

## Supporting Information

*for*

### **Hydrogen passivation strategy for electrocatalytic chlorine evolution reaction on metal-organic frameworks: A theoretical insight**

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**Table S1.** The cell information of  $\text{TM}_3(\text{THT})_2$  (TM=Mn, Fe, Co, Ni, Tc, Ru, Rh, Pd, Re, Os, Ir, Pt).

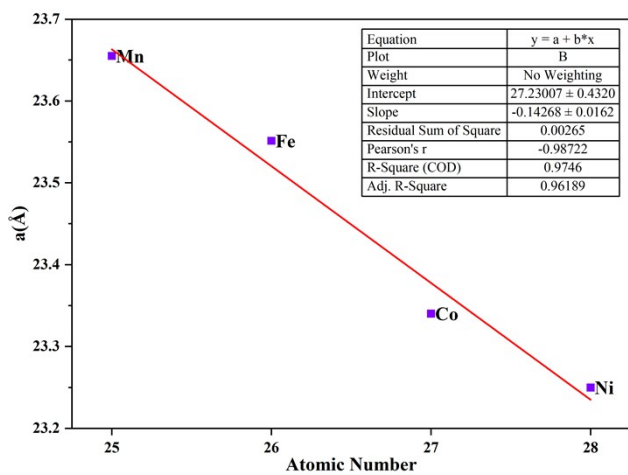
|    | a/Å     | b/Å     | c/Å    | alpha/° | beta/° | gamma/° |
|----|---------|---------|--------|---------|--------|---------|
| Mn | 23.655  | 23.655  | 3.4855 |         |        |         |
| Fe | 23.5513 | 23.5513 | 3.4333 |         |        |         |
| Co | 23.3401 | 23.3401 | 3.3756 |         |        |         |
| Ni | 23.2498 | 23.2498 | 3.4061 |         |        |         |
| Tc | 23.839  | 23.839  | 3.3233 |         |        |         |
| Ru | 23.7616 | 23.7616 | 3.2356 | 90      | 90     | 120     |
| Rh | 23.7055 | 23.7055 | 3.2784 |         |        |         |
| Pd | 23.7065 | 23.7065 | 3.3768 |         |        |         |
| Re | 23.8565 | 23.8565 | 3.3528 |         |        |         |
| Os | 23.7774 | 23.7774 | 3.2454 |         |        |         |
| Ir | 23.7222 | 23.7222 | 3.2819 |         |        |         |
| Pt | 23.6815 | 23.6815 | 3.3921 |         |        |         |

**Table S2.** Charge changes of the main atoms of different intermediates during CER and OER after hydrogen passivation of  $\text{Re}_3(\text{THT})_2$  (Re is the metal site, H corresponds to the hydrogen atom used for passivation of Re, S corresponds to the site used for subsequent CER and OER reactions, and Cl/HO/O/HOO corresponds to the different adsorbates)

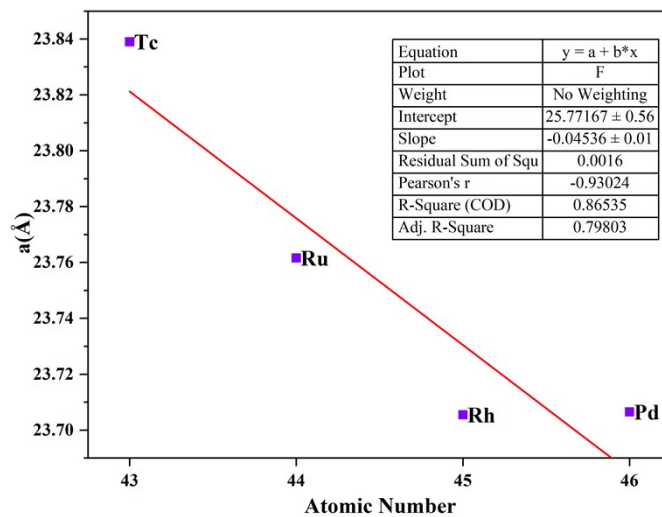
|      | Re     | H     | S     | Cl/HO/O/HOO |
|------|--------|-------|-------|-------------|
| *Cl  | -0.312 | 0.077 | 0.092 | -0.208      |
| HO*  | -0.336 | 0.074 | 0.233 | -0.101      |
| O*   | -0.176 | 0.13  | 0.177 | -0.364      |
| HOO* | -0.324 | 0.069 | 0.164 | -0.159      |

**Table S3.** The adsorption energy of hydrogen atoms on metal sites before hydrogen passivation ( $E_{*-\text{H}}$ ) and the adsorption energy of hydrogen atoms on sulfur sites after hydrogen passivation ( $E_{*-\text{H-H}}$ ).

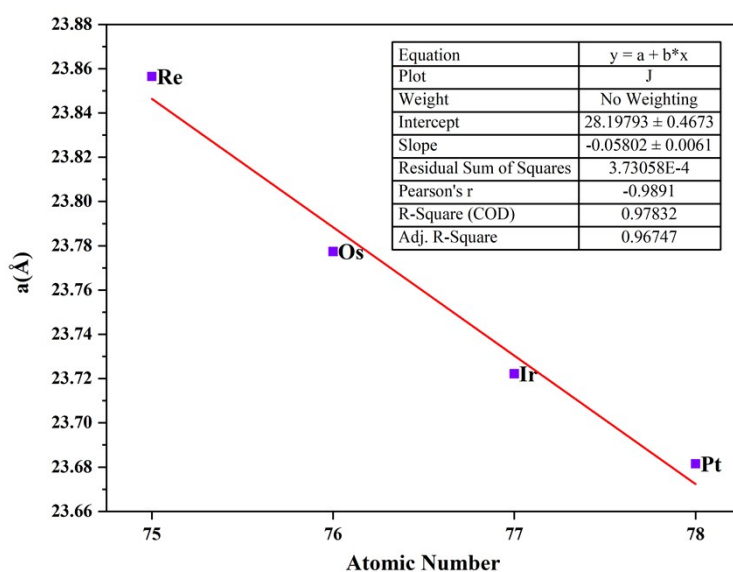
|                             | $E_{*-\text{H}}/\text{eV}$ | $E_{*-\text{H-H}}/\text{eV}$ |
|-----------------------------|----------------------------|------------------------------|
| $\text{Fe}_3(\text{THT})_2$ | -0.06                      | 0.02                         |
| $\text{Co}_3(\text{THT})_2$ | -0.27                      | -0.01                        |
| $\text{Tc}_3(\text{THT})_2$ | -0.81                      | 0.27                         |
| $\text{Ru}_3(\text{THT})_2$ | -0.79                      | 0.02                         |
| $\text{Rh}_3(\text{THT})_2$ | -0.50                      | -0.07                        |
| $\text{Re}_3(\text{THT})_2$ | -1.47                      | 0.36                         |
| $\text{Os}_3(\text{THT})_2$ | -0.96                      | 0.22                         |
| $\text{Ir}_3(\text{THT})_2$ | -0.69                      | 0.10                         |



(a)

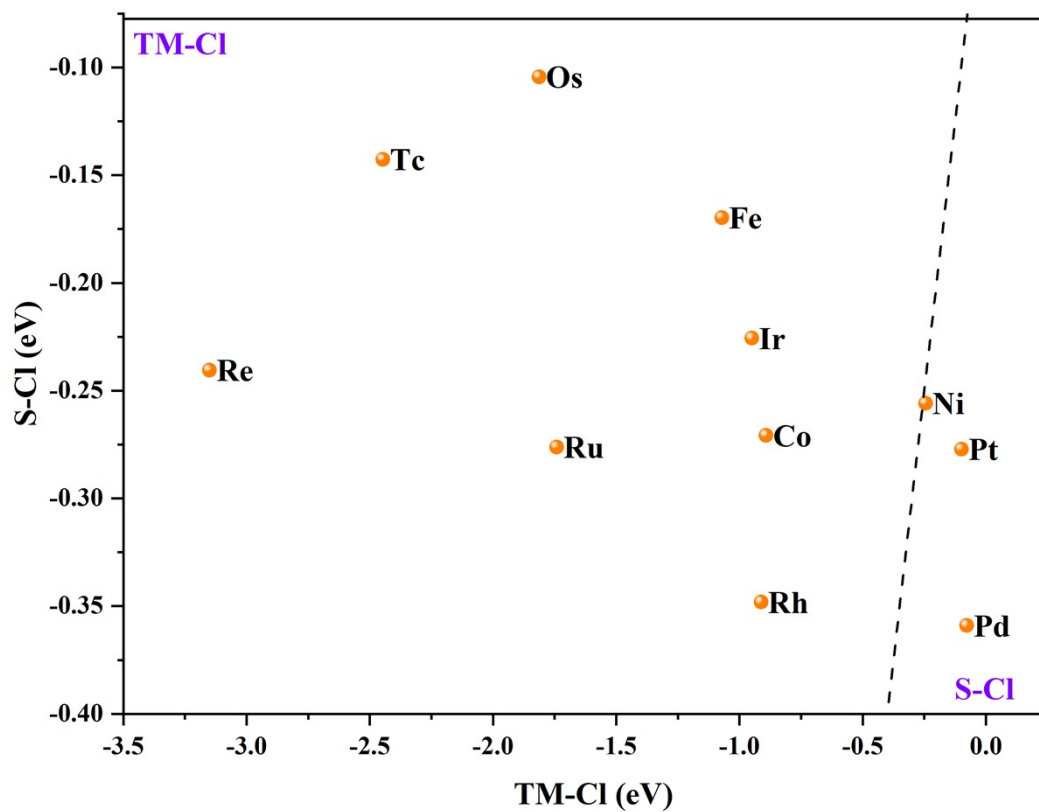


(b)

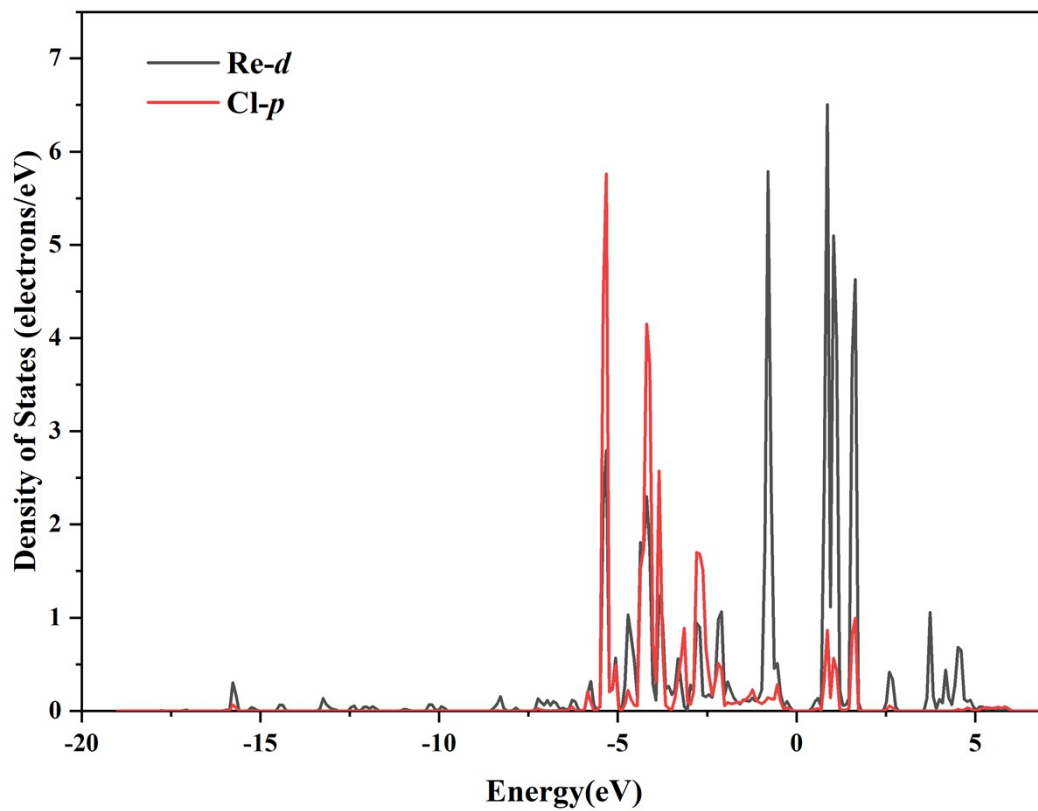


(c)

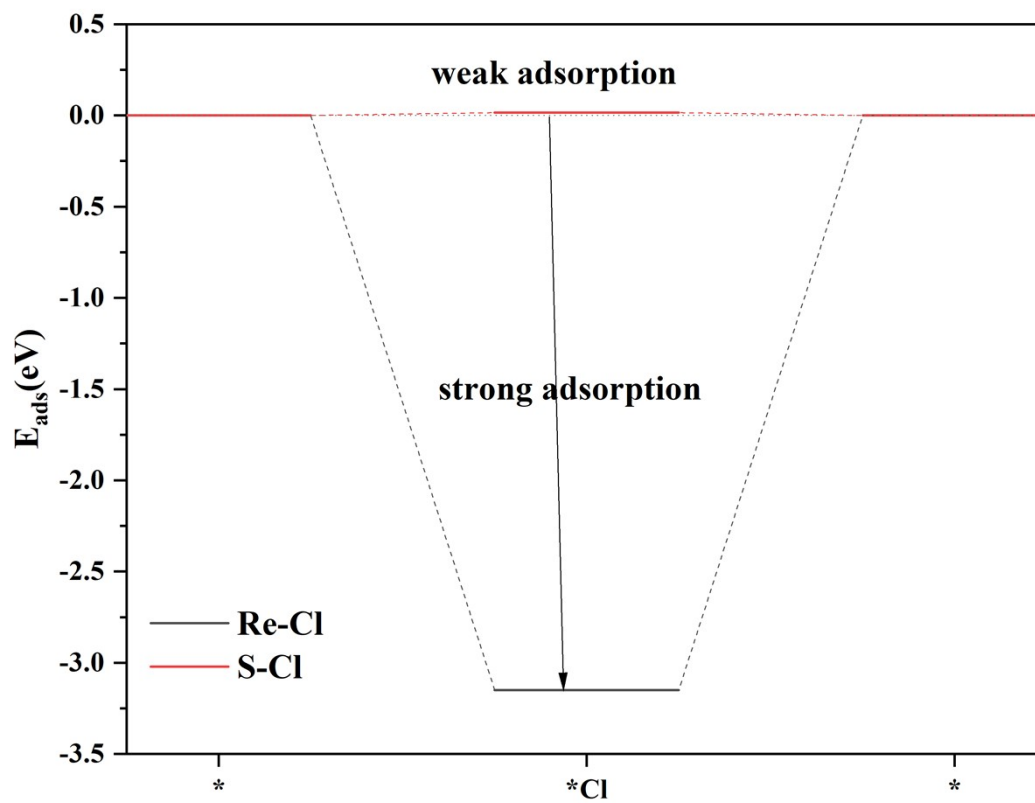
**Figure S1.** Relationship between the atomic number of transition metals in  $\text{TM}_3(\text{THT})_2$  and the unit cell “a” of  $\text{TM}_3(\text{THT})_2$ .



**Figure S2.** Adsorption energy of Cl atoms on transition metal sites and sulfur sites. (the sulfur sites of  $\text{Mn}_3(\text{THT})_2$  cannot adsorb Cl atom and the corresponding point cannot be marked in this figure).

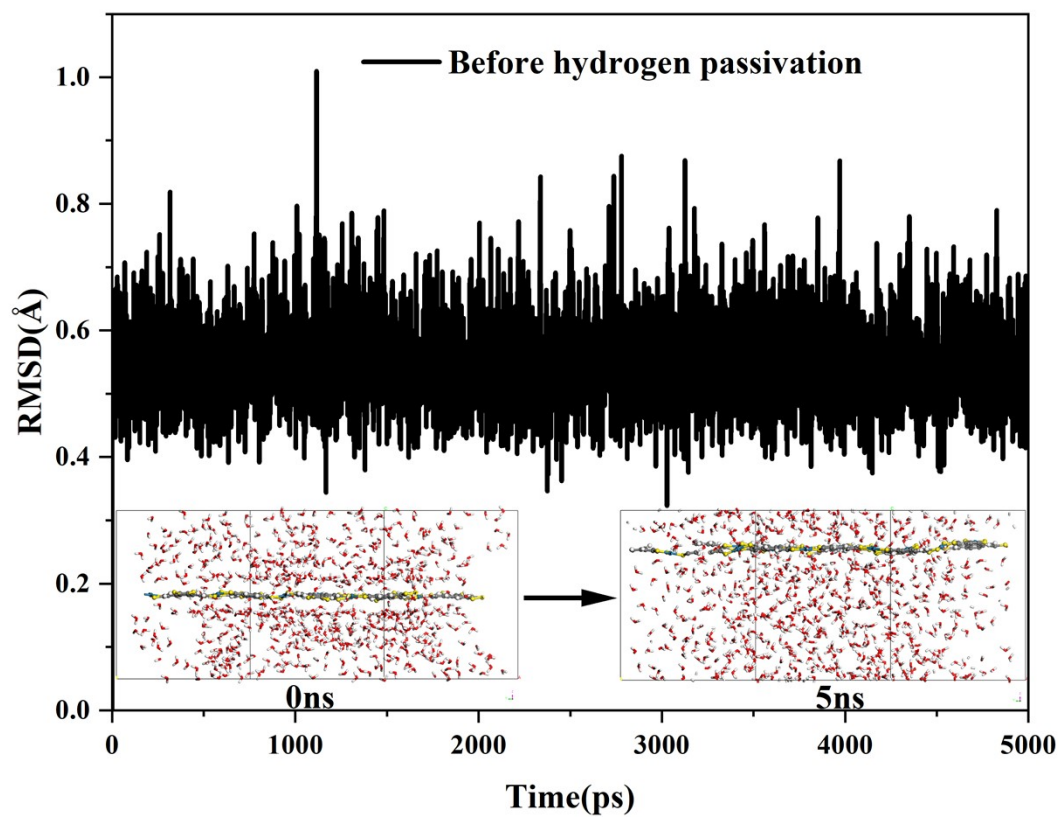


**Figure S3.** Density states of the p orbital of Cl and the d orbital of Re when Cl is adsorbed on the Re site of  $\text{Re}_3(\text{THT})_2$ .

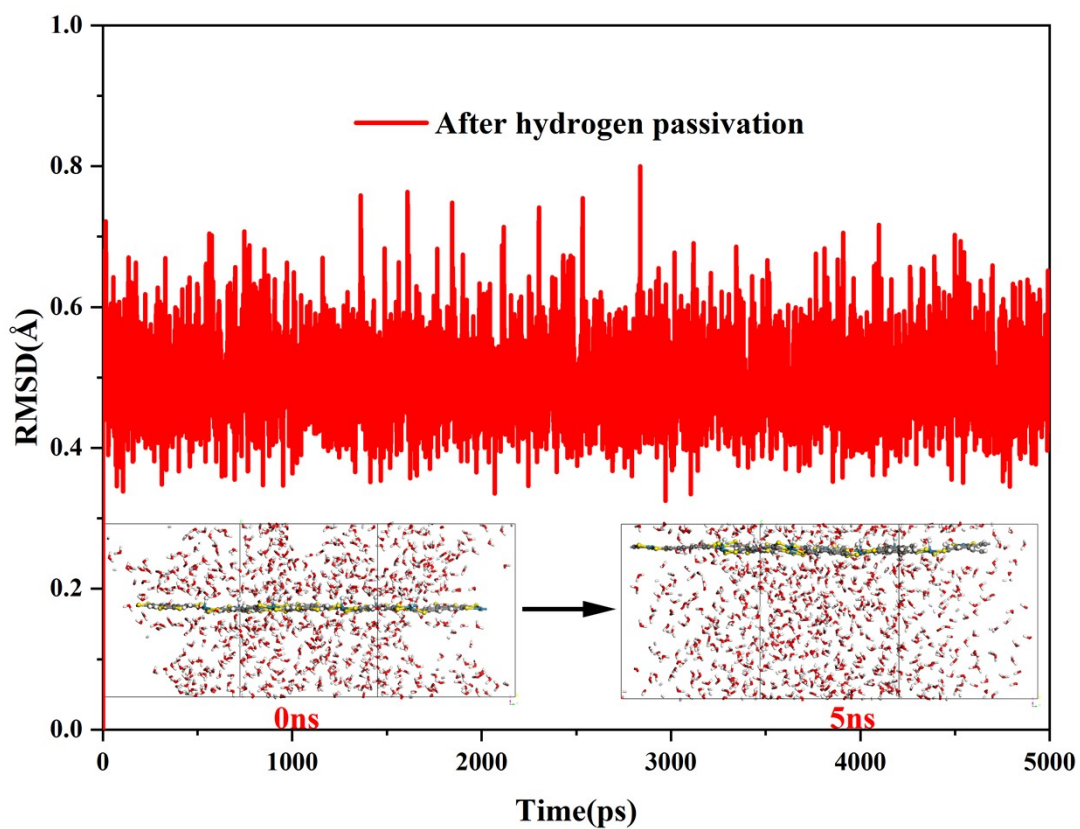


**Figure S4.** Adsorption energy of chlorine on the S site of  $\text{Re}_3(\text{THT})_2$  after H passivation; adsorption energy of chlorine on the metal site of  $\text{Re}_3(\text{THT})_2$  before H passivation.



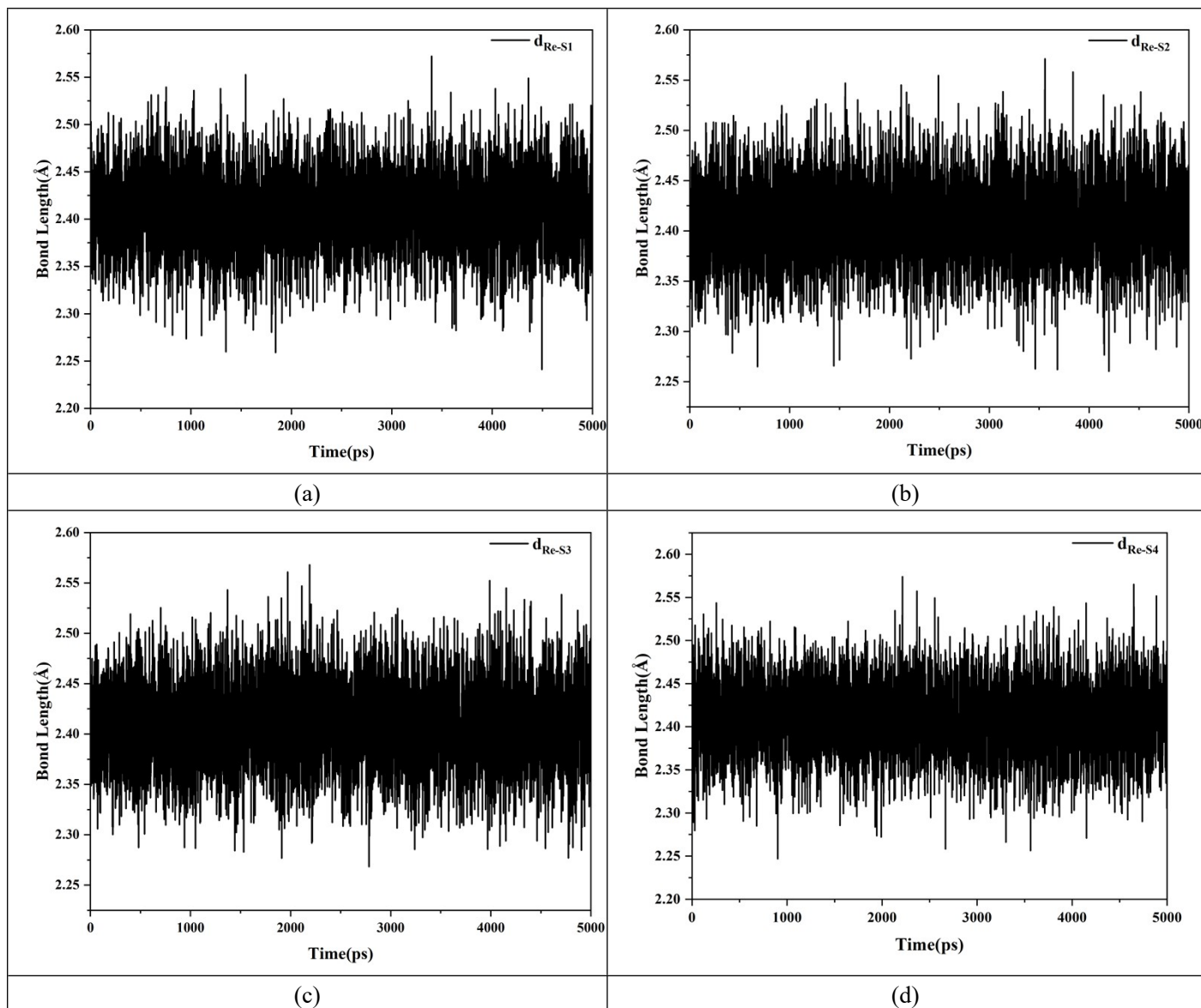


(a)

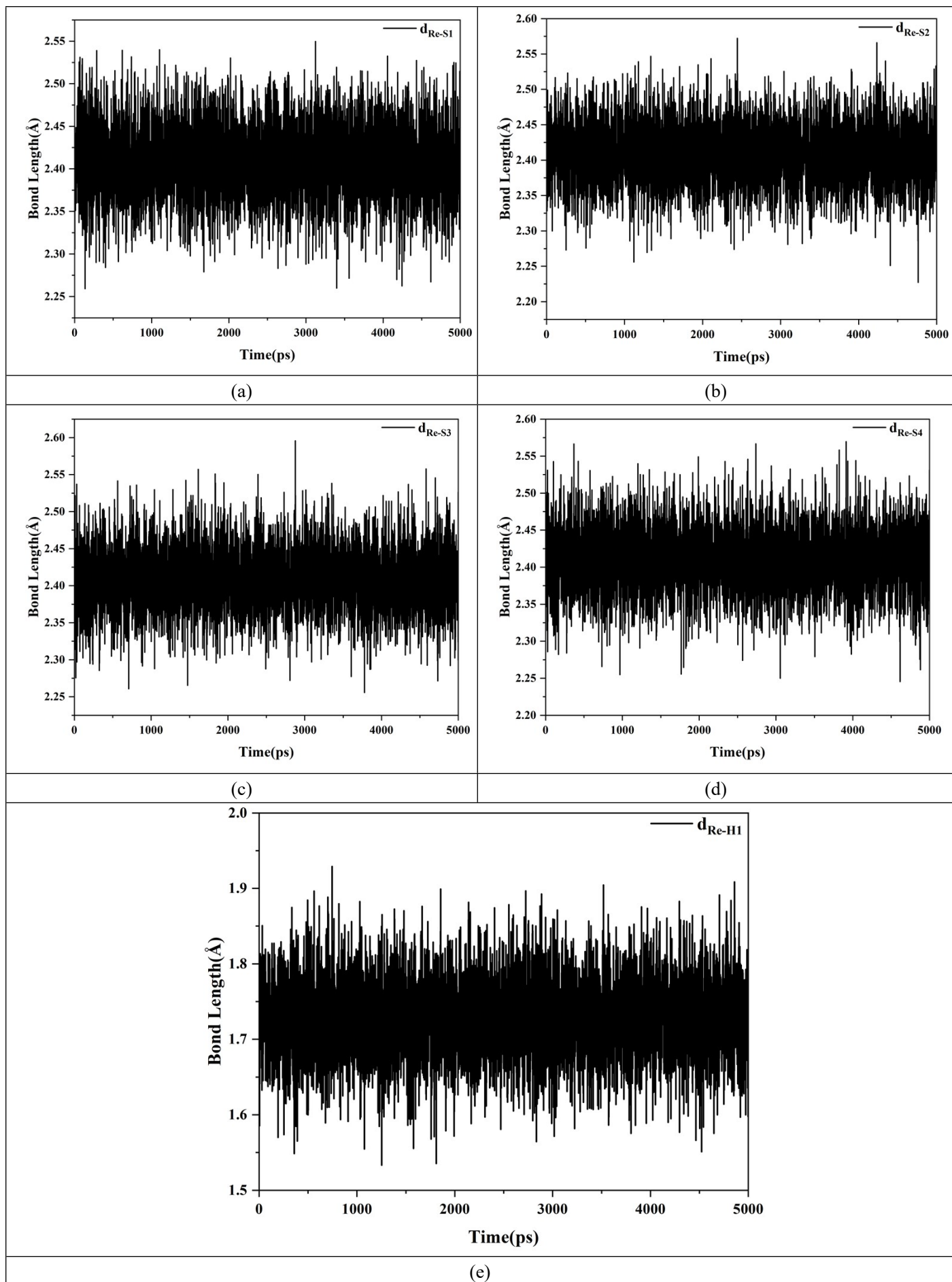


(b)

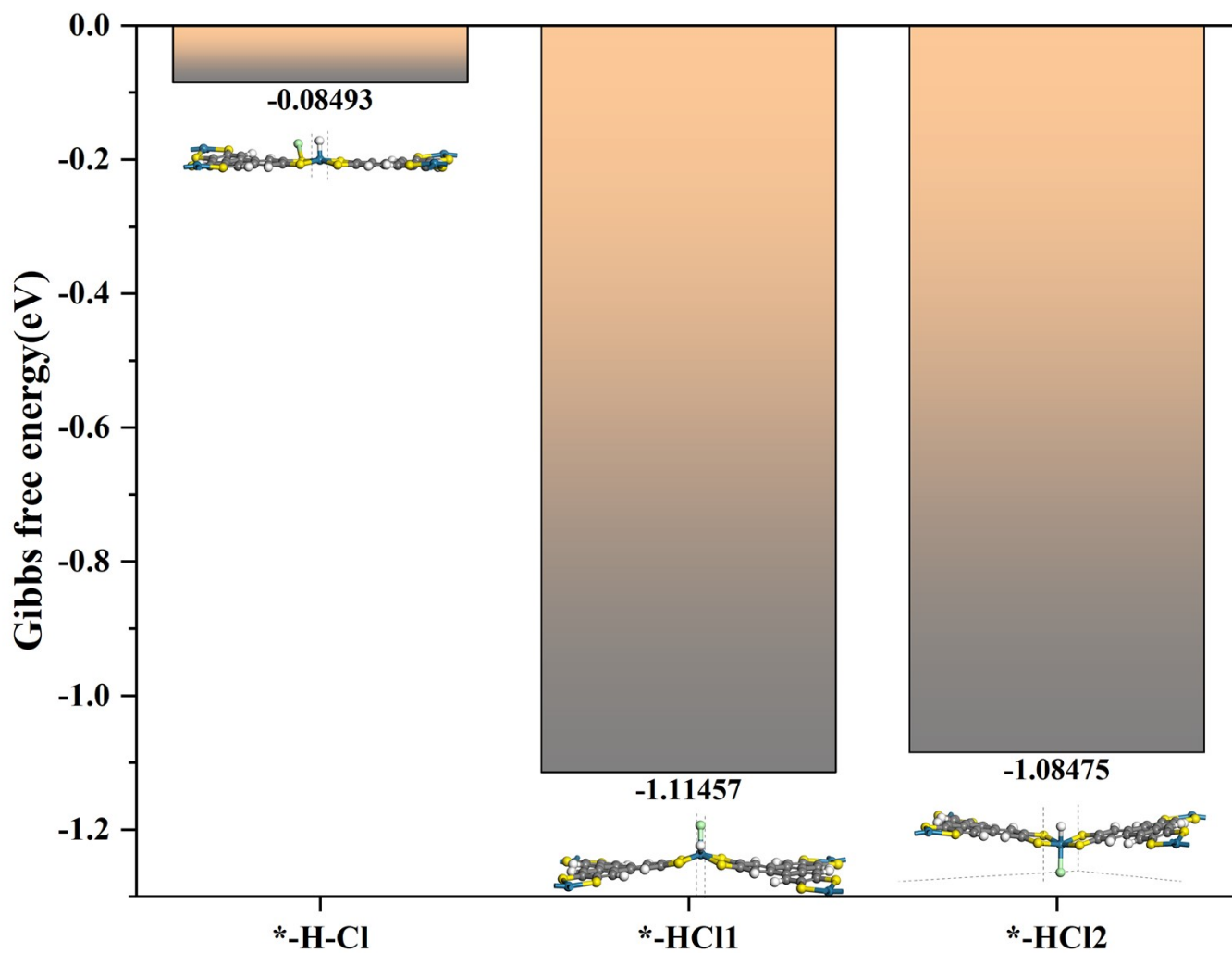
**Figure S5.** RMSD curve obtained by molecular dynamics trajectory analysis of  $\text{Re}_3(\text{THT})_2$  in aqueous solution for 5 ns (a) before hydrogen passivation and (b) after hydrogen passivation.



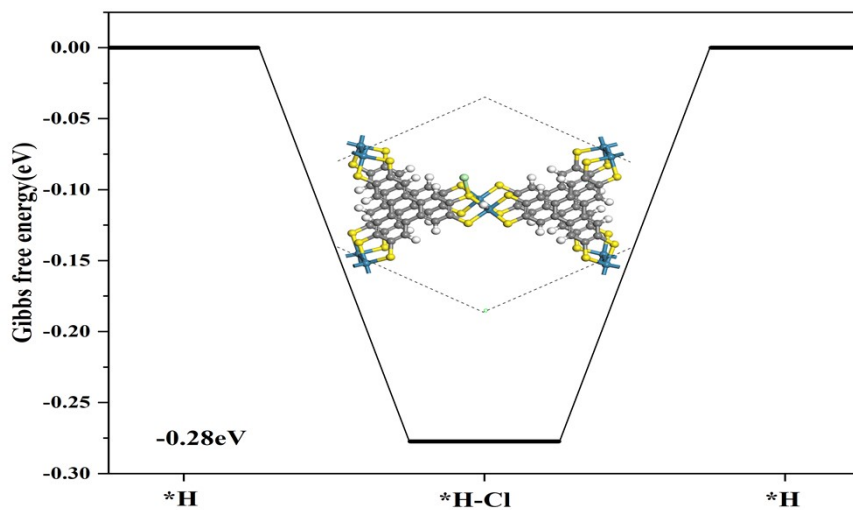
**Figure S6.** Evolution of the bond lengths between Re and S atoms during molecular dynamics simulation of  $\text{Re}_3(\text{THT})_2$  in aqueous solution before hydrogen passivation.



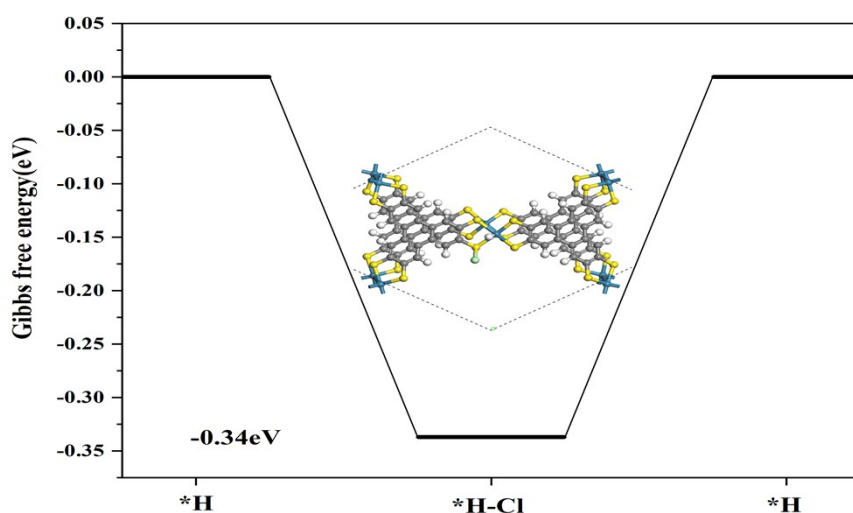
**Figure S7.** Evolution of the bond lengths (a)~(d) between Re and S atoms and (e) between Re and H atoms during molecular dynamics simulation of  $\text{Re}_3(\text{THT})_2$  in aqueous solution after hydrogen passivation.



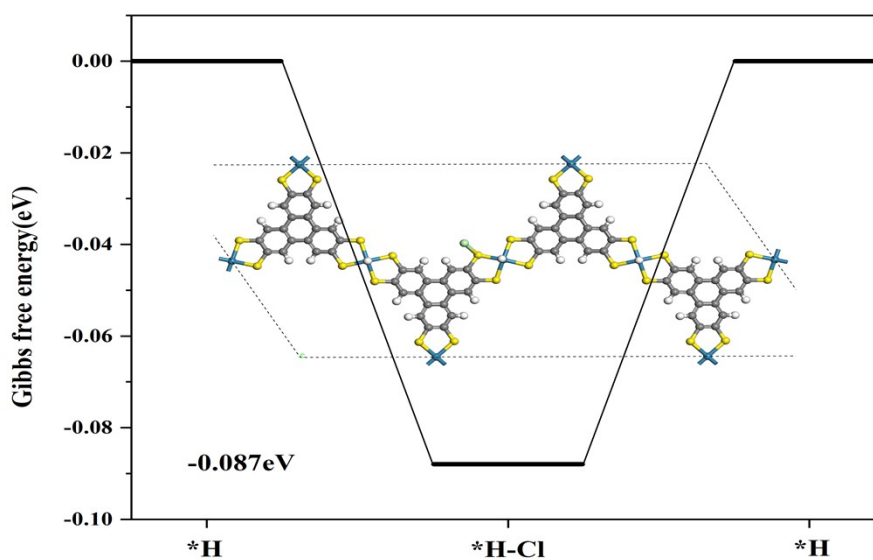
**Figure S8.** The Gibbs free energy change of chlorine evolution reaction on Re metal site and S site. (\*-H-Cl corresponds to Cl adsorbed on the sulfur site; \*-HCl1 corresponds to Cl adsorbed on Re, on the same side of H; \*-HCl2 corresponds to Cl adsorbed on Re, on the opposite side of H)



(a)



(b)



(c)

**Figure S9.** Gibbs free energy change of CER on the double layer  $\text{Re}_3(\text{THT})_2$  after passivation (a) (configuration 1) and (b) (configuration 2); and Gibbs free energy change of CER on the  $2 \times 1 \times 1$   $\text{Re}_3(\text{THT})_2$  after passivation (c).