Electronic Supplemental Information (SI) For:

Molybdenum-titanium oxo-cluster, an efficient electrochemical catalyst for a facile preparation of black titanium dioxide film

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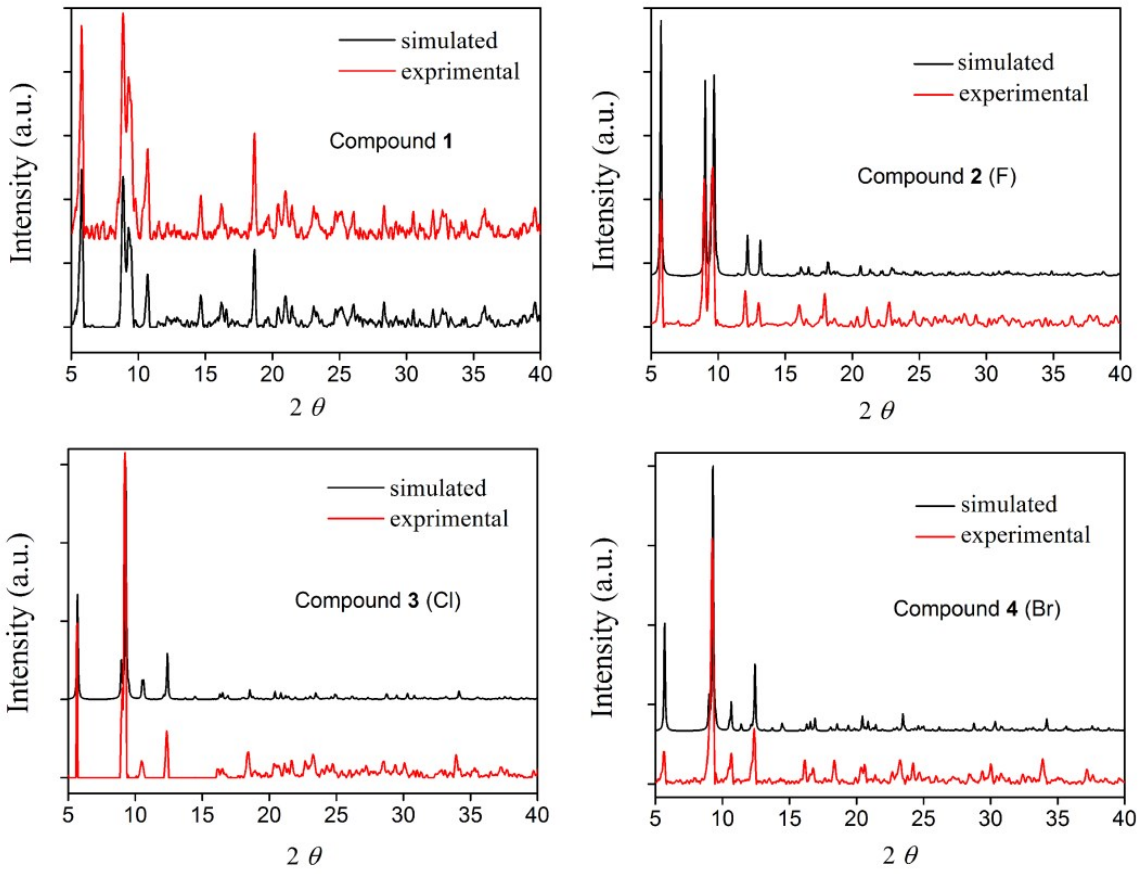


Fig. S1. XRD patterns of **1**−**4** and those simulated from the single-crystal X-ray data.

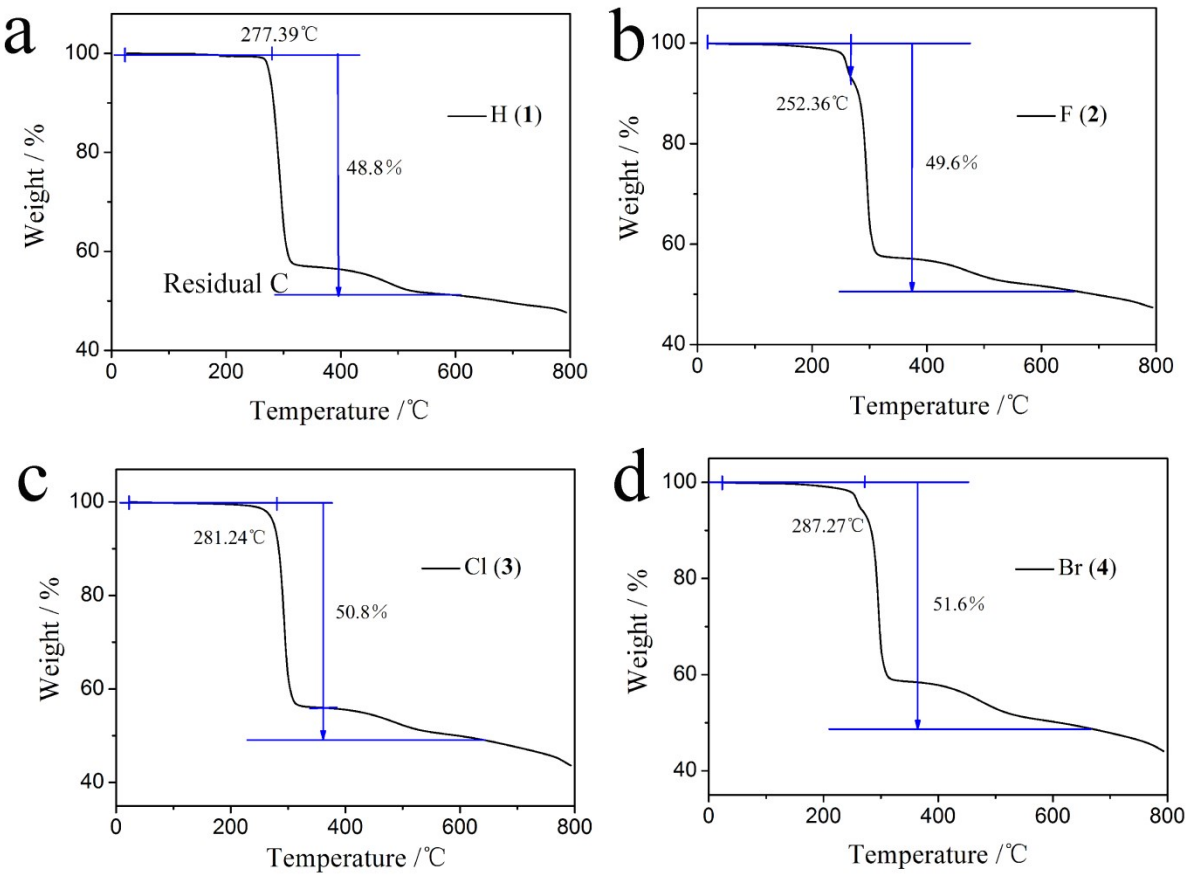


Fig. S2. Thermogravimetric analysis of **1**−**4**.

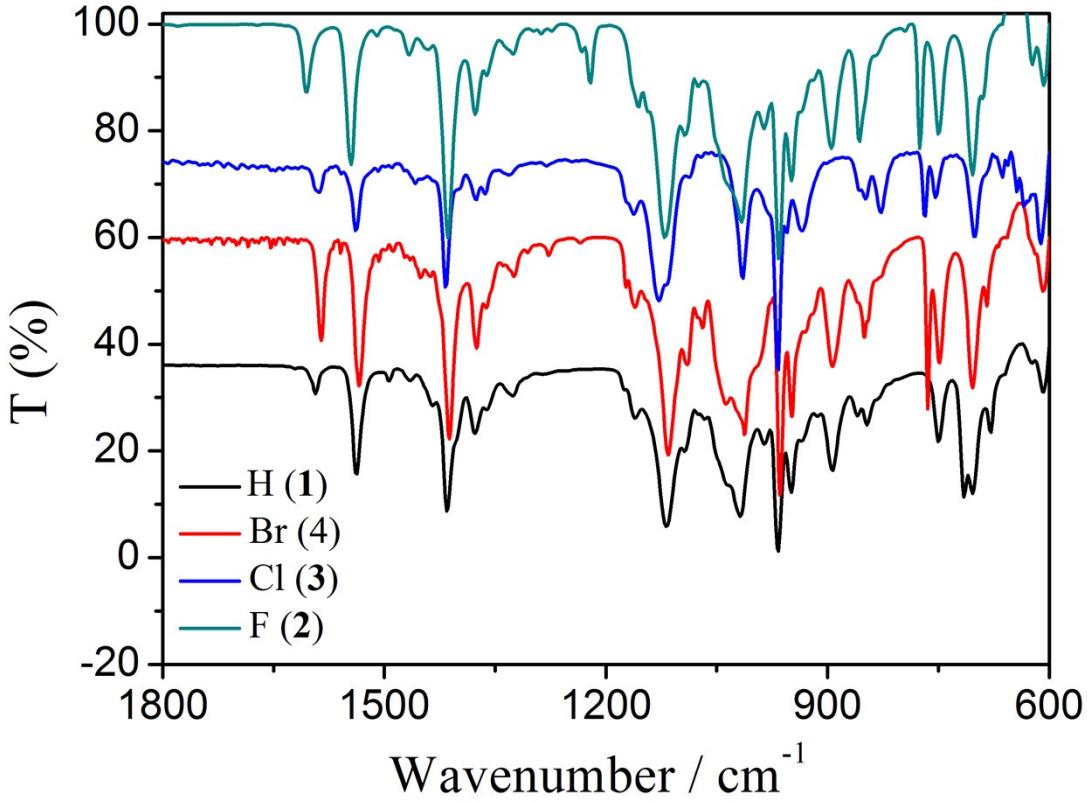
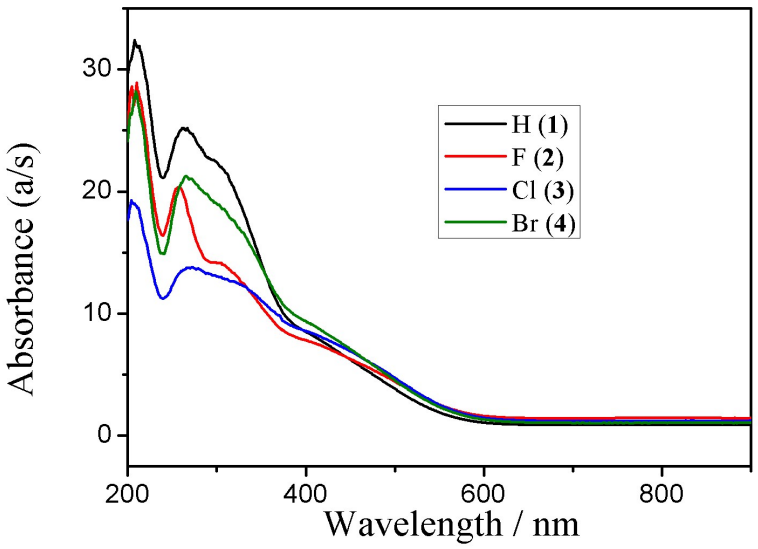
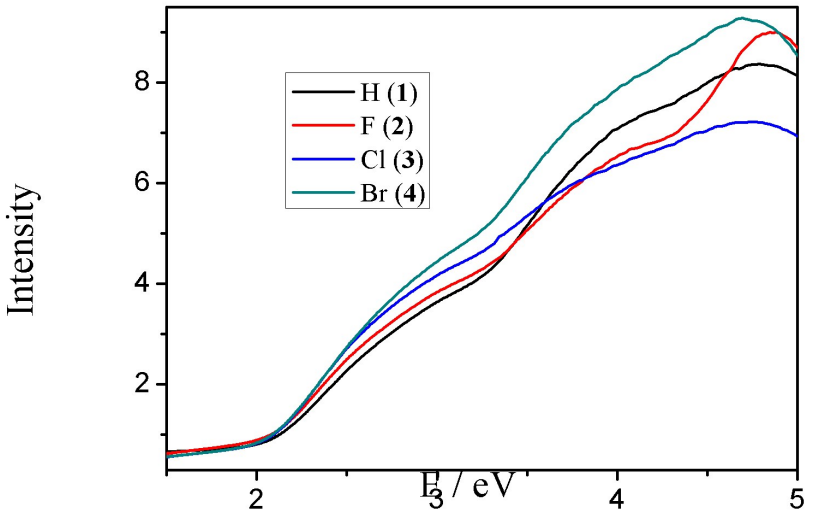


Fig. S3. IR spectra of copmpounds **1**−**4**.

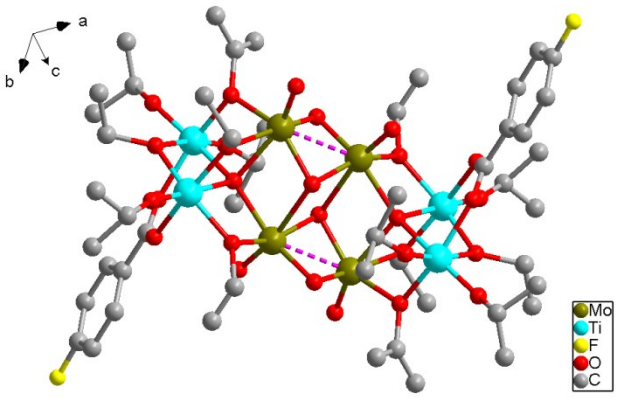


(a)

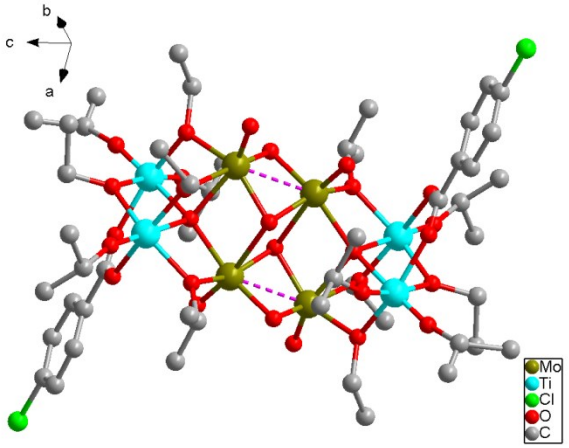


(b)

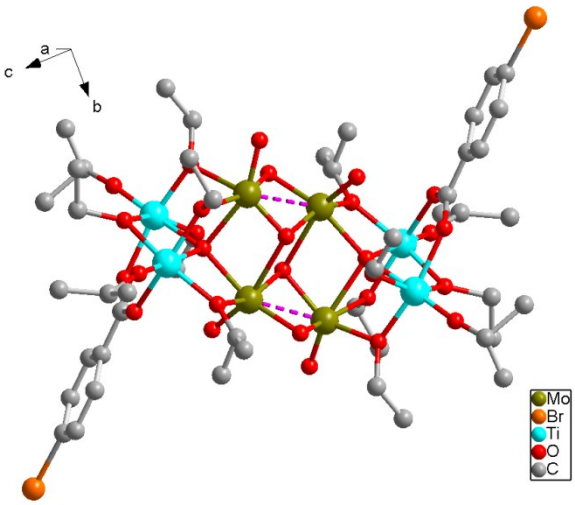
Fig. S4. UV-vis spectra of compounds **1**−**4** in nm (a) and eV (b) presentation.



Compound **2**

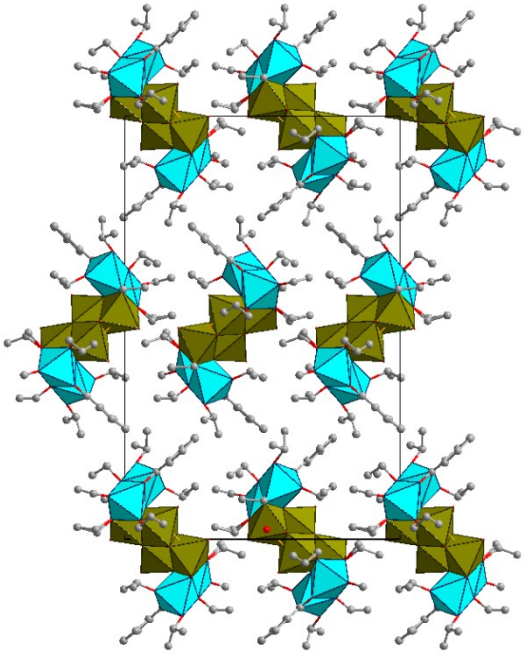


Compound **3**

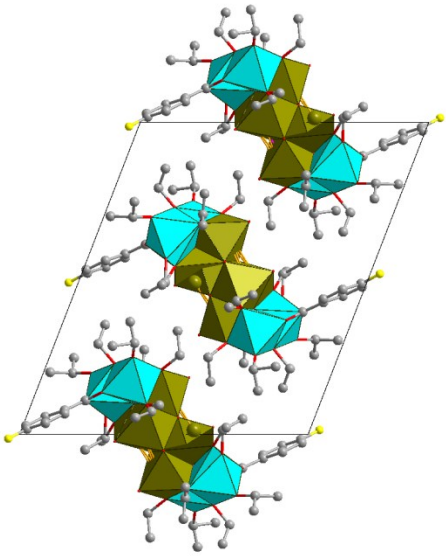


Compound **4**

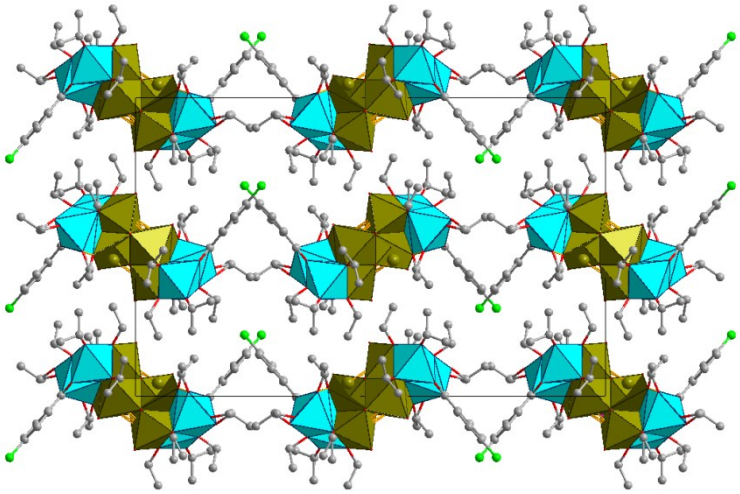
Fig. S5. Structures of compound **2**, **3** and **4** in ball-stick model. Hydrogen atoms are omitted for clarity.



(**1**)



(**2**)



(**3**)

Fig. S6. Molecular packing of compounds **1**−**3**.

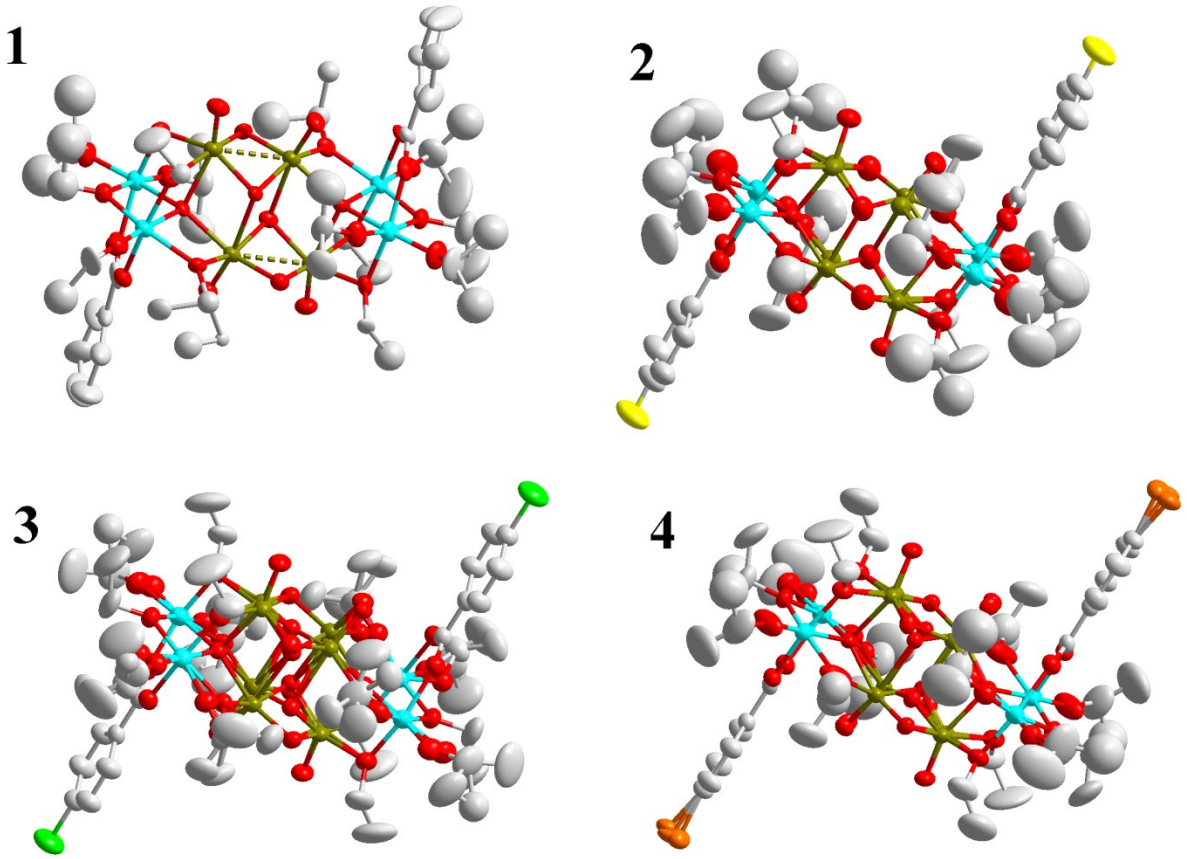


Fig. S7. X-ray crystal structures of compounds **1**–**4** with displacement ellipsoids drawn at the 50% probability level, showing the disordered structures. H atoms are omitted for clarity.

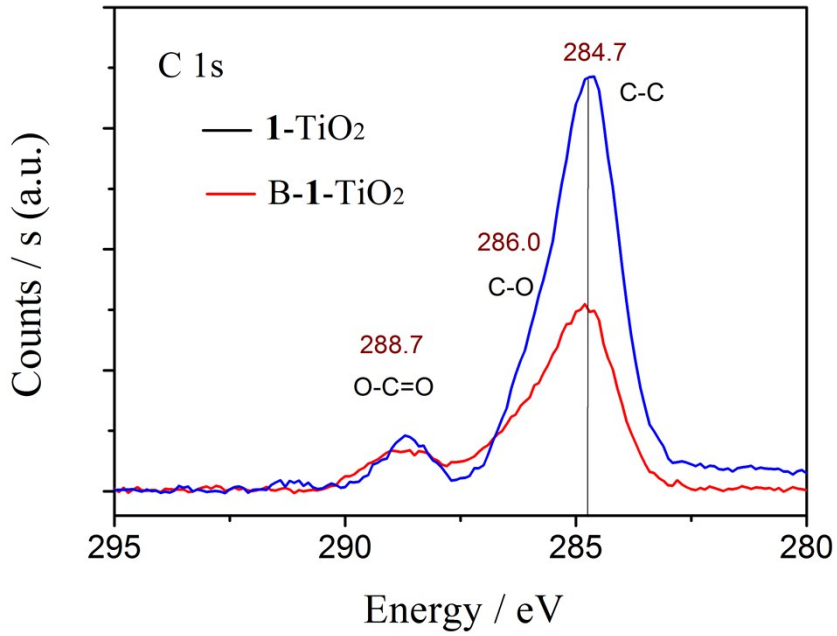


Fig. S8. The C1s XPS spectra of the **1**-TiO_2 (yellow) and B-**1**-TiO_2 (black) electrodes.

Tables

Table S1. Crystal data and structural refinement parameters for compounds **1**–**4**.

	1*	**2**	**3**	**4**
formula	$C_{50}H_{96}Mo_4O_{29}Ti_4$	$C_{50}H_{94}F_2Mo_4O_{28}Ti_4$	$C_{50}H_{94}Cl_2Mo_4O_{28}Ti_4$	$C_{50}H_{106}Br_2Mo_4O_{28}Ti_4$
fw	1736.51	1756.49	1789.51	1962.46
cryst size (mm^3)	0.24×0.20×0.10	0.35×0.30×0.20	0.30×0.22×0.18	0.30×0.20×0.14
cryst syst	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	$Pna2_1$	$P2_1/c$	$Pbca$	$Pbca$
a (Å)	19.4496(15)	16.582(2)	11.592(3)	11.6103(8)
b (Å)	11.4429(9)	11.7633(19)	19.701(5)	19.6212(14)
c (Å)	29.881(2)	19.247(3)	30.995(7)	31.014(2)
α (deg)	90	90	90	90
β (deg)	90	111.121(4)	90	90
γ (deg)	90	90	90	90
V ($Å^3$)	6650.4(9)	3502.0(9)	7078(3)	7065.3(8)
Z	4	2	4	4
ρ_{calcd} (g cm^{-3})	1.638	1.666	1.679	1.766
F(000)	3152	1784	3232	3776
μ (mm^{-1})	1.261	1.204	1.262	2.320
T (K)	120(2)	192(2)	192(2)	192(2)
reflns collected	124982	129254	242181	105608
unique reflns	13640	7166	7342	8134
observed reflns	10925	5271	5915	5488
no. params	738	461	582	486
GOF on F^2	1.172	1.040	1.164	1.145
R_1 [I>2σ(I)]	0.0814	0.0690	0.0691	0.0633
$_wR_2$	0.2010	0.1705	0.1810	0.1572

*The quality of crystal of **1** is not good enough, therefore, the data of **1** are only referred as a supplemental information.

Table S2 Summary of Bond-Valence calculations.

Atom	Coord	D_aver Sigm	Distort(x10-4)	Valence	BVSum(Sigma)
Mo1	6.00	2.0169(57)	80.895	5.000	5.070(89)
Mo2	5.00	1.9510(63)	55.354	5.000	4.830(95)
Mo3	5.00	1.9509(63)	51.372	5.000	4.794(92)
Mo4	6.00	2.0165(56)	86.020	5.000	5.120(91)
Ti1	6.00	1.9686(63)	43.070	4.000	4.227(79)
Ti2	6.00	1.9668(60)	32.983	4.000	4.187(76)
Ti3	6.00	1.9557(59)	29.698	4.000	4.292(76)
Ti4	6.00	1.9596(63)	44.458	4.000	4.332(84)
O1	2.00	2.0658(92)	45.446	-2.000	1.186(31)
O2	2.00	1.9638(90)	0.036	-2.000	1.715(42)
O3	4.00	2.1144(62)	12.097	-2.000	2.039(35)
O4	2.00	2.0474(107)	1.127	-2.000	1.211(35)
O5	2.00	2.0628(92)	42.893	-2.000	1.193(31)
O6	2.00	1.9544(90)	0.003	-2.000	1.759(43)
O7	2.00	2.0610(123)	1.231	-2.000	1.167(39)
O8	2.00	1.9305(98)	0.614	-2.000	1.878(50)
O9	2.00	2.0116(94)	12.250	-2.000	1.197(31)
O10	2.00	2.0090(97)	8.532	-2.000	1.199(32)
O11	2.00	1.9354(104)	0.196	-2.000	1.853(52)
O12	1.00	2.0708(155)	0.000	-2.000	0.501(21)
O13	2.00	2.0303(107)	6.258	-2.000	1.266(37)
O14	1.00	1.7636(162)	0.000	-2.000	1.149(50)
O15	4.00	2.1146(62)	9.140	-2.000	2.029(34)
O16	1.00	2.0477(161)	0.000	-2.000	0.533(23)
O17	1.00	1.7081(153)	0.000	-2.000	1.712(71)
O18	1.00	1.6909(140)	0.000	-2.000	1.793(68)
O19	2.00	2.0438(109)	4.347	-2.000	1.220(36)
O20	1.00	2.0536(158)	-0.001	-2.000	0.525(22)
O21	1.00	1.7490(176)	0.000	-2.000	1.195(57)
O22	1.00	2.0908(158)	0.000	-2.000	0.475(20)
O23	1.00	1.6903(154)	0.000	-2.000	1.796(75)
O24	1.00	1.8119(162)	0.000	-2.000	1.008(44)
O25	1.00	1.6773(140)	0.000	-2.000	1.860(71)
O26	1.00	1.7577(161)	0.000	-2.000	1.168(51)
O27	1.00	1.7468(170)	0.000	-2.000	1.202(55)
O28	1.00	1.8074(185)	0.000	-2.000	1.021(51)

=> Old Global Instability Index (GII=SQRT{SUM{|BVS-abs(q)|^2}/Num_Atoms}) = 73.31 /100

=> Normalized GII(a)= SUM {|BVS-abs(q)| *mult} /N_Atoms_UCell = 58.02 /100

=> Normalized GII(b)= SUM {|BVS-abs(q)| *mult/abs(q)}/N_Atoms_UCell = 27.82 %

=> Normalized GII(c)= SQRT{ SUM {|BVS-abs(q)|^2*mult} /N_Atoms_UCell}= 73.31 /100

Subroutine Calc_BVS (JRC-LLB, version: March-2005)