Supporting Information

Theoretical Insights into Lanthanide Rare Earth Single-Atom Catalysts for Electrochemical CO_2 Reduction

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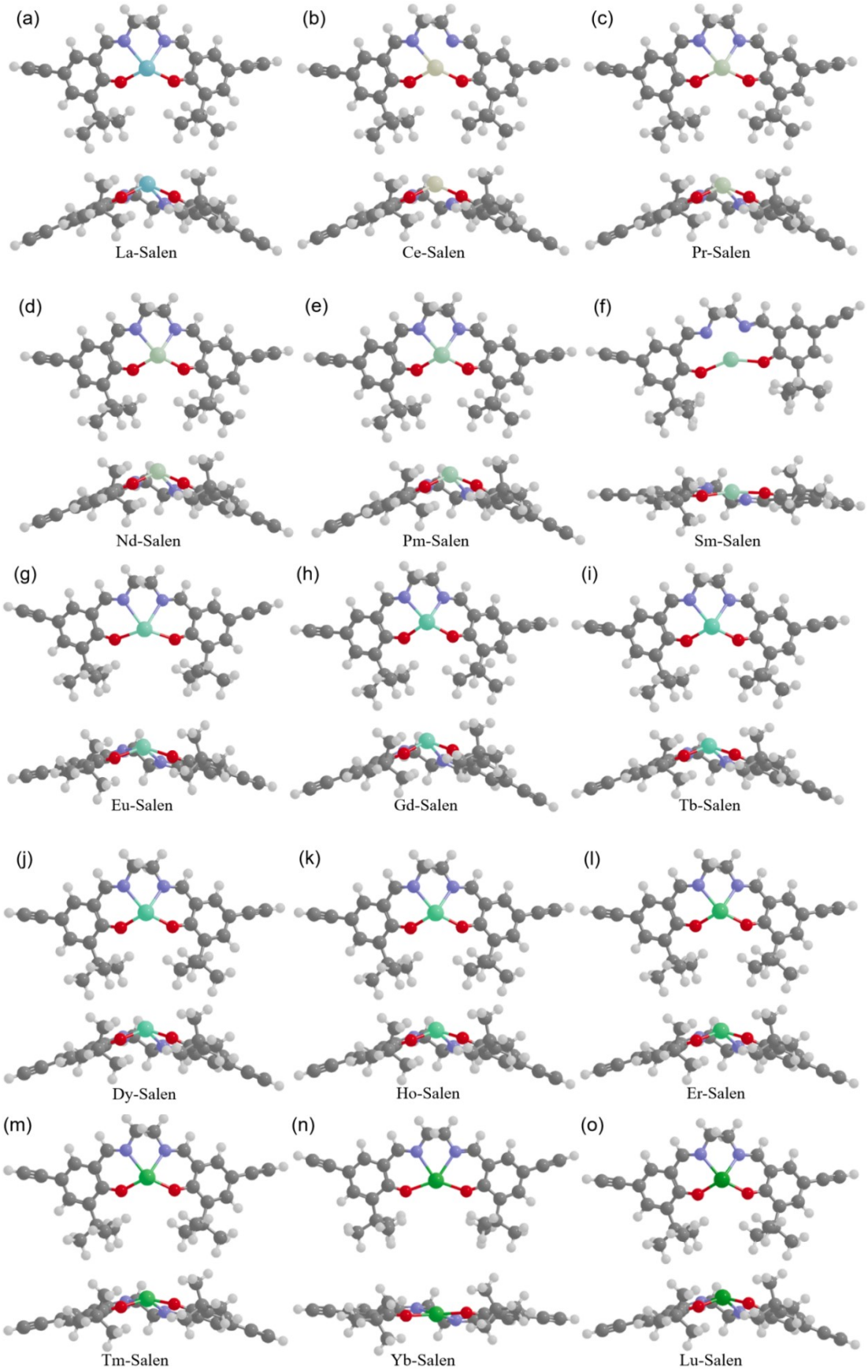

Figure S1. Top and side views of 15 REM-Salen catalyst structures, respectively.

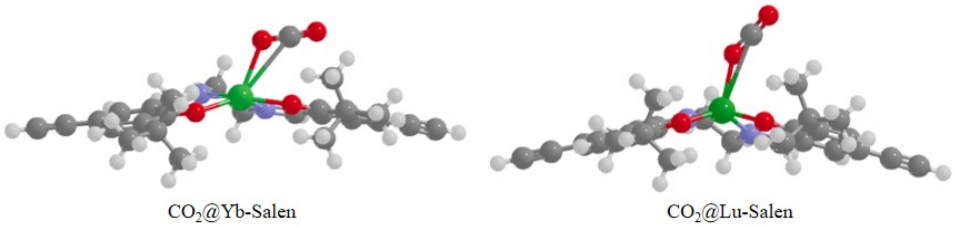

Figure S2. Side-on chemisorption on REM-Salen surfaces.

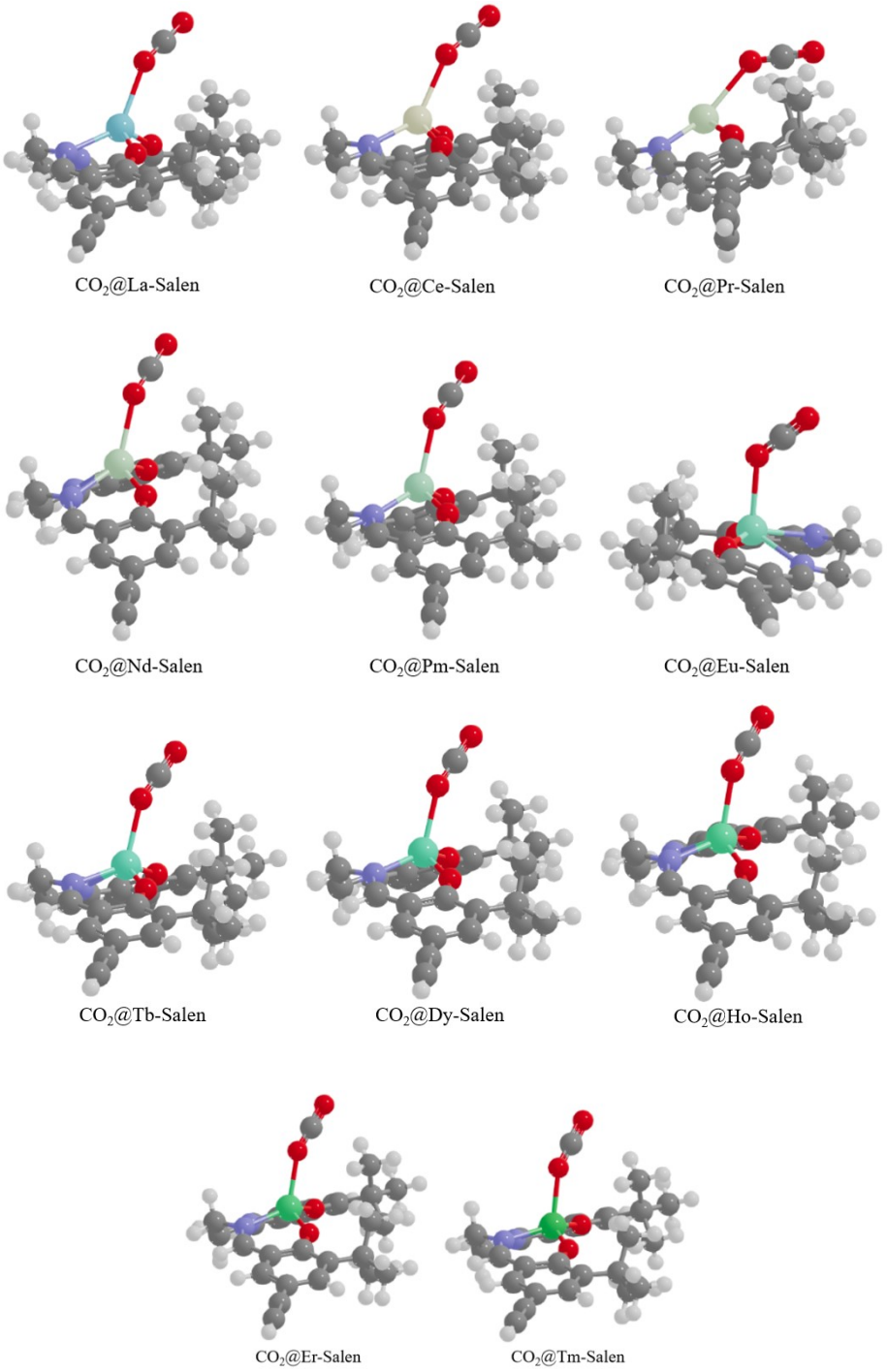

Figure S3. End-on chemisorption on REM-Salen surfaces.

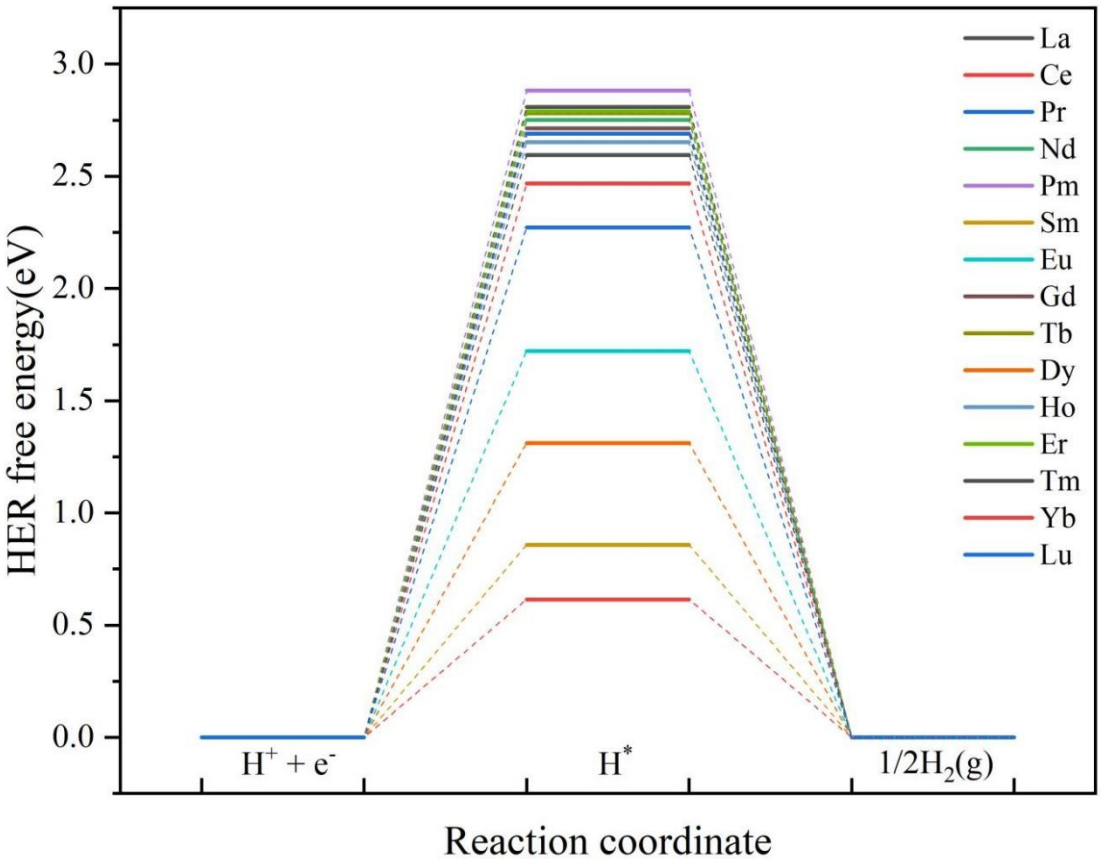

Figure S4. Hydrogen evolution reaction (HER) mechanisms on REM-Salen.

Table S1. Formation energies E_f of REM-Salen.

REM-Salen	**E_f (eV)**
La-Salen	-1.06
Ce-Salen	-1.33
Pr-Salen	-1.85
Nd-Salen	-2.97
Pm-Salen	-3.82
Sm-Salen	-5.10
Eu-Salen	-2.38
Gd-Salen	-1.40
Tb-Salen	-2.08
Dy-Salen	-1.57
Ho-Salen	-3.16
Er-Salen	-3.48
Tm-Salen	-2.22
Yb-Salen	-1.77
Lu-Salen	-2.73

Table S2. The specific parameters including bond lengths of REM-O and REM-C, ∠O-C-O, and adsorption configurations when CO2 adsorbed on the surface of REM-Salen.

Catalyst	**REM-O(Å)**	**REM-C(Å)**	**C-O_1(Å)**	**C-O_2(Å)**	**∠O-C-O(°)**	**Adsorption configuration**
CO_2 molecule	--	--	1.166	1.166	180	--
La-Salen	2.734	--	1.178	1.152	180	End-on
Ce-Salen	2.71	--	1.177	1.153	180	End-on
Pr-Salen	2.666	--	1.177	1.152	180	End-on
Nd-Salen	2.636	--	1.178	1.152	180	End-on
Pm-Salen	2.587	--	1.177	1.152	180	End-on
Sm-Salen	2.271	2.56	1.251	1.195	143.1	Side-on
Eu-Salen	2.688	--	1.171	1.158	180	End-on
Gd-Salen	2.512	--	1.179	1.151	180	End-on
Tb-Salen	2.498	--	1.179	1.15	180	End-on
Dy-Salen	2.47	--	1.179	1.15	180	End-on
Ho-Salen	2.438	--	1.18	1.15	180	End-on
Er-Salen	2.389	--	1.18	1.149	180	End-on
Tm-Salen	2.368	--	1.179	1.149	180	End-on
Yb-Salen	2.555	3.282	1.176	1.156	177	Side-on
Lu-Salen	2.368	3.417	1.181	1.149	178.7	Side-on

Table S3. $U_L(CO_2RR)$ and *COOH adsorption energy by DFT for 15 REM-Salen catalysts.

REM-Salen	**E_{ad}(*COOH)(eV)**	**U_L(V)**
La-Salen	0.39	-2.92
Ce-Salen	-0.18	-2.48
Pr-Salen	-0.23	-2.23
Nd-Salen	-0.36	-2.11
Pm-Salen	-0.33	-2.13
Sm-Salen	-1.92	-0.77
Eu-Salen	-1.02	-1.67
Gd-Salen	0.24	-2.77
Tb-Salen	0.17	-2.73
Dy-Salen	-1.29	-1.27
Ho-Salen	0.12	-2.70
Er-Salen	0.11	-2.68
Tm-Salen	0.03	-2.61
Yb-Salen	-2.07	-0.56
Lu-Salen	-0.34	-2.23

Table S4. CO_2RR Gibbs free energy by DFT for each step of 15 REM-Salen catalysts with unit eV.

	ΔG_1	ΔG_2	ΔG_3
La-Salen	2.92	-1.97	-0.21
Ce-Salen	2.48	-1.54	-0.21
Pr-Salen	2.23	-1.28	-0.22
Nd-Salen	2.11	-1.12	-0.26
Pm-Salen	2.13	-1.04	-0.36
Sm-Salen	0.77	0.17	-0.20
Eu-Salen	1.67	-0.77	-0.16
Gd-Salen	2.77	-1.79	-0.25
Tb-Salen	2.73	-1.78	-0.21
Dy-Salen	1.27	-0.35	-0.19
Ho-Salen	2.70	-1.72	-0.25
Er-Salen	2.68	-1.73	-0.21
Tm-Salen	2.61	-1.67	-0.21
Yb-Salen	0.56	0.25	-0.07
Lu-Salen	2.23	-1.44	-0.06

Table S5. The energy gap (HOMO and LUMO) for 15 REM-Salen catalysts with unit eV.

	HOMO	**LUMO**	**Energy gap**
La-Salen	-5.035	-8.547	3.51
Ce-Salen	-5.088	-8.574	3.49
Pr-Salen	-5.196	-8.612	3.42
Nd-Salen	-5.216	-8.587	3.37
Pm-Salen	-5.622	-8.566	2.94
Sm-Salen	-1.461	-3.981	2.52
Eu-Salen	-1.559	-5.161	3.60
Gd-Salen	-5.236	-8.592	3.36
Tb-Salen	-5.298	-8.658	3.36
Dy-Salen	-5.270	-8.660	3.39
Ho-Salen	-5.226	-8.651	3.42
Er-Salen	-5.230	-8.662	3.43
Tm-Salen	-5.821	-8.688	2.87
Yb-Salen	-1.510	-4.368	2.86
Lu-Salen	-5.311	-8.704	3.39