Supplementary Information

Solvent-Modulated Assembly of Peptide and Cerium Functionalized Gigantic $\{Mo_{120}Ce_6\}_2$ Dimers for High-Efficiency Photocatalytic Oxidation

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1. Materials

All chemicals were purchased commercially and used without further purification.

2. Instrumentation

Crystallography: Suitable single crystals were selected and mounted onto a rubber loop using Fomblin oil. Single crystal X-ray diffraction data of **1**-**2** were recorded on a Bruker/ARINAX MD2 diffractometer equipped with a MarCCD-300 detector at beam line station BL17B of Shanghai Synchrotron Radiation Facility (SSRF) at 150 K. The structures were solved by the direct methods and refined with OLEX 2-1.5[1]. All non-hydrogen atoms are anisotropic refined by the least square method, and the hydrogen atoms are determined by the ideal geometry by the theoretical hydrogenation method. CCDC-2330175 (**1**), CCDC-2330176 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Element Analyses: Element analyses C, N and H content were determined by VARIDEL III Elemental Analyzer.

Thermogravimetric Analysis (TGA): Thermogravimetric analysis was performed on a METTLER TOLEDO TG8000 Thermogravimetric Analyzer under nitrogen flow at a typical heating rate of 10 ℃·min^{-1}.

Powder X-ray Diffraction (PXRD): Powder XRD was recorded on a Haoyuan DX-2700B diffractometer equipped with monochromatized Cu-Kα (λ = 1.5418 Å) radiation in the range of $3° \leq 2\theta \leq 40º$, with a scanning rate of 0.02° s^{-1}.

Fourier-transform infrared (FT-IR) spectroscopy: The samples were prepared as a KBr pellet and the FT-IR spectrum was collected in transmission mode in the range of 600-4000 cm^{-1} using a NEXUS-670 spectrometer. Wavenumbers are given in cm^{-1}. Intensities are denoted as w = weak, m = medium, s = strong, vs = very strong, br = broad.

Solid-state UV-Vis absorption spectroscopy: All compounds were prepared into powders, which were tested in wavelength mode by integrating sphere attachment in UV3600 UV-Vis spectrometer.

GC-Mass spectra: GC-Mass analysis was carried out on Agilent 8860 GC system and 5977B GC/MSD system with EI mode.

Mott-Schottky: Mott-Schottky plot was conducted on an electrochemical workstation CHI 760D. Firstly, the lapping sample (5 mg) was dispersed in ethanol (1 mL), and Nafion (100 μL) was added to the sample for ultrasonic mixing. Appropriate suspension droplets were taken on the fluoride-tin oxide (FTO) glass plate (1 × 2 cm^2, 50 Ω/cm^2) as the working electrode, Pt wire as the counter electrode. Ag/AgCl was used as the reference electrode and 0.2 mol/L Na_2SO_4 solution was used as the electrolyte. Under a certain pressure range, frequencies of 1000, 1500 and 2000 Hz were selected for testing.

3. Synthesis

Synthesis of $Na_4H_6[Mo_{96}^{VI}Mo_{24}^{V}Ce_6^{III}O_{366}H_{12}(H_2O)_{74}(C_9H_{15}N_4O_3)(C_9H_{16}N_4O_3)]_2$·ca 476 H_2O (1)

L-carnosine (1.4 mg, 0.007 mmol), $CeCl_3·7H_2O$ (19 mg, 0.02 mmol) and an aqueous solution of 0.1 M $[N_2H_4]$·2HCl (0.1 mL) were added to a solution of $Na_2MoO_4·2H_2O$ (50 mg, 0.2 mmol) in water (4 mL) under stirred. The mixture was then acidified with 6 M $HClO_4$ (0.15 mL) to pH ~1.7. After that, the mixture was transferred to a 10 mL vial with a metallic lid with a rubber septum, which was then heated at 80°C in an oven for four days. The deep-blue rhombic crystal crystals were collected by filtration, washed with ice-cold H_2O, and dried under inert atmosphere (yield 15 % based on Mo). Elemental analysis (ICP) % calcd (found): H 2.77 (2.73), N 0.05 (0.04), C 0.09 (0.09), Na 0.02 (0.04), Mo 47.28 (47.46), Ce 3.45 (3.39). IR (KBr pellet, 4000-400 cm^{-1}):3252(br), 1721(w), 1608(m), 1410(w), 1258(w), 967(m), 858(m), 810(m), 620(m), 521(m).

Synthesis of $(C_9H_{16}N_4O_3)_2H_8[Mo_{96}^{VI}Mo_{24}^{V}Ce_6^{III}O_{366}H_{12}(H_2O)_{75}(CH_3OH)]_2$·ca 338 H_2O (2)

L-carnosine (1.0 mg, 0.005 mmol), $CeCl_3·7H_2O$ (19 mg, 0.02 mmol) and an aqueous solution of 0.1 M $[N_2H_4]·2HCl$ (0.1 mL) were added to a solution of $Na_2MoO_4·2H_2O$ (50 mg, 0.2 mmol) in water (2 mL) and methanol (2 mL) under stirred. The mixture was then acidified with 1 M $HClO_4$ (0.15 mL) to pH ~1.1. After that, the mixture was transferred to a 10 mL vial with a metallic lid with a rubber septum, which was then heated at 80°C in an oven for 1 week. Then, at room temperature, the vial stood for 24 hours. The deep-blue diamond-shaped flake crystals were collected by filtration, washed with ice-cold H_2O, and dried under inert atmosphere (yield 7 % based on Mo). Elemental analysis (ICP) % calcd (found): H 2.31 (2.30), N 0.02 (0.03), C 0.05 (0.05), Na 0.00 (0.01), Mo 50.31 (49.98), Ce 3.67 (3.62). IR (KBr pellet, 4000-400 cm^{-1}):3260(br), 1723(w), 1608(m), 1436(w), 1243(w), 1187(w), 995(m), 738(w),649(m), 543(s).

4. Crystallographic data and crystal structures of 1-2.

Table S1 Crystallographic Details for **1-2.**

Compound	**1**	**2**
Empirical formula	$C_{36}H_{1136}Ce_{12}Mo_{240}N_{16}Na_4O_{1266}$	$C_{20}H_{1340}Ce_{12}Mo_{240}N_8O_{1374}$
Formula weight	46855.66	48098.71
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a /Å	26.945(17) Å	30.69(9) Å
b /Å	28.15(2) Å	31.23(10) Å
c /Å	45.76(4) Å	33.38(8) Å
α/°	96.39(4)°	70.03(8)°.
β/°	96.72(3)°	88.40(5)°
γ/°	117.654(19)°	70.33(19)°
V /Å^3	29988(40) Å^3	28172(147) Å^3
Z	1	1
ρ calc /g·cm^{-3}	2.568 Mg/m^3	2.824 Mg/m^3
μ(MoKα) /mm^{-1}	2.642 mm^{-1}	2.822 mm^{-1}
F(000)	21932	22804
2θ range /°	0.806 to 24.037°	0.686 to 24.171°
Index ranges	-31<=h<=31, -33<=k<=33, -53<=l<=54	-36<=h<=36, -36<=k<=36, -39<=l<=39
Reflections collected	808739	770008
Data / restraints / parameters	100439 / 833 / 5539	94461 / 811 / 5442
R_1/wR_2 (I>2σ(I))[a]	R_1 = 0.1190, wR_2 = 0.2722	R_1 = 0.1502, wR_2 = 0.3968
R_1/wR_2 (all data)	R_1 = 0.1247, wR_2 = 0.2754	R_1 = 0.1605, wR_2 = 0.4046
GooF (all data)[b]	1.031	1.053
Data completeness	96.7 %	95.3 %

[a] $R_1 = \sum||Fo|-|Fc|\,|/\sum|Fo|$; $wR_2 = \{\sum w[(Fo)^2-(Fc)^2]^2/\sum w[(Fo)^2]^2\}^{1/2}$

[b] $GooF = \{\sum w[(Fo)^2-(Fc)^2]^2/(n-p)\}^{1/2}$

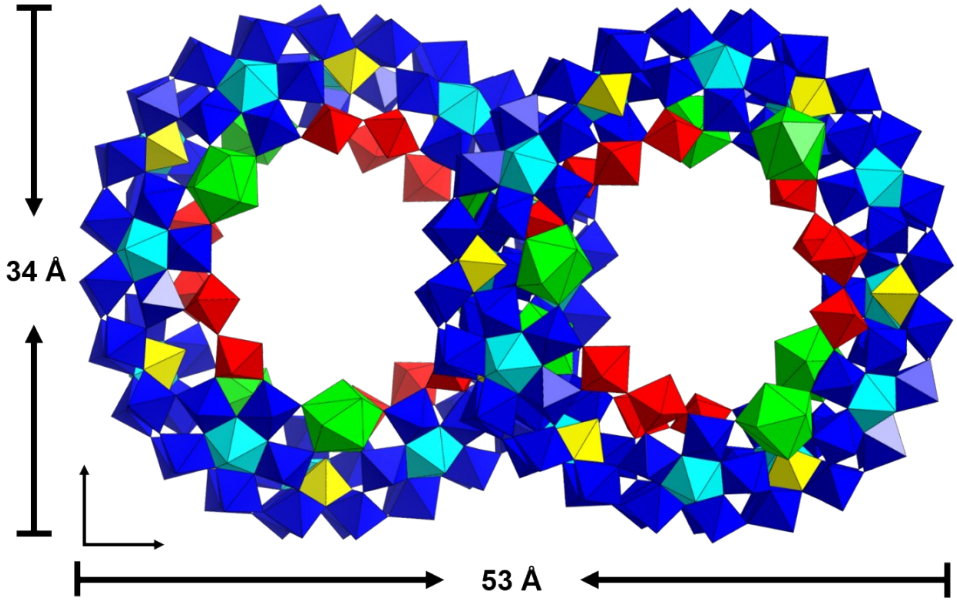


Fig.S1 The length and width dimensions of **1a**. The framework of **1a** is presented in polyhedron mode. Color scheme: {Mo_1}, yellow polyhedron; {Mo_2}, red polyhedron; {Mo_8}, blue polyhedron with central pentagonal unit in cyan polyhedron.

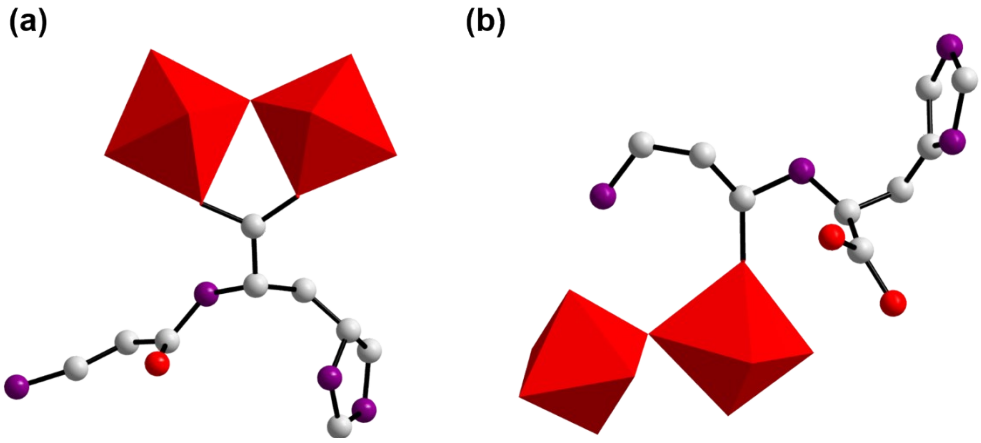


Fig.S2 View of the coordination modes of L-carnosine in **1a**. Color scheme: {Mo_2}, red polyhedron; red, O; gray, C; purple, N.

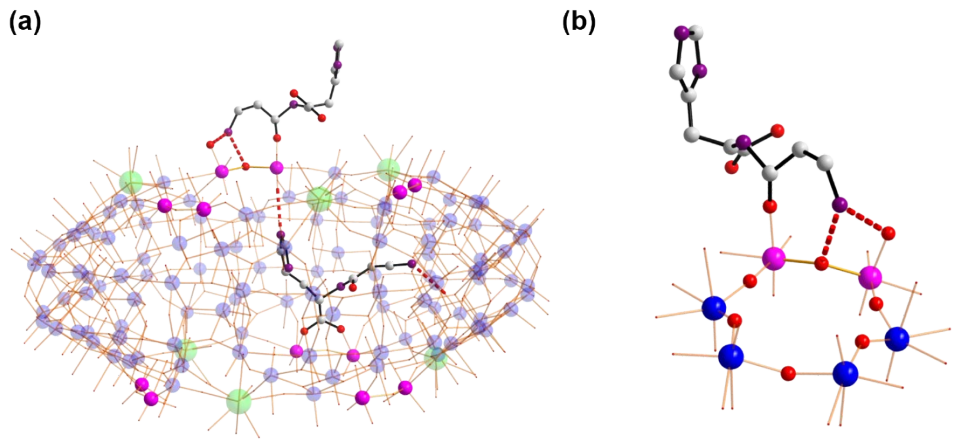


Fig.S3 (a) Ball-and-Stick representation of half **1a** with highlight of the two L-carnosine. (b) View of multiple hydrogen bonds formed by outer surface-attached L-carnosine with $\{Mo_6O_6\}$. Colour code: red, O; purple, N; grey, C; bule, Mo; green, Ce; pink, $\{Mo_2\}$ BB. Hydrogen bonds between L-carnosine and $\{Mo_6O_6\}$ are highlighted in red dash line.

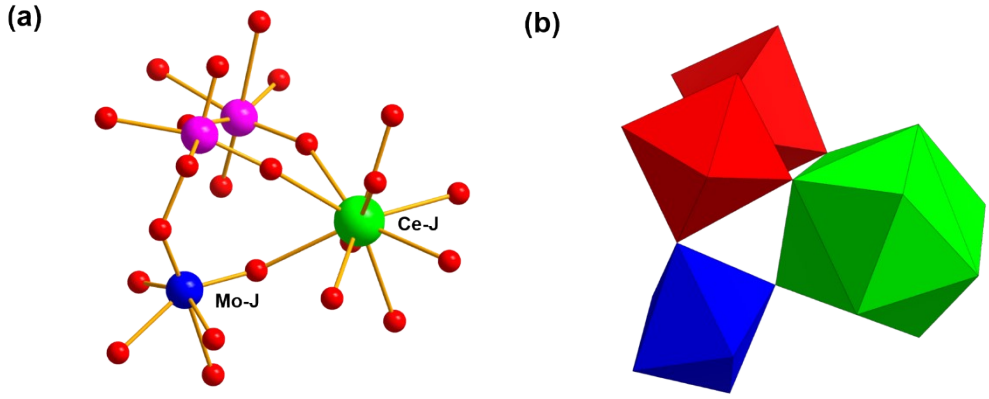


Fig.S4 (a) Ball-and-Stick and (b) polyhedron representation of local diagram of **2a** junction. Colour code is the same as Fig. S1 and Fig S3.

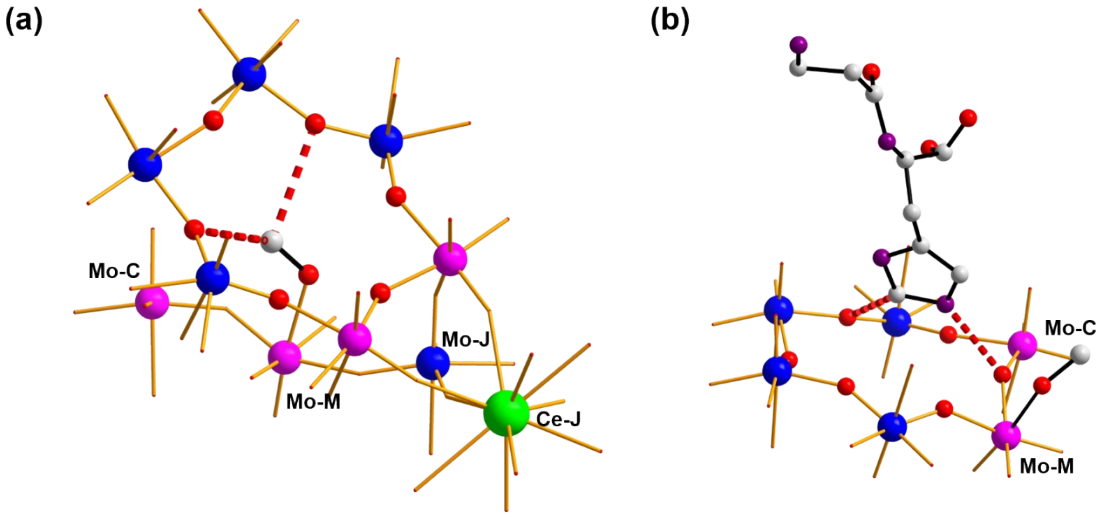


Fig.S5 View of hydrogen bonds formed by methanol (a) and L-carnosine (b) with $\{Mo_6O_6\}$ in **2a**. Colour code is the same as Fig. S3. Hydrogen bonds are highlighted in red dash line.

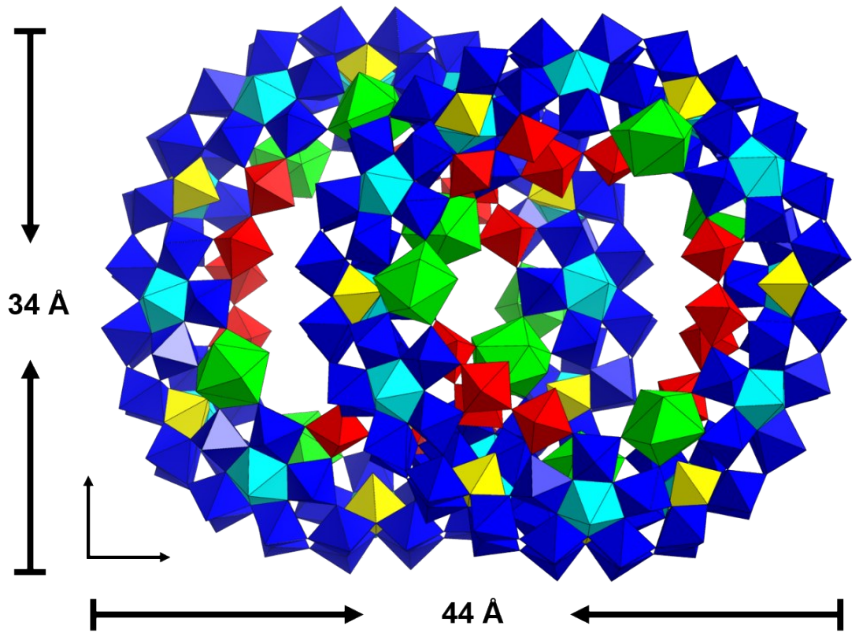


Fig. S6 The length and width dimensions of **2a**. The framework of **2a** is presented in polyhedron mode. Color scheme: {Mo_1}, yellow polyhedron; {Mo_2}, red polyhedron; {Mo_8}, blue polyhedron with central pentagonal unit in cyan polyhedron.

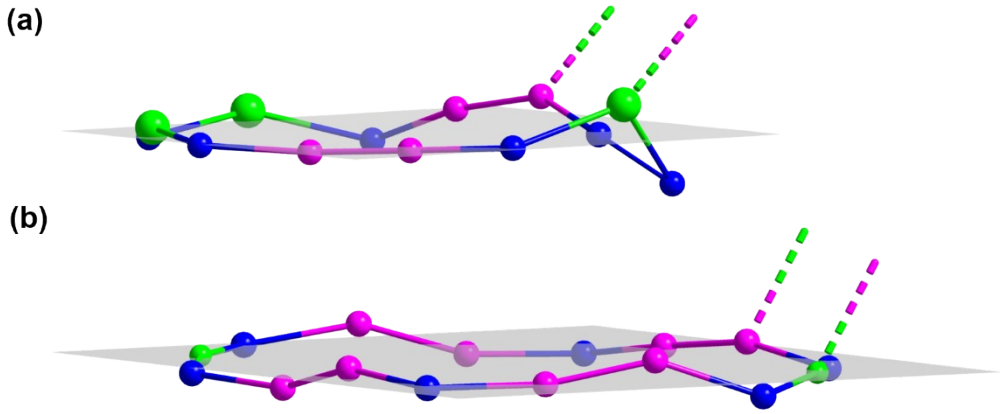


Fig. S7 Simplified contact rims of {$(Mo_{100}Ce_6)_2$} (a) and {$(Mo_{124}Eu_4)_2$} (b). Colour code: red, O; grey, C; pink, Mo_2; green, Ce; dash line, connection bond.

5. Structural analysis of 1-2.

Although the wheel-type molybdenum blue architectures are very complex, the general approach to the structural analysis and formula determination is well documented. The structural analysis requires the following lines of evidence / information to allow the assignment of formula and the structural details coupled with Single-crystal X-ray diffraction.

(i) Redox titration to help determine the number of reduced Mo^{V} centres (UV-vis-NIR) spectroscopy also can help corroborate this data via the analysis of the extinction coefficient for the IVCT associated with the reduced Mo^{V} centres.

(ii) Bond valence sum analysis to confirm the terminal oxo positions, reduced Mo^{V} centres and the positions of the hydroxide ligands.

(iii) Elemental analysis of sodium, molybdenum, cerium and C, H, N analysis.

(iv) TGA to estimate the number of ligand and solvent water molecules.

Therefore, the analysis below both presents this data and demonstrates how the structural assignment is consistent with this data.

Redox titrations

Because of the rather poor solubility of compounds **1**-**2**, it is impossible to perform redox tritration to determine the reduced eletrons on them.

Bond valence sum (BVS) analysis

Bond valence calculations were performed for each bond using the bond distance (R) measured and empirical parameters R_0 and B: bond valence = EXP((R_0-R)/B). BVS for each metal centre was then summed from all bond valences of the bonds listed. The parameters R_0 and B were taken from Gagne & Hawthorne. Mo(6+) and Mo(5+) centres were calculated separately using corresponding parameters listed below.

Parameter list:

Bond	R_0	B
Mo(6+)-O	1.903	0.349
Mo(5+)-O	1.888	0.314

Table S2. Average Bond valence sum values for the Mo centres which span the incomplete $\{Mo_5O_6\}$-type double cubanes and the μ_3-O atoms of the $\{(\mu_3\text{-}O)_2O_2\}$-type compartments in **1** and **2**.

Compounds	BVS(Mo)	BVS(μ_3-O)
1	**5.56**	**1.29**
2	**5.57**	**1.23**

Table S3. BVS values for Mo atoms in compound **1**.

Atom	BVS value	Atom	BVS value	Atom	BVS value	Atom	BVS value
M1	**6.10**	M2	**5.96**	M3	**6.11**	M4	**6.10**
M5	**5.89**	M6	**6.23**	M7	**6.26**	M8	**5.41**
M9	**5.51**	M10	**5.98**	M11	**5.79**	M12	**5.88**
M13	**6.12**	M14	**6.18**	M15	**5.59**	M16	**5.76**
M17	**6.11**	M18	**6.23**	M19	**5.93**	M20	**6.13**
M21	**6.19**	Mo1	**6.11**	Mo2	**6.02**	Mo3	**5.75**
Mo4	**5.42**	Mo5	**6.07**	Mo6	**6.01**	Mo7	**6.03**
Mo8	**5.57**	Mo9	**5.71**	Mo10	**5.81**	Mo11	**5.98**
Mo12	**6.14**	Mo13	**5.48**	Mo14	**5.59**	Mo15	**5.67**
Mo16	**5.51**	Mo17	**5.65**	Mo18	**5.92**	Mo19	**5.93**
Mo20	**5.46**	Mo21	**5.90**	Mo22	**5.71**	Mo23	**6.29**
Mo24	**5.66**	Mo25	**5.45**	Mo26	**5.80**	Mo27	**6.34**
Mo28	**5.51**	Mo29	**6.26**	Mo30	**5.62**	Mo31	**6.16**
Mo32	**5.51**	Mo33	**5.72**	Mo34	**5.72**	Mo35	**6.22**
Mo36	**5.65**	Mo37	**6.20**	Mo38	**5.67**	Mo39	**5.84**
Mo40	**5.44**	Mo41	**6.05**	Mo42	**5.48**	Mo43	**5.43**
Mo44	**5.38**	Mo45	**5.52**	Mo46	**5.49**	Mo47	**5.46**
Mo48	**6.29**	Mo49	**6.16**	Mo50	**5.50**	Mo51	**5.62**
Mo52	**5.39**	Mo53	**5.71**	Mo54	**5.79**	Mo55	**5.91**
Mo56	**5.19**	Mo57	**5.52**	Mo58	**5.92**	Mo59	**6.29**
Mo60	**6.19**	Mo61	**5.43**	Mo62	**6.17**	Mo63	**5.76**
Mo64	**6.16**	Mo65	**5.80**	Mo66	**5.65**	Mo67	**5.94**
Mo68	**5.66**	Mo69	**6.17**	Mo70	**5.26**	Mo71	**6.00**
Mo72	**5.51**	Mo73	**5.82**	Mo74	**5.82**	Mo75	**5.64**
Mo76	**5.13**	Mo77	**6.10**	Mo78	**6.13**	Mo79	**5.68**
Mo80	**5.55**	Mo81	**5.54**	Mo82	**5.49**	Mo83	**5.34**
Mo84	**5.56**	Mo85	**5.79**	Mo86	**5.90**	Mo87	**5.60**
Mo88	**6.07**	Mo89	**6.15**	Mo90	**5.47**	Mo91	**5.36**
Mo92	**5.47**	Mo93	**6.28**	Mo94	**6.19**	Mo95	**6.20**

Mo96	**6.21**	Mo97	**5.49**	Mo98	**5.36**	Mo99	**5.90**

Table S4. BVS values for O atoms in compound **1**.

Atom	**BVS value**	**Atom**	**BVS value**	**Atom**	**BVS value**	**Atom**	**BVS value**
O1	**2.01**	O2	**1.95**	O3	**0.13**	O4	**1.90**
O5	**2.05**	O6	**2.02**	O7	**0.11**	O8	**1.76**
O9	**1.86**	O10	**2.25**	O11	**0.25**	O12	**2.02**
O13	**1.88**	O14	**2.00**	O15	**1.95**	O16	**0.40**
O17	**1.60**	O18	**1.91**	O19	**2.11**	O20	**1.86**
O21	**2.13**	O22	**1.82**	O23	**1.94**	O24	**2.18**
O25	**1.89**	O26	**1.90**	O27	**2.06**	O28	**2.13**
O29	**0.11**	O30	**1.95**	O31	**1.94**	O32	**1.92**
O33	**1.98**	O34	**1.87**	O35	**1.93**	O36	**1.78**
O37	**2.12**	O38	**1.90**	O39	**1.84**	O40	**2.01**
O41	**2.00**	O42	**2.07**	O43	**0.19**	O44	**0.28**
O45	**1.87**	O46	**1.97**	O47	**1.91**	O48	**0.29**
O49	**2.13**	O50	**1.86**	O51	**2.04**	O52	**1.75**
O53	**2.15**	O54	**2.08**	O55	**1.17**	O56	**1.98**
O57	**0.10**	O58	**1.61**	O59	**1.31**	O60	**2.01**
O61	**2.02**	O62	**2.02**	O63	**1.57**	O64	**2.24**
O65	**1.80**	O66	**2.07**	O67	**2.12**	O68	**2.00**
O69	**1.97**	O70	**0.29**	O71	**2.13**	O72	**1.38**
O73	**1.96**	O74	**2.11**	O75	**2.09**	O76	**1.39**
O77	**2.10**	O78	**2.10**	O79	**2.17**	O80	**1.90**
O81	**1.83**	O82	**0.29**	O83	**2.09**	O84	**2.06**
O85	**2.09**	O86	**1.99**	O87	**2.21**	O88	**2.10**
O89	**1.32**	O90	**2.06**	O91	**1.79**	O92	**1.06**
O93	**2.19**	O94	**2.17**	O95	**2.03**	O96	**2.07**
O97	**2.01**	O98	**0.53**	O99	**0.30**	O100	**1.72**
O101	**2.05**	O102	**1.82**	O103	**1.99**	O104	**1.95**
O105	**1.96**	O106	**0.38**	O107	**0.38**	O108	**1.89**
O109	**1.87**	O110	**1.90**	O111	**1.85**	O112	**2.01**
O113	**0.12**	O114	**2.09**	O115	**0.11**	O116	**0.21**
O117	**0.13**	O118	**1.25**	O119	**2.00**	O120	**1.90**
O121	**2.14**	O122	**2.11**	O123	**0.78**	O124	**2.14**
O125	**1.92**	O126	**1.91**	O127	**1.92**	O128	**1.51**
O129	**2.01**	O130	**1.98**	O131	**1.92**	O132	**2.16**
O133	**1.93**	O134	**1.37**	O135	**2.02**	O136	**2.19**
O137	**2.11**	O138	**1.28**	O139	**1.84**	O140	**2.13**
O141	**2.13**	O142	**1.96**	O143	**1.79**	O144	**2.11**
O145	**2.10**	O146	**2.16**	O147	**1.93**	O148	**1.76**
O149	**1.93**	O150	**2.11**	O151	**1.88**	O152	**1.93**

O153	**2.02**	O154	**2.13**	O155	**2.09**	O156	**2.01**
O157	**2.05**	O158	**1.97**	O159	**1.93**	O160	**1.78**
O161	**1.88**	O162	**2.02**	O163	**1.83**	O164	**2.28**
O165	**2.08**	O166	**2.03**	O167	**2.19**	O168	**0.24**
O169	**2.06**	O170	**1.80**	O171	**2.26**	O172	**0.42**
O173	**2.06**	O174	**1.37**	O175	**2.00**	O176	**0.31**
O177	**2.00**	O178	**2.16**	O179	**1.97**	O180	**0.31**
O181	**1.99**	O182	**2.10**	O183	**2.31**	O184	**2.13**
O185	**0.36**	O186	**1.26**	O187	**2.16**	O188	**0.41**
O189	**0.25**	O190	**1.91**	O191	**2.36**	O192	**0.27**
O193	**1.73**	O194	**1.99**	O195	**1.82**	O196	**0.36**
O197	**0.32**	O198	**1.90**	O199	**0.39**	O200	**1.74**
O201	**2.18**	O202	**2.13**	O203	**2.00**	O204	**0.37**
O205	**1.59**	O206	**2.03**	O207	**2.15**	O208	**1.64**
O209	**1.72**	O210	**1.99**	O211	**2.11**	O212	**0.38**
O213	**1.96**	O214	**2.06**	O215	**1.77**	O216	**2.17**
O217	**2.04**	O218	**0.41**	O219	**2.18**	O220	**1.89**
O221	**2.17**	O222	**1.99**	O223	**0.12**	O224	**2.03**
O225	**0.14**	O226	**0.34**	O227	**0.21**	O228	**2.16**
O229	**0.16**	O230	**2.04**	O231	**0.15**	O232	**1.99**
O233	**0.17**	O234	**1.52**	O235	**1.96**	O236	**2.14**
O237	**1.92**	O238	**2.02**	O239	**0.33**	O240	**2.13**
O241	**1.85**	O242	**1.96**	O243	**2.25**	O244	**1.23**
O245	**1.47**	O246	**1.88**	O247	**0.23**	O248	**2.11**
O249	**1.97**	O250	**2.16**	O251	**1.87**	O252	**2.12**
O253	**0.32**	O254	**2.12**	O255	**2.19**	O256	**2.12**
O257	**1.71**	O258	**2.16**	O259	**0.38**	O260	**2.15**
O261	**2.09**	O262	**2.15**	O263	**0.12**	O264	**2.07**
O265	**2.06**	O266	**1.91**	O267	**1.94**	O268	**2.00**
O269	**2.07**	O270	**2.05**	O271	**2.09**	O272	**1.96**
O273	**2.02**	O274	**1.94**	O275	**2.01**	O276	**1.28**
O277	**1.96**	O278	**2.09**	O279	**1.91**	O280	**2.06**
O281	**2.06**	O282	**2.06**	O283	**1.95**	O284	**2.03**
O285	**2.27**	O286	**2.24**	O287	**1.92**	O288	**2.08**
O289	**2.14**	O290	**2.26**	O291	**1.21**	O292	**1.86**
O293	**2.01**	O294	**2.09**	O295	**2.05**	O296	**1.06**
O297	**0.19**	O298	**2.00**	O299	**2.05**	O300	**2.01**
O301	**1.52**	O302	**1.72**	O303	**0.48**	O304	**1.25**
O305	**2.27**	O306	**1.74**	O307	**2.15**	O308	**2.00**
O309	**0.34**	O310	**1.555**	O311	**2.19**	O312	**0.29**
O313	**0.32**	O314	**2.19**	O315	**1.75**	O316	**1.83**
O317	**2.11**	O318	**1.87**	O319	**2.05**	O320	**2.19**
O321	**2.06**	O322	**2.07**	O323	**2.02**	O324	**2.10**
O325	**2.02**	O326	**2.21**	O327	**1.81**	O328	**2.12**

O329	**1.31**	O330	**0.33**	O331	**1.96**	O332	**2.07**
O333	**1.95**	O334	**0.23**	O335	**0.15**	O336	**1.84**
O337	**0.34**	O338	**2.23**	O339	**1.39**	O340	**2.17**
O341	**2.07**	O342	**2.09**	O343	**0.44**	O344	**1.95**
O345	**0.29**	O346	**1.64**	O347	**0.62**	O348	**2.09**
O349	**0.36**	O350	**0.44**	O351	**0.31**	O352	**2.05**
O353	**1.59**	O354	**0.36**	O355	**2.18**	O356	**1.75**
O357	**0.28**	O358	**2.27**	O359	**0.93**	O360	**0.34**
O361	**0.33**	O362	**0.34**	O363	**0.37**	O364	**1.49**
O365	**2.00**	O366	**0.52**	O367	**0.25**	O368	**2.25**
O369	**0.30**	O370	**1.89**	O371	**2.21**	O372	**1.80**
O373	**1.91**	O374	**0.33**	O375	**0.37**	O376	**1.06**
O377	**1.06**	O378	**0.30**	O379	**2.08**	O380	**2.05**
O381	**0.32**	O382	**1.34**	O383	**2.21**	O384	**1.86**
O385	**0.60**	O386	**2.03**	O387	**2.22**	O388	**1.87**
O389	**0.32**	O390	**0.47**	O391	**2.28**	O392	**0.35**
O393	**2.16**	O394	**0.36**	O395	**0.34**	O396	**1.86**
O397	**2.06**	O398	**0.69**	O399	**0.92**	O400	**2.09**
O401	**0.71**	O402	**2.24**	O403	**0.46**	O404	**1.70**
O405	**2.06**	O406	**0.45**	O407	**0.29**	O408	**1.99**
O409	**2.11**	O410	**0.48**	O411	**2.19**	O412	**2.05**
O413	**0.27**	O414	**0.38**	O415	**0.41**	O416	**2.10**
O417	**0.45**	O418	**1.06**	O419	**2.29**	O420	**1.79**
O421	**0.30**	O422	**0.37**	O423	**1.22**	O424	**1.99**
O425	**1.02**	O426	**1.33**	O427	**2.13**	O428	**1.18**
O429	**2.21**	O430	**2.16**	O431	**1.28**	O432	**1.86**
O433	**2.08**	O434	**1.15**	O435	**0.12**	O436	**1.97**
O437	**0.14**	O438	**0.16**	O439	**2.18**	O440	**1.99**
O441	**2.13**	O442	**2.02**	O443	**1.95**	O444	**1.93**
O445	**1.28**	O446	**2.20**	O447	**0.13**	O448	**2.23**
O449	**0.12**	O450	**2.11**	O451	**0.13**	O452	**1.61**
O453	**0.15**	O454	**2.03**	O455	**0.10**	O456	**2.11**
O457	**0.11**	O458	**2.13**	O459	**0.17**	O460	**2.15**
O461	**0.13**	O462	**1.93**	O463	**0.15**	O464	**1.53**
O465	**0.17**	O466	**2.15**	O467	**0.11**	O468	**1.99**
O469	**1.85**						

Table S5 BVS values for Mo atoms in compound **2**.

Atom	BVS value	Atom	BVS value	Atom	BVS value	Atom	BVS value
M1	**5.93**	M2	**6.18**	M3	**6.11**	M4	**6.08**
M5	**5.21**	M6	**5.00**	M7	**5.78**	M8	**5.88**
M9	**5.99**	M10	**6.06**	M11	**5.60**	M12	**5.89**
M13	**5.69**	M14	**5.98**	M15	**5.94**	M16	**5.61**

M17	**5.93**	M18	**5.71**	M19	**6.11**	M20	**5.95**
M21	**5.64**	Mo1	**6.17**	Mo2	**5.62**	Mo3	**5.98**
Mo4	**5.35**	Mo5	**5.53**	Mo6	**5.21**	Mo7	**5.58**
Mo8	**5.53**	Mo9	**6.29**	Mo10	**5.37**	Mo11	**5.64**
Mo12	**5.99**	Mo13	**5.72**	Mo14	**5.08**	Mo15	**5.79**
Mo16	**5.64**	Mo17	**5.66**	Mo18	**5.53**	Mo19	**5.50**
Mo20	**5.09**	Mo21	**5.77**	Mo22	**5.56**	Mo23	**5.61**
Mo24	**5.79**	Mo25	**5.80**	Mo26	**5.38**	Mo27	**5.39**
Mo28	**5.82**	Mo29	**5.62**	Mo30	**5.86**	Mo31	**5.61**
Mo32	**5.49**	Mo33	**5.45**	Mo34	**5.80**	Mo35	**5.58**
Mo36	**5.49**	Mo37	**5.62**	Mo38	**5.62**	Mo39	**5.84**
Mo40	**6.13**	Mo41	**5.75**	Mo42	**6.13**	Mo43	**5.87**
Mo44	**5.87**	Mo45	**5.77**	Mo46	**6.04**	Mo47	**5.77**
Mo48	**5.73**	Mo49	**5.83**	Mo50	**5.73**	Mo51	**6.21**
Mo52	**5.21**	Mo53	**5.81**	Mo54	**6.09**	Mo55	**5.98**
Mo56	**5.50**	Mo57	**5.76**	Mo58	**5.55**	Mo59	**5.75**
Mo60	**5.62**	Mo61	**5.24**	Mo62	**5.45**	Mo63	**5.98**
Mo64	**6.26**	Mo65	**6.04**	Mo66	**5.62**	Mo67	**6.03**
Mo68	**5.99**	Mo69	**6.29**	Mo70	**5.75**	Mo71	**6.00**
Mo72	**5.56**	Mo73	**5.86**	Mo74	**5.86**	Mo75	**5.86**
Mo76	**5.05**	Mo77	**6.03**	Mo78	**5.40**	Mo79	**5.76**
Mo80	**5.24**	Mo81	**5.60**	Mo82	**6.18**	Mo83	**5.67**
Mo84	**6.23**	Mo85	**5.85**	Mo86	**5.83**	Mo87	**5.43**
Mo88	**6.22**	Mo89	**5.56**	Mo90	**5,75**	Mo91	**6.04**
Mo92	**5.44**	Mo93	**6.17**	Mo94	**5.90**	Mo95	**6.16**
Mo96	**6.28**	Mo97	**6.24**	Mo98	**6.25**	Mo99	**5.90**

Table S6 BVS values for O atoms in compound **2**.

Atom	**BVS value**	**Atom**	**BVS value**	**Atom**	**BVS value**	**Atom**	**BVS value**
O1	**1.90**	O2	**2.07**	O3	**1.07**	O4	**1.88**
O5	**2.39**	O6	**1.95**	O7	**0.11**	O8	**1.23**
O9	**0.26**	O10	**1.15**	O11	**2.01**	O12	**1.92**
O13	**0.36**	O14	**1.71**	O15	**1.91**	O16	**1.27**
O17	**1.45**	O18	**1.92**	O19	**1.77**	O20	**1.29**
O21	**1.90**	O22	**2.00**	O23	**1.71**	O24	**1.97**
O25	**2.13**	O26	**2.01**	O27	**0.44**	O28	**1.30**
O29	**0.10**	O30	**1.97**	O31	**1.82**	O32	**0.22**
O33	**2.12**	O34	**2.21**	O35	**2.20**	O36	**1.21**
O37	**2.31**	O38	**1.29**	O39	**1.98**	O40	**1.87**
O41	**2.18**	O42	**2.07**	O43	**2.03**	O44	**1.81**
O45	**0.39**	O46	**1.80**	O47	**2.11**	O48	**1.85**
O49	**0.97**	O50	**2.01**	O51	**0.31**	O52	**1.84**
O53	**0.30**	O54	**1.97**	O55	**0.24**	O56	**1.91**

O57	**0.10**	O58	**2.15**	O59	**2.00**	O60	**1.83**
O61	**2.22**	O62	**2.05**	O63	**2.04**	O64	**2.17**
O65	**2.01**	O66	**1.87**	O67	**2.05**	O68	**2.09**
O69	**2.04**	O70	**1.22**	O71	**2.08**	O72	**1.82**
O73	**1.64**	O74	**1.99**	O75	**0.18**	O76	**1.87**
O77	**2.02**	O78	**1.26**	O79	**2.01**	O80	**2.07**
O81	**0.29**	O82	**1.98**	O83	**1.47**	O84	**1.67**
O85	**0.28**	O86	**1.16**	O87	**1.36**	O88	**1.95**
O89	**2.32**	O90	**1.44**	O91	**1.87**	O92	**2.18**
O93	**0.30**	O94	**1.82**	O95	**1.30**	O96	**1.73**
O97	**0.29**	O98	**2.15**	O99	**1.15**	O100	**1.99**
O101	**0.94**	O102	**1.92**	O103	**0.28**	O104	**1.97**
O105	**1.25**	O106	**2.14**	O107	**0.93**	O108	**1.79**
O109	**1.86**	O110	**1.75**	O111	**0.10**	O112	**1.58**
O113	**0.10**	O114	**0.32**	O115	**0.10**	O116	**1.48**
O117	**0.10**	O118	**1.29**	O119	**2.13**	O120	**1.89**
O121	**2.04**	O122	**1.96**	O123	**1.71**	O124	**1.98**
O125	**1.93**	O126	**1.75**	O127	**1.95**	O128	**2.00**
O129	**2.11**	O130	**2.15**	O131	**2.02**	O132	**1.98**
O133	**0.20**	O134	**2.06**	O135	**2.29**	O136	**1.92**
O137	**1.88**	O138	**1.89**	O139	**2.10**	O140	**2.33**
O141	**1.36**	O142	**1.70**	O143	**1.72**	O144	**1.81**
O145	**2.10**	O146	**1.91**	O147	**0.27**	O148	**1.94**
O149	**2.00**	O150	**1.98**	O151	**2.13**	O152	**2.15**
O153	**0.34**	O154	**1.97**	O155	**0.44**	O156	**1.95**
O157	**1.87**	O158	**1.83**	O159	**2.28**	O160	**1.63**
O161	**1.78**	O162	**1.77**	O163	**2.32**	O164	**1.93**
O165	**1.98**	O166	**1.88**	O167	**1.89**	O168	**1.87**
O169	**1.95**	O170	**1.23**	O171	**0.22**	O172	**1.84**
O173	**1.80**	O174	**2.04**	O175	**1.95**	O176	**0.27**
O177	**2.18**	O178	**1.95**	O179	**2.16**	O180	**2.14**
O181	**2.01**	O182	**1.71**	O183	**2.17**	O184	**2.05**
O185	**1.86**	O186	**0.24**	O187	**1.94**	O188	**1.86**
O189	**1.49**	O190	**0.27**	O191	**1.97**	O192	**1.86**
O193	**2.04**	O194	**1.84**	O195	**1.89**	O196	**2.00**
O197	**0.75**	O198	**1.99**	O199	**1.91**	O200	**1.89**
O201	**0.35**	O202	**1.90**	O203	**0.26**	O204	**1.97**
O205	**0.25**	O206	**2.24**	O207	**0.41**	O208	**1.85**
O209	**0.47**	O210	**1.75**	O211	**0.39**	O212	**1.98**
O213	**0.33**	O214	**2.01**	O215	**0.26**	O216	**0.67**
O217	**0.17**	O218	**2.10**	O219	**0.96**	O220	**0.98**
O221	**0.10**	O222	**1.90**	O223	**0.11**	O224	**2.12**
O225	**0.11**	O226	**2.09**	O227	**0.10**	O228	**1.90**
O229	**0.11**	O230	**1.54**	O231	**0.11**	O232	**1.84**

O233	**0.13**	O234	**2.09**	O235	**0.12**	O236	**1.94**
O237	**2.15**	O238	**1.95**	O239	**1.61**	O240	**1.93**
O241	**2.01**	O242	**2.11**	O243	**1.65**	O244	**1.87**
O245	**1.70**	O246	**1.82**	O247	**1.90**	O248	**1.89**
O249	**1.40**	O250	**1.97**	O251	**2.07**	O252	**2.02**
O253	**1.11**	O254	**2.09**	O255	**1.82**	O256	**2.02**
O257	**0.26**	O258	**2.19**	O259	**2.03**	O260	**1.70**
O261	**2.06**	O262	**1.90**	O263	**0.23**	O264	**2.19**
O265	**2.08**	O266	**1.98**	O267	**1.85**	O268	**1.84**
O269	**2.18**	O270	**1.94**	O271	**2.18**	O272	**1.69**
O273	**1.83**	O274	**1.54**	O275	**1.95**	O276	**1.75**
O277	**1.79**	O278	**1.94**	O279	**2.06**	O280	**1.94**
O281	**1.81**	O282	**1.91**	O283	**1.94**	O284	**2.07**
O285	**2.36**	O286	**1.90**	O287	**1.83**	O288	**2.17**
O289	**1.79**	O290	**1.39**	O291	**1.73**	O292	**1.98**
O293	**2.01**	O294	**1.91**	O295	**2.11**	O296	**2.09**
O297	**0.25**	O298	**1.95**	O299	**0.23**	O300	**1.93**
O301	**2.08**	O302	**1.75**	O303	**1.24**	O304	**1.85**
O305	**2.24**	O306	**2.17**	O307	**0.29**	O308	**1.87**
O309	**2.11**	O310	**1.81**	O311	**1.99**	O312	**1.92**
O313	**1.86**	O314	**1.99**	O315	**2.34**	O316	**2.16**
O317	**0.35**	O318	**1.94**	O319	**2.03**	O320	**1.84**
O321	**1.57**	O322	**0.77**	O323	**1.85**	O324	**1.98**
O325	**2.13**	O326	**1.91**	O327	**0.75**	O328	**2.12**
O329	**0.28**	O330	**2.10**	O331	**0.49**	O332	**1.77**
O333	**1.93**	O334	**1.94**	O335	**0.24**	O336	**1.75**
O337	**2.10**	O338	**1.89**	O339	**2.14**	O340	**1.99**
O341	**0.28**	O342	**1.98**	O343	**2.29**	O344	**1.77**
O345	**2.12**	O346	**2.02**	O347	**1.89**	O348	**2.25**
O349	**0.41**	O350	**2.02**	O351	**0.30**	O352	**1.87**
O353	**0.32**	O354	**1.35**	O355	**1.83**	O356	**1.21**
O357	**1.74**	O358	**1.94**	O359	**1.92**	O360	**0.19**
O361	**1.97**	O362	**2.11**	O363	**0.33**	O364	**1.93**
O365	**0.71**	O366	**2.01**	O367	**1.12**	O368	**2.08**
O369	**0.26**	O370	**1.99**	O371	**0.39**	O372	**1.97**
O373	**2.27**	O374	**2.04**	O375	**2.13**	O376	**0.29**
O377	**0.38**	O378	**1.86**	O379	**0.35**	O380	**2.07**
O381	**1.78**	O382	**1.97**	O383	**0.32**	O384	**2.07**
O385	**2.29**	O386	**2.01**	O387	**1.67**	O388	**2.05**
O389	**1.60**	O390	**2.00**	O391	**1.73**	O392	**1.73**
O393	**0.21**	O394	**1.97**	O395	**1.93**	O396	**1.05**
O397	**0.28**	O398	**2.24**	O399	**0.51**	O400	**2.07**
O401	**0.40**	O402	**2.08**	O403	**0.38**	O404	**2.09**
O405	**0.43**	O406	**1.80**	O407	**2.26**	O408	**0.29**

O409	**0.37**	O410	**2.11**	O411	**0.32**	O412	**1.80**
O413	**1.38**	O414	**1.74**	O415	**1.10**	O416	**2.23**
O417	**0.23**	O418	**1.84**	O419	**2.15**	O420	**2.06**
O421	**0.48**	O422	**2.09**	O423	**0.36**	O424	**1.86**
O425	**0.34**	O426	**1.75**	O427	**2.17**	O428	**1.87**
O429	**0.21**	O430	**0.27**	O431	**0.35**	O432	**2.01**
O433	**2.24**	O434	**1.80**	O435	**1.82**	O436	**1.32**
O437	**0.29**	O438	**1.93**	O439	**0.27**	O440	**1.64**
O441	**0.10**	O442	**2.04**	O443	**0.11**	O444	**2.04**
O445	**0.14**	O446	**1.92**	O447	**0.17**	O448	**1.89**
O449	**1.15**	O450	**2.13**	O451	**1.12**	O452	**2.11**
O453	**1.11**	O454	**2.36**	O455	**1.13**	O456	**1.87**
O457	**0.19**	O458	**2.11**	O459	**0.11**	O460	**2.20**
O461	**0.10**	O462	**1.32**	O463	**0.13**	O464	**2.09**
O465	**0.22**	O466	**0.23**	O467	**0.16**	O468	**2.00**
O469	**0.11**	O470	**1.31**	O471	**0.14**	O472	**1.71**

Elemental analysis and C, H, N analysis

See Section **3**. Synthetic procedure of **1-2.**

UV-vis-NIR spectra in water

Because of the rather poor solubility of compounds **1-2**, we could not prepare the related solution with accurate concentration. Therefore, the UV-vis spectra of **1-2** were recorded in saturated aqueous solution S9 and ε was not caculated. All the UV-vis spectra of **1-2** show the characteristic band of Mo Blue which is centered around 745 nm.

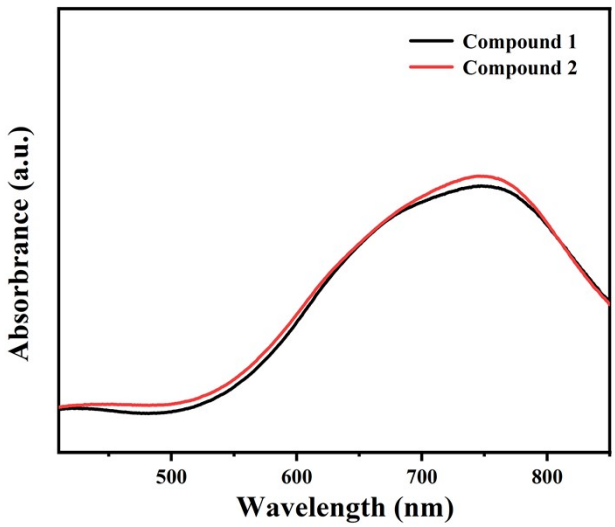


Fig. S8 Uv-vis spectra of Compound **1** and **2.**

TGA results of 1-2

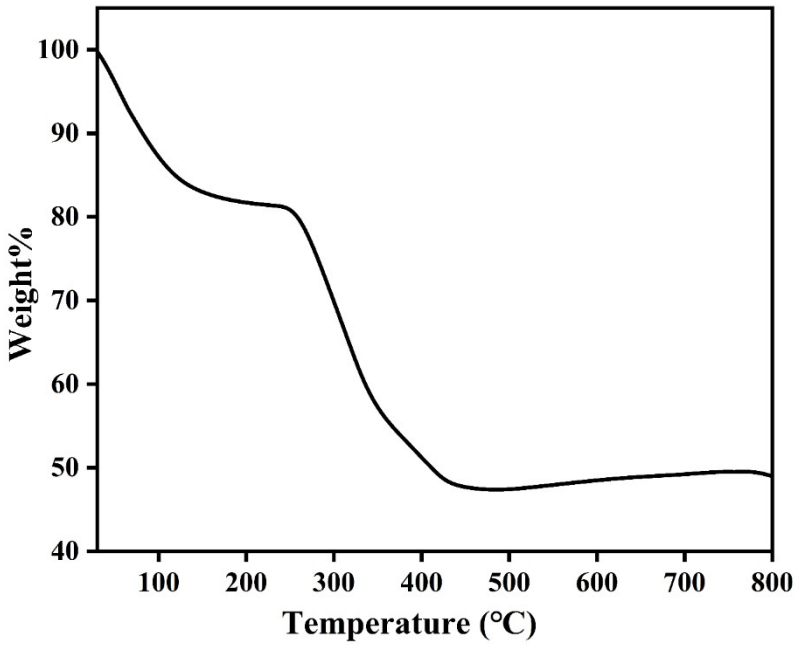


Fig. S9 TGA curve of Compound **1**. 19.1% weight loss between r.t. to 250 °C corresponds to ~476 guest H_2O and four L-carnosine ligands on the frame.

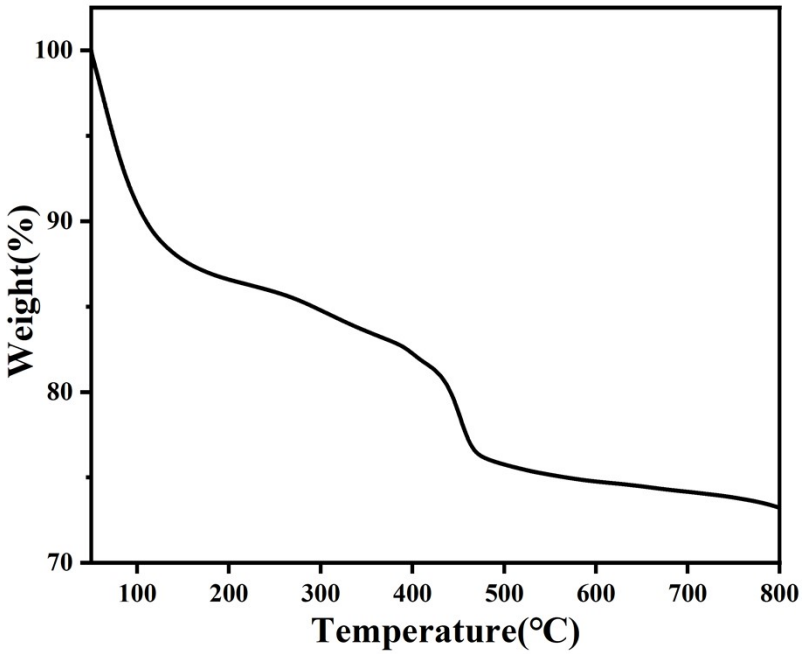


Fig S10 .TGA curve of Compound **2**. 14.3% weight loss between r.t. to 255 °C corresponds to ~338 guest H_2O and countercation L-carnosine ligands.

6. PXRD spectra of 1-2.

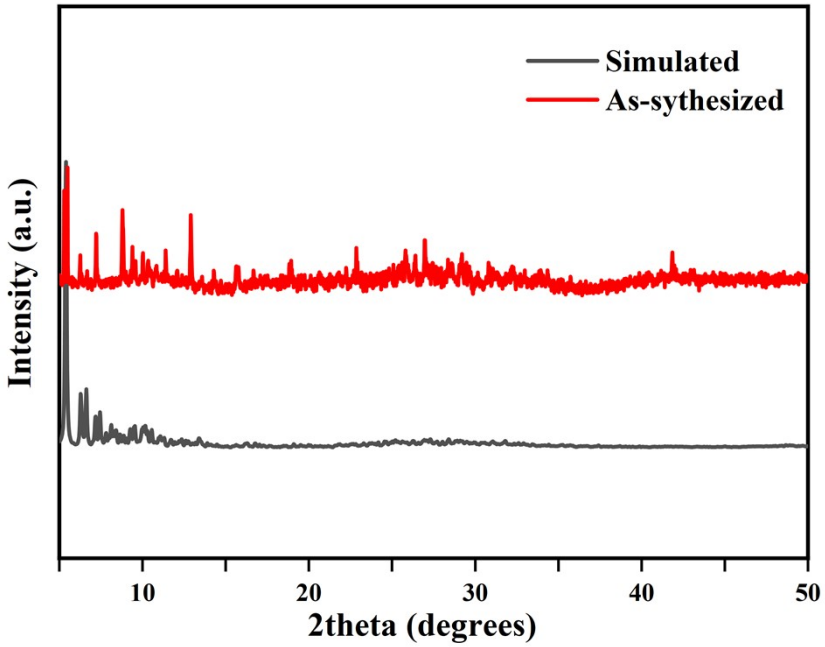


Fig. S11 Experimental and simulated PXRD patterns of **1**.

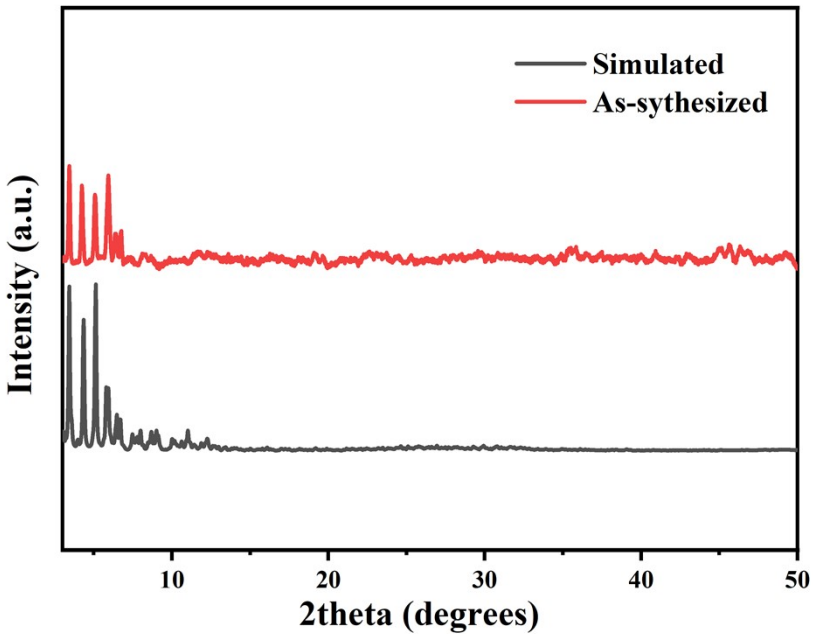


Fig. S12 Experimental and simulated PXRD patterns of **2.**

7. FT-IR spectra of 1-2.

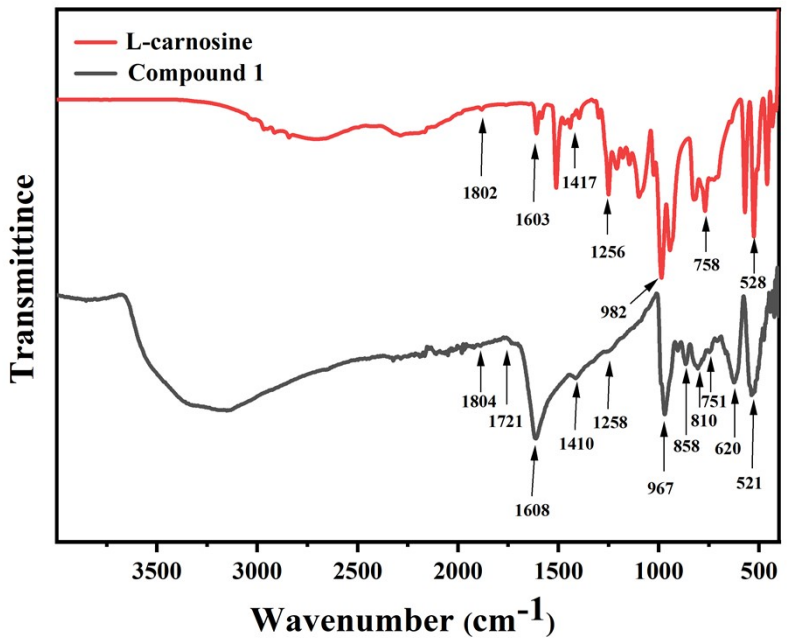


Fig. S13 FT-IR spectra of compound **1** (black line) and L-carnosine (red line).

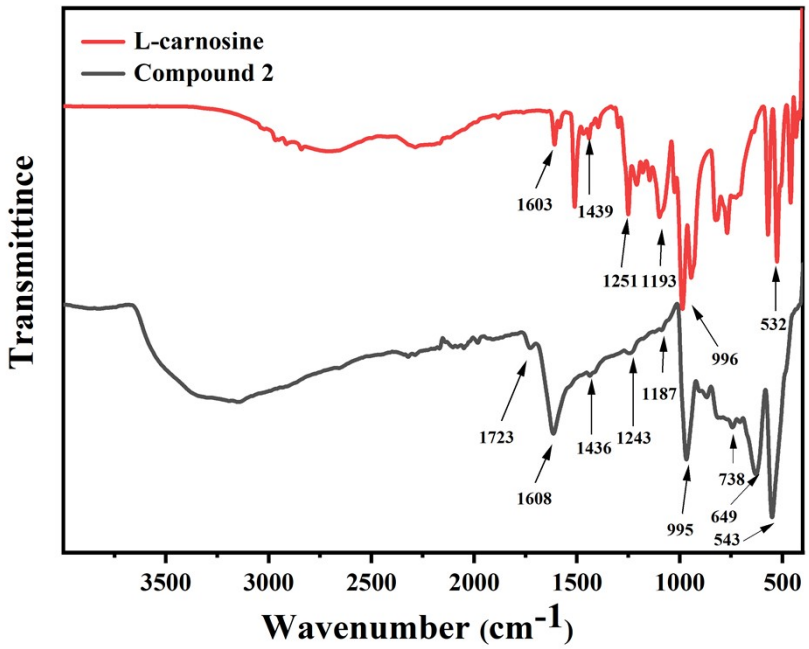


Fig.S14 FT-IR spectra of compound **2** (black line) and L-carnosine (red line).

8. Solid-state UV-Vis spectra and band gap results of 1 and 2.

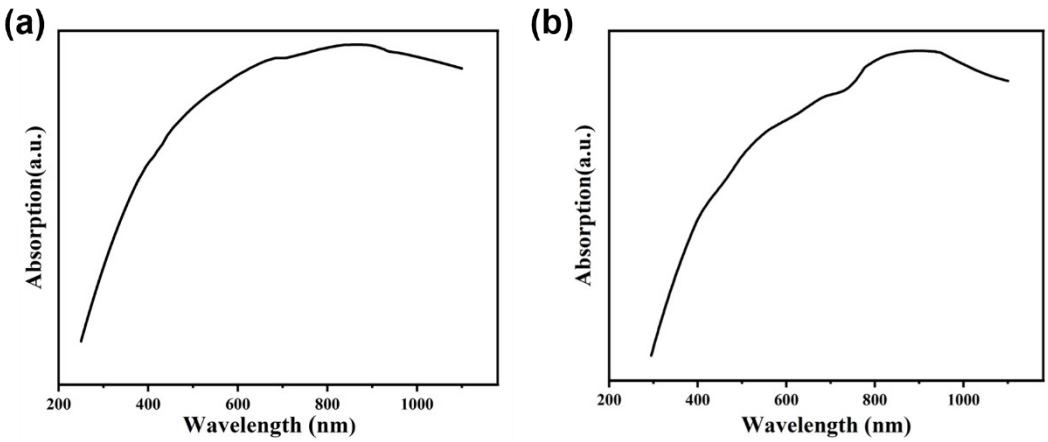


Fig. S15 The solid-state UV-Vis spectra of compound **1** and **2.**

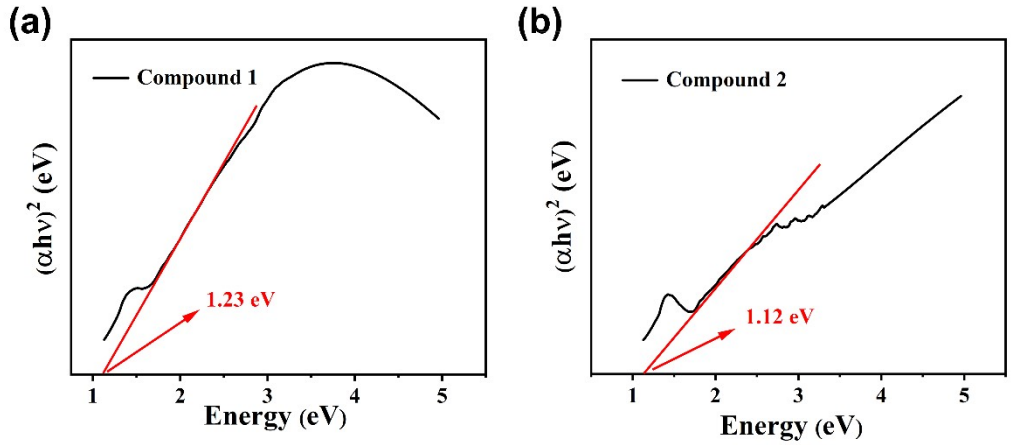


Fig. S16 The band gap results of compound **1** and **2**.

9. The band gap and the Mott-Schottky results of {Mo_{132}}, {Mo_{154}} and {Mo_{240}}.

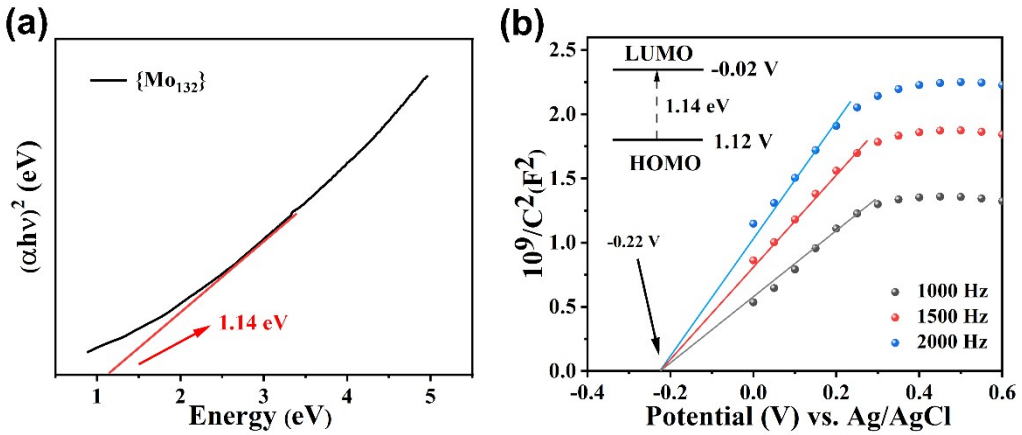


Fig. S17 (a) The band gap result of Mo_{132}; (b) the Mott-Schottky spots of Mo_{132} in 0.5 M Na_2SO_4 aqueous solution.

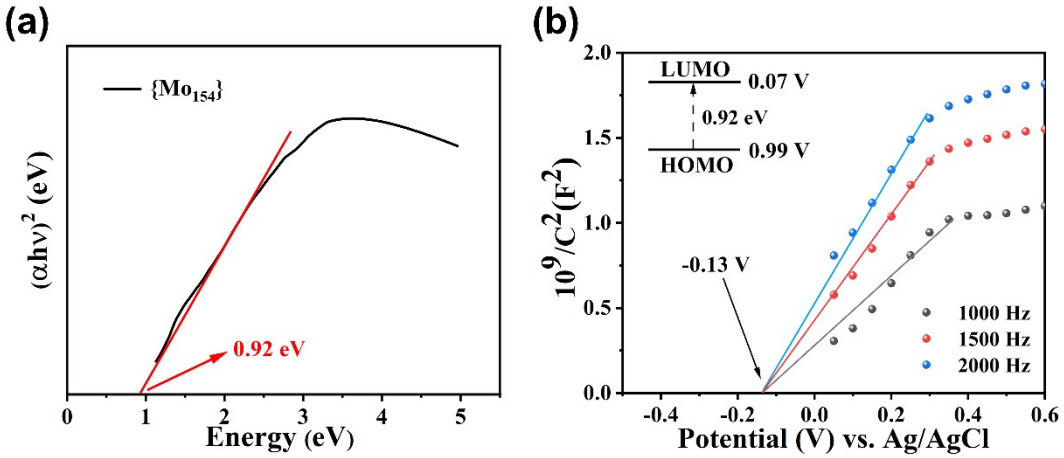


Fig. S18 (a) The band gap result of Mo_{154}; (b) the Mott-Schottky spots of Mo_{154} in 0.5 M Na_2SO_4 aqueous solution.

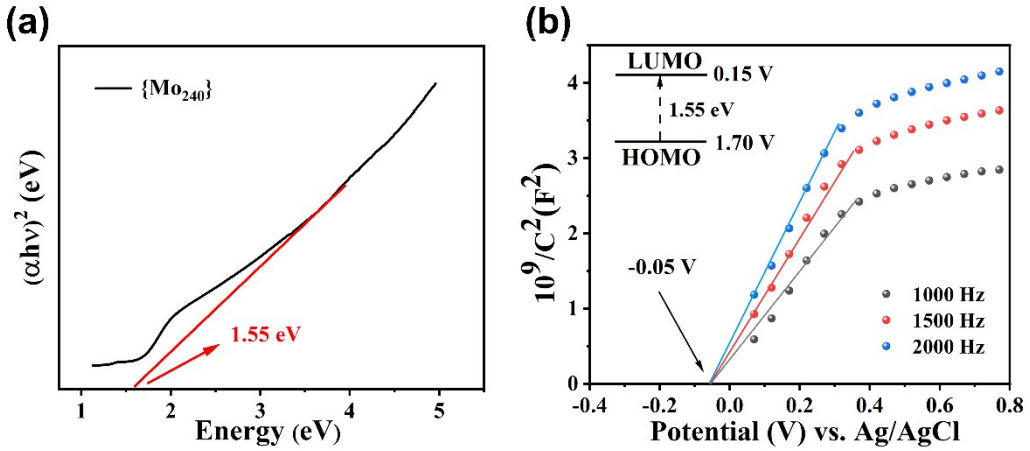


Fig. S19 (a) The band gap result of Mo_{240}; (b) the Mott-Schottky spots of Mo_{240} in 0.5 M Na_2SO_4 aqueous solution.

10.The Mott-Schottky results of 2, $\{Mo_{120}Ce_6\}$, $\{Mo_{124}Ce_4\}$, $\{Mo_{100}Ce_6\}_2$ and $\{Mo_{128}Ce_4\}_2$.

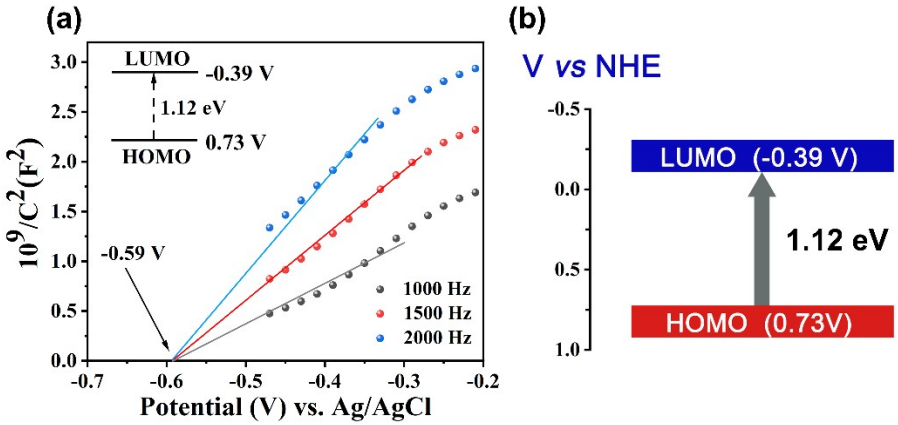


Fig. S20 (a) The Mott-Schottky spots of **2** in 0.5 M Na_2SO_4 aqueous solution. (b) Energy band position of **2.**

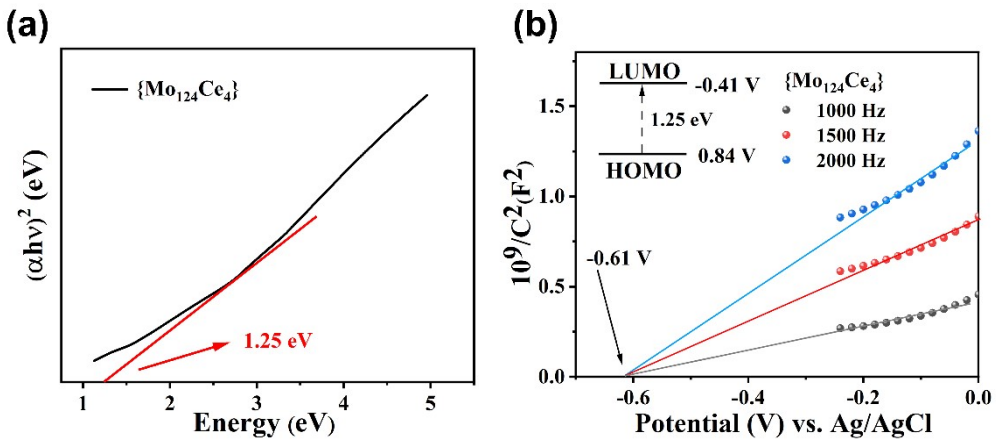


Fig. S21 (a) The band gap result of $\{Mo_{124}Ce_4\}$; (b) the Mott-Schottky spots of $\{Mo_{124}Ce_4\}$ in 0.5 M Na_2SO_4 aqueous solution.

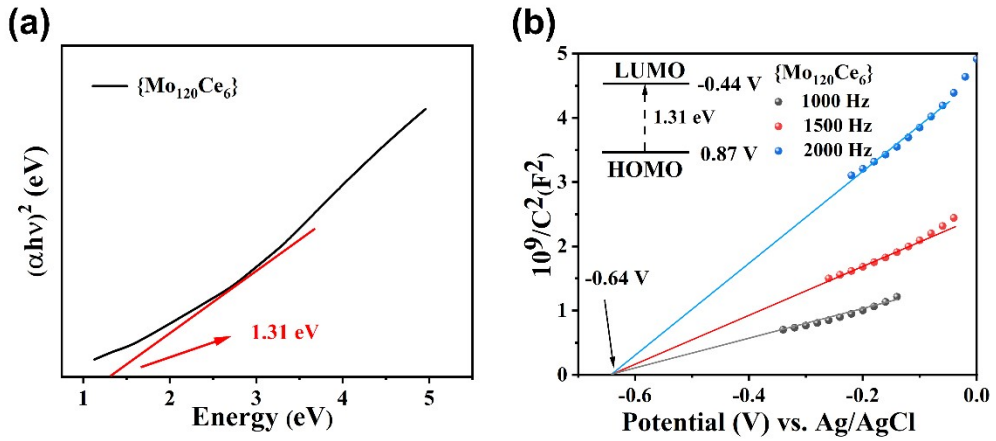


Fig. S22 (a) The band gap result of $\{Mo_{120}Ce_6\}$; (b) the Mott-Schottky spots of $\{Mo_{120}Ce_6\}$ in 0.5 M Na_2SO_4 aqueous solution.

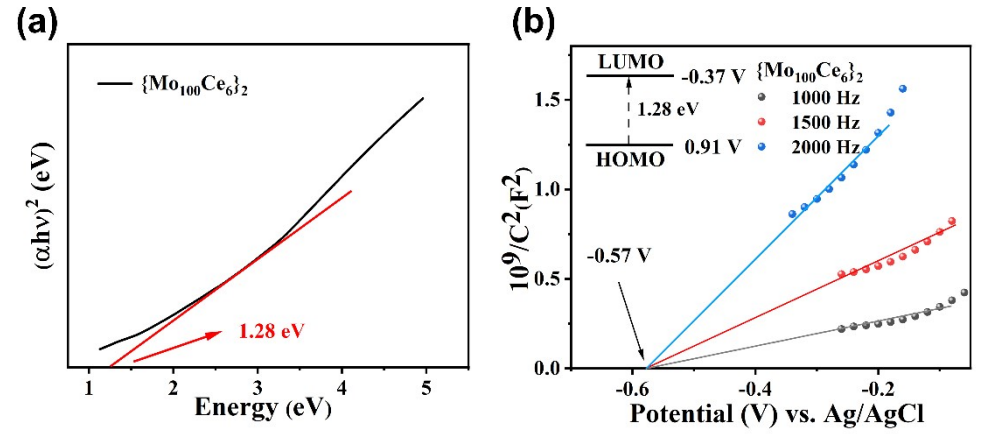


Fig. S23 (a) The band gap result of $\{Mo_{100}Ce_6\}_2$; (b) the Mott-Schottky spots of $\{Mo_{100}Ce_6\}_2$ in 0.5 M Na_2SO_4 aqueous solution.

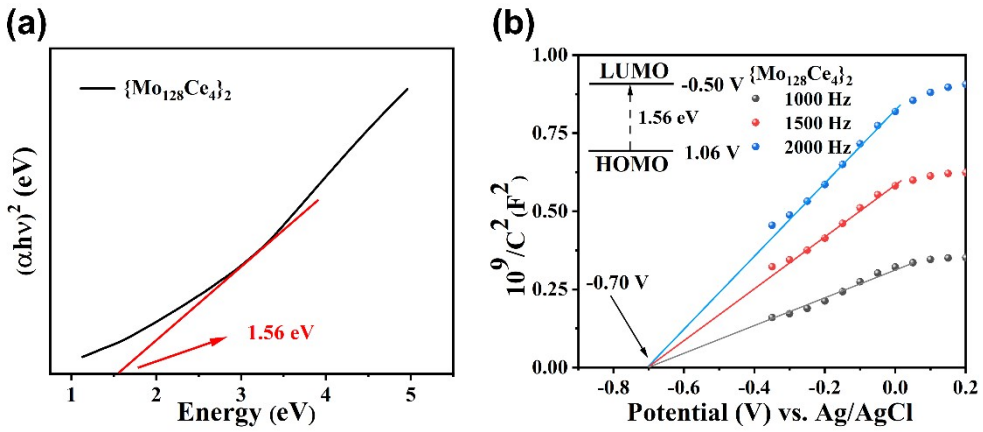


Fig. S24 (a) The band gap result of $\{Mo_{128}Ce_4\}_2$; (b) the Mott-Schottky spots of $\{Mo_{128}Ce_4\}_2$ in 0.5 M Na_2SO_4 aqueous solution.

11. Synthesis of $\{Mo_{128}Ce_4\}_2$

Synthesis of $[\{Mo^{V/IV}_{128}Ce_4O_{388}H_{10}(H_2O)_{81}\}_2]^{20-}$ ……$\{Mo_{128}Ce_4\}_2$

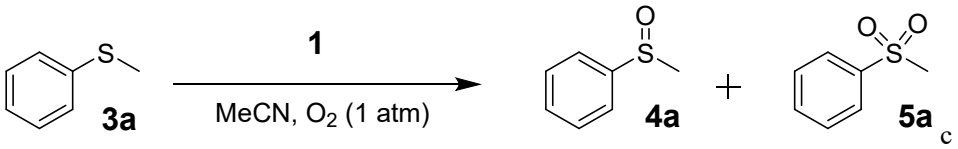
A solution of $CeCl_3 \cdot 7H_2O$ (6.15 g, 16.4 mmol) in H_2O (500 mL) was quickly added under stirring to an aqueous solution of K_2MoO_4 (5.90 g, 24.8 mmol) in H_2O (500 mL). After stirring for 30 min the practically colorless precipitate was collected by filtration, washed with ice-cold H_2O, and dried at 120 ℃ for 5 h. (yield: 6.2 g) To the solution of this precipitate (1.5 g), in a mixture of H_2O (15 mL) and 1 M HCl (12.5 mL), an aqueous solution (1.5 mL) of $[N_2H_4] \cdot 2HCl$ (10 $g \cdot L^{-1}$) was added. The solution was heated (without stirring) in a 100-mL Erlenmeyer flask (wide necked; covered with a watch glass) in a preheated oil bath at 60 ± 65℃ for 1 h. The resulting deep-blue solution cooled to room temperature, and kept in a closed flask for 24 hours. After a small amount of a colorless precipitation was removed by filtration the filtrate was kept in a closed 100-mL Erlenmeyer flask for two weeks. The deep blue (longish) platelike crystals were collected by filtration, washed with ice-cold H_2O, and dried under inert atmosphere over $CaCl_2$, yield: 0.15 g (14.3% based on Mo). IR (KBr pellet, 4000-400 cm^{-1}):3193(br), 1625(s), 993(s), 954(s), 873(m), 829(m),732(m),627(s),547(s).

Crystal data for $\{Mo_{128}Ce_4\}_2$: $Ce_8H_{736}Mo_{256}O_{1314}$, Mr = 47436.86, triclinic, space group *P*-1, a = 31.860(16) Å, b = 33.876(12) Å, c = 36.328 Å, α = 111.051(8)°, β = 97.071(10)°, γ = 97.071(13)°, V = 35721(29) $Å^3$, Z = 1, ρ = 2.205 $g \cdot cm^{-3}$, μ = 2.516 mm^{-1}, F(000) = 22458.

12. General procedures for photocatalytic oxidation of sulphides to sulfoxides.

All manipulations were conducted under aerobic condition. Into a test tube (φ 20 mm × 170 mm) equipped with an O_2 balloon (1 atm) were successively placed compound **1** (0.025 mol%), sulfides (0.2 mmol), internal standard (n-hexadecane, 0.2 mmol) and solvent (2 mL). A Teflon-coated magnetic stir bar was added, and was irradiated with light sources with stirring at room temperature. When performing quenching experiments, 5 eq. scavenger was added to the above reactants. The products were confirmed by comparison of their GC-Mass spectra with those of authentic data. The yield was calculated with respect to the internal standard. Thioanisole was taken as a model compound. Similarly, we use the above procedure to screen light sources, solvents and the amount of photocatalyst. After the reaction, the catalysts deposited at the bottom of the centrifuge tube by centrifugation, which is conducive to the recovery of the catalyst. The retrieved catalyst was washed with diethyl ether, and then air-dried prior to being used for the cycle experiment.

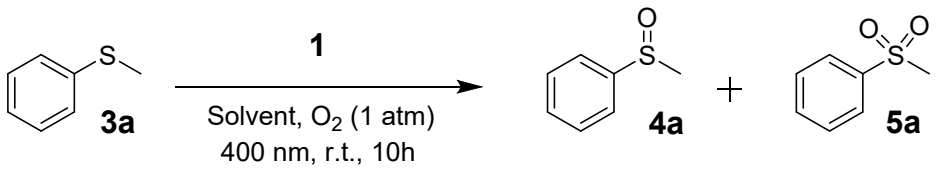
Table S7 Screening the light sources for photocatalytic oxidation of sulfides[a]



		Yields (%)[b]	
Entry	Light sources	**5a**	**6a**
1	365 nm	58	41
2	380 nm	67	32
3	400 nm	98	trace
4	420 nm	15	n.d.
5	505 nm	n.d.	n.d.

[a]Reaction conditions: **3a** (0.2 mmol), **1** (0.025 mol%), O_2 (1 atm), r.t., acetonitrile (2 mL), 10 h. [b]Yields were determined by GC-MS using mesitylene as an internal standard.

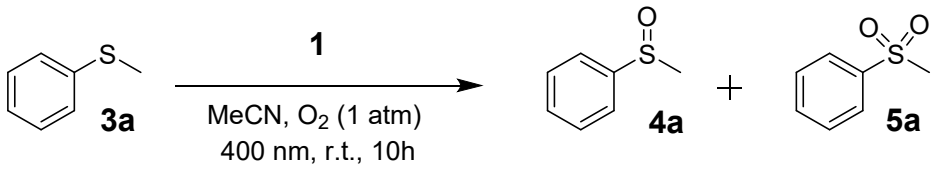
Table S8 Screening the solvents for photocatalytic oxidation of sulfides[a].



		Yields (%)[b]	
Entry	Solvent	**4a**	**5a**
1	Acetonitrile	98	trace
2	Methanol	87	trace
3	Ethanol	82	trace
4	Acetone	43	trace
5	Tetrahydrofuran	7	n.d.
6	Ethyl acetate	n.d.	n.d.

[a]Reaction conditions: **3a** (0.2 mmol), **1** (0.025 mol%), 400 nm, O_2 (1 atm), solvent (2 mL), r.t., 10 h. [b]Yields were determined by GC-MS using mesitylene as an internal standard.

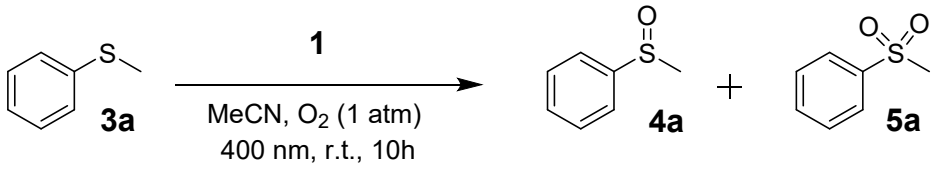
Table S9 Screening the amount of photocatalyst for photocatalytic oxidation of sulfides



		Yields (%)[b]	
Entry	Amount of photocatalyst (mol%)	**4a**	**5a**
1	0.010	43	trace
2	0.015	76	trace
3	0.025	97	trace
4	0.05	75	24
5	0.075	33	66

[a]Reaction conditions: **3a** (0.2 mmol), 400 nm, O_2 (1 atm), acetonitrile (2 mL), r.t., 10h. [b]Yields were determined by GC-MS using mesitylene as an internal standard.

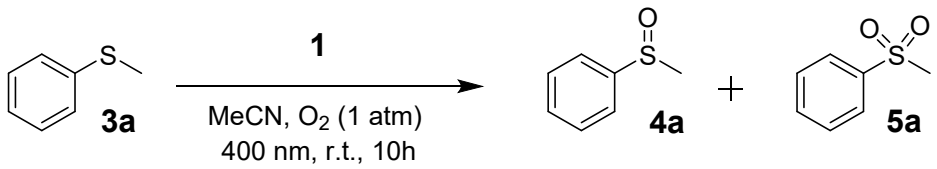
Table S10 Different types of high-nuclear molybdenum clusters for photocatalytic oxidation of sulfides



		Yields (%)[b]	
Entry	Catalyst (mol%)	**4a**	**5a**
1	**1**	98	trace
2	Mo_{154}	n.d.	n.d.
3	Mo_{240}	n.d.	n.d.
4	Mo_{132}	n.d.	n.d.
5	$Mo_{124}Ce_4$	32	n.d.
6	$Mo_{120}Ce_6$	38	n.d.
7	$(Mo_{100}Ce_6)_2$	62	trace
8	$(Mo_{124}Ce_4)_2$	72	trace

[a]Reaction conditions: **3a** (0.2 mmol), catalyst (0.025 mol%), 400 nm, O_2 (1 atm), acetonitrile (2 mL), r.t., 10h. [b]Yields were determined by GC-MS using mesitylene as an internal standard.

Table S11 Quenching experiments to determine the reactive oxygen species (ROS) for photocatalytic oxidation of sulfides



			Yields (%)[b]	
Entry	Scavenger (eq.)	Roles	**4a**	**5a**
1	Standard	--	98	trace
2	*p*-Benzoquinone	$O_2^{\bullet-}$ scavenger	63	trace
3	1,4-Diazabicyclooctane	$^1O_2$ scavenger	trace	n.d.
4	t-BuOH	·OH scavenger	97	trace
5	KI	hole scavenger	n.d.	n.d.

[a]Reaction conditions: **3a** (0.2 mmol), **1** (0.025 mol%), 400 nm, O_2 (1 atm), r.t., acetonitrile (2 mL), scavenger (5 eq.), 10 h. [b]Yields were determined by GC-MS using mesitylene as an internal standard.

Recycling experiments.

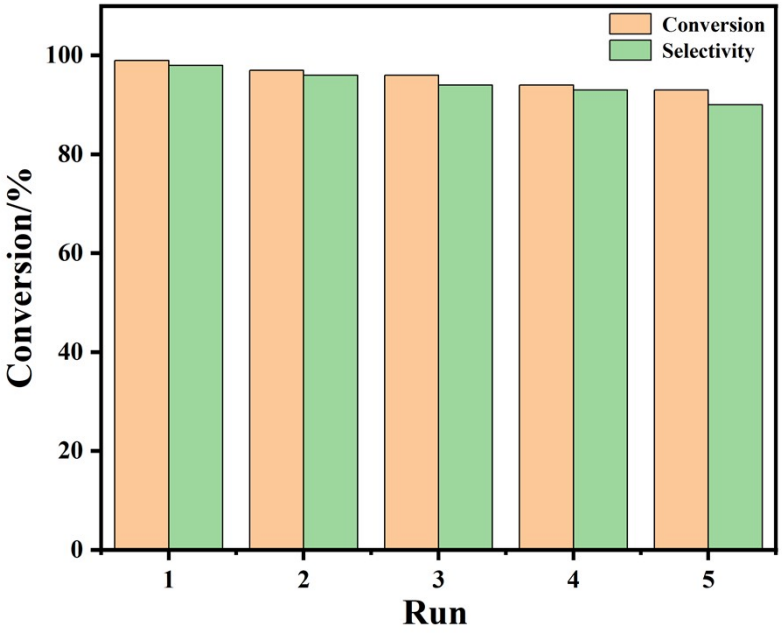


Fig. S25 Recycling experiments for the photocatalytic oxidation of thioanisole.

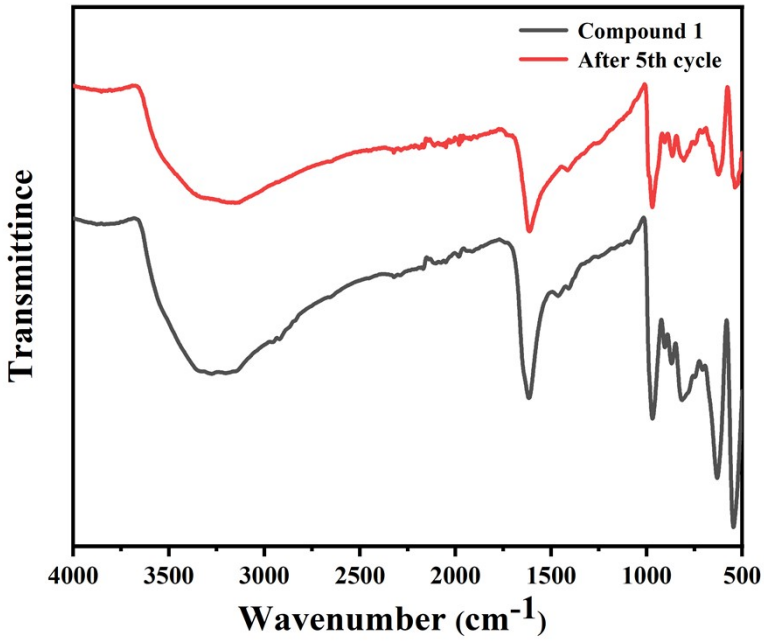


Fig. S26 IR spectra of **1** before and after photocatalytic oxidation of thioanisole.

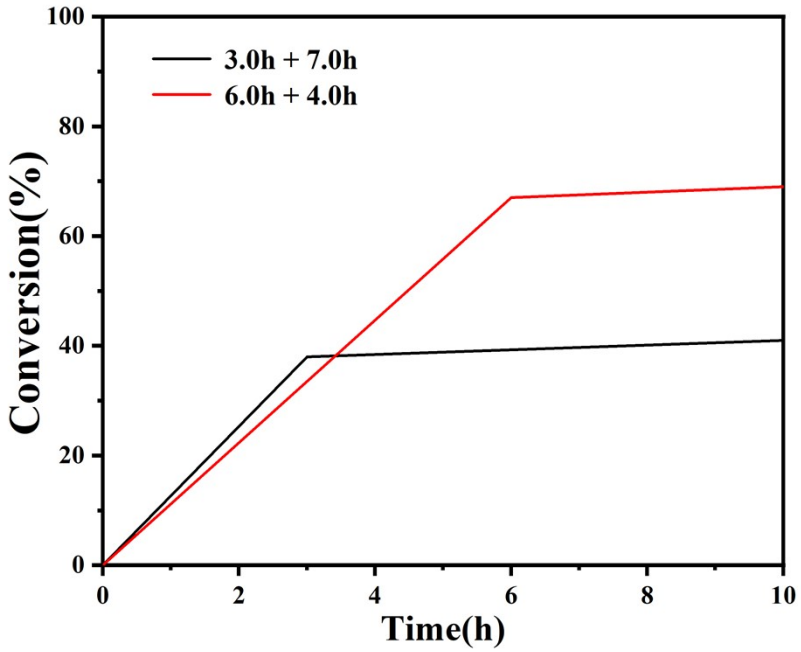


Fig. S27 Filtration experiment using **1** for the catalytic oxidation of thioanisole.

Table S12 Elemental Analysis of 1 after Catalysis

Element	Mo	Ce	Na	C	N	H
Calcuated value (%)	47.28	3.45	0.02	0.09	0.05	2.77
Actual value (%)	47.46	3.39	0.04	0.09	0.04	2.73
After catalysis (%)	47.33	3.32	0.03	0.08	0.04	2.70
Mother liquor after catalyst filtration (%)	< 0.01	< 0.01	< 0.01	-	-	-

13. References

1 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann. “OLEX2: a complete structure solution, refinement and analysis program”. *J. Appl. Cryst.* 2009,42, 339-341.