Supporting Information for

Vanadium polyoxoanion-bridged macrocyclic metal complexes: from one-dimensional to three-dimensional structures

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Table S1. Selected Bond Distances (Å) and Angles(°) for **1-4**

		1			
N(3)-Cu(2)	1.987(3)	O(4)-V(5)	1.687(3)	V(5)-O(8)	2.089(2)
N(4)-Cu(2)	2.097(3)	O(4)-V(3)	2.041(3)	V(5)-O(8)#2	2.100(2)
N(1)-Cu(1)	2.040(3)	O(5)-V(3)	1.610(3)	O(9)-V(2)	1.743(3)
N(2)-Cu(1)	2.027(3)	O(6)-V(1)	1.829(3)	O(9)-V(1)	1.940(3)
O(1)-V(4)	1.610(3)	O(6)-V(3)	1.833(3)	O(10)-V(2)	1.606(3)
O(2)-V(4)	1.827(3)	O(7)-V(3)	1.834(3)	O(11)-V(5)	2.051(2)
O(2)-V(1)	1.836(3)	O(7)-V(2)	1.866(3)	O(11)-V(4)#2	2.095(2)
O(3)-V(5)	1.881(2)	V(2)-O(8)	2.289(2)	O(11)-V(2)	2.128(3)
O(3)-V(2)#2	1.974(2)	V(3)-O(8)	2.333(2)	O(12)-V(5)	1.686(3)
O(3)-V(4)	2.011(2)	V(4)-O(8)	2.269(2)	O(12)-V(1)#2	2.043(3)
O(14)-V(4)	1.766(3)	O(8)-V(1)	2.368(2)	O(13)-V(1)	1.591(3)
O(14)-V(3)	1.939(3)				
N(3)-Cu(2)-N(3)#1	180.00(11)	N(3)-Cu(2)-N(4)#1	94.25(13)	N(3)-Cu(2)-N(4)	85.75(13)
N(4)#1-Cu(2)-N(4)	180.00(16)	N(2)-Cu(1)-N(2)#3	180.00(13)	N(2)-Cu(1)-N(1)#3	89.64(13)
V(4)-O(2)-V(1)	114.70(13)	N(2)-Cu(1)-N(1)	90.36(13)	O(13)-V(1)-O(6)	104.84(15)
V(5)-O(3)-V(2)#2	107.13(11)	N(1)#3-Cu(1)-N(1)	180.000(1)	O(13)-V(1)-O(2)	101.94(14)
V(5)-O(3)-V(4)	106.45(11)	V(2)-O(9)-V(1)	115.83(13)	O(6)-V(1)-O(2)	92.77(12)
V(2)#2-O(3)-V(4)	107.21(11)	V(5)-O(11)-V(4)#2	105.54(11)	O(13)-V(1)-O(9)	102.15(14)
V(5)-O(4)-V(3)	110.52(13)	V(5)-O(11)-V(2)	106.28(11)	O(6)-V(1)-O(9)	89.07(12)
V(1)-O(6)-V(3)	115.02(13)	V(4)#2-O(11)-V(2)	98.83(10)	O(2)-V(1)-O(9)	154.50(11)
V(3)-O(7)-V(2)	114.60(13)	V(5)-O(12)-V(1)#2	111.97(13)	O(13)-V(1)-O(12)#2	101.19(14)
V(1)#2-V(5)-V(4)	122.37(3)	V(4)-O(14)-V(3)	114.40(13)	O(6)-V(1)-O(12)#2	153.71(11)
V(2)#2-V(5)-V(4)	62.08(2)	O(6)-V(1)-O(8)	80.97(10)	O(9)-V(1)-O(8)	76.66(10)
O(2)-V(1)-O(12)#2	85.34(11)	O(2)-V(1)-O(8)	78.52(10)	O(12)#2-V(1)-O(8)	72.95(9)
O(9)-V(1)-O(12)#2	81.91(11)	O(13)-V(1)-O(8)	174.10(14)		

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N(3)-Ni(2)	2.098(8)	O(1)-V(3)	1.873(3)	O(6)-V(3)	1.894(3)
N(4)-Ni(2)	2.122(7)	O(1)-V(1)	1.903(3)	O(6)-V(4)	1.895(3)
Ni(1)-O(4)	2.051(3)	O(1)-V(2)	1.964(3)	O(6)-V(2)#3	1.979(3)
Ni(1)-N(2)#1	2.086(7)	O(2)-V(7)	1.874(3)	O(7)-V(8)	1.594(3)
Ni(1)-N(1)#1	2.099(6)	O(2)-V(8)	1.931(3)	O(8)-V(2)	1.591(4)
Ni(2)-N(3)#2	2.098(8)	O(2)-V(6)	1.965(3)	O(9)-V(1)	1.915(3)
Ni(2)-O(18)	2.101(3)	O(3)-V(7)#3	1.851(4)	O(9)-V(6)	1.941(3)
Ni(2)-N(4)#2	2.122(7)	O(3)-V(5)	1.921(3)	O(9)-V(8)	1.946(3)
Ni(3)-N(7)#3	1.925(8)	O(3)-V(6)	1.955(3)	O(10)-V(3)	1.604(4)
Ni(3)-N(7)	2.001(7)	O(4)-V(5)	1.615(3)	O(11)-V(4)	1.595(3)
Ni(3)-N(6)	2.017(8)	O(5)-V(4)	1.865(3)	O(12)-V(4)	1.822(3)
Ni(3)-N(8)	2.017(7)	O(5)-V(5)	1.951(3)	O(12)-V(1)	1.906(3)
Ni(3)-N(5)	2.042(7)	O(5)-V(6)	1.956(3)	O(12)-V(3)	2.090(4)
O(13)-V(8)	1.884(3)	O(15)-V(5)#3	1.881(3)	O(20)-V(3)	1.833(2)
O(13)-V(1)	1.959(3)	O(15)-V(7)	2.329(4)	V(2)-O(14)#3	1.952(3)
O(13)-V(2)	1.959(3)	O(16)-V(6)	1.599(3)	V(2)-O(6)#3	1.979(3)
O(14)-V(5)	1.911(3)	O(17)-V(7)	1.597(4)	V(5)-O(15)#3	1.881(3)
O(14)-V(4)	1.929(3)	O(18)-V(1)	1.627(3)	V(7)-O(3)#3	1.851(4)
O(14)-V(2)#3	1.952(3)	O(19)-V(7)#3	1.844(3)	O(19)-V(7)	1.844(3)
O(15)-V(8)	1.797(3)				
O(4)#1-Ni(1)-O(4)	180.00(6)	O(18)-Ni(2)-O(18)#2	177.6(2)	N(7)-Ni(3)-N(6)	95.8(3)
O(4)#1-Ni(1)-N(2)	92.0(2)	O(18)-Ni(2)-N(4)#2	88.2(3)	Ni(3)#3-Ni(3)-N(8)	155.8(3)
O(4)-Ni(1)-N(2)	88.0(2)	N(3)#2-Ni(2)-N(4)	165.5(5)	N(6)#3-Ni(3)-N(8)	31.5(5)
N(2)-Ni(1)-N(2)#1	180.0(4)	N(3)-Ni(2)-N(4)	88.6(6)	N(7)#3-Ni(3)-N(8)	125.3(4)
O(4)#1-Ni(1)-N(1)	91.4(2)	O(18)-Ni(2)-N(4)	90.4(3)	N(7)-Ni(3)-N(8)	87.5(3)
O(4)-Ni(1)-N(1)	88.6(2)	O(18)#2-Ni(2)-N(4)	88.2(3)	N(6)-Ni(3)-N(8)	176.7(4)
N(2)-Ni(1)-N(1)	93.8(3)	N(4)#2-Ni(2)-N(4)	105.8(4)	Ni(3)#3-Ni(3)-N(5)	112.2(3)
O(4)-Ni(1)-N(1)#1	91.4(2)	Ni(3)#3-Ni(3)-N(7)	70.7(3)	N(6)#3-Ni(3)-N(5)	118.3(6)
N(2)-Ni(1)-N(1)#1	86.2(3)	N(6)#3-Ni(3)-N(7)	58.8(5)	N(7)#3-Ni(3)-N(5)	41.1(4)
N(1)-Ni(1)-N(1)#1	180.0(3)	N(7)#3-Ni(3)-N(7)	143.3(3)	N(7)-Ni(3)-N(5)	175.6(4)
N(3)#2-Ni(2)-N(3)	77.2(11)	Ni(3)#3-Ni(3)-N(6)	27.2(3)	N(6)-Ni(3)-N(5)	87.7(4)
N(3)#2-Ni(2)-O(18)	87.8(9)	N(6)#3-Ni(3)-N(6)	151.7(5)	N(8)-Ni(3)-N(5)	88.9(4)
N(3)-Ni(2)-O(18)	94.1(9)	N(7)#3-Ni(3)-N(6)	51.6(4)	O(18)-V(1)-O(1)	111.77(17)
N(3)-Ni(2)-O(18)#2	87.8(9)	O(1)-V(1)-O(13)	80.09(14)	O(18)-V(1)-O(12)	105.98(16)
O(1)-V(1)-O(12)	84.77(14)	O(12)-V(1)-O(13)	143.22(14)	O(8)-V(2)-O(1)	110.93(18)
O(18)-V(1)-O(9)	111.12(17)	O(9)-V(1)-O(13)	78.49(13)	O(14)#3-V(2)-O(1)	139.61(14)
O(1)-V(1)-O(9)	136.50(15)	O(8)-V(2)-O(14)#3	109.29(17)	O(13)-V(2)-O(1)	78.61(13)
O(12)-V(1)-O(9)	90.31(14)	O(8)-V(2)-O(13)	108.70(17)	O(10)-V(3)-O(12)	98.60(18)
O(18)-V(1)-O(13)	110.75(15)	O(14)#3-V(2)-O(13)	92.07(14)	O(20)-V(3)-O(12)	156.64(17)
O(8)-V(2)-O(6)#3	109.08(17)	O(10)-V(3)-O(20)	104.7(2)	O(1)-V(3)-O(12)	80.55(13)
O(10)-V(3)-O(1)	111.93(18)	O(6)-V(3)-O(12)	77.95(14)	O(20)-V(3)-O(6)	91.81(12)
O(13)-V(2)-O(6)#3	142.21(14)	O(20)-V(3)-O(1)	91.56(12)	O(11)-V(4)-O(12)	108.57(17)
O(1)-V(2)-O(6)#3	87.19(14)	O(10)-V(3)-O(6)	113.00(17)	O(11)-V(4)-O(5)	108.39(17)

O(12)-V(4)-O(5)	92.23(15)	O(16)-V(6)-O(2)	108.95(16)	O(1)-V(3)-O(6)	132.34(15)
O(11)-V(4)-O(6)	108.80(17)	O(15)#3-V(5)-O(14)	89.91(15)	O(9)-V(6)-O(2)	77.23(13)
O(12)-V(4)-O(6)	84.96(15)	O(4)-V(5)-O(3)	110.62(17)	O(3)-V(6)-O(2)	88.10(14)
O(5)-V(4)-O(6)	141.57(14)	O(15)#3-V(5)-O(3)	87.32(16)	O(5)-V(6)-O(2)	143.15(14)
O(11)-V(4)-O(14)	106.89(16)	O(14)-V(5)-O(3)	138.39(14)	O(17)-V(7)-O(19)	104.2(2)
O(12)-V(4)-O(14)	144.17(14)	O(4)-V(5)-O(5)	108.53(16)	O(17)-V(7)-O(3)#3	115.33(19)
O(5)-V(4)-O(14)	81.40(14)	O(15)#3-V(5)-O(5)	145.68(14)	O(19)-V(7)-O(3)#3	94.98(13)
O(6)-V(4)-O(14)	78.96(14)	O(14)-V(5)-O(5)	79.69(14)	O(17)-V(7)-O(2)	115.53(19)
O(3)-V(5)-O(5)	79.61(14)	O(4)-V(5)-O(14)	110.06(16)	O(19)-V(7)-O(2)	95.53(13)
O(4)-V(5)-O(15)#3	105.77(16)	O(3)#3-V(7)-O(2)	123.26(16)	O(9)-V(6)-O(3)	140.98(15)
O(3)-V(6)-O(5)	78.66(14)	O(17)-V(7)-O(15)	95.9(2)	O(16)-V(6)-O(5)	107.90(16)
O(9)-V(6)-O(5)	91.71(14)	O(16)-V(6)-O(9)	107.77(18)	O(19)-V(7)-O(15)	159.84(17)
O(7)-V(8)-O(15)	107.29(17)	O(16)-V(6)-O(3)	111.19(18)	O(3)#3-V(7)-O(15)	76.85(14)
O(7)-V(8)-O(13)	108.94(17)	O(7)-V(8)-O(9)	107.00(16)	O(2)-V(7)-O(15)	74.61(13)
O(15)-V(8)-O(13)	94.42(15)	O(15)-V(8)-O(9)	145.26(15)	O(2)-V(8)-O(9)	77.93(14)
O(7)-V(8)-O(2)	106.59(17)	O(13)-V(8)-O(9)	79.60(13)	O(15)-V(8)-O(2)	87.19(16)
O(13)-V(8)-O(2)	142.13(14)				

3

Ni(1)-N(1)	2.071(2)	V(1)-O(3)	1.619(2)	V(1)-O(2)	1.797(2)
Ni(1)-N(2)	2.078(2)	V(1)-O(1)	1.659(2)	V(1)-O(2)#2	1.821(2)
Ni(1)-O(1)	2.117(2)				
N(1)-Ni(1)-N(1)#1	180.00(13)	N(2)-Ni(1)-O(1)#1	94.14(9)	O(2)-V(1)-O(2)#2	112.20(14)
N(1)-Ni(1)-N(2)#1	86.12(10)	O(1)-Ni(1)-O(1)#1	180.00(11)	V(1)-O(2)-V(1)#3	134.10(12)
N(1)-Ni(1)-N(2)	93.88(10)	O(3)-V(1)-O(1)	109.16(11)	V(1)-O(1)-Ni(1)	150.86(12)
N(2)#1-Ni(1)-N(2)	180.00(14)	O(3)-V(1)-O(2)	108.42(10)	O(1)-V(1)-O(2)	107.73(10)
N(1)-Ni(1)-O(1)	87.05(9)	N(2)-Ni(1)-O(1)	85.86(9)	O(1)-V(1)-O(2)#2	110.82(10)
N(1)#1-Ni(1)-O(1)	92.95(9)				

4

Cu(1)-N(1)	2.032(3)	Cu(1)-N(2)	2.038(3)	Cu(1)-O(2)	2.534(3)
V(1)-O(1)	1.629(3)	V(1)-O(3)	1.793(3)	V(1)-O(2)	1.648(3)
V(1)-O(3)#2	1.814(3)				
N(1)#1-Cu(1)-N(1)	180.0(2)	O(1)-V(1)-O(2)	109.94(17)	O(2)-V(1)-O(3)#2	110.69(14)
N(1)-Cu(1)-N(2)	94.41(13)	O(1)-V(1)-O(3)	110.01(14)	O(3)-V(1)-O(3)#2	111.14(7)
N(1)-Cu(1)-N(2)#1	85.59(13)	O(2)-V(1)-O(3)	106.58(14)	V(1)-O(3)-V(1)#3	138.93(17)
N(2)-Cu(1)-N(2)#1	180.00(18)	O(1)-V(1)-O(3)#2	108.48(15)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z ; #2 -x+1,-y+1,-z+1; #3 -x,-y,-z+1 for **1**; #1 -x+1,-y,-z+1, #2 -x,y,-z+1/2, #3 -x+1,y,-z+1/2 for **2**; #1 -x+1,-y,-z+1, #2 x-y+1/3,x-1/3,-z+2/3, #3 y+1/3,-x+y+2/3,-z+2/3 for **3**; #1 -x+1,-y+1,-z, #2 -y+2/3,x-y+1/3,z+1/3, #3 -x+y+1/3,-x+2/3,z-1/3, #4 -x+4/3,-y+2/3,-z+5/3 for **4**.

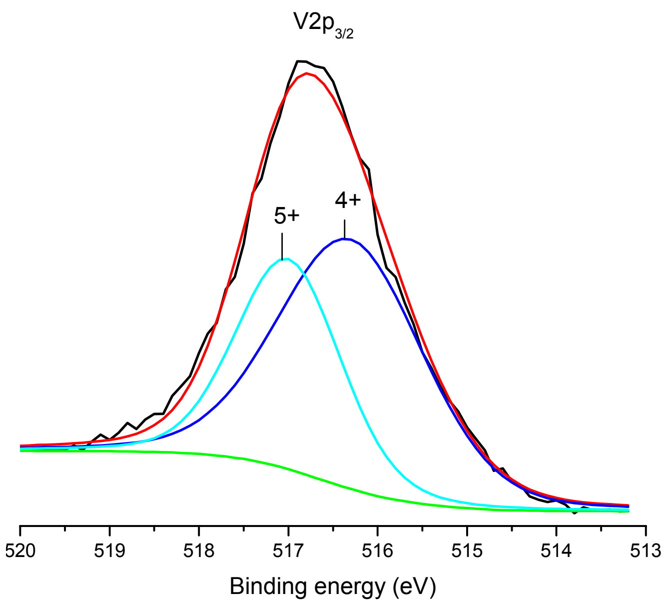
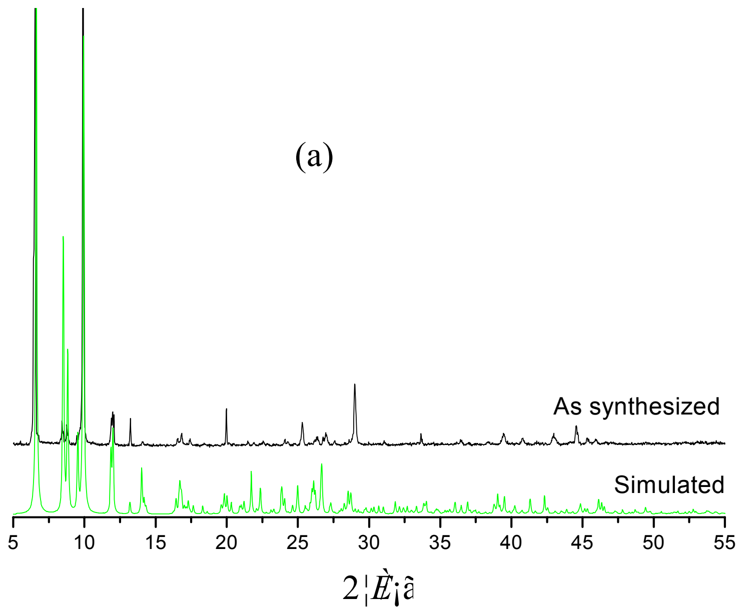


Figure S1. The XPS spectrum of **2**.



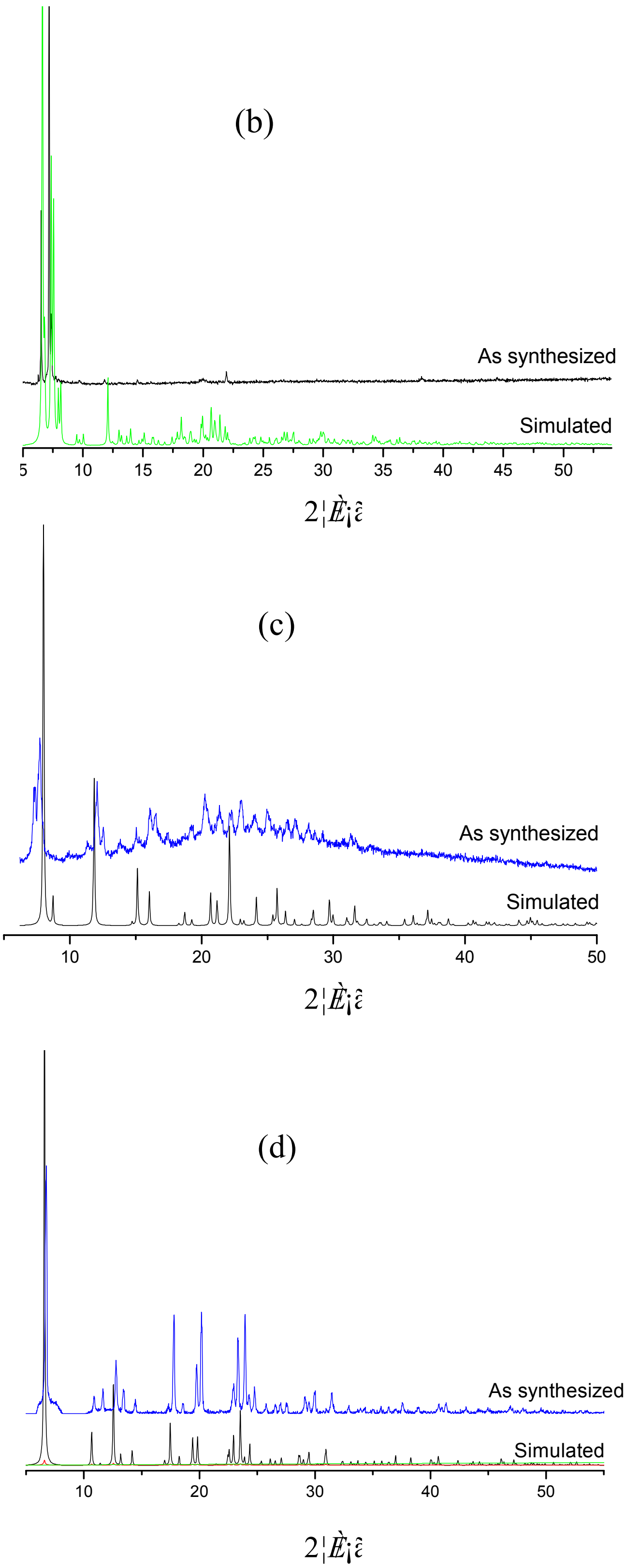
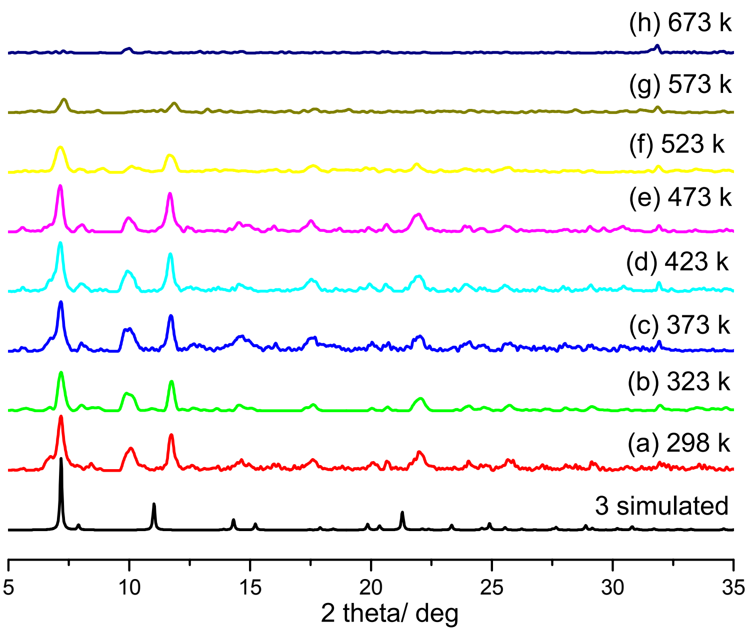


Figure S2. The XRD patterns of the simulated from the single-crystal diffraction data and as-synthesized for (a) **1**, (b) **2**, (c) **3**, and (d) **4**.



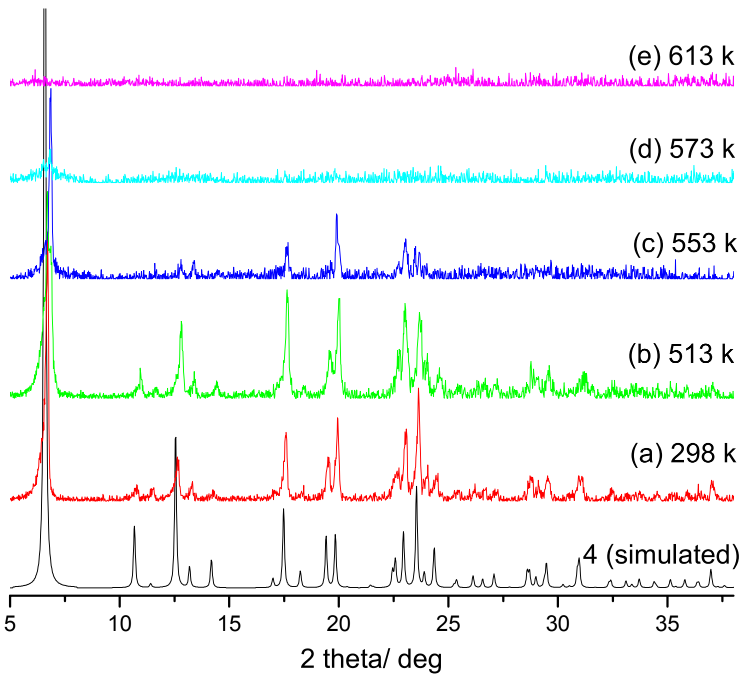


Figure S3. The variable temperature X-ray powder diffraction measurements for **3** (top) and **4** (bottom). (The peaks shift between the simulated and as synthesized patterns (298 K) in **3** may be due to the lost of guest water molecules, as the crystals of **3** are easy to collapse to powder at room temperature.)