# **Electronic Supplementary Information**

### for

# Understanding homogeneous hydrogen evolution reactivity and deactivation pathways of molecular molybdenum sulfide catalysts

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#### 1. Instrumentation

**UV-Vis spectroscopy:** UV-Vis spectroscopy was performed on a Shimadzu UV-2450 spectrophotometer, Varian Cary 50 spectrophotometer or Varian Cary 5G spectrophotometer. All systems were used with standard cuvettes (d = 10.0 mm).

**Emission spectroscopy:** Emission spectroscopy was performed on a Jasco FP-8500 spectrofluorometer. Standard emission cuvettes (d = 10.0 mm, V = 3 ml) were used.

**Single-crystal X-Ray Diffraction (XRD):** single-crystal XRD data was collected on an Agilent SuperNova CCD single-crystal X-ray diffractometer ( $\lambda$ (Mo K $\alpha$ ) = 0.71073 Å) equipped with a graphite monochromator.

**Dynamic light scattering (DLS):** DLS measurements were performed on a Malvern Instruments Zetasizer ZEN 3600 with a particle size detection limit of 0.6 nm - 6000 nm and a particle concentration detection limit of 0.001 - 1 mass-% (for particles in the 100-1000 nm size range).

**Inductively coupled plasma atomic emission spectrometry (ICP-AES)** was performed on a Perkin Elmer Plasma 400 spectrometer.

**Gas chromatography:** Gas-chromatography was performed on a Bruker Scion GC/MS, with a thermal conductivity detector 15 (column: molecular sieve 5A 75 m × 0.53 mm, oven temperature 70 °C, flow rate 25 ml min<sup>-1</sup>, detector temperature 200 °C) with Argon as carrier gas. The GC was calibrated by direct injection of known amounts of  $H_2$  gas.

**Scanning electron microscopy / energy dispersive X-ray spectroscopy (SEM-EDX)**: SEM was performed on a Zeiss DSM 962 electron microscope in combination with an EDAX EDS unit for energy dispersive X-Ray spectroscopy. The samples were mounted on carbon tabs and sputtered with carbon before the measurement. SEM studies were performed at an acceleration voltage of 5 kV. EDX measurements were performed at an acceleration voltage of 10 kV.

**FT-IR spectroscopy:** FT-IR spectroscopy was performed on a Shimadzu IR Prestige-21 FTIR spectrophotometer with a Golden Gate ATR unit. Signals are given as wavenumbers in cm<sup>-1</sup> using the following abbreviations: vs = very strong, s = strong, m = medium, w = weak and b = broad.

**Elemental analysis:** Elemental analysis was performed on a Euro Vector Euro EA 3000 Elemental Analyzer.

**Raman Spectroscopy:** Raman spectroscopy was performed on a Renishaw In Via Raman dual-laser system equipped with a He-Ne laser (633 nm, 17 mW) and a frequency-doubled Nd:YAG laser (532 nm, 50 mW), coupled with a Leica DM 2500 confocal microscope. The system was calibrated using a silicon wafer reference in air with an N PLAN EPI 50×/0.75 objective before every measurement Raman spectra were taken in Static Mode with  $\lambda$  = 633 nm at 10% power (~1.7 mW) and 200 seconds exposure time. The samples were placed in a single cavity glass microscope slide, and a glass cover slip was placed on top to prevent solvent evaporation. A long-distance objective (HC PL FLUOTAR L50×/0.55) was used for optimum laser focusing through the solvent and cover slip.

**Theoretical calculations:** Density functional theory calculations were performed using the Jaguar electronic structure program.<sup>1</sup> Mo atoms were described using effective core potentials with LACVP-type basis sets, all other atoms are described using the 6-31G++ basis set. Geometry optimizations were performed and the resulting minimum energy configurations were used for calculating solvation free energies, making use of the SM 8 solvation model.<sup>1,2</sup>

**Electrochemistry:** Linear sweep voltammetry was performed on a CHI instruments 600E potentiostat with three-electrode setup, using a glassy carbon or Pt working electrode and a Pt wire as pseudo-reference electrode and counter-electrode, respectively. The experiments were performed under argon in dry, de-gassed MeOH. Potentials are referenced against Ferrocene/Ferrocenium (Fc<sup>+</sup>/Fc).

**Electrospray ionization mass spectrometry (ESI-MS):** MS measurements were performed on a UHR-TOF Bruker Daltonik maXis ESI-ToF MS. Detection was in negative-ion mode and the source voltage was 4 kV. The drying gas ( $N_2$ ) was held at 180 °C. The machine was calibrated prior to every experiment using the Agilent ESI-TOF low concentration tuning mixture.

**General remarks:** All chemicals were purchased from Sigma Aldrich, ABCR or ACROS and were of reagent grade. The chemicals were used without further purification unless stated otherwise. **{Mo<sub>3</sub>}**, **{Mo<sub>3</sub>}-CI** and **{Mo<sub>3</sub>}-Br** were prepared based on modified literature references, see section 2.

## 2. Synthetic section

**2.1. Synthesis of {Mo<sub>3</sub>}:** The thiomolybdate  $(NH_4)_2[Mo_3S_{13}] \times 2H_2O$  was prepared by a modification of the synthesis reported by Müller *et al.*<sup>3</sup> ( $NH_4$ )<sub>6</sub>[Mo<sub>7</sub>O<sub>24</sub>] x 4H<sub>2</sub>O (4.0 g, 3.2 mmol) were dissolved in water (20 ml) in a round bottom flask. An ammonium polysulfide ( $(NH_4)_2S_x$ ) solution (120 ml, 25 wt.-%) was added and the flask was covered with a watch glass. The solution was heated to 96 °C for five days without stirring. Dark-red crystals of ( $NH_4$ )<sub>2</sub>[Mo<sub>3</sub>S<sub>13</sub>] x 2H<sub>2</sub>O formed and were removed by filtration, washed with water, ethanol, carbon disulfide and ether. The product was air-dried. Yield: 5.6 g (7.16 mmol, 97.9 % based on Mo).

Elemental analysis for  $(NH_4)_2[Mo_3S_{13}] \times 2H_2O$  in wt.-% (calcd.): Mo 37.22 (37.06), S 54.12 (53.66), N 3.43 (3.61), H 2.11 (1.56).

Characteristic IR bands (in cm<sup>-1</sup>): 3343 (s), 545 (m), 511 (m), 459 (w).

	Found	Literature		Found	Literature
a/Å	11.582(6) Å	11.577(6) Å	α/°	90	90
b/Å	16.453(5) Å	16.448(7) Å	β/°	117.34(4)	117.30(3)
c/Å	5.712 (4) Å	5.716(2) Å	γ/°	90	90

Single-crystal XRD: unit cell data (literature values based on ICSD no 10003<sup>3</sup>)

**2.2. Synthesis of**  $\{Mo_3\}$ -**CI:**  $(nBu_4N)_2[Mo_3S_7CI_6]$  was prepared by a modification of the synthesis reported by Fedin *et al*.<sup>4</sup>  $(NH_4)_2[Mo_3S_{13}] \times 2H_2O$  (1.0 g, 1.28 mmol) was refluxed in 100 ml of aqueous hydrochloric acid (37 %) for 30 min. The solution was filtered. To the warm solution, tetra-*n*-butyl ammonium chloride ( $nBu_4NCI$ , 2.0 g, 7.19 mmol) was added. The target compound, ( $nBu_4N)_2[Mo_3S_7CI_6]$  was obtained as a yellow precipitate which was recovered by filtration and washed with water, ethanol and diethyl ether. The product was then air dried. Yield: 1.2 g (0.99 mmol, 75 % based on Mo). Single crystals of ( $nBu_4N)_2[Mo_3S_7CI_6]$  were obtained by diffusion of ethyl acetate into an acetonitrile solution of ( $nBu_4N)_2[Mo_3S_7CI_6]$ .

**Elemental analysis** for (*n*Bu<sub>4</sub>N)<sub>2</sub>[Mo<sub>3</sub>S<sub>7</sub>Cl<sub>6</sub>] in wt.-% (calcd.): Mo 23.78 (22.95), S 18.55 (18.58), N 2.31(2.80), H 5.98 (5.87), C 31.76 (32.17)

Characteristic IR bands (in cm<sup>-1</sup>): 2789(s), 560 (m), 566 (s), 461 (w), 392(m).

**2.3. Synthesis of {Mo<sub>3</sub>}-Br:**  $(PPh_4)_2[Mo_3S_7Br_6]$  was prepared by a modification of the synthesis reported by Fedin *et al*.<sup>4</sup> (NH<sub>4</sub>)<sub>2</sub>[Mo<sub>3</sub>S<sub>13</sub>] x 2H<sub>2</sub>O (1.0 g, 1.28 mmol) was refluxed in 100 ml of aqueous hydrobromic acid (48 %) for 30 min. The hot solution was filtered. To this hot filtrate, tetraphenylphosphonium bromide (PPh<sub>4</sub>Br, 2.0 g, 4.76 mmol) was added. The target product,  $(PPh_4)_2[Mo_3S_7Br_6]$  was obtained as an orange precipitate and was recovered by filtration, washed with water, ethanol and diethyl ether. The product was then air dried. Yield: 1.3 g (1.03 mmol, 80 % based on Mo). Single crystals were obtained by diffusion of ethyl acetate into the acetonitrile solution of  $(PPh_4)_2[Mo_3S_7Br_6]$ .

**Elemental analysis for in wt.-% (calcd.):** Mo 17.22 (17.89), S 13.44 (13.41), P 3.71 (3.61), H 2.41 (2.41), C 34.51 (33.81)

Characteristic IR bands (in cm<sup>-1</sup>): 2975 (w), 2358 (s), 686 (m), 562 (s), 464 (w).

**2.4.** Synthesis of {Mo<sub>3</sub>}-Br as  $nBu_4N^+$  salt for electrochemical studies: due to the electrochemical (reductive) instability of the PPh<sub>4</sub><sup>+</sup> cation, the cation was exchanged for tetra-*n*-butyl ammonium for the electrochemical characterization to avoid cation-related artefacts. ( $nBu_4N$ )<sub>2</sub>[Mo<sub>3</sub>S<sub>7</sub>Br<sub>6</sub>] was prepared by a modification of the synthesis reported by Fedin *et al*:<sup>4</sup> (NH<sub>4</sub>)<sub>2</sub>[Mo<sub>3</sub>S<sub>13</sub>] x 2H<sub>2</sub>O (1.0 g, 1.28 mmol) was

refluxed in aqueous hydrobromic acid (48 %, 100 ml) for 30 min. The hot solution was filtered. To this hot filtrate, tetra-*n*-butyl ammonium bromide ( $nBu_4NBr$ , 2.0 g, 6.20 mmol) was added. The target compound, ( $nBu_4N)_2[Mo_3S_7Br_6]$ , was obtained as an orange precipitate and was recovered by filtration, washed with water, ethanol and diethyl ether. The product was then air dried. Yield: 1.53 g (1.04 mmol, 80% based on Mo). Single crystals were obtained by diffusion of ethyl acetate into the acetonitrile solution of ( $nBu_4N)_2[Mo_3S_7Br_6]$ .

**Elemental analysis for in wt.-% (calcd.):** Mo 19.49 (18.89), S 15.00 (15.28), Br 32.46 (33.01), N 1.89 (1.52), H 4.91 (5.00), C 26.03 (26.81).

Characteristic IR bands (in cm<sup>-1</sup>): 2789 (s), 686 (m), 562 (s), 464 (w).

#### 3. Crystallographic information

**Single-crystal structure determination:** Suitable single-crystals of the respective compound were mounted onto a microloop using Fomblin oil. X-ray diffraction intensity data were measured at 150 K on a Agilent SuperNova diffractometer  $\lambda$ (MoK<sub>a</sub> = 0.71073 Å) equipped with a graphite monochromator. Structure solution was carried out using SHELX-2013<sup>5</sup> *via* OLEX2.<sup>6</sup> Corrections for incident and diffracted beam absorption effects were applied using empirical methods.<sup>7</sup> Structures were solved by a combination of direct methods and difference Fourier syntheses and refined against *F*<sup>2</sup> by the full matrix least-squares technique. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added using a riding model. Crystal data, data collection parameters and refinement statistics are listed in Table S 1. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk. CCDC reference number 1533537 (**{Mo<sub>3</sub>}-CI**) and 1533536 (**{Mo<sub>3</sub>}-Br**).

	Mo <sub>3</sub> -Cl	Mo <sub>3</sub> -Br
CCDC reference no	1533537	1533536
Chemical formula	C <sub>32</sub> H <sub>72</sub> N <sub>2</sub> Mo <sub>3</sub> S <sub>7</sub> Cl <sub>6</sub>	$C_{48}H_{40}P_2Mo_3S_7Br_6$
Formula Mass	1209.85	1670.44
Crystal system	Orthorhombic	Orthorhombic
a/Å	18.3547(3)	17.9676(3)
b/Å	18.6200(3)	25.7114(6)
c/Å	29.2421(5)	27.2220(5)
α/°	90.00	90.00
β/°	90.00	90.00
<i>γ</i> /°	90.00	90.00
Unit cell volume/Å <sup>3</sup>	9993.9(3)	12575.8(4)
Temperature/K	150	150
Space group	Pbca	Pbca
No. of formula units per unit cell, Z	8	8
No. of reflections measured	54440	58921
No. of parameters	459	595
R <sub>int</sub>	0.0382	0.0312
Final $R_1$ values ( $l > 2\sigma(l)$ )	0.0641	0.0451
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.0881	0.0668
Goodness of fit on <i>F</i> <sup>2</sup>	1.067	1.135
Max/min resd electron density (e Å-3)	3.44/-1.31	2.15/-1.46

Table S 1: Summary of the crystallographic data for {Mo<sub>3</sub>}-Cl and {Mo<sub>3</sub>}-Br



**Figure S 3:** ORTEP representation of  $(nBu_4N)_2[Mo_3S_7CI_6]$  (left) and  $(PPh_4)_2[Mo_3S_7Br_6]$  (right), probability ellipsoids given at 50 %.

#### 4. Catalytic section

#### 4.1. Photocatalytic hydrogen evolution studies:

**Solvents**: All solvents were purged with high-purity argon before each measurement to remove traces of oxygen.

**Standard reaction setup:** 5 mL GC vials were filled with 2 mL of the reaction mixture under inert conditions (containing solvent, the respective catalyst, photosensitizer ([Ru(bpy)<sub>3</sub>]PF<sub>6</sub>) and electron donor (ascorbic acid) at the concentrations specified. *Standard conditions:* solvent: MeOH:H<sub>2</sub>O, 10:1, v:v; [catalyst] =  $3.1 \times 10^{-7}$  M, [Ru(bpy)<sub>3</sub>]<sup>2+</sup> =  $2 \times 10^{-5}$  M, [ascorbic acid] = 0.1 M). The vials were sealed with a septum cap. The samples were irradiated with a LED light source ( $\lambda_{max}$  = 470 nm) in a custombuilt, air-cooled photoreactor. Hydrogen evolution was quantified by gas-chromatography. Each measurement was carried out in triplicate, the values reported are the resulting average. **Control experiments** were performed and showed no hydrogen evolution when the samples are not irradiated, or when catalyst, [Ru(bpy)<sub>3</sub>]<sup>2+</sup> or ascorbic acid are absent.

**Definitions:**  $TON = n(H_2) / n(catalyst)$   $TOF = TON / t_{irradiation}$ .

**4.2. Colloid detection procedure:** To exclude the formation of colloidal particles (e.g. by precipitation of  $[Ru(bpy)_3]^{2+}/[Mo_3S_{13}]^{2-}$  salts) in the above reaction system, a literature-known colloid detection procedure using dynamic light scattering (DLS), micro-filtration (using a 0.2 µm pore size PTFE syringe filter), UV-Vis spectrometry and scanning electron microscopy / energy-dispersive X-ray spectroscopy was performed.<sup>8</sup> For all samples reported, no colloid formation was observed over the course of the catalytic reaction.

**Micro-filtration** of the solutions using a 0.2  $\mu$ m pore size PTFE syringe filter and UV-Vis spectroscopic analysis of the solutions before and after filtration show no significant change in the UV-Vis spectroscopic trace of the catalyst-containing solutions. **SEM-EDX analysis** of the filter membrane show no particles and do not feature EDX signals for Mo, S or Ru, see below.



**Figure S1: Left:** UV-Vis spectroscopic analysis of the reaction solution before and after micro-filtration. Virtually no changes are observed after filtration. **Right:** SEM and EDX analysis of the filter membrane (fibrous structure) after filtration shows that no colloidal particles (no Mo, S, Ru detected by EDX) are retained on the membrane.

**Dynamic light scattering** verified the initial observations and no particles were detected in the reaction solution, see Table S2.

**Table S2:** Dynamic light scattering for standard HER reaction solutions containing [{**Mo**<sub>3</sub>}] = 5 × 10<sup>-8</sup> M, [[Ru(bpy)<sub>3</sub>]<sup>2+</sup>] = 1 × 10<sup>-5</sup> M, [ascorbic acid] = 0.01 M solvent: MeOH:H<sub>2</sub>O (10:1, v:v) before and after irradiation ( $\lambda_{max}$  =470 nm,  $t_{irradiation}$  = 25 min) at room temperature.

Condition	DLS average particle size/ nm	DLS mean count rate / kcps
Pure solvent	not detected	18.86
Reaction solution before irradiation	not detected	22.08
Reaction solution after irradiation	not detected	23.18

Particle detection by DLS can be related back to the amount of light scattered by the sample, these values are reported as "DLS mean count rate" in kilo-counts per second, kcps. Based on extensive analyses, this represents the most reliable particle size identification method by DLS, since DLS measurements are prone to reporting "false positive" results.<sup>9</sup>

#### 4.3. Ligand exchange studies on {Mo<sub>3</sub>}.

**4.3.1. Solvent and ascorbic acid effects.** The effects of the reaction medium (MeOH:H<sub>2</sub>O, 10:1 vs pure H<sub>2</sub>O) were examined by carrying out the standard HER reaction using **{Mo<sub>3</sub>}** as catalyst in MeOH:H<sub>2</sub>O, 10:1, v:v and in pure H<sub>2</sub>O. The results show significantly lower *TONs* and a significantly faster drop in *TOFs* for the reaction carried out in water. This is in line with the suggested mechanism where terminal disulfide ligands are replaced by water ligands, see main manuscript for details.



**Figure S2: Left:** Change of turnover frequency for the HER catalysis by  $\{Mo_3\}$  in MeOH:H<sub>2</sub>O (10:1, v:v) and in H<sub>2</sub>O, showing significant differences in TOFs during the first 60 min of HER catalysis. **Right:** UV-Vis spectroscopy gives no indication of ascorbic acid coordination to  $\{Mo_3\}$ .

#### 5. ESI-Mass spectrometry

High-resolution ESI-mass spectrometry (negative ion mode) of  $\{Mo_3\}$  in MeOH:H<sub>2</sub>O (10:1, v:v) showed the presence of thiomolybdate species featuring oxo ligands. This reactivity is literature-known and based on the exchange of terminal disulfides with water ligands.<sup>10</sup> The conversion to oxo ligands occurs by deprotonation, either in solution or during the ESI-MS process. These findings support the proposed ligand exchange for  $\{Mo_3\}$  described in the main manuscript.



**Figure S3:** ESI mass spectrometry of **{Mo<sub>3</sub>}** based on an aqueous methanolic solution of **{Mo<sub>3</sub>}** under catalytic conditions, highlighting the observation of oxo-substituted species which are in line with the proposed disulfide exchange. Note that ESI-MS is a gas phase measurement, i.e. ionization and transfer of the species from solution into the gas phase can result in chemical changes such as loss of ligands, deprotonation, etc. Note that care has to be taken when comparing ESI-MS results with the solution behaviour of the species under investigation as the ESI process involves transfer of species from solution to the gas phase.



**Figure S4: Left:** UV-Vis spectrometric analysis of the stability of  $\{Mo_3\}$  in pure MeOH solution. Ligand exchange on  $\{Mo_3\}$  is known<sup>3</sup> to lead to characteristic changes in the UV-Vis spectrum. No changes of the UV-vis spectral signatures were observed over the standard reaction time of 6 h. Conditions: solvent: water-free MeOH, [ $\{Mo_3\}\}$ ] = 1 mM. **Right:** UV-Vis spectroscopy of the standard reaction solution containing  $\{Mo_3\}$ , [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and ascorbic acid at different irradiation times. After the standard 6 h irradiation period, only minor degradation of the photosensitizer is observed. After 24 h irradiation, significant photosensitizer degradation is noted.

#### 6. Theoretical calculations

Density functional theory calculations were performed using the B3LYP exchange–correlation functional with unrestricted Kohn–Sham wave functions as implemented in the Jaguar electronic structure program.<sup>1</sup> Mo atoms are described using effective core potentials with LACVP-type basis sets, all other atoms are described using the 6-31G++ basis set. Geometry optimizations were performed and the resulting minimum energy configurations were used for calculating solvation free energies in methanol, making use of the SM 8 solvation model as implemented in the Jaguar code.<sup>1,2</sup> To gain further insights into the reaction process, all possible intermediate steps for the HER (shown in Figure S5) were calculated.



**Figure S5:** Overview over the possible reaction intermediates for a) the Volmer-Tafel and b) the Volmer-Heyrovsky HER for the cluster  $[Mo_3S_7X_6]^n$  with charge *n*. Each step downwards (blue arrow) corresponds to a reduction; each step to the right (red arrows) to a protonation. The diagonal steps (black arrows) describe proton-coupled electron transfers.

For a cluster  $[Mo_3S_7X_6]^n$  with charge *n* three different types of reaction steps are possible. A reduction step

$$[Mo_3S_7X_6]^n + e^- \rightarrow [Mo_3S_7X_6]^{n-1}$$
(1)

a proton transfer

$$[Mo_3S_7X_6]^n + H^+ \to H[Mo_3S_7X_6]^{n+1},$$
(2)

and a coupled proton electron transfer

$$[Mo_{3}S_{7}X_{6}]^{n} + H^{+} + e^{-} \rightarrow H[Mo_{3}S_{7}X_{6}]^{n}.$$
(3)

The free energy changes for these processes are

$$\Delta G_{\text{ET}} = \Delta G([\text{Mo}_3\text{S}_7\text{X}_6]^{n-1}) - \Delta G([\text{Mo}_3\text{S}_7\text{X}_6]^n) - \Delta G(\text{e}^-)$$
(4)

for the electron transfer,

$$\Delta G_{\mathsf{PT}} = \Delta G \left( \mathsf{H} [\mathsf{Mo}_3 \mathsf{S}_7 \mathsf{X}_6]^{n+1} \right) - \Delta G \left( [\mathsf{Mo}_3 \mathsf{S}_7 \mathsf{X}_6]^n \right) - \Delta G \left( \mathsf{H}^+ \right)$$
(5)

for the proton transfer, and

$$\Delta G_{\text{CPET}} = \Delta G \left( \mathsf{H} [\mathsf{Mo}_3 \mathsf{S}_7 \mathsf{X}_6]^n \right) - \Delta G \left( [\mathsf{Mo}_3 \mathsf{S}_7 \mathsf{X}_6]^n \right) - \Delta G \left( \mathsf{e}^- \right) - \Delta G \left( \mathsf{H}^+ \right)$$
(6)

for the coupled proton electron transfer.

The electron source for these processes is the reduced photosensitizer  $[Ru(bpy)_3]^{1+}$ , which provides an electron *via* the oxidation

$$[Ru(bpy)_3]^{1+} \to [Ru(bpy)_3]^{2+} + e^{-}.$$
(7)

Thus, the reference value for the free energy of the electron  $\Delta G(e^{-})$  is calculated as

$$\Delta G(\mathbf{e}^{-}) = \Delta G([Ru(bpy)_{3}]^{2+}) - \Delta G([Ru(bpy)_{3}]^{1+}) = -76.9 \text{ kcal/mol}.$$
(8)

The free energy of the proton at a concentration c = 0.5 mM in methanol is given by

$$\Delta G(H^{+}, 0.5 \text{ mM}) = \Delta G_{gas}(H^{+}) + \Delta G_{solv}(H^{+}, 1M) + R \cdot T \cdot \ln\left(\frac{c}{c_{0}}\right) = -288.6 \text{ kcal/mol},$$
(8)

where  $\Delta G_{gas}(H^+) = -6.3 \text{ kcal/mol}$  is the free energy of the proton in gas phase,<sup>11</sup>  $\Delta G_{solv}(H^+, 1M) = -263.5 \text{ kcal/mol}$  is the solvation free energy of the proton at  $c_0 = 1 \text{ M}$ ,<sup>12</sup> T = 298.15 K is the room temperature, and  $R = 8.314 \frac{J}{\text{mol K}}$  is the ideal gas constant.



**Figure S6:** Reaction pathways for  $[Mo_3S_{13}]^{2^-}$ . Red dotted lines correspond to proton transfers, blue dashed lines to electron transfers, and black dash dotted lines describe proton-coupled electron transfers. A protonation of the  $[Mo_3S_{13}]^{2^-}$  cluster is energetically not favored and would lead to  $\Delta G_{\rm PT}(H_t[Mo_3S_{13}]^{1^-}) = 40.8 \, \rm kcal/mol$  (proton binding to terminal disulfide), or  $G_{\rm PT}(H_b[Mo_3S_{13}]^{1^-}) = 70.3 \, \rm kcal/mol$  (proton binding to bridging disulfide). Thermodynamically, an electron transfer would be possible ( $\Delta G_{\rm ET}([Mo_3S_{13}]^{3^-}) = -26.2 \, \rm kcal/mol$ ), but subsequent protonation of the resulting  $[Mo_3S_{13}]^{3^-}$  cluster is energetically highly unfavored. The same argument holds for the 2-electron-reduced species  $[Mo_3S_{13}]^{4^-}$ . Thus, the only remaining possibility is a coupled proton electron transfer to the native cluster  $[Mo_3S_{13}]^{2^-}$ . For this process, proton transfer to the bridging disulfide position ( $G_{\rm CPET}(H_b[Mo_3S_{13}]^{2^-}) = 7.5 \, \rm kcal/mol$ ) is slightly preferred compared with the terminal disulfide position ( $G_{\rm CPET}(H_t[Mo_3S_{13}]^{2^-}) = 8.0 \, \rm kcal/mol$ ). Hence, theoretical analyses suggest that the first reaction step (Volmer step) is realized by a coupled proton electron transfer to a bridging disulfide ligand. This is in line with literature studies on related thiomolybdates.<sup>13</sup> To verify that the reaction proceeds as a Volmer- Heyrovsky reaction, we also calculated the intermediate products for the Volmer-Tafel reaction (gray dash-dotted lines). However, as shown

above, all products with two adsorbed hydrogen atoms are energetically unfavored compared with the Volmer-Heyrovsky process leading to  $[Mo_3S_{13}]^{2^-} + H_2$ .



**Figure S7:** Reaction pathways for  $[Mo_3S_{11}(H_2O)_2]^0$ . As described in Figure S6 for the  $[Mo_3S_{13}]^{2-}$  cluster, the only possibility for the HER are two proton-coupled electron transfers in a Volmer- Heyrovsky type manner. Color coding: Proton transfer: red dotted lines; electron transfer: blue dashed lines; proton-coupled electron transfer: black dash dotted lines.



**Figure S8:** Reaction pathways for  $[Mo_3S_9(H_2O)_4]^{2+}$ . As described in Figure S6 for the  $[Mo_3S_{13}]^{2-}$  cluster, the only possibility for the HER are two proton-coupled electron transfers in a Volmer- Heyrovsky type manner. Color coding: Proton transfer: red dotted lines; electron transfer: blue dashed lines; proton-coupled electron transfer: black dash dotted lines.



**Figure S9:** Reaction pathways for  $[Mo_3S_7(H_2O)_6]^{4+}$ . As described in Figure S6 for the  $[Mo_3S_{13}]^{2-}$  cluster, the only possibility for the HER are two proton-coupled electron transfers in a Volmer- Heyrovsky type manner. Color coding: Proton transfer: red dotted lines; electron transfer: blue dashed lines; proton-coupled electron transfer: black dash dotted lines.



**Figure S10:** Reaction pathways for  $[Mo_3S_7Cl_6]^{2^-}$ . As described in Figure S6 for the  $[Mo_3S_{13}]^{2^-}$  cluster, the only possibility for the HER are two proton-coupled electron transfers in a Volmer- Heyrovsky type manner. Color coding: Proton transfer: red dotted lines; electron transfer: blue dashed lines; proton-coupled electron transfer: black dash dotted lines.



**Figure S11:** Reaction pathways for  $[Mo_3S_{11}]$  (i.e. a **{Mo**<sub>3</sub>**}** species with a vacant terminal coordination site). For this species, hydrogen evolution by two proton-coupled electron transfers in a Volmer- Heyrovsky type manner is possible. Note that three Hydrogen atom binding sites were assessed. Hydrogen evolution based on hydrogen atom binding at a bridging disulfide or at a Mo centre (leading to a Mo-hydride ( $H_{Mo}$ )) seems energetically feasible. In contrast, H atom binding at a terminal disulfide ( $H_t$ ) or cluster reorganization after hydrogen atom binding at a terminal disulfide ( $H_{teorg}$ ) leads to energetically stabilized species for which subsequent  $H_2$  desorption is energetically highly unfavored. Color coding: Proton transfer: red dotted lines; electron transfer: blue dashed lines; proton-coupled electron transfer: black dash dotted lines.



**Figure S12:** Illustration of the calculated structures of the hydrogen-atom-bound species  $[Mo_3S_{13-x}(H_2O)_x]^{(2-x)}$ , x = 0, 2, 4, 6. Note that H atom binding is energetically most favored at the briding disulfide ligands, resulting in a reductive cleavage of the disulfide bond and formation of a hydrogen sulfide (HS<sup>-</sup>) ligand. Also note that weak S<sup>...</sup>H hydrogen bonds ( $d(S^{...}H) \sim 2.6-2.8$  Å, dashed magenta lines) are observed for x = 0, 2, 4 but not for the species with x = 6, which also shows the highest calculated activation barrier for hydrogen evolution in a Volmer-Heyrovsky mechanism (see main text). Further studies are required to assess whether a correlation between these observations exists. Colour scheme: Mo: teal, S: yellow, O: red, water-bound hydrogens: grey, sulfur-bound hydrogens: pink.

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