Supporting Information

Inorganic–Organic Hybrid Supramolecular Architectures Based on Keggin Polyoxometalates and Crown Ether： Synthesis, Crystal Structure and Electrochemical Properties

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Contents

Table S1. Selected bond lengths (Å) for compound **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mo1	O29	1.799(6)	K2	N1	2.874(14)
Mo1	O31[a]	2.400(7)	K2	C25	3.393(18)
Mo1	O32[a]	1.979(7)	Si1	O22[a]	1.537(7)
Mo2	O24	2.377(7)	Si1	O24[a]	1.691(7)
Mo2	O27	1.805(5)	Si1	O30	1.622(7)
Mo2	O30[a]	2.440(7)	Si1	O31[a]	1.686(7)
Mo2	O33	1.990(5)	Si1	O31	1.686(7)
Mo3	O13	1.663(5)	O1	C14	1.407(9)
Mo4	O30[a]	2.454(7)	O6	C13	1.400(9)
Mo6	O19	1.997(5)	O12	C1	1.434(12)
Mo6	O20	1.654(5)	O12	C12	1.421(13)
Mo6	O22	2.409(7)	O22	O30	1.694(9)
K1	O10	2.801(6)	C11	C12	1.499(15)
K1	O13	2.948(5)	C17	C18	1.470(12)
K1	C10	3.540(9)	C19	C20	1.474(14)
K2	O1	2.965(6)	C21	C22	1.457(14)
K2	O3	2.975(6)	C25	C26	1.54(2)

Symmetry transformation for **1**: *a, -x,1-y,1-z*

Table S2. Selected angles (º) for compound **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O25	Mo2	O33	98.2(3)	O22[1]	Si1	O24	110.9(3)
O27	Mo2	O16	87.4(2)	O22	Si1	O30[a]	115.2(3)
O27	Mo2	O24	65.1(3)	O22[a]	Si1	O30[a]	64.8(3)
O34	Mo4	O21	103.2(4)	C6	O9	C7	116.3(11)
O34	Mo4	O23[a]	97.2(3)	C7	O9	K1	116.7(7)
O34	Mo4	O29[a]	97.7(3)	C8	O10	K1	116.7(6)
O34	Mo4	O30[a]	154.7(2)	C9	O10	K1	116.9(6)
O34	Mo4	O31	155.1(3)	C9	O10	C8	114.3(9)
O12	K1	O13	93.6(2)	O1	C14	C13	109.5(6)
O12	K1	C10	79.8(2)	O6	C15	C16	110.0(6)
O13	K1	C10	69.20(19)	O5	C16	C15	108.3(7)
O1	K2	O3	106.35(17)	O5	C17	C18	109.5(7)
O3	K2	O25	126.08(16)	O1	C24	C23	109.2(8)
O3	K2	C25	80.7(3)	N1	C25	K2	53.6(11)
O4	K2	O1	146.63(17)	N1	C25	C26	169(2)
O4	K2	O2	114.23(18)	C26	C25	K2	137.5(12)

Symmetry transformation for **1**: *a, -x,1-y,1-z*

Table S3. Selected bond lengths (Å) for compound **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	O1	1.679(6)	K1	O24	2.840(7)
W1[a]	O9	1.868(8)	K1	N1	2.828(17)
W1[a]	O10	1.901(6)	K1	C25	3.42(2)
W2	O18	1.905(7)	Si1	O20[a]	1.605(9)
W2	O19	2.313(10)	Si1	O19	1.685(9)
W3	O20	2.454(10)	O23	C15	1.419(13)
W4	O8	1.905(6)	O24	C13	1.413(13)
W5	O11	1.671(6)	C15	C16	1.482(15)
W5	O12	1.872(8)	C17	C18	1.470(15)
W5	O17	1.916(7)	K2[b]	O5	2.946(9)
W6	O19	2.404(11)	K2	O32	2.800(8)
W6	O18	1.960(13)	O29	C7	1.40(2)
W6	O3	1.776(10)	O30	C8	1.391(19)
W6	O2	1.676(7)	O30	C9	1.406(19)
K1	O1	3.062(7)	C5	C6	1.53(2)
K1	O21	2.965(8)	C7	C8	1.45(2)
K1	O22	2.807(7)	C9	C10	1.48(2)
K1	O23	2.855(7)	C11	C12	1.46(2)

Symmetry transformation for **2**: *a, 1-x,1-y,1-z*; b, *1-x, 1-y, -z.*

Table S4. Selected angles (º) for compound **2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	W1	O10[a]	100.9(4)	O28	K2	O30	118.7(3)
O4	W1	O19	61.4(4)	O28	K2	O31	159.2(3)
O4	W1	O20[a]	96.1(4)	O31	C11	C12	110.6(14)
O9[a]	W1	O3	89.0(4)	O32	C12	C11	108.7(13)
O9[a]	W1	O4	158.2(4)	C18	O21	K1	108.3(6)
O7	W6[a]	O19[a]	93.5(4)	C18	O21	C19	113.1(9)
O7	W6[a]	O18[a]	158.3(4)	C19	O21	K1	110.7(7)
O19	Si1	O19[a]	104.8(5)	C16	O22	K1	119.9(6)
O20	Si1	O19	69.3(5)	C17	O22	K1	122.6(6)
O19	Si1	O20[a]	110.8(5)	C17	O22	C16	110.8(8)
K2[b]	O5	W2	166.9(4)	C14	O23	K1	108.9(6)
C13	O24	K1	117.7(6)	C15	O23	K1	109.3(6)
C15	O23	C14	111.0(8)	O29	C6	C5	106.7(13)
O27	C3	C4	107.3(11	O29	C7	C8	110.7(14)

Symmetry transformation for **2**: *a, 1-x,1-y,1-z*; b, *1-x, 1-y, -z.*

Table S5. Hydrogen bonds (Å and °) in complex **1**.

D−H···A	d(D−H)	d(H···A)	d(D···A)	∠ DHA	Symmetry Code
C9–H9B···O1	0.970	2.698	3.549	146.76	*1+x, -1+y, z;* *1/2+x, 1/2-y, -1/2+z*
C23–H23B···O23	0.970	2.546	3.439	152.96	*1+x, -1+y, z;* *1/2+x, 1/2-y, -1/2+z*
C22–H22A···O29	0.970	2.504	3.387	151.18	*1/2+x, 1/2-y, -1/2+z;* *1+x, -1+y, z*
C10–H10B···O18	0.970	2.623	3.320	128.95	*1-x, -y,1-z;* *1+x, -1+y,1+z*
C10–H9A···O18	0.970	3.341	3.793	110.62	*1-x, -y,1-z;* *1+x, -1+y,1+z*
C1–H1A··N1	0.970	2.626	3.533	155.83	*1/2+x, 1/2-y, 1/2+z;* *1/2+x, 1/2-y, -1/2+z*

Table S6. Hydrogen bonds (Å and °) in complex **2**.

D−H···A	d(D−H)	d(H···A)	d(D···A)	∠ DHA	Symmetry Code
C13–H13B···O12	0.970	2.624	3.375	134.47	*x, y, z;* *-1+x, y, z*
C20–H20A···O13	0.970	2.541	3.464	159	*1-x, 1-y, 1-z;* *1/2-x, -1/2+y, 1/2-z*
C21–H21A···O17	0.970	2.464	3.365	154.45	*1-x, 1-y, 1-z;* *1/2-x, -1/2+y, 1/2-z*
C2–H2A ···O6	0.970	2.608	3.321	130.59	*x, y, z;* *1-x, 1-y, -z*
C26–H26B···O27	0.962	2.469	3.318	146.97	*x, y, z;* *x, y,-1+z*
C5–H5B··N1	0.969	2.676	3.589	157.29	*x, y, z;* *x, y, -1+z;*

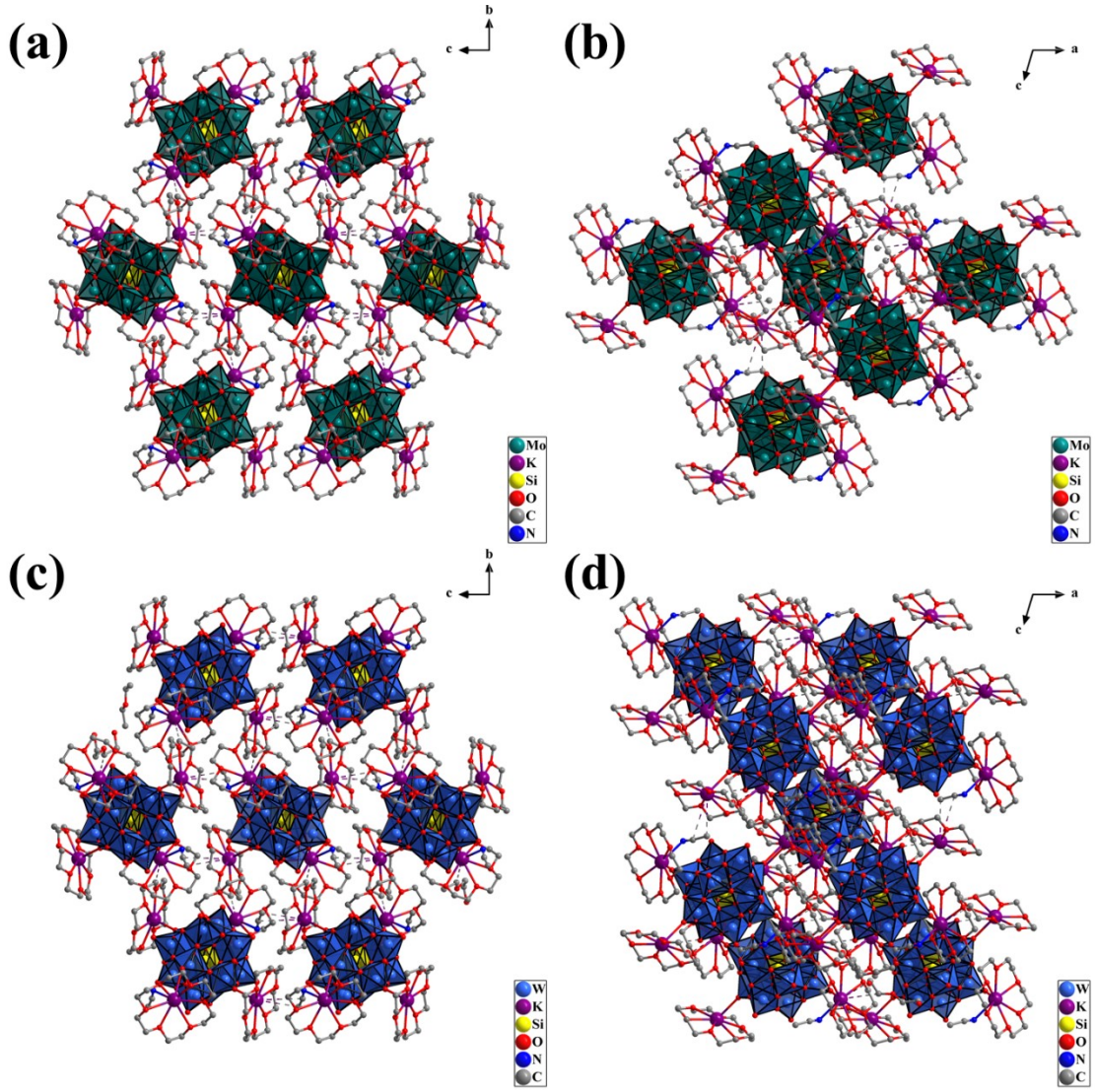

Fig S1. Three-dimensional stacking diagram of compound **1** along the *a*-axis (a) and the *b*-axis (b) and compound **2** along the *a*-axis (c) and the *b*-axis (d).

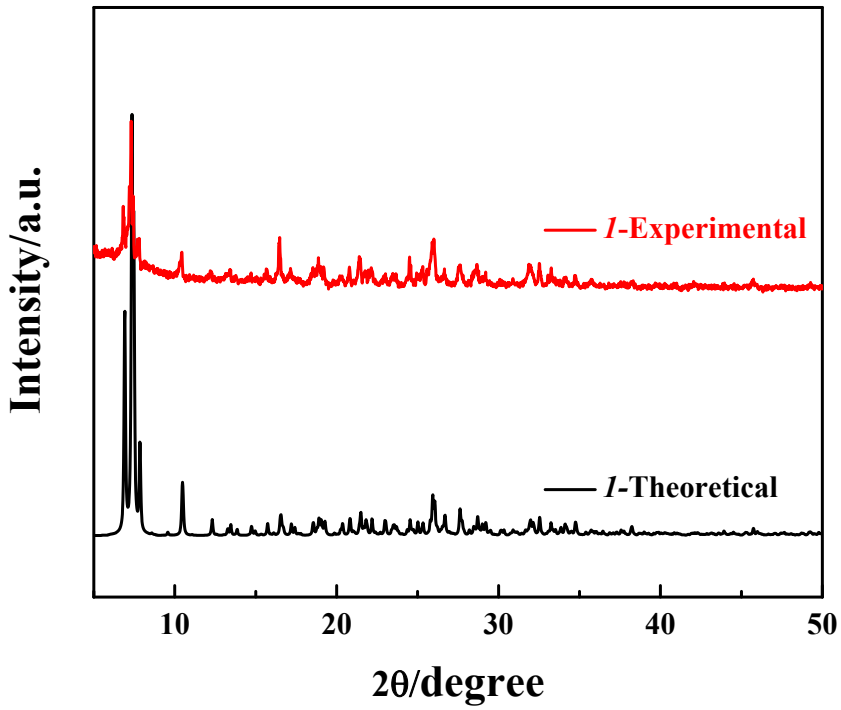

Fig S2. X-ray powder pattern of complex **1** vs. the calculated pattern. Peak positions are in good agreement, indicating the phase purity of the compound. Differences in intensity are due to preferred orientation of the powder sample.

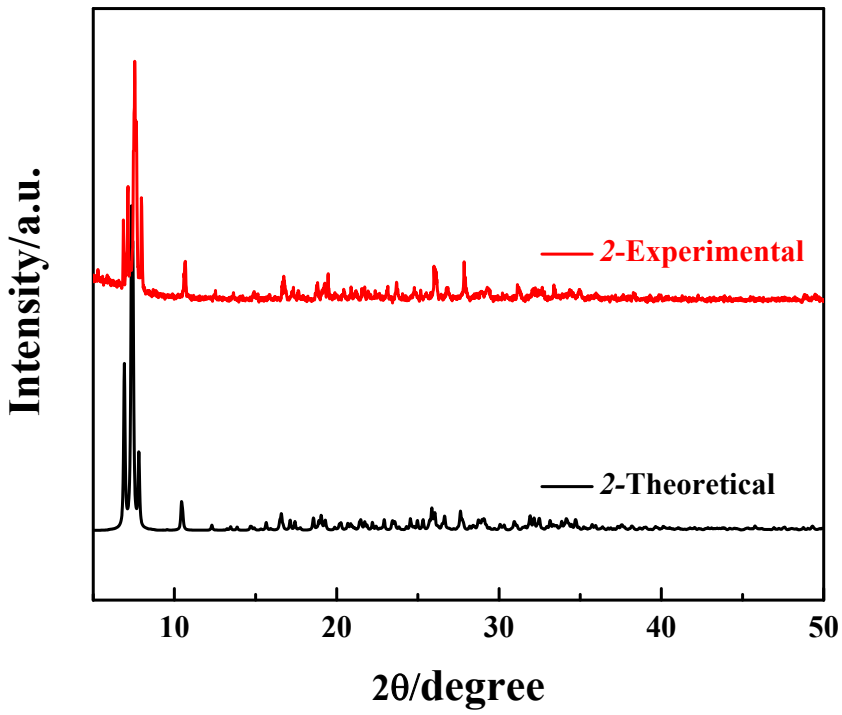

Fig S3. X-ray powder pattern of complex **2** vs. the calculated pattern. Peak positions are in good agreement, indicating the phase purity of the compound. Differences in intensity are due to preferred orientation of the powder sample.

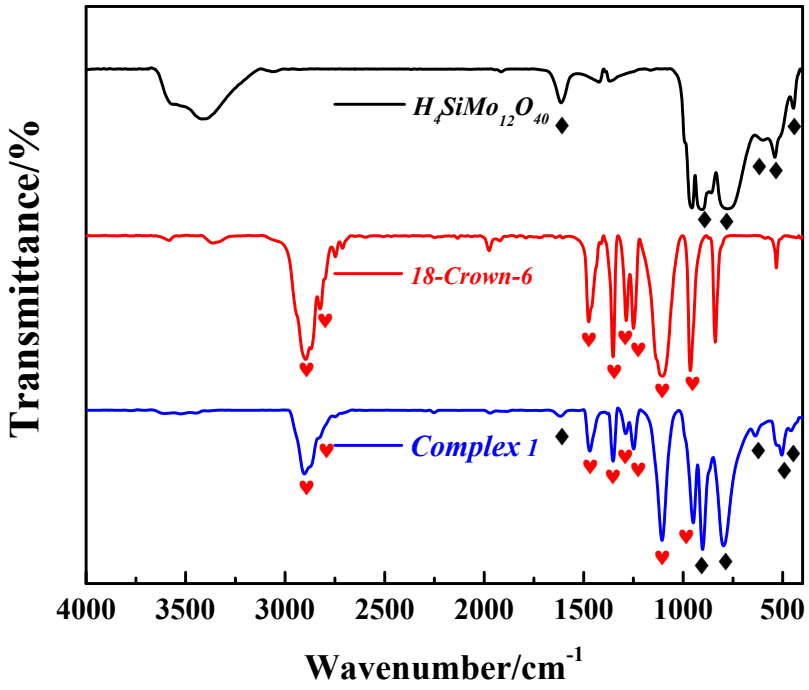

Fig S4. FT-IR spectra of free $H_4SiMo_{12}O_{40}$ ($SiMo_{12}$), [18]crown-6**,** and complex **1** in solid state.

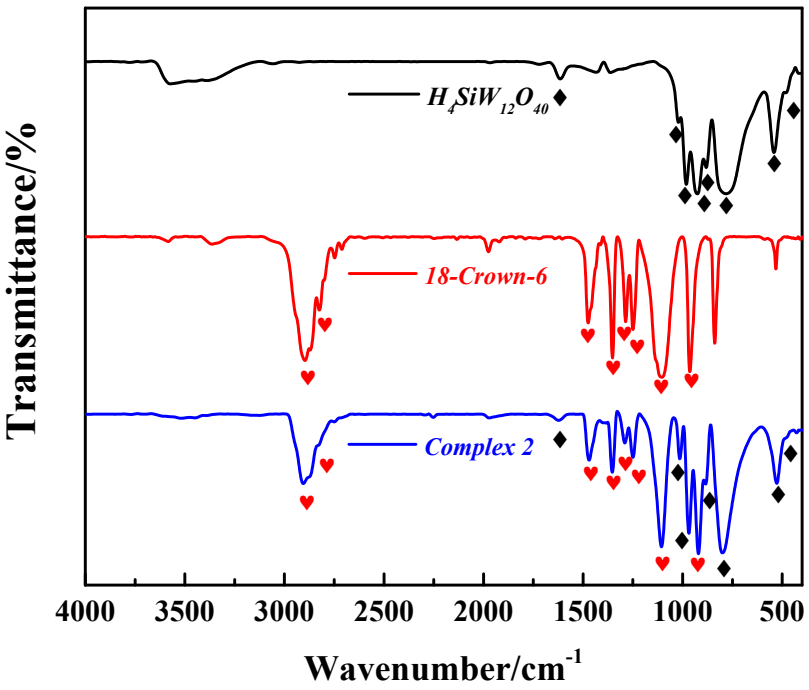

Fig S5. FT-IR spectra of free $H_4SiW_{12}O_{40}$ (SiW_{12}), [18]crown-6**,** and complex **2** in solid state.

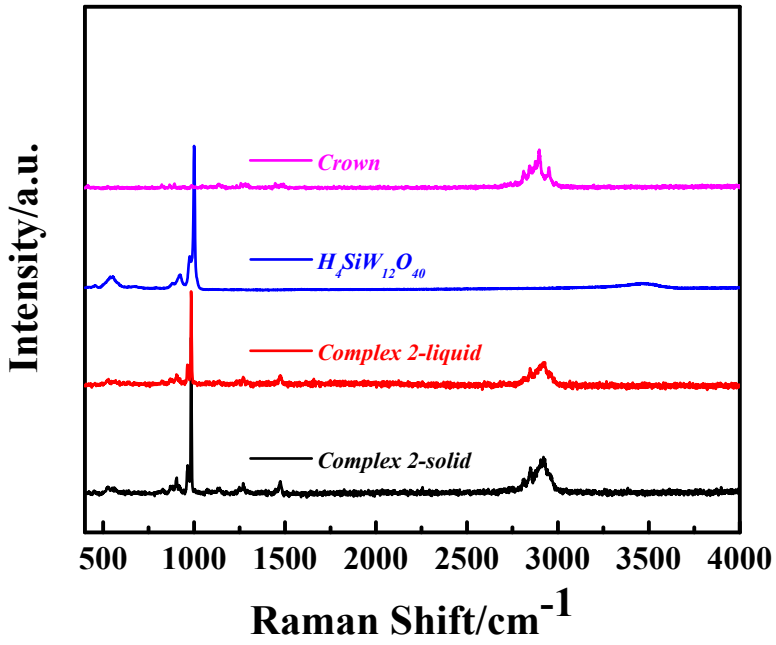

Fig S6. Raman spectra of free [18]crown-6, free $H_4SiW_{12}O_{40}$ (SiW_{12}), and complex **2** in solid state/aqueous solution.

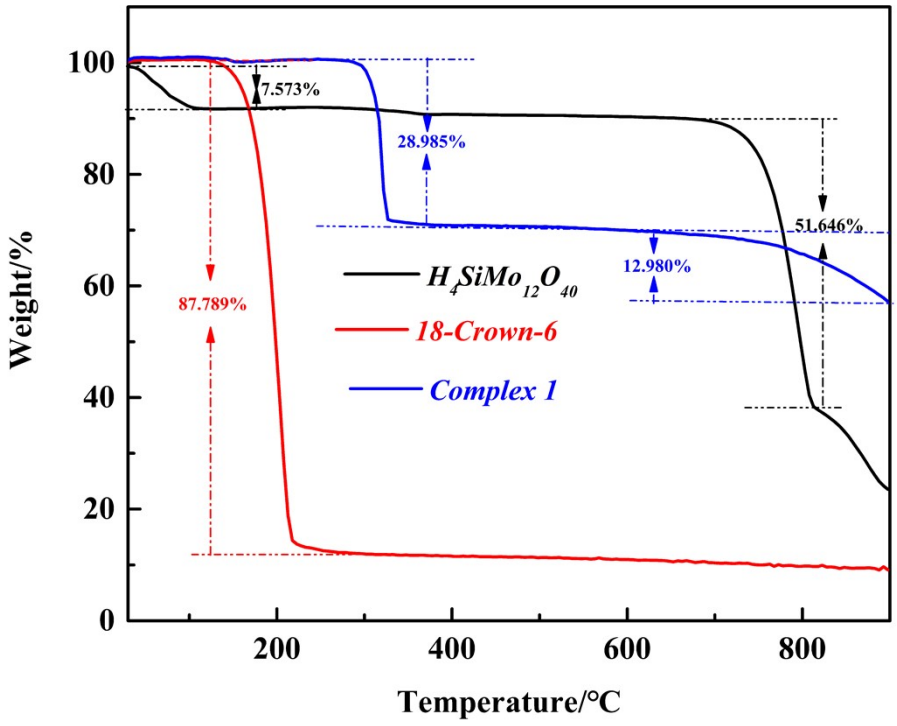

Fig S7. Thermogravimetric curve of free $H_4SiMo_{12}O_{40}$ ($SiMo_{12}$), [18]crown-6**,** and complex **1**.

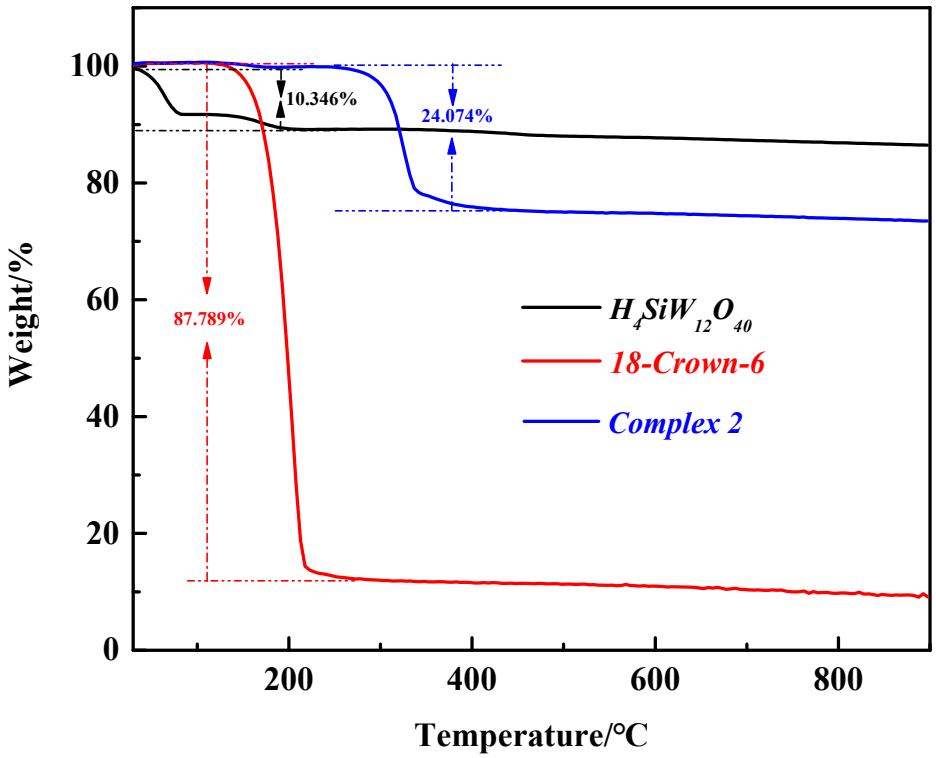

Fig S8. Thermogravimetric curve of free $H_4SiW_{12}O_{40}$ (SiW_{12}), [18]crown-6**,** and complex **2**.

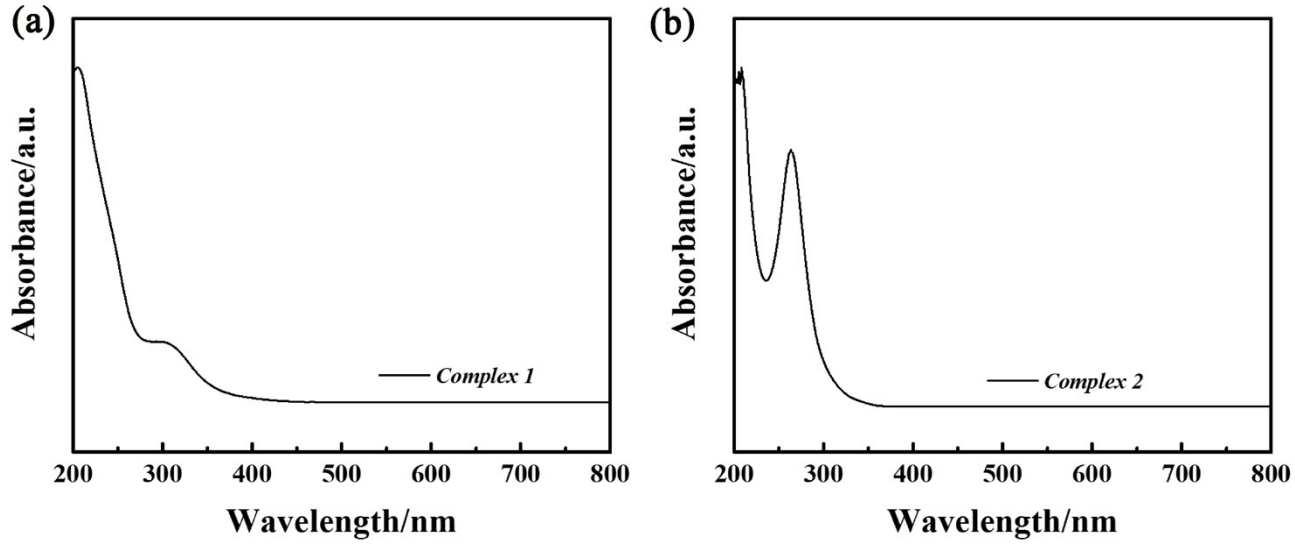

Fig S9. UV/vis spectra of (a) complex **1** and (b) complex **2** in aqueous solution.

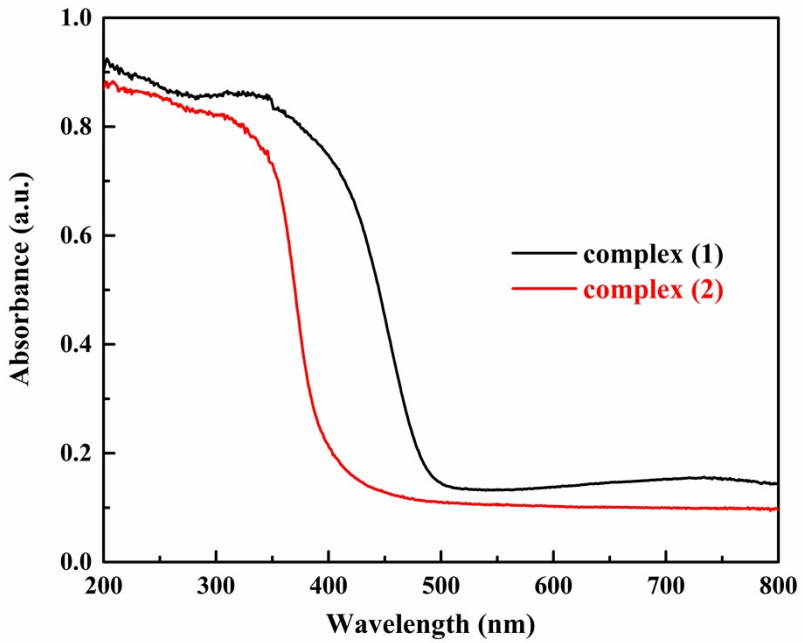

Fig S10. Solid state UV/vis spectra of complex **1** and complex **2**. (Band gap: E_g (eV) = hc / λ ≈ 1240 / λ_{onset}, h Planck's constant; c the speed of light in vacuum.)

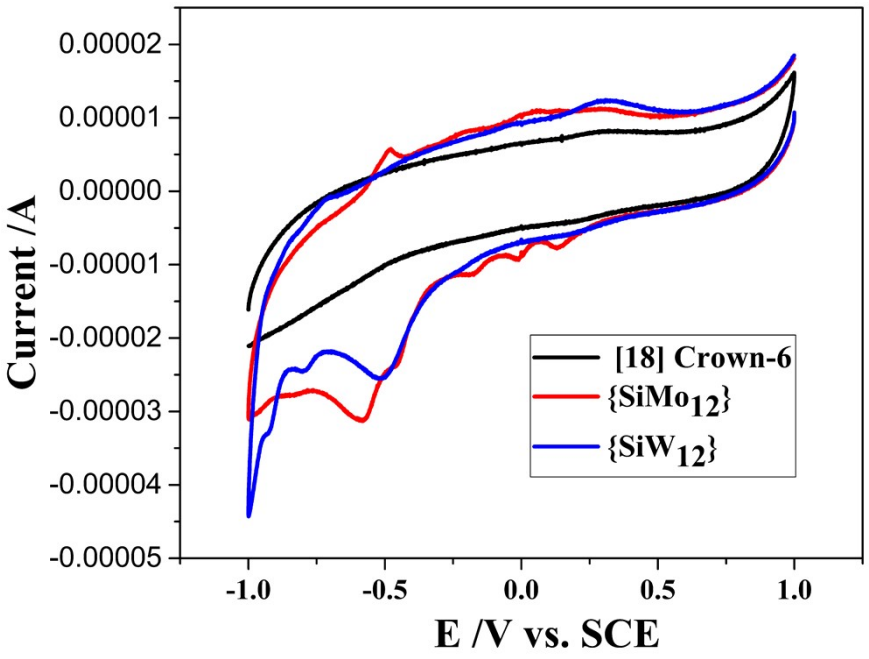

Fig S11. Cyclic voltammograms of 0.1 mM aqueous solutions of the free $H_4SiMo_{12}O_{40}$ ($SiMo_{12}$), $H_4SiW_{12}O_{40}$ (SiW_{12}), and [18]crown-6 in 0.5 M NaCl/HCl buffer solution at pH 3.0. (scan rate 100 mV/s, GCE working electrode, SCE reference electrode.