/1000$$

The total sum value of $(xi - xa)^2$ = 2.231×10^{-6}

Equation **1** written as, $S = \sqrt{\frac{\sum(xi-xa)^2}{n-1}}$

$$S = \sqrt{\frac{\sum 2.231 \times 10\text{^}(-6)}{4-1}}$$

$$S = \sqrt{7.438 \times 10\text{^}(-7)}$$

*Standard deviation for compound **1** (S)* = $\mathbf{8.62\times10^{-4}}$ Scm^{-1}

For compound **2**:

The same calculation procedure of compound **1** followed to calculate the standard deviation of compound **2**.

Cycle number	xi	xa	$(xi - xa)$	$(xi - xa)^2$
1^{st}	1.97×10^{-4}	2.16×10^{-4}	1.9×10^{-5}	3.61×10^{-10}
2^{nd}	1.86×10^{-4}		3.0×10^{-5}	9.0×10^{-10}
3^{rd}	1.96×10^{-4}		2.0×10^{-5}	4.0×10^{-10}
4^{th}	2.85×10^{-4}		6.9×10^{-5}	4.76×10^{-9}

The total sum value of $(xi - xa)^2$= 6.421×10^{-9}

*Standard deviation for compound **2** (S)* =$\mathbf{4.621\times10^{-5}}$ Scm^{-1}

c) Controlled experiments on residual electrolyte of compounds 1 and 2 after EIS measurements

(1) FTIR spectra:

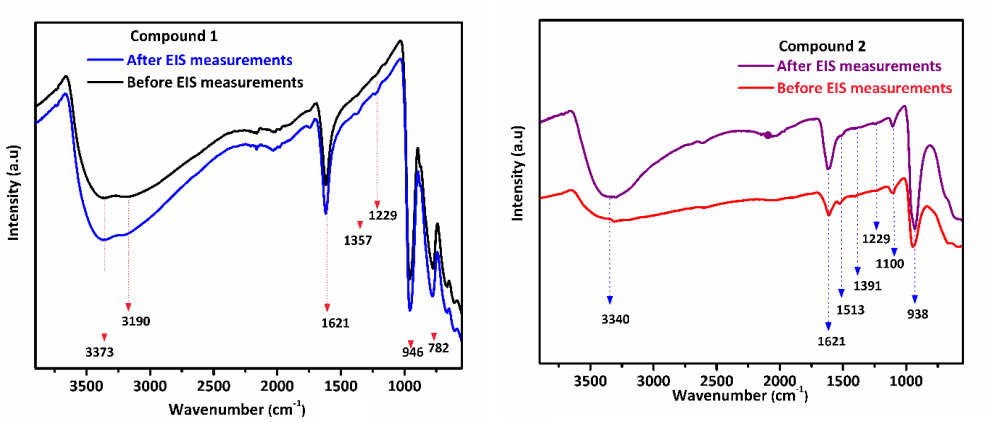


Fig. S16 FTIR spectra of compound **1** (left) and compound **2** (right) before and after EIS measurements.

(2) Raman spectra:

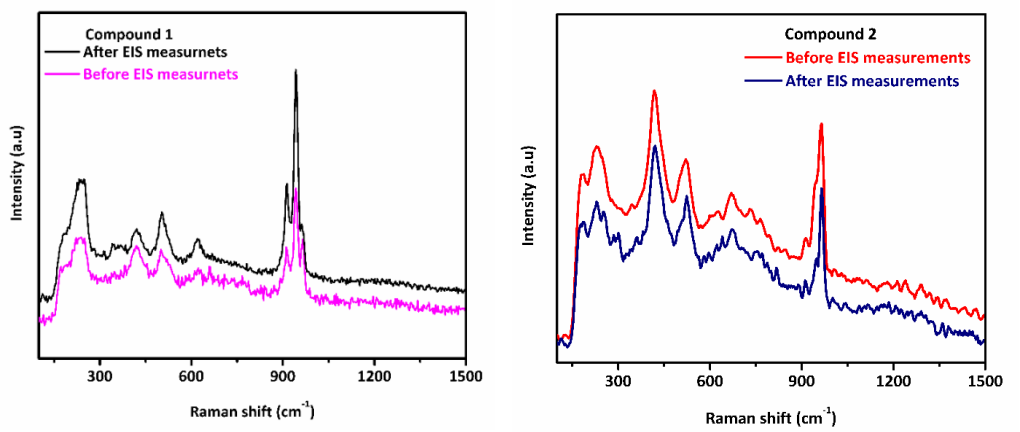


Fig. S17 Raman spectra of compound **1**(left) and compound **2** (right) before and after EIS measurements.

(3) UV-Vis absorption spectra:

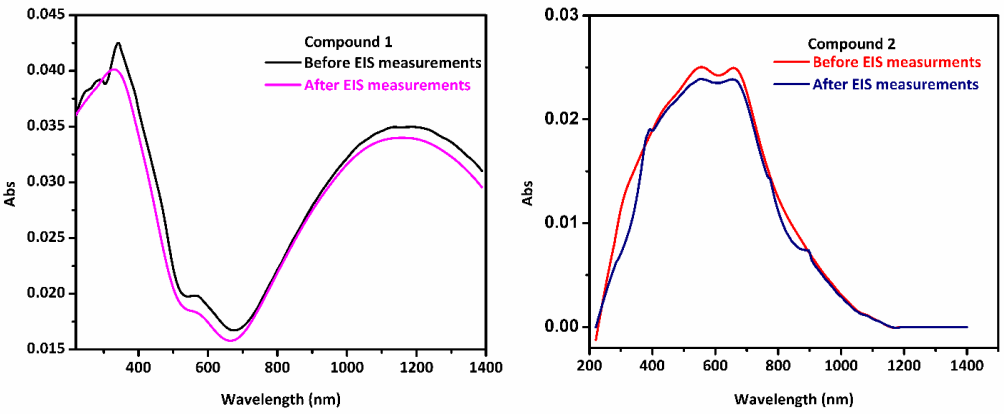


Fig. S18 UV-visible spectra of compound **1** (left) and compound **2** (right) before and after EIS measurements.

(4) PXRD profiles:

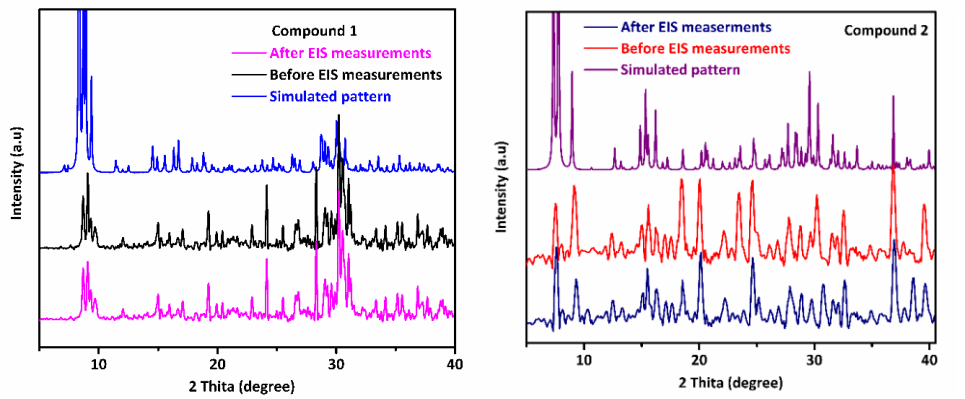


Fig. S19 Powder X-ray diffraction analysis of compound **1** (left) and compound **2** (right) before and after EIS measurements.

(5) XPS spectra:

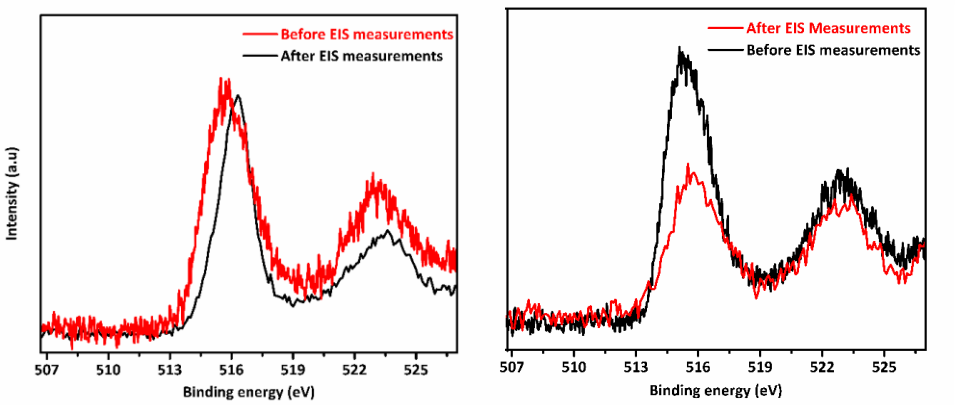


Fig. S20 XPS spectra of compound **1**(left) and compound **2** (right) before and after EIS measurements.

Table S5. Comparison of proton conductivity values of compounds **1** and **2** with those of other reported POMs

S.No	Compound Name/formula	Conductivity (S cm^{-1})	E_a (kJ $mole^{-1}$)	Conditions	References	Type
1	$H_3[PMo_{12}O_{40}].29H_2O$	1.8×10^{-1}	15.5	25°C, 85% RH	**S1**	POM
2	$[I_3\subset(Mo^{V}{}_2O_2S_2)_8(Se^{IV}O_3)_8(OH)_8]^{9-}$	1.2×10^{-2}	74.29	55 °C, 97% RH	**S2**	POM
3	$[Zn(P_3Mo_6O_{29})_2]^{12-}$	1.04×10^{-2}	21.22	80 °C, 75% RH	**S3**	POM
4	$[H_8P_2W_{16}V_2O_{62}].20H_2O$	1.89×10^{-2}	31.91	18 °C, 80% RH	**S4**	POM
5	$[H_7SiW_9V_3O_{40}].9H_2O$	8.11×10^{-3}	26.69	58 °C, 50% RH	**S5**	POM
6	**$[H_8V_{18}O_{42}(VO_4)]^{7-}$ (1)**	**3.01×10^{-3}**	**23.34**	**50 °C, 70% RH**	**This work**	**POM**
7	**$[H_8V_{18}O_{42}(VO_4)]^{5-}$ (2)**	**2.16×10^{-4}**	**18.40**	**50 °C, 70% RH**	**This work**	**POM**
8	$[MnV_{13}O_{38}]^{7-}$	4.68×10^{-3}	43.41	61 °C, 97% RH	**S6**	POM
9	$[PMo^{V}{}_{18}Mo^{V}{}_4V^{IV}{}_4O_{42}]^{11-}$	1.5×10^{-3}	31.83	75 °C, 98% RH	**S7**	POM-MOF
10	$H_6[SiW_9MoV_2O_{40}]\cdot15H_2O$	6.01×10^{-3}	27.5	22 °C, 80% RH	**S8**	POM
11	$NbO_2(OH)$-PW_{12}	7.3×10^{-3}	37.62	77 °C, 97% RH	**S9**	POM
12	$[\varepsilon$-$H_2PMo_8{}^{V}Mo_4{}^{VI}O_{40}Zn_4]^{3-}$	1.5×10^{-5}	114.81	90 °C, 85% RH	**S10**	POM
13	$[Mo_6O_{16}(OH)(H_2O)_4]_4^{12-}$	2.19×10^{-2}	62.39	90 °C, 98% RH	**S11**	ATMP-POM
14	(HPW-*meso-silica*)	1.104×10^{-1}	~14	90 °C, 100% RH	**S12**	POM-PEM
15	TiO_2-P_2O_5	1.6×10^{-2}	8.68	160 °C, 100% RH	**S13**	CGMN
16	EB-COF:PW_{12}	3.32×10^{-3}	23.15	25 °C, 97% RH	**S14**	POM-COF
17	POM-SVP_{97}K-5	2.21×10^{-4}	13.50	25 – 65 °C, 0% RH	**S15**	POM-PEM

Abbreviations:

- *(**POM-OF**) a Polyoxometalate Based Open Framework.*
- ***(ATMP-POM)** Amino trimethylene phosphonic acid based polyoxometalate.*
- ***(POMOF)** polyoxometalates based metal organic frame work.*
- ***(POM-PEM)** polyoxometalates proton exchange membrane.*
- ***(POM-COF)** polyoxometalates based covalent organic frame work.*
- ***(CGMN)** Crystalline Glass, Mesoporous Nanocomposite.*

Section S9. References

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End