Electronic supplementary information for

"Heptamolybdate: A Highly Active Sulfide Oxygenation Catalyst"

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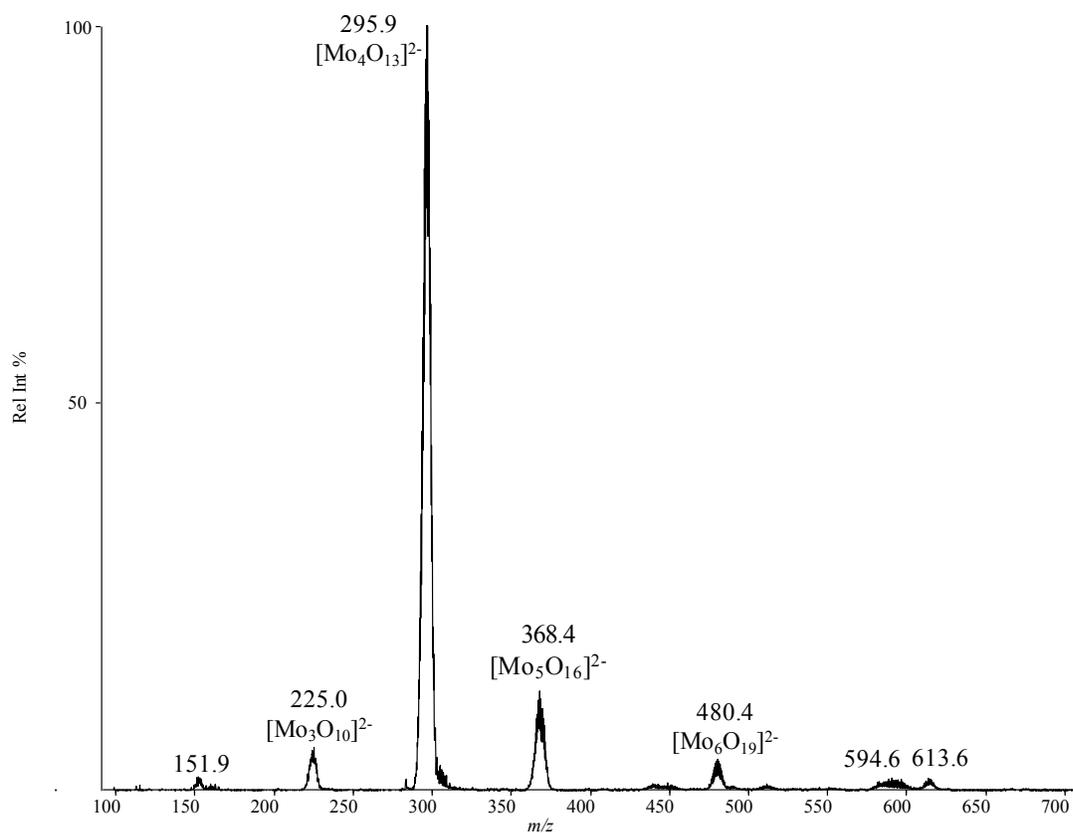   Xi'an Shiyou University, Xi'an
       Shaanxi Province,710065, China

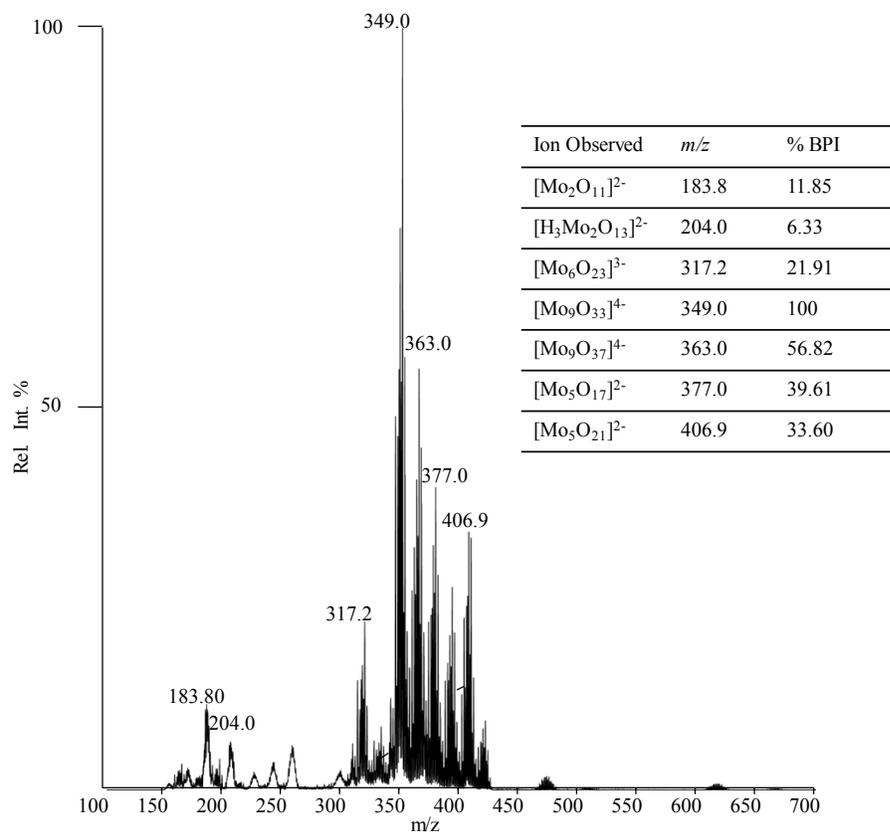**Fig. S1** NanoESI mass spectrum of $[Mo_7O_{24}]^{6-}$ (0.034 nmol) in MeCN solution in the negative ion mode.

Ion Observed	m/z	% BPI
$[Mo_2O_{11}]^{2-}$	183.8	11.85
$[H_3Mo_2O_{13}]^{2-}$	204.0	6.33
$[Mo_6O_{23}]^{3-}$	317.2	21.91
$[Mo_9O_{33}]^{4-}$	349.0	100
$[Mo_9O_{37}]^{4-}$	363.0	56.82
$[Mo_5O_{17}]^{2-}$	377.0	39.61
$[Mo_5O_{21}]^{2-}$	406.9	33.60

Fig. S2 NanoESI mass spectrum of $[Mo_7O_{22}(O_2)_2]^{6-}$ **2b** (0.034 nmol) in MeCN solution in the negative ion mode.
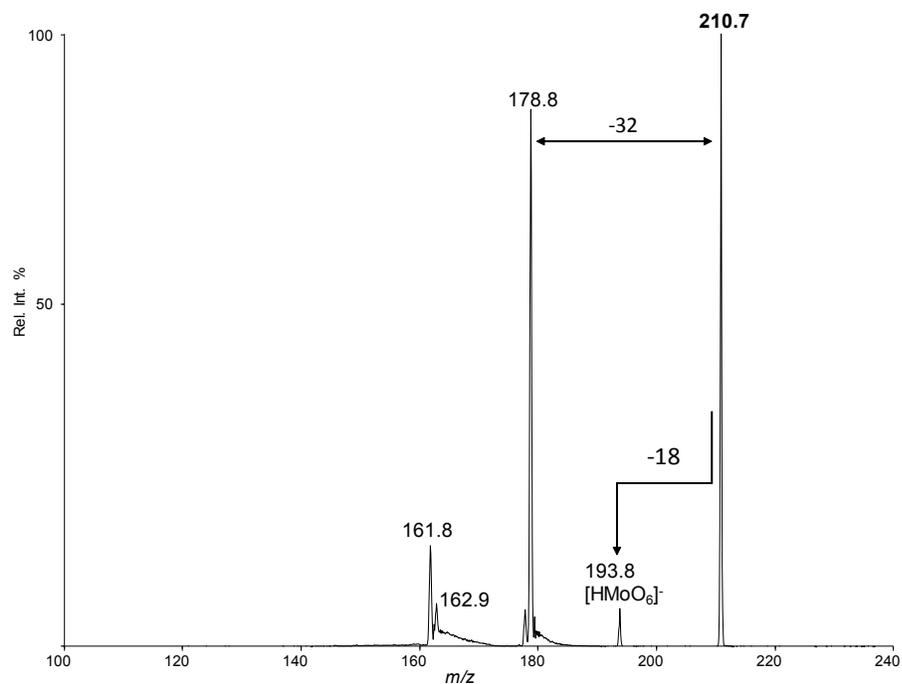
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Fig. S3 Tandem mass spectrum of the peak at *m/z* 210.7 via collision-induced dissociation from Figure 5b. Collision-induced dissociation (CID) was performed using beam type CID. Beam-type CID was performed by precursor ion selection in Q1, ion acceleration for fragmentation in q2 collision cell and followed by fragment analysis in Q3 linear ion trap. Collision energy (CE) of 25 V was used for analysis. m/z range of 100-1000 Da was used.
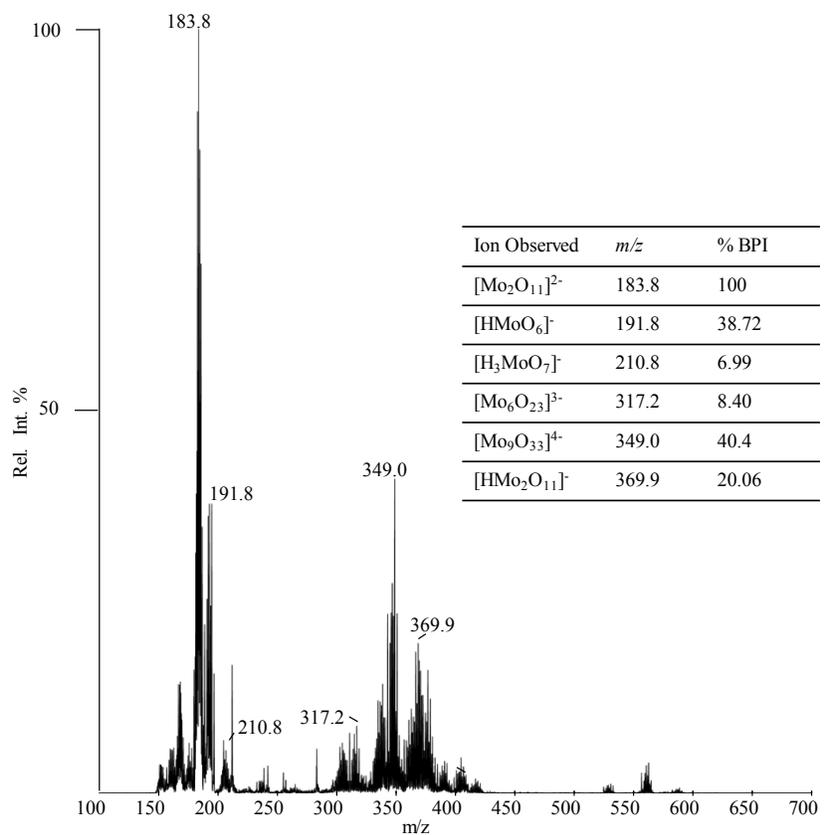
Ion Observed	m/z	% BPI
$[Mo_2O_{11}]^{2-}$	183.8	100
$[HMoO_6]^-$	191.8	38.72
$[H_3MoO_7]^-$	210.8	6.99
$[Mo_6O_{23}]^{3-}$	317.2	8.40
$[Mo_9O_{33}]^{4-}$	349.0	40.4
$[HMo_2O_{11}]^-$	369.9	20.06

Fig. S4. NanoESI mass spectra of **2b** 1 min after the addition of H_2O_2.

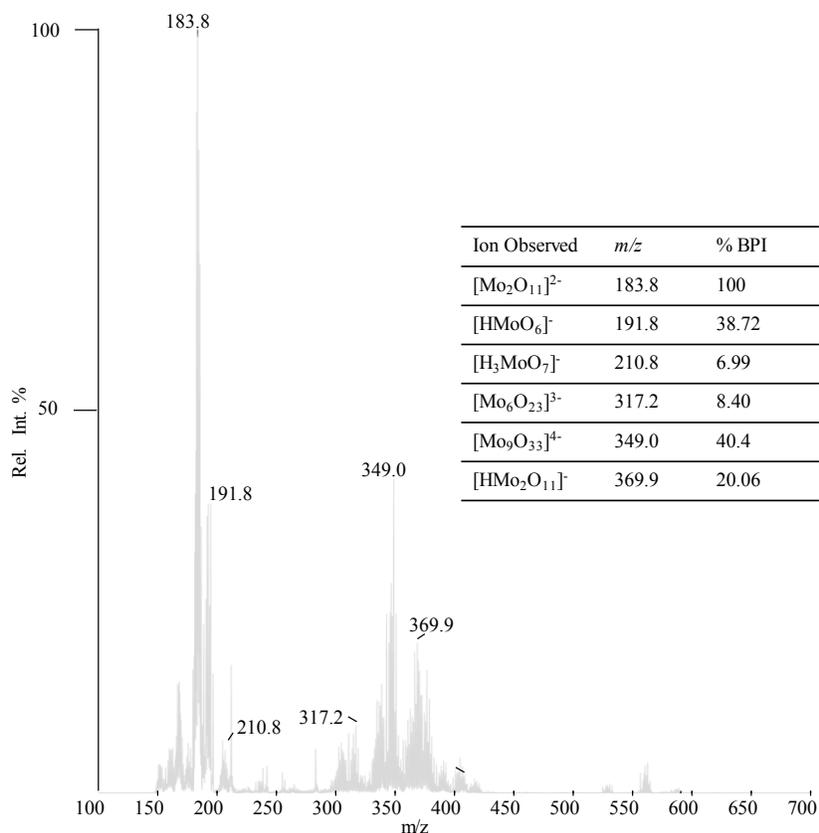| Ion Observed	*m/z*	% BPI
$[Mo_2O_{11}]^{2-}$	183.8	100
$[HMoO_6]^-$	191.8	38.72
$[H_3MoO_7]^-$	210.8	6.99
$[Mo_6O_{23}]^{3-}$	317.2	8.40
$[Mo_9O_{33}]^{4-}$	349.0	40.4
$[HMo_2O_{11}]^-$	369.9	20.06

Fig. S5. NanoESI mass spectra of **2b** 1 min after the addition of both H_2O_2 and MPS.
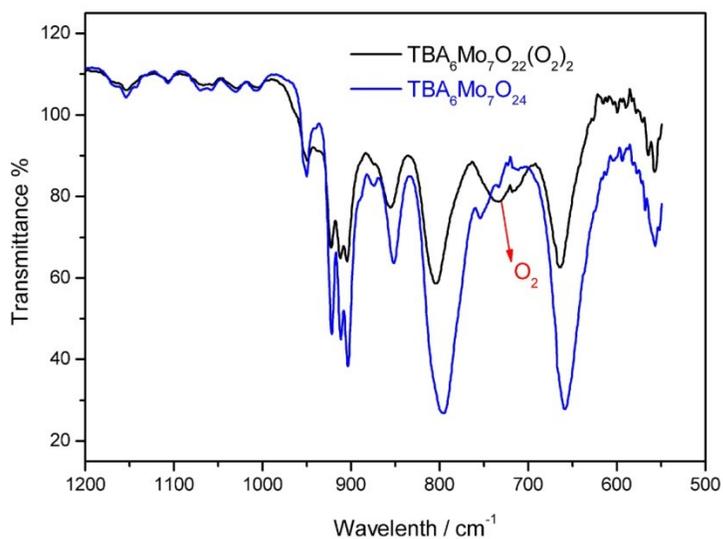

Fig. S6. FT-IR spectra of **1b** and **2b**

7. Instrumental information for all ESI-MS of **2b**

   All the MS data were collected using a QTRAP 4000 hybrid triple quadrupole/linear ion using nano-electrospray ionization in the negative ion mode. The characteristic

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parameters of the MS were: spray voltage, -1400-1600 V, curtain gas, 20 psi; declustering potential (DP), 20V. Data shown here were typically averages of 50-100 scans. MS1 mass analysis was performed in LIT mode in Q3. Data acquisition, processing, and instrument control were performed using Analyst software.

8   Crystallographic Details

Crystallization: Ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ 2.472 g (2.0 mmol) was dissolved in 20 mL water, then excessive 30% hydrogen peroxide 2.0 mL (20 mmol) and $CH_5N_3\cdot HCl$ 0.478 g (5.0 mmol) were added. The resultant reaction mixture was further stirred for 1h. After filtration, the yellow filtration was sealed by parafilm with a few tiny pores and very slowly evaporated at the room temperature. Two weeks later, yellow single-crystalline blocks suitable for X-ray crystallography products were obtained and afforded powder samples 1.687 g (yield 65% based on Mo)

Structural characterization: Crystal structure of compound 1 consists of heptamolybdate anion, two guanidine $CH_6N_3^+$, four ammonium NH_4^+ cations and lattice water molecules. The heptamolybdate $Mo_7O_{24}^{6-}$ is well-known as the fundamental units in the polyoxomolybdate anions. The molybdenum atom coordinated by peroxo group was hepta-coordinated. The pentagonal bipyramidal arrangement of coordination was frequently observed in peroxo complexes. The bond distances of the peroxo groups in 1 are 1.443(16) and 1.342(19) Å, respectively, falling in the range of peroxo compounds.

Crystal data for 1: Monoclinic, space group *P*21/c, a = 13.6678(14) Å, b = 10.8474(11) Å, c = 30.014(3) Å, β = 113.895(4), V = 4068.5(7) Å^3, Z = 4, ρ_{calcd} = 2.102 g·cm^{-3}, μ = 2.178 mm^{-1}. A single crystal of dimensions 0.35 x 0.28 x 0.24 mm^3 for 1 was selected for indexing and intensity data collection on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature. Numbers of collected and observed independent [I > 2σ(I)] reflections are 21742 and 6213 (R_{int} = 0.038). Full matrix least-squares refinements were based on F^2 and converged at R_1 = 0.0599 and wR_2 = 0.1878.

9   Packing diagram