

Supporting Information

A new polyoxometalate-based Mo/V coordinated crystalline hybrid and its catalytic activity in aerobic hydroxylation of benzene

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Table S1 Bond valence sum for selected V and Mo of [MoVbpy]HPMoV₂.

V7	3.69
Mo7	5.51

Table S2. Bonds distances (Å) and angles (°) for [MoVbpy]HPMoV₂

Mo(1)-O(3)	1.644(5)	O(14)#1-Mo(2)-O(4A)#1	91.6(3)	O(3A)-O(1A)-V(3)#1	131.4(6)
Mo(1)-O(12)	1.804(6)	O(11)#1-Mo(2)-O(4A)#1	64.8(3)	P(1)-O(1A)-Mo(3)#1	124.9(5)
Mo(1)-O(5)	1.870(6)	O(17)-Mo(2)-O(1A)	160.2(4)	O(4A)#1-O(1A)-Mo(3)#1	131.5(6)
Mo(1)-O(21)	1.932(6)	O(16)-Mo(2)-O(1A)	64.9(3)	O(2A)#1-O(1A)-Mo(3)#1	68.8(4)
Mo(1)-O(20)	2.009(7)	O(13)-Mo(2)-O(1A)	94.8(3)	O(3A)-O(1A)-Mo(3)#1	131.4(6)
Mo(1)-O(3A)	2.476(9)	O(14)#1-Mo(2)-O(1A)	63.6(3)	V(3)#1-O(1A)-Mo(3)#1	0.00(4)
Mo(1)-O(2A)	2.488(9)	O(11)#1-Mo(2)-O(1A)	92.3(3)	P(1)-O(1A)-Mo(2)	125.1(5)
Mo(2)-O(17)	1.640(6)	O(4A)#1-Mo(2)-O(1A)	40.6(3)	O(4A)#1-O(1A)-Mo(2)	69.4(4)
Mo(2)-O(16)	1.844(6)	O(15)-Mo(3)-O(21)	102.8(3)	O(2A)#1-O(1A)-Mo(2)	136.8(6)
Mo(2)-O(13)	1.874(6)	O(15)-Mo(3)-O(14)	101.9(3)	O(3A)-O(1A)-Mo(2)	128.3(6)
Mo(2)-O(14)#1	1.919(6)	O(21)-Mo(3)-O(14)	90.4(3)	V(3)#1-O(1A)-Mo(2)	92.9(3)
Mo(2)-O(11)#1	1.941(6)	O(15)-Mo(3)-O(18)#1	100.1(3)	Mo(3)#1-O(1A)-Mo(2)	92.9(3)
Mo(2)-O(4A)#1	2.452(8)	O(21)-Mo(3)-O(18)#1	157.1(3)	P(1)-O(1A)-Mo(5)	121.4(5)
Mo(2)-O(1A)	2.460(9)	O(14)-Mo(3)-O(18)#1	86.1(3)	O(4A)#1-O(1A)-Mo(5)	131.9(6)
Mo(3)-O(15)	1.643(5)	O(15)-Mo(3)-O(19)	100.7(4)	O(2A)#1-O(1A)-Mo(5)	126.1(6)
Mo(3)-O(21)	1.840(6)	O(21)-Mo(3)-O(19)	89.1(3)	O(3A)-O(1A)-Mo(5)	66.0(4)
Mo(3)-O(14)	1.884(6)	O(14)-Mo(3)-O(19)	156.9(3)	V(3)#1-O(1A)-Mo(5)	91.6(3)
Mo(3)-O(18)#1	1.904(6)	O(18)#1-Mo(3)-O(19)	85.4(3)	Mo(3)#1-O(1A)-Mo(5)	91.6(3)
Mo(3)-O(19)	1.912(6)	O(15)-Mo(3)-O(2A)	160.2(3)	Mo(2)-O(1A)-Mo(5)	91.6(3)
Mo(3)-O(2A)	2.430(9)	O(21)-Mo(3)-O(2A)	66.7(3)	P(1)-O(2A)-O(1A)#1	55.1(4)
Mo(3)-O(1A)#1	2.453(9)	O(14)-Mo(3)-O(2A)	95.0(3)	P(1)-O(2A)-O(4A)#1	54.8(4)
Mo(4)-O(10)	1.658(6)	O(18)#1-Mo(3)-O(2A)	91.0(3)	O(1A)#1-O(2A)-O(4A)#1	92.3(6)
Mo(4)-O(9)	1.789(6)	O(19)-Mo(3)-O(2A)	63.7(3)	P(1)-O(2A)-Mo(3)	125.2(5)
Mo(4)-O(19)	1.882(6)	O(15)-Mo(3)-O(1A)#1	158.4(3)	O(1A)#1-O(2A)-Mo(3)	70.2(4)
Mo(4)-O(13)	1.902(6)	O(21)-Mo(3)-O(1A)#1	94.1(3)	O(4A)#1-O(2A)-Mo(3)	136.7(6)
Mo(4)-O(12)	2.012(6)	O(14)-Mo(3)-O(1A)#1	64.1(3)	P(1)-O(2A)-Mo(4)	123.9(5)

Mo(4)-O(4A)#1	2.475(9)	O(18)#1-Mo(3)-O(1A)#1	64.0(3)	O(1A)#1-O(2A)-Mo(4)	131.9(6)
Mo(4)-O(2A)	2.487(9)	O(19)-Mo(3)-O(1A)#1	92.9(3)	O(4A)#1-O(2A)-Mo(4)	69.1(4)
Mo(5)-O(6)	1.657(6)	O(2A)-Mo(3)-O(1A)#1	41.0(3)	Mo(3)-O(2A)-Mo(4)	93.1(3)
Mo(5)-O(22)	1.847(7)	O(10)-Mo(4)-O(9)	103.7(3)	P(1)-O(2A)-Mo(1)	122.6(5)
Mo(5)-O(18)	1.859(6)	O(10)-Mo(4)-O(19)	101.2(3)	O(1A)#1-O(2A)-Mo(1)	131.7(6)
Mo(5)-O(5)	1.929(6)	O(9)-Mo(4)-O(19)	93.1(3)	O(4A)#1-O(2A)-Mo(1)	127.2(5)
Mo(5)-O(16)	1.938(6)	O(10)-Mo(4)-O(13)	102.3(3)	Mo(3)-O(2A)-Mo(1)	90.9(3)
Mo(5)-O(3A)	2.412(9)	O(9)-Mo(4)-O(13)	91.0(3)	Mo(4)-O(2A)-Mo(1)	91.7(3)
Mo(5)-O(1A)	2.490(9)	O(19)-Mo(4)-O(13)	154.4(3)	P(1)-O(4A)-O(1A)#1	55.3(4)
Mo(6)-O(8)	1.643(6)	O(10)-Mo(4)-O(12)	98.9(3)	P(1)-O(4A)-O(2A)#1	55.3(4)
Mo(6)-O(20)	1.792(6)	O(9)-Mo(4)-O(12)	157.3(3)	O(1A)#1-O(4A)-O(2A)#1	92.9(6)
Mo(6)-O(11)	1.857(6)	O(19)-Mo(4)-O(12)	84.2(3)	P(1)-O(4A)-O(3A)	56.1(4)
Mo(6)-O(22)	1.941(6)	O(13)-Mo(4)-O(12)	82.4(3)	O(1A)#1-O(4A)-O(3A)	90.7(6)
Mo(6)-O(9)#1	2.025(6)	O(10)-Mo(4)-O(4A)#1	162.4(3)	O(2A)#1-O(4A)-O(3A)	90.0(6)
Mo(6)-O(3A)	2.445(9)	O(9)-Mo(4)-O(4A)#1	67.1(3)	P(1)-O(4A)-Mo(2)#1	125.2(5)
Mo(7)-O(7)	1.683(5)	O(19)-Mo(4)-O(4A)#1	94.5(3)	O(1A)#1-O(4A)-Mo(2)#1	69.9(4)
Mo(7)-O(2)	1.774(5)	O(13)-Mo(4)-O(4A)#1	64.0(3)	O(2A)#1-O(4A)-Mo(2)#1	131.2(5)
Mo(7)-O(1)	1.817(5)	O(12)-Mo(4)-O(4A)#1	90.6(3)	O(3A)-O(4A)-Mo(2)#1	133.6(5)
Mo(7)-O(1)#2	2.130(5)	O(10)-Mo(4)-O(2A)	156.1(3)	P(1)-O(4A)-V(2)#1	125.2(5)
Mo(7)-N(1)	2.236(6)	O(9)-Mo(4)-O(2A)	95.2(3)	O(1A)#1-O(4A)-V(2)#1	69.9(4)
Mo(7)-N(2)	2.328(6)	O(19)-Mo(4)-O(2A)	62.8(3)	O(2A)#1-O(4A)-V(2)#1	131.2(5)
Mo(7)-Mo(7)#2	3.0746(14)	O(13)-Mo(4)-O(2A)	91.7(3)	O(3A)-O(4A)-V(2)#1	133.6(5)
P(1)-O(1A)#1	1.503(9)	O(12)-Mo(4)-O(2A)	63.6(3)	Mo(2)#1-O(4A)-V(2)#1	0.00(6)
P(1)-O(1A)	1.503(9)	O(4A)#1-Mo(4)-O(2A)	41.0(3)	P(1)-O(4A)-Mo(4)#1	125.1(4)
P(1)-O(4A)#1	1.511(8)	O(6)-Mo(5)-O(22)	101.9(3)	O(1A)#1-O(4A)-Mo(4)#1	136.6(6)
P(1)-O(4A)	1.511(8)	O(6)-Mo(5)-O(18)	101.9(3)	O(2A)#1-O(4A)-Mo(4)#1	69.9(4)
P(1)-O(2A)	1.522(8)	O(22)-Mo(5)-O(18)	92.8(3)	O(3A)-O(4A)-Mo(4)#1	127.2(5)
P(1)-O(2A)#1	1.522(8)	O(6)-Mo(5)-O(5)	100.4(3)	Mo(2)#1-O(4A)-Mo(4)#1	91.5(3)
P(1)-O(3A)#1	1.564(9)	O(22)-Mo(5)-O(5)	88.0(3)	V(2)#1-O(4A)-Mo(4)#1	91.5(3)
P(1)-O(3A)	1.564(9)	O(18)-Mo(5)-O(5)	157.0(3)	P(1)-O(3A)-O(4A)	53.4(4)
V(7)-O(4)	1.588(5)	O(6)-Mo(5)-O(16)	100.8(3)	P(1)-O(3A)-O(1A)	52.3(4)
V(7)-O(2)	1.948(5)	O(22)-Mo(5)-O(16)	157.0(3)	O(4A)-O(3A)-O(1A)	87.8(6)
V(7)-N(6)	2.087(6)	O(18)-Mo(5)-O(16)	86.2(3)	P(1)-O(3A)-Mo(5)	122.9(5)
V(7)-N(5)	2.097(6)	O(5)-Mo(5)-O(16)	84.3(3)	O(4A)-O(3A)-Mo(5)	130.3(5)
V(7)-N(4)	2.112(6)	O(6)-Mo(5)-O(3A)	158.7(3)	O(1A)-O(3A)-Mo(5)	70.7(4)
V(7)-N(3)	2.310(6)	O(22)-Mo(5)-O(3A)	64.7(3)	P(1)-O(3A)-Mo(6)	124.7(5)
O(1)-Mo(7)#2	2.130(5)	O(18)-Mo(5)-O(3A)	95.5(3)	O(4A)-O(3A)-Mo(6)	71.5(4)
O(9)-V(6)#1	2.025(6)	O(5)-Mo(5)-O(3A)	64.1(3)	O(1A)-O(3A)-Mo(6)	135.9(5)
O(9)-Mo(6)#1	2.025(6)	O(16)-Mo(5)-O(3A)	92.5(3)	Mo(5)-O(3A)-Mo(6)	93.4(3)
O(11)-V(2)#1	1.941(6)	O(6)-Mo(5)-O(1A)	157.8(3)	P(1)-O(3A)-Mo(1)	121.1(5)
O(11)-Mo(2)#1	1.941(6)	O(22)-Mo(5)-O(1A)	95.8(3)	O(4A)-O(3A)-Mo(1)	133.1(5)
O(14)-V(2)#1	1.919(6)	O(18)-Mo(5)-O(1A)	63.7(3)	O(1A)-O(3A)-Mo(1)	127.8(5)
O(14)-Mo(2)#1	1.919(6)	O(5)-Mo(5)-O(1A)	93.4(3)	Mo(5)-O(3A)-Mo(1)	93.5(3)
O(18)-V(3)#1	1.904(6)	O(16)-Mo(5)-O(1A)	63.2(3)	Mo(6)-O(3A)-Mo(1)	92.9(3)
O(18)-Mo(3)#1	1.904(6)	O(3A)-Mo(5)-O(1A)	43.3(3)	C(30)-N(5)-C(26)	118.7(7)
O(1A)-O(4A)#1	1.706(13)	O(8)-Mo(6)-O(20)	103.9(4)	C(30)-N(5)-V(7)	124.8(6)

O(1A)-O(2A)#1	1.710(13)	O(8)-Mo(6)-O(11)	102.0(3)	C(26)-N(5)-V(7)	116.4(5)
O(1A)-O(3A)	1.810(13)	O(20)-Mo(6)-O(11)	95.2(3)	C(16)-N(4)-C(20)	118.2(7)
O(1A)-V(3)#1	2.453(9)	O(8)-Mo(6)-O(22)	101.3(3)	C(16)-N(4)-V(7)	120.8(5)
O(1A)-Mo(3)#1	2.453(9)	O(20)-Mo(6)-O(22)	89.5(3)	C(20)-N(4)-V(7)	121.0(5)
O(2A)-O(1A)#1	1.710(13)	O(11)-Mo(6)-O(22)	154.3(3)	C(11)-N(3)-C(15)	117.4(7)
O(2A)-O(4A)#1	1.737(12)	O(8)-Mo(6)-O(9)#1	99.6(3)	C(11)-N(3)-V(7)	128.0(6)
O(4A)-O(1A)#1	1.706(13)	O(20)-Mo(6)-O(9)#1	156.0(3)	C(15)-N(3)-V(7)	114.5(5)
O(4A)-O(2A)#1	1.737(12)	O(11)-Mo(6)-O(9)#1	84.8(3)	C(1)-N(1)-C(5)	119.2(7)
O(4A)-O(3A)	1.776(12)	O(22)-Mo(6)-O(9)#1	80.8(3)	C(1)-N(1)-Mo(7)	119.6(5)
O(4A)-Mo(2)#1	2.452(8)	O(8)-Mo(6)-O(3A)	159.6(3)	C(5)-N(1)-Mo(7)	120.8(5)
O(4A)-V(2)#1	2.452(8)	O(20)-Mo(6)-O(3A)	65.2(3)	C(21)-N(6)-C(25)	118.2(7)
O(4A)-Mo(4)#1	2.475(9)	O(11)-Mo(6)-O(3A)	96.3(3)	C(21)-N(6)-V(7)	124.7(5)
N(5)-C(30)	1.343(9)	O(22)-Mo(6)-O(3A)	62.9(3)	C(25)-N(6)-V(7)	117.0(5)
N(5)-C(26)	1.355(9)	O(9)#1-Mo(6)-O(3A)	90.9(3)	C(10)-N(2)-C(6)	119.4(7)
N(4)-C(16)	1.344(9)	O(7)-Mo(7)-O(2)	102.9(3)	C(10)-N(2)-Mo(7)	122.9(5)
N(4)-C(20)	1.351(9)	O(7)-Mo(7)-O(1)	106.6(2)	C(6)-N(2)-Mo(7)	117.6(5)
N(3)-C(11)	1.335(9)	O(2)-Mo(7)-O(1)	103.9(2)	C(28)-C(27)-C(26)	120.4(8)
N(3)-C(15)	1.349(10)	O(7)-Mo(7)-O(1)#2	92.6(2)	C(28)-C(27)-H(27A)	119.8
N(1)-C(1)	1.335(10)	O(2)-Mo(7)-O(1)#2	162.9(2)	C(26)-C(27)-H(27A)	119.8
N(1)-C(5)	1.343(10)	O(1)-Mo(7)-O(1)#2	78.0(2)	N(4)-C(20)-C(19)	122.6(8)
N(6)-C(21)	1.333(9)	O(7)-Mo(7)-N(1)	87.4(2)	N(4)-C(20)-H(20A)	118.7
N(6)-C(25)	1.368(9)	O(2)-Mo(7)-N(1)	93.0(2)	C(19)-C(20)-H(20A)	118.7
N(2)-C(10)	1.326(10)	O(1)-Mo(7)-N(1)	154.7(2)	N(6)-C(25)-C(24)	121.5(7)
N(2)-C(6)	1.349(9)	O(1)#2-Mo(7)-N(1)	80.5(2)	N(6)-C(25)-C(26)	114.0(7)
C(27)-C(28)	1.376(11)	O(7)-Mo(7)-N(2)	156.9(2)	C(24)-C(25)-C(26)	124.6(7)
C(27)-C(26)	1.379(10)	O(2)-Mo(7)-N(2)	84.6(2)	C(25)-C(24)-C(23)	119.4(8)
C(27)-H(27A)	0.93	O(1)-Mo(7)-N(2)	92.4(2)	C(25)-C(24)-H(24A)	120.3
C(20)-C(19)	1.355(11)	O(1)#2-Mo(7)-N(2)	78.3(2)	C(23)-C(24)-H(24A)	120.3
C(20)-H(20A)	0.93	N(1)-Mo(7)-N(2)	70.3(2)	N(5)-C(30)-C(29)	122.6(8)
C(25)-C(24)	1.376(10)	O(7)-Mo(7)-Mo(7)#2	101.6(2)	N(5)-C(30)-H(30A)	118.7
C(25)-C(26)	1.480(10)	O(2)-Mo(7)-Mo(7)#2	143.51(19)	C(29)-C(30)-H(30A)	118.7
C(24)-C(23)	1.378(12)	O(1)-Mo(7)-Mo(7)#2	42.67(15)	N(6)-C(21)-C(22)	122.6(8)
C(24)-H(24A)	0.93	O(1)#2-Mo(7)-Mo(7)#2	35.31(13)	N(6)-C(21)-H(21A)	118.7
C(30)-C(29)	1.389(11)	N(1)-Mo(7)-Mo(7)#2	114.81(17)	C(22)-C(21)-H(21A)	118.7
C(30)-H(30A)	0.93	N(2)-Mo(7)-Mo(7)#2	83.36(15)	N(5)-C(26)-C(27)	120.9(7)
C(21)-C(22)	1.391(11)	O(1A)#1-P(1)-O(1A)	180.0(10)	N(5)-C(26)-C(25)	115.3(7)
C(21)-H(21A)	0.93	O(1A)#1-P(1)-O(4A)#1	111.1(5)	C(27)-C(26)-C(25)	123.8(7)
C(1)-C(2)	1.386(12)	O(1A)-P(1)-O(4A)#1	68.9(5)	N(1)-C(1)-C(2)	122.9(9)
C(1)-H(1A)	0.93	O(1A)#1-P(1)-O(4A)	68.9(5)	N(1)-C(1)-H(1A)	118.6
C(22)-C(23)	1.369(12)	O(1A)-P(1)-O(4A)	111.1(5)	C(2)-C(1)-H(1A)	118.6
C(22)-H(22A)	0.93	O(4A)#1-P(1)-O(4A)	180.0(10)	C(23)-C(22)-C(21)	118.6(8)
C(11)-C(12)	1.371(11)	O(1A)#1-P(1)-O(2A)	68.8(5)	C(23)-C(22)-H(22A)	120.7
C(11)-H(11A)	0.93	O(1A)-P(1)-O(2A)	111.2(5)	C(21)-C(22)-H(22A)	120.7
C(5)-C(4)	1.377(12)	O(4A)#1-P(1)-O(2A)	69.9(5)	N(3)-C(11)-C(12)	124.0(8)
C(5)-C(6)	1.467(11)	O(4A)-P(1)-O(2A)	110.1(5)	N(3)-C(11)-H(11A)	118
C(28)-C(29)	1.382(12)	O(1A)#1-P(1)-O(2A)#1	111.2(5)	C(12)-C(11)-H(11A)	118

C(28)-H(28A)	0.93	O(1A)-P(1)-O(2A)#1	68.8(5)	N(1)-C(5)-C(4)	121.3(9)
C(10)-C(9)	1.381(12)	O(4A)#1-P(1)-O(2A)#1	110.1(5)	N(1)-C(5)-C(6)	115.8(7)
C(10)-H(10A)	0.93	O(4A)-P(1)-O(2A)#1	69.9(5)	C(4)-C(5)-C(6)	122.9(8)
C(15)-C(14)	1.379(11)	O(2A)-P(1)-O(2A)#1	180.0(8)	C(27)-C(28)-C(29)	119.0(8)
C(15)-C(16)	1.483(10)	O(1A)#1-P(1)-O(3A)#1	72.3(5)	C(27)-C(28)-H(28A)	120.5
C(16)-C(17)	1.392(11)	O(1A)-P(1)-O(3A)#1	107.7(5)	C(29)-C(28)-H(28A)	120.5
C(6)-C(7)	1.397(11)	O(4A)#1-P(1)-O(3A)#1	70.5(5)	N(2)-C(10)-C(9)	122.2(8)
C(12)-C(13)	1.365(13)	O(4A)-P(1)-O(3A)#1	109.5(5)	N(2)-C(10)-H(10A)	118.9
C(12)-H(12A)	0.93	O(2A)-P(1)-O(3A)#1	107.2(5)	C(9)-C(10)-H(10A)	118.9
C(29)-H(29A)	0.93	O(2A)#1-P(1)-O(3A)#1	72.8(5)	N(3)-C(15)-C(14)	121.7(7)
C(23)-H(23A)	0.93	O(1A)#1-P(1)-O(3A)	107.7(5)	N(3)-C(15)-C(16)	114.9(7)
C(17)-C(18)	1.381(12)	O(1A)-P(1)-O(3A)	72.3(5)	C(14)-C(15)-C(16)	123.4(8)
C(17)-H(17A)	0.93	O(4A)#1-P(1)-O(3A)	109.5(5)	N(4)-C(16)-C(17)	121.5(7)
C(19)-C(18)	1.373(12)	O(4A)-P(1)-O(3A)	70.5(5)	N(4)-C(16)-C(15)	116.2(7)
C(19)-H(19A)	0.93	O(2A)-P(1)-O(3A)	72.8(5)	C(17)-C(16)-C(15)	122.2(7)
C(14)-C(13)	1.380(12)	O(2A)#1-P(1)-O(3A)	107.2(5)	N(2)-C(6)-C(7)	120.8(8)
C(14)-H(14A)	0.93	O(3A)#1-P(1)-O(3A)	180.0(9)	N(2)-C(6)-C(5)	115.2(7)
C(9)-C(8)	1.372(14)	O(4)-V(7)-O(2)	99.0(3)	C(7)-C(6)-C(5)	124.0(8)
C(9)-H(9A)	0.93	O(4)-V(7)-N(6)	95.6(3)	C(13)-C(12)-C(11)	118.3(8)
C(7)-C(8)	1.363(13)	O(2)-V(7)-N(6)	163.5(2)	C(13)-C(12)-H(12A)	120.9
C(7)-H(7A)	0.93	O(4)-V(7)-N(5)	105.8(3)	C(11)-C(12)-H(12A)	120.9
C(18)-H(18A)	0.93	O(2)-V(7)-N(5)	91.1(2)	C(28)-C(29)-C(30)	118.4(8)
C(2)-C(3)	1.372(15)	N(6)-V(7)-N(5)	77.3(2)	C(28)-C(29)-H(29A)	120.8
C(2)-H(2A)	0.93	O(4)-V(7)-N(4)	94.9(3)	C(30)-C(29)-H(29A)	120.8
C(13)-H(13A)	0.93	O(2)-V(7)-N(4)	93.8(2)	C(22)-C(23)-C(24)	119.7(8)
C(8)-H(8A)	0.93	N(6)-V(7)-N(4)	92.7(2)	C(22)-C(23)-H(23A)	120.2
C(3)-C(4)	1.374(14)	N(5)-V(7)-N(4)	157.6(2)	C(24)-C(23)-H(23A)	120.2
C(3)-H(3A)	0.93	O(4)-V(7)-N(3)	168.1(3)	C(18)-C(17)-C(16)	119.1(8)
C(4)-H(4A)	0.93	O(2)-V(7)-N(3)	84.0(2)	C(18)-C(17)-H(17A)	120.4
O(3)-Mo(1)-O(12)	103.3(3)	N(6)-V(7)-N(3)	83.3(2)	C(16)-C(17)-H(17A)	120.4
O(3)-Mo(1)-O(5)	101.4(3)	N(5)-V(7)-N(3)	85.5(2)	C(20)-C(19)-C(18)	119.8(8)
O(12)-Mo(1)-O(5)	94.2(3)	N(4)-V(7)-N(3)	73.4(2)	C(20)-C(19)-H(19A)	120.1
O(3)-Mo(1)-O(21)	101.1(3)	Mo(7)-O(1)-Mo(7)#2	102.0(2)	C(18)-C(19)-H(19A)	120.1
O(12)-Mo(1)-O(21)	90.6(3)	Mo(7)-O(2)-V(7)	161.9(3)	C(15)-C(14)-C(13)	119.4(9)
O(5)-Mo(1)-O(21)	155.2(3)	Mo(1)-O(5)-Mo(5)	139.0(4)	C(15)-C(14)-H(14A)	120.3
O(3)-Mo(1)-O(20)	99.0(3)	Mo(4)-O(9)-V(6)#1	137.9(4)	C(13)-C(14)-H(14A)	120.3
O(12)-Mo(1)-O(20)	157.5(3)	Mo(4)-O(9)-Mo(6)#1	137.9(4)	C(8)-C(9)-C(10)	118.7(9)
O(5)-Mo(1)-O(20)	84.4(3)	V(6)#1-O(9)-Mo(6)#1	0.00(4)	C(8)-C(9)-H(9A)	120.7
O(21)-Mo(1)-O(20)	82.0(3)	Mo(6)-O(11)-V(2)#1	139.6(4)	C(10)-C(9)-H(9A)	120.7
O(3)-Mo(1)-O(3A)	155.5(3)	Mo(6)-O(11)-Mo(2)#1	139.6(4)	C(8)-C(7)-C(6)	119.0(9)
O(12)-Mo(1)-O(3A)	97.2(3)	V(2)#1-O(11)-Mo(2)#1	0.00(6)	C(8)-C(7)-H(7A)	120.5
O(5)-Mo(1)-O(3A)	63.3(3)	Mo(1)-O(12)-Mo(4)	138.5(4)	C(6)-C(7)-H(7A)	120.5
O(21)-Mo(1)-O(3A)	92.0(3)	Mo(2)-O(13)-Mo(4)	138.3(4)	C(19)-C(18)-C(17)	118.7(9)
O(20)-Mo(1)-O(3A)	62.1(3)	Mo(3)-O(14)-V(2)#1	138.8(4)	C(19)-C(18)-H(18A)	120.7
O(3)-Mo(1)-O(2A)	160.5(3)	Mo(3)-O(14)-Mo(2)#1	138.8(4)	C(17)-C(18)-H(18A)	120.7
O(12)-Mo(1)-O(2A)	65.9(3)	V(2)#1-O(14)-Mo(2)#1	0.00(5)	C(3)-C(2)-C(1)	116.8(10)

O(5)-Mo(1)-O(2A)	95.7(3)	Mo(2)-O(16)-Mo(5)	139.6(4)	C(3)-C(2)-H(2A)	121.6
O(21)-Mo(1)-O(2A)	64.3(3)	Mo(5)-O(18)-V(3)#1	140.6(4)	C(1)-C(2)-H(2A)	121.6
O(20)-Mo(1)-O(2A)	91.9(3)	Mo(5)-O(18)-Mo(3)#1	140.6(4)	C(12)-C(13)-C(14)	119.2(9)
O(3A)-Mo(1)-O(2A)	43.3(3)	V(3)#1-O(18)-Mo(3)#1	0.00(5)	C(12)-C(13)-H(13A)	120.4
O(17)-Mo(2)-O(16)	102.5(3)	Mo(4)-O(19)-Mo(3)	140.2(5)	C(14)-C(13)-H(13A)	120.4
O(17)-Mo(2)-O(13)	100.9(4)	Mo(6)-O(20)-Mo(1)	139.5(4)	C(7)-C(8)-C(9)	119.9(9)
O(16)-Mo(2)-O(13)	91.1(3)	Mo(3)-O(21)-Mo(1)	136.8(4)	C(7)-C(8)-H(8A)	120.1
O(17)-Mo(2)-O(14)#1	102.3(3)	Mo(5)-O(22)-Mo(6)	137.8(4)	C(9)-C(8)-H(8A)	120.1
O(16)-Mo(2)-O(14)#1	88.1(3)	P(1)-O(1A)-O(4A)#1	55.8(4)	C(2)-C(3)-C(4)	121.2(10)
O(13)-Mo(2)-O(14)#1	156.4(3)	P(1)-O(1A)-O(2A)#1	56.1(4)	C(2)-C(3)-H(3A)	119.4
O(17)-Mo(2)-O(11)#1	100.5(3)	O(4A)#1-O(1A)-O(2A)#1	93.4(6)	C(4)-C(3)-H(3A)	119.4
O(16)-Mo(2)-O(11)#1	156.9(3)	P(1)-O(1A)-O(3A)	55.4(4)	C(3)-C(4)-C(5)	118.5(10)
O(13)-Mo(2)-O(11)#1	86.4(2)	O(4A)#1-O(1A)-O(3A)	91.2(6)	C(3)-C(4)-H(4A)	120.7
O(14)#1-Mo(2)-O(11)#1	85.2(3)	O(2A)#1-O(1A)-O(3A)	89.7(6)	C(5)-C(4)-H(4A)	120.7
O(17)-Mo(2)-O(4A)#1	159.1(4)	P(1)-O(1A)-V(3)#1	124.9(5)		
O(16)-Mo(2)-O(4A)#1	93.4(3)	O(4A)#1-O(1A)-V(3)#1	131.5(6)		
O(13)-Mo(2)-O(4A)#1	64.9(3)	O(2A)#1-O(1A)-V(3)#1	68.8(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z+2; #2 -x,-y+1,-z+2; #3 -x+1,-y+1,-z+2; #4 -x+1,-y,-z+3; #5 -x,-y,-z+3; #6 x+1,y,z; #7 -x+1,-y,-z+2; #8 x-1,y,z

Table S3. Catalytic performance of [MoVbpy]HPMoV₂ in different condition ^[a]

Entry	m _{cat} (g)	m _{vc} (g)	O ₂ (MPa)	T(K)	Time(h)	Yield(%)
1	0.1	0.3	1	373	6	8
2	0.1	0.3	1.5	373	6	8.5
3	0.1	0.35	1.5	373	8	7.4
4 ^[b]	0.1	0.25	1.5	373	8	11.9/6.4
5	0.1	0.25	1.5	383	8	9.8
6	0.12	0.25	1.5	373	8	11.8
7	0.1	0.25	1.5	373	10	12.5

[a] Reaction solution: 3ml acetic acid and 2ml deionized water. [b] Yield of first/second run of catalytic test

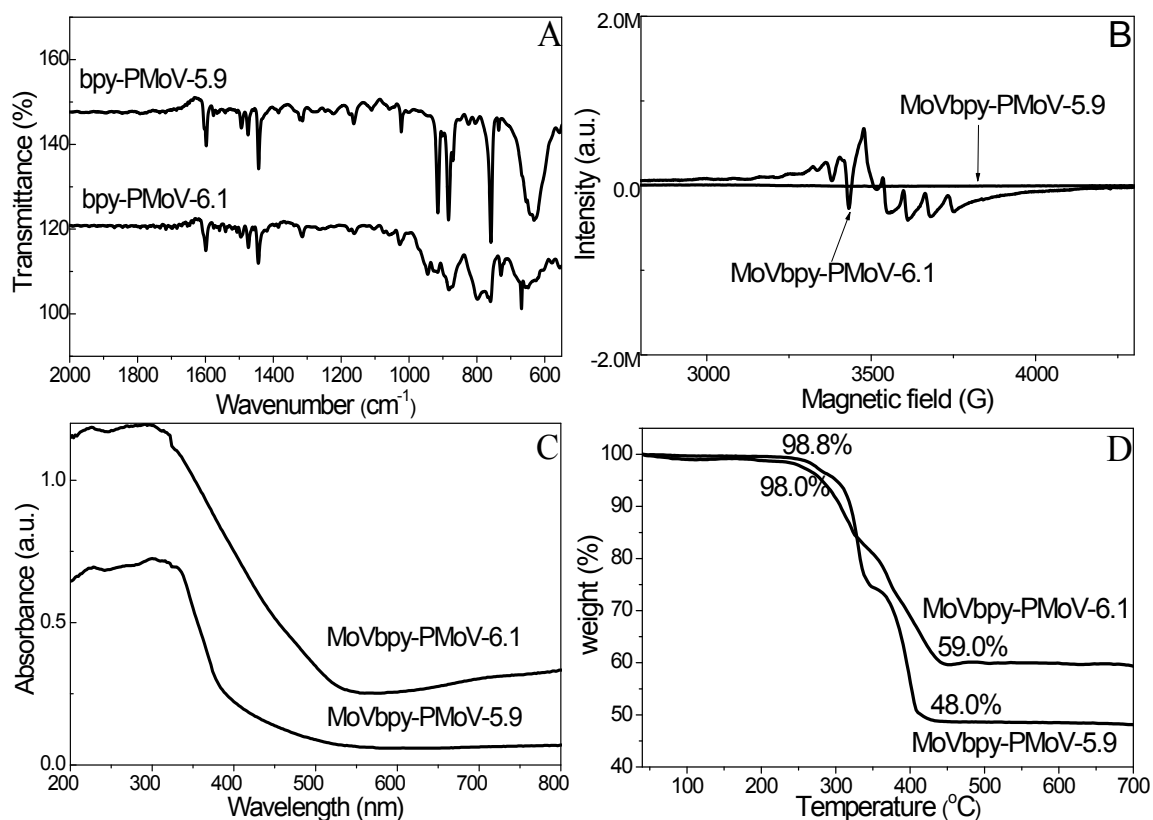


Figure S1. FT-IR spectra (A), ESR spectra (B), UV-vis DR spectra (C) and TG curves (D) for MoVbpy-PMoV-5.9 and MoVbpy-PMoV-6.1 samples.

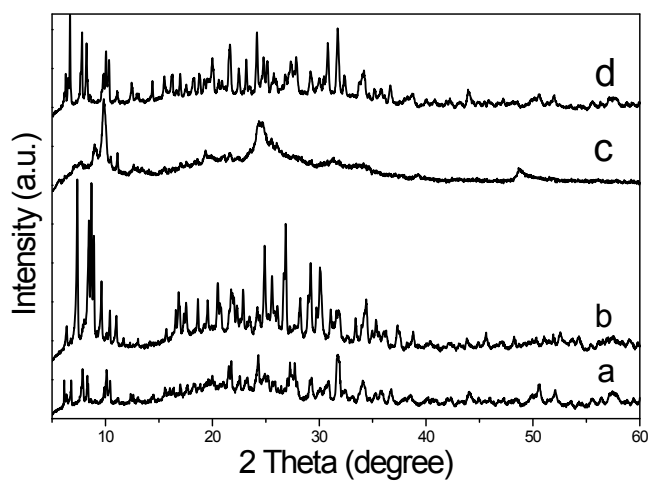


Figure S2. XRD patterns for a) fresh [MoVbpy]HPMoV₂, b) reused [MoVbpy]HPMoV₂, c) MoVbpy-PMoV-6.1 and d) MoVbpy-PMoV-5.9.

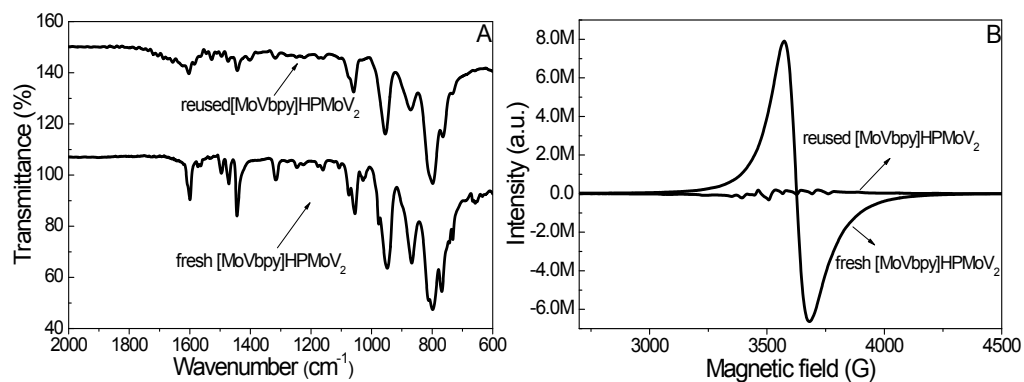
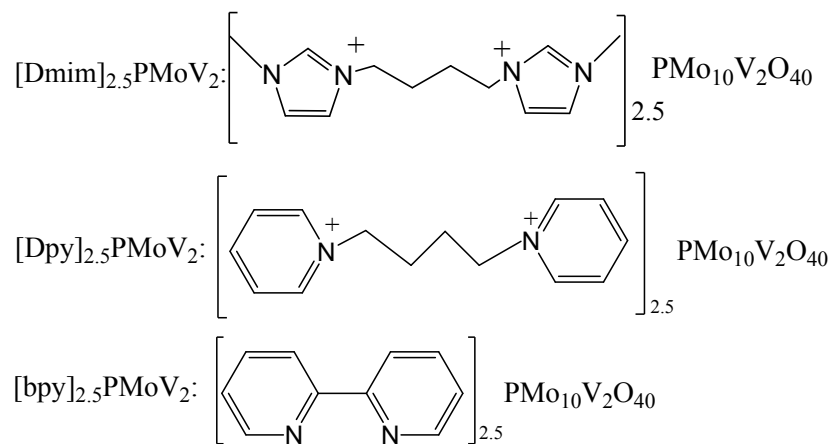


Figure S3. FT-IR (A) and ESR (B) spectra for fresh and reused [MoVbpy]HPMoV₂



Scheme S1. Chemical structures of [Dmim]_{2.5}PMo₁₀V₂, [Dpy]_{2.5}PMo₁₀V₂ and [bpy]_{2.5}PMo₁₀V₂.