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A series of new polyoxometalate-based metal-organic complexes with different rigid pyridyl-bis(triazole) ligands: Assembly, structures and electrochemical properties

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Table S1 Selected bond distances (Å) and angles (°) for complexes **1–5**.

Complex **1**			
Co(1)-O(3W)	2.072(4)	N(2)-Co(1)-O(2W)	89.76(17)
Co(1)-O(1W)	2.091(5)	O(3W)-Co(1)-O(1)	89.02(15)
Co(1)-N(2)	2.103(4)	O(1W)-Co(1)-O(1)	90.06(17)
Co(1)-O(2W)	2.113(4)	N(2)-Co(1)-O(1)	99.01(15)
Co(1)-O(1)	2.114(4)	O(2W)-Co(1)-O(1)	86.45(14)
Co(1)-N(1)	2.139(4)	O(3W)-Co(1)-N(1)	94.28(17)
O(3W)-Co(1)-O(1W)	87.5(2)	O(1W)-Co(1)-N(1)	90.17(19)
O(3W)-Co(1)-N(2)	169.81(18)	N(2)-Co(1)-N(1)	77.71(16)
O(1W)-Co(1)-N(2)	98.7(2)	O(2W)-Co(1)-N(1)	93.78(15)
O(3W)-Co(1)-O(2W)	84.45(16)	O(1)-Co(1)-N(1)	176.70(15)
O(1W)-Co(1)-O(2W)	171.25(19)		
Complex **2**			
Co(1)-O(2W)	2.046(3)	O(2)-Co(1)-N(1)	92.00(16)
Co(1)-O(2)	2.068(3)	O(1)-Co(1)-N(1)	99.76(15)
Co(1)-O(1)	2.088(3)	O(2W)-Co(1)-O(1W)	90.59(14)
Co(1)-N(1)	2.118(4)	O(2)-Co(1)-O(1W)	86.05(14)
Co(1)-O(1W)	2.129(4)	O(1)-Co(1)-O(1W)	83.05(14)
Co(1)-N(2)	2.142(4)	N(1)-Co(1)-O(1W)	176.60(15)
Co(2)-O(3W)	2.073(3)	O(2W)-Co(1)-N(2)	89.80(15)
Co(2)-O(4W)	2.089(4)	O(2)-Co(1)-N(2)	93.53(14)
Co(2)-O(3)	2.098(3)	O(1)-Co(1)-N(2)	175.42(15)
Co(2)-N(8)	2.100(5)	N(1)-Co(1)-N(2)	77.71(16)
Co(2)-O(4)	2.115(3)	O(1W)-Co(1)-N(2)	99.62(15)
Co(2)-N(9)	2.171(4)	O(3W)-Co(2)-O(4W)	87.67(15)
Co(3)-O(7W)	2.052(4)	O(3W)-Co(2)-O(3)	173.51(14)
Co(3)-O(5W)	2.065(4)	O(4W)-Co(2)-O(3)	87.70(14)
Co(3)-O(9W)	2.073(4)	O(3W)-Co(2)-N(8)	96.80(16)
Co(3)-O(8W)	2.085(4)	O(4W)-Co(2)-N(8)	174.47(16)
Co(3)-O(6W)	2.095(3)	O(3)-Co(2)-N(8)	88.09(15)
Co(3)-O(10W)	2.139(4)	O(3W)-Co(2)-O(4)	88.03(14)
O(2W)-Co(1)-O(2)	175.63(14)	O(4W)-Co(2)-O(4)	88.71(14)
O(2W)-Co(1)-O(1)	86.44(13)	O(3)-Co(2)-O(4)	87.32(13)
O(2)-Co(1)-O(1)	90.37(13)	N(8)-Co(2)-O(4)	94.68(15)
O(2W)-Co(1)-N(1)	91.49(16)	O(3W)-Co(2)-N(9)	89.57(15)

O(4W)-Co(2)-N(9)	98.60(15)	O(7W)-Co(3)-O(6W)	86.34(15)
O(3)-Co(2)-N(9)	95.62(14)	O(5W)-Co(3)-O(6W)	92.56(15)
N(8)-Co(2)-N(9)	78.25(16)	O(9W)-Co(3)-O(6W)	175.24(16)
O(4)-Co(2)-N(9)	172.21(15)	O(8W)-Co(3)-O(6W)	94.50(14)
O(7W)-Co(3)-O(5W)	91.09(17)	O(7W)-Co(3)-O(10W)	95.97(16)
O(7W)-Co(3)-O(9W)	90.45(16)	O(5W)-Co(3)-O(10W)	172.89(16)
O(5W)-Co(3)-O(9W)	91.02(16)	O(9W)-Co(3)-O(10W)	89.77(15)
O(7W)-Co(3)-O(8W)	176.14(17)	O(8W)-Co(3)-O(10W)	87.84(14)
O(5W)-Co(3)-O(8W)	85.11(16)	O(6W)-Co(3)-O(10W)	87.07(14)
O(9W)-Co(3)-O(8W)	88.94(15)		
Complex **3**			
Co(1)-O(1W)	2.053(5)	Co(2)-O(3W)#3	2.071(6)
Co(1)-O(2)	2.085(5)	Co(2)-O(3W)	2.071(6)
Co(1)-O(2W)	2.099(5)	Co(2)-N(1)#3	2.084(6)
Co(1)-N(7)#1	2.134(7)	Co(2)-N(1)	2.084(6)
Co(1)-O(1)#2	2.135(5)	Co(2)-N(2)#3	2.194(6)
Co(1)-N(4)	2.152(7)	Co(2)-N(2)	2.194(6)
O(1W)-Co(1)-O(2)	176.8(2)	O(3W)#3-Co(2)-O(3W)	180.0
O(1W)-Co(1)-O(2W)	87.8(2)	O(3W)#3-Co(2)-N(1)#3	91.0(3)
O(2)-Co(1)-O(2W)	89.6(2)	O(3W)-Co(2)-N(1)#3	89.0(3)
O(1W)-Co(1)-N(7)#1	90.4(2)	O(3W)#3-Co(2)-N(1)	89.0(3)
O(2)-Co(1)-N(7)#1	91.7(2)	O(3W)-Co(2)-N(1)	91.0(3)
O(2W)-Co(1)-N(7)#1	99.1(2)	N(1)#3-Co(2)-N(1)	180.0
O(1W)-Co(1)-O(1)#2	87.4(2)	O(3W)#3-Co(2)-N(2)#3	92.3(3)
O(2)-Co(1)-O(1)#2	95.03(19)	O(3W)-Co(2)-N(2)#3	87.7(3)
O(2W)-Co(1)-O(1)#2	172.2(2)	N(1)#3-Co(2)-N(2)#3	76.7(2)
N(7)#1-Co(1)-O(1)#2	87.1(2)	N(1)-Co(2)-N(2)#3	103.3(2)
O(1W)-Co(1)-N(4)	97.4(2)	O(3W)#3-Co(2)-N(2)	87.7(3)
O(2)-Co(1)-N(4)	80.7(2)	O(3W)-Co(2)-N(2)	92.3(3)
O(2W)-Co(1)-N(4)	88.1(2)	N(1)#3-Co(2)-N(2)	103.3(2)
N(7)#1-Co(1)-N(4)	169.6(2)	N(1)-Co(2)-N(2)	76.7(2)
O(1)#2-Co(1)-N(4)	86.4(2)	N(2)#3-Co(2)-N(2)	180.0(3)
Symmetry code for **3**: #1 -x+2,-y+2,-z+1; #2 -x+1,-y+2,-z+1; #3 -x+1,-y+1,-z+1			
Complex **4**			
Ni(1)-O(1W)	2.030(2)	Ni(2)-N(1)#3	2.047(2)
Ni(1)-O(2)	2.050(2)	Ni(2)-N(1)	2.047(2)
Ni(1)-O(2W)	2.070(2)	Ni(2)-O(3W)	2.063(3)
Ni(1)-N(7)#1	2.089(2)	Ni(2)-O(3W)#3	2.063(3)
Ni(1)-O(1)#2	2.092(2)	Ni(2)-N(2)	2.154(3)
Ni(1)-N(4)	2.110(2)	Ni(2)-N(2)#3	2.154(3)
O(1W)-Ni(1)-O(2)	177.73(9)	O(2)-Ni(1)-N(7)#1	91.10(9)
O(1W)-Ni(1)-O(2W)	88.11(9)	O(2W)-Ni(1)-N(7)#1	97.62(10)
O(2)-Ni(1)-O(2W)	90.10(9)	O(1W)-Ni(1)-O(1)#2	87.46(9)
O(1W)-Ni(1)-N(7)#1	90.52(9)	O(2)-Ni(1)-O(1)#2	94.20(8)

O(2W)-Ni(1)-O(1)#2	173.17(9)	N(1)-Ni(2)-O(3W)#3	88.71(11)
N(7)#1-Ni(1)-O(1)#2	87.61(9)	O(3W)-Ni(2)-O(3W)#3	180.0
O(1W)-Ni(1)-N(4)	96.92(9)	N(1)#3-Ni(2)-N(2)	101.80(10)
O(2)-Ni(1)-N(4)	81.63(9)	N(1)-Ni(2)-N(2)	78.20(10)
O(2W)-Ni(1)-N(4)	88.31(10)	O(3W)-Ni(2)-N(2)	91.80(11)
N(7)#1-Ni(1)-N(4)	170.66(10)	O(3W)#3-Ni(2)-N(2)	88.20(11)
O(1)#2-Ni(1)-N(4)	87.08(9)	N(1)#3-Ni(2)-N(2)#3	78.20(10)
N(1)#3-Ni(2)-N(1)	180.0	N(1)-Ni(2)-N(2)#3	101.79(10)
N(1)#3-Ni(2)-O(3W)	88.71(11)	O(3W)-Ni(2)-N(2)#3	88.20(11)
N(1)-Ni(2)-O(3W)	91.29(10)	O(3W)#3-Ni(2)-N(2)#3	91.80(11)
N(1)#3-Ni(2)-O(3W)#3	91.29(10)		
Symmetry code for **4**: #1 -x+2,-y+2,-z+1; #2 -x+1,-y+2,-z+1; #3 -x+1,-y+1,-z+1			
Complex **5**			
Ni(1)-O(1W)	2.000(3)	Ni(2)-N(3)#2	2.055(3)
Ni(1)-O(2W)	2.039(3)	Ni(2)-N(4)#2	2.057(3)
Ni(1)-N(1)	2.054(3)	Ni(2)-O(6W)#2	2.092(3)
Ni(1)-O(8)	2.069(2)	Ni(2)-O(6W)	2.092(3)
Ni(1)-O(3W)	2.072(2)	Ni(2)-N(4)	2.057(3)
Ni(1)-O(1)#1	2.082(2)	Ni(2)-N(3)	2.055(3)
O(1W)-Ni(1)-O(2W)	180.0	N(3)#2-Ni(2)-N(3)	180.0
O(1W)-Ni(1)-N(1)	100.97(12)	N(3)#2-Ni(2)-N(4)	100.97(12)
O(2W)-Ni(1)-N(1)	79.03(12)	N(3)-Ni(2)-N(4)	79.03(12)
O(1W)-Ni(1)-O(8)	79.03(12)	N(3)#2-Ni(2)-N(4)#2	79.03(12)
O(2W)-Ni(1)-O(8)	100.97(12)	N(3)-Ni(2)-N(4)#2	100.97(12)
N(1)-Ni(1)-O(8)	180.0	N(4)-Ni(2)-N(4)#2	180.0
O(1W)-Ni(1)-O(3W)	86.68(13)	N(3)#2-Ni(2)-O(6W)	86.68(13)
O(2W)-Ni(1)-O(3W)	93.32(13)	N(3)-Ni(2)-O(6W)	93.32(13)
N(1)-Ni(1)-O(3W)	91.80(15)	N(4)-Ni(2)-O(6W)	91.80(15)
O(8)-Ni(1)-O(3W)	88.20(15)	N(4)#2-Ni(2)-O(6W)	88.20(15)
O(1W)-Ni(1)-O(1)#1	93.32(13)	N(3)#2-Ni(2)-O(6W)#2	93.32(13)
O(2W)-Ni(1)-O(1)#1	86.68(13)	N(3)-Ni(2)-O(6W)#2	86.68(13)
N(1)-Ni(1)-O(1)#1	88.20(15)	N(4)-Ni(2)-O(6W)#2	88.20(15)
O(8)-Ni(1)-O(1)#1	91.80(15)	N(4)#2-Ni(2)-O(6W)#2	91.80(15)
O(3W)-Ni(1)-O(1)#1	180.0	O(6W)-Ni(2)-O(6W)#2	180.0
Symmetry code for **5**: #1 -x,-y,-z+2; #2 -x,-y+1,-z+2			

Table S2. Selected hydrogen-bonding geometry (Å, º) for complexes **1**–**2**

Complex	D–H···A	D–H	H···A	D···A	D–H···A
1	C(3)–H(3A)···O(10)	0.86	1.98	3.2540	143
	N(6)–H(6A)···O(8)	0.93	2.46	2.7150	143
2	N(3)–H(3A) ···O(7)	0.86	1.90	2.7170	157
	C(18)–H(18A) ···O(17)	0.93	2.16	3.0100	151

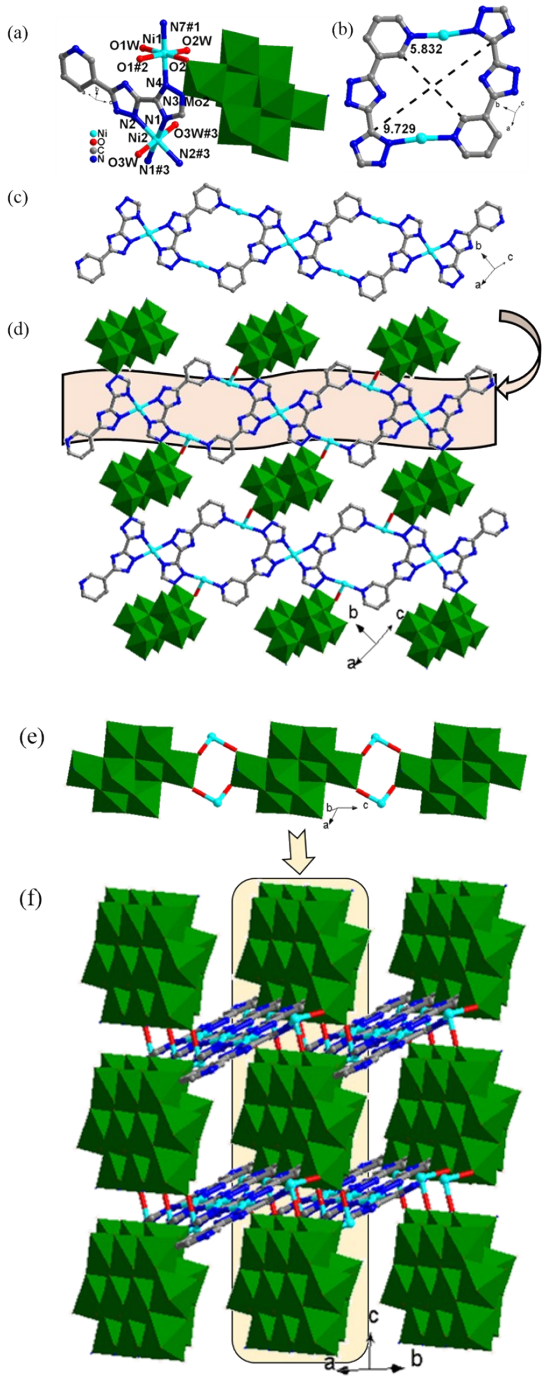

Fig. S1 (a) The coordination geometry of the Ni^{II} ions in **4**. The hydrogen atoms and lattice water molecules are omitted for clarity; Symmetry code for **4**: #1 -x+2,-y+2,-z+1; #2 -x+1,-y+2,-z+1; #3 -x+1,-y+1,-z+1. (b) [$Ni_2(H_2pyttz\text{-}II)_2$] loop in **4**. (c) The 1D Co-H_2pyttz-II chain in **4.** (d) View of the 2D layer in **4**. (e) A view of Ni-γ-Mo_8O_{26} inorganic chain in complex **4**. (e) The 3D Mo_8O_{26}-based metal-organic framework of **4**.

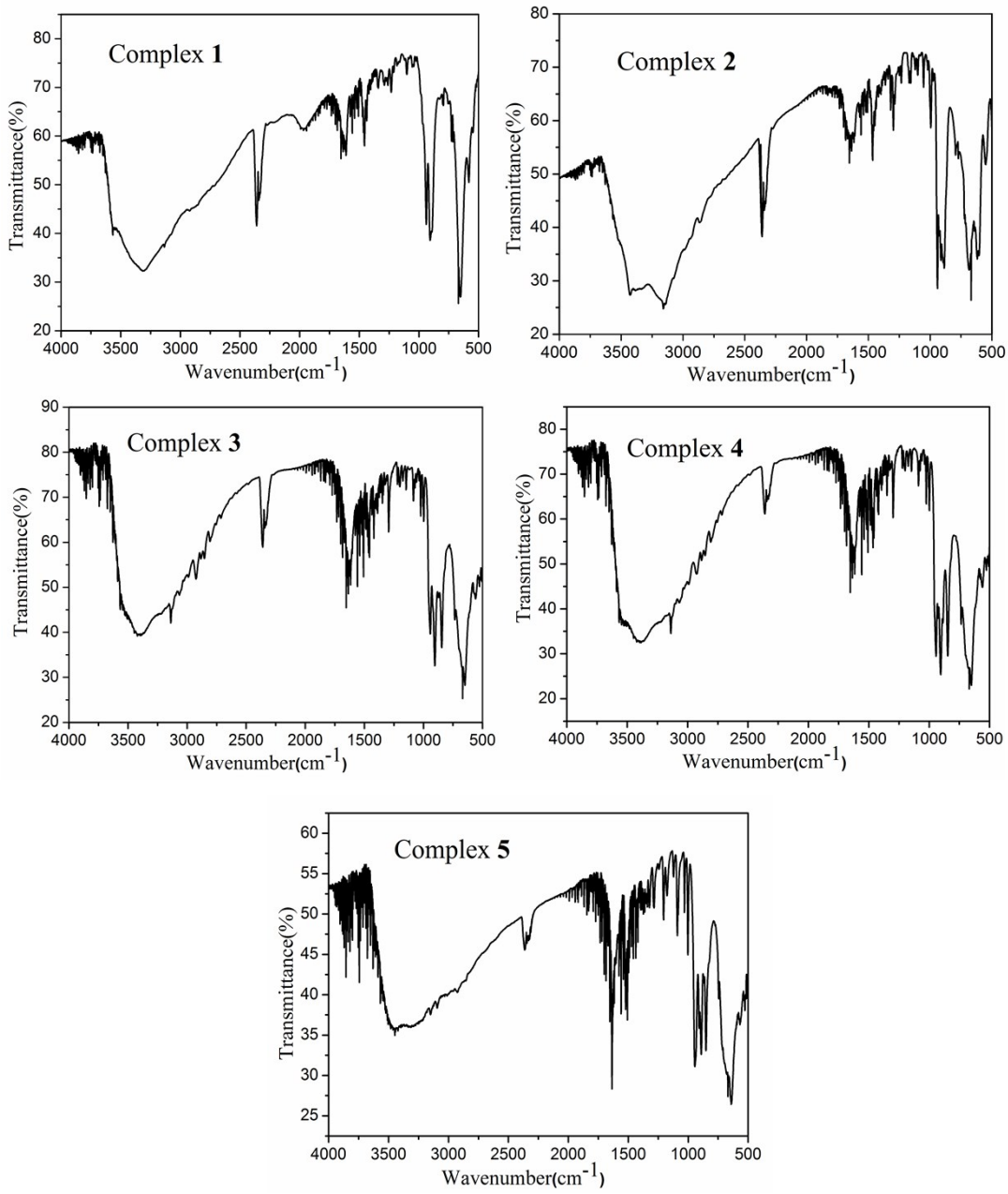

Fig. S2 The IR spectra of complexes **1–5**.

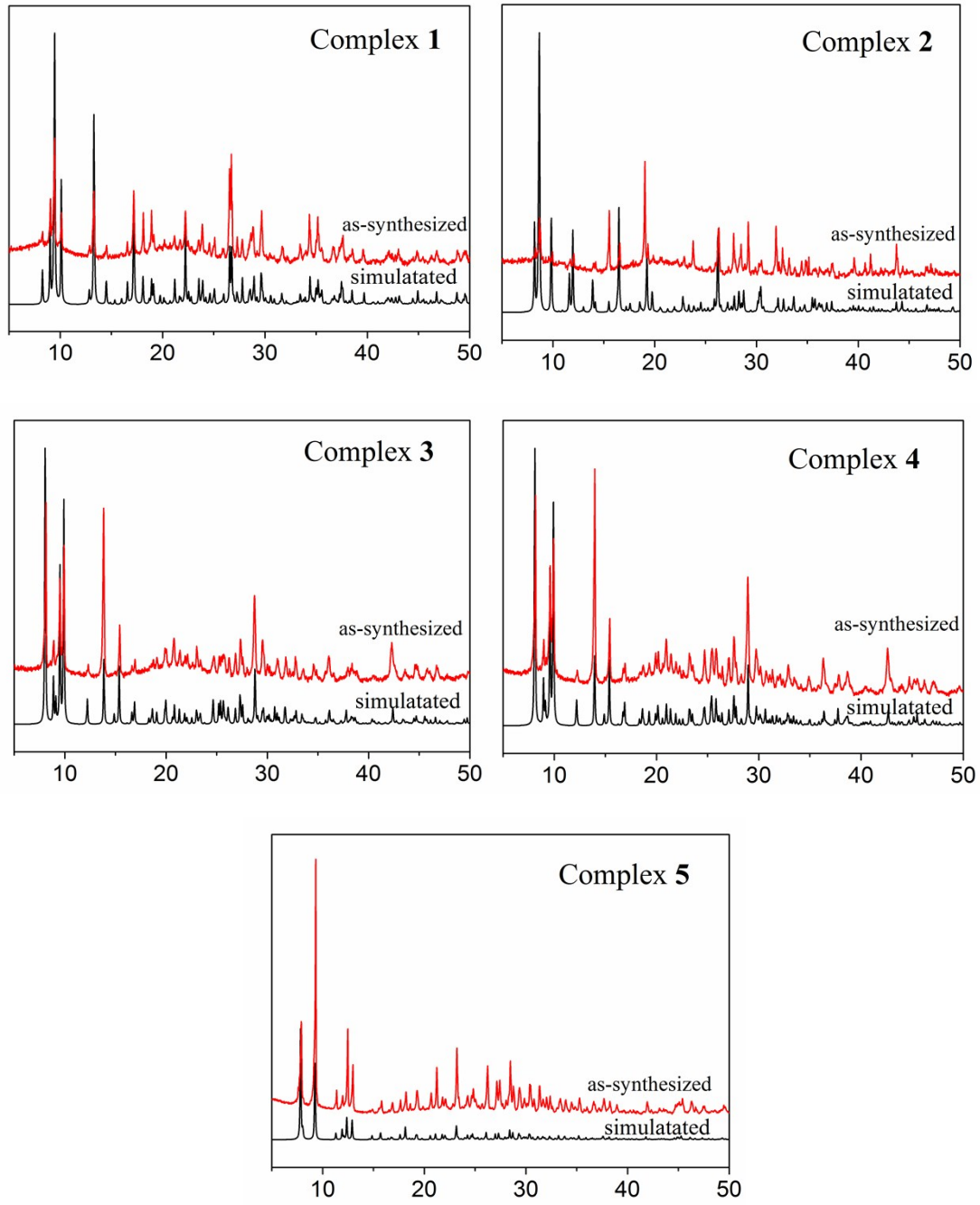

Fig. S3 The PXRD patterns of complexes **1**–**5**.

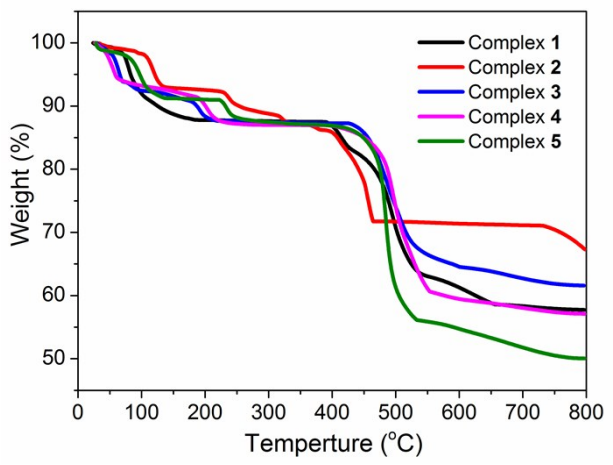

Fig. S4 The TG curves of complexes **1**–**5**.

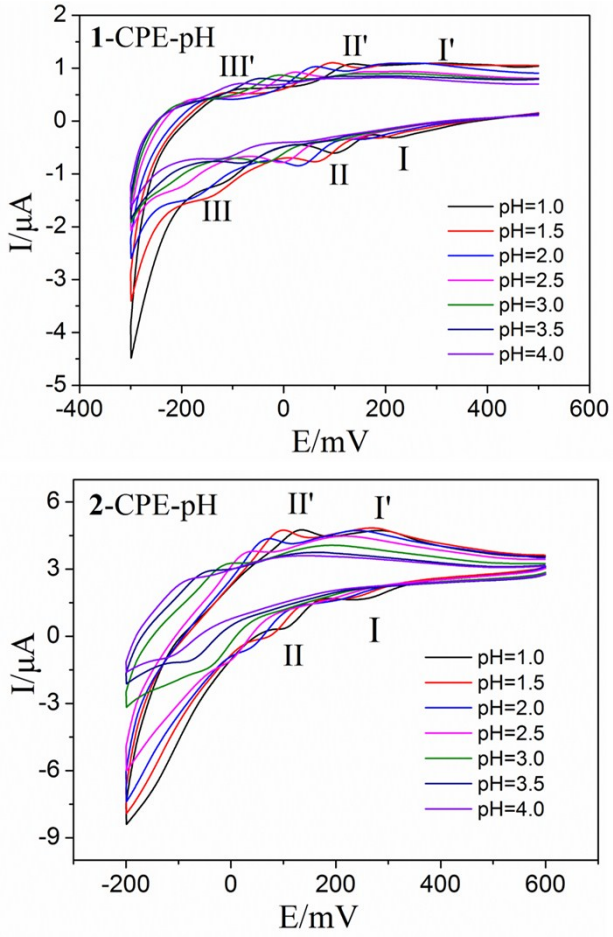

Fig. S5 Cyclic voltammograms of **1**-CPE and **2**-CPE at different pH values (Scan rate: 40 $mV \cdot s^{-1}$).

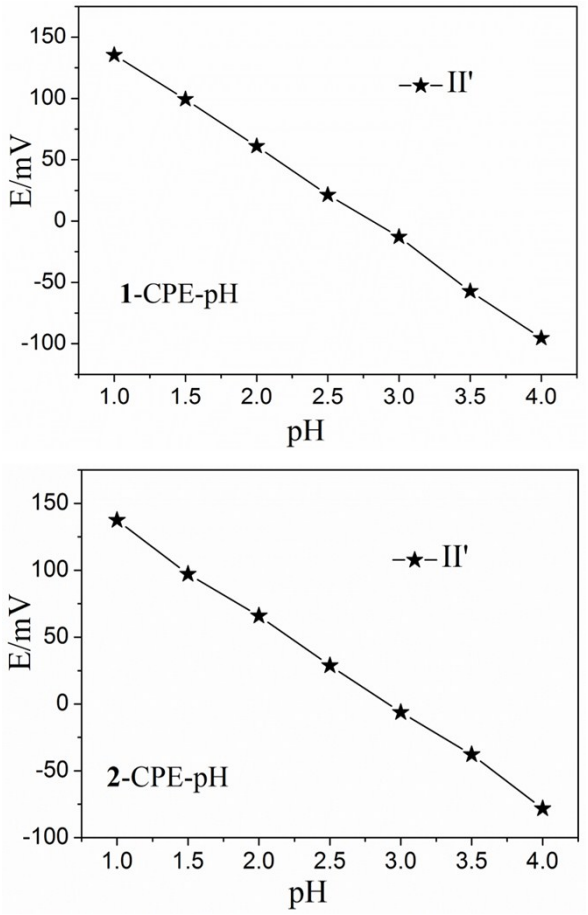

Fig. S6 Variation of anodic peak potentials of the Mo^{VI}-based wave (II′) with different pH for **1**-CPE and **2**-CPE