Supplementary Information

Computational Study of OH, NH_2-Functionalized Iron-Doped Tetraphenylporphyrin as a Photocatalyst for CO_2 Reduction to C_1 Fuels

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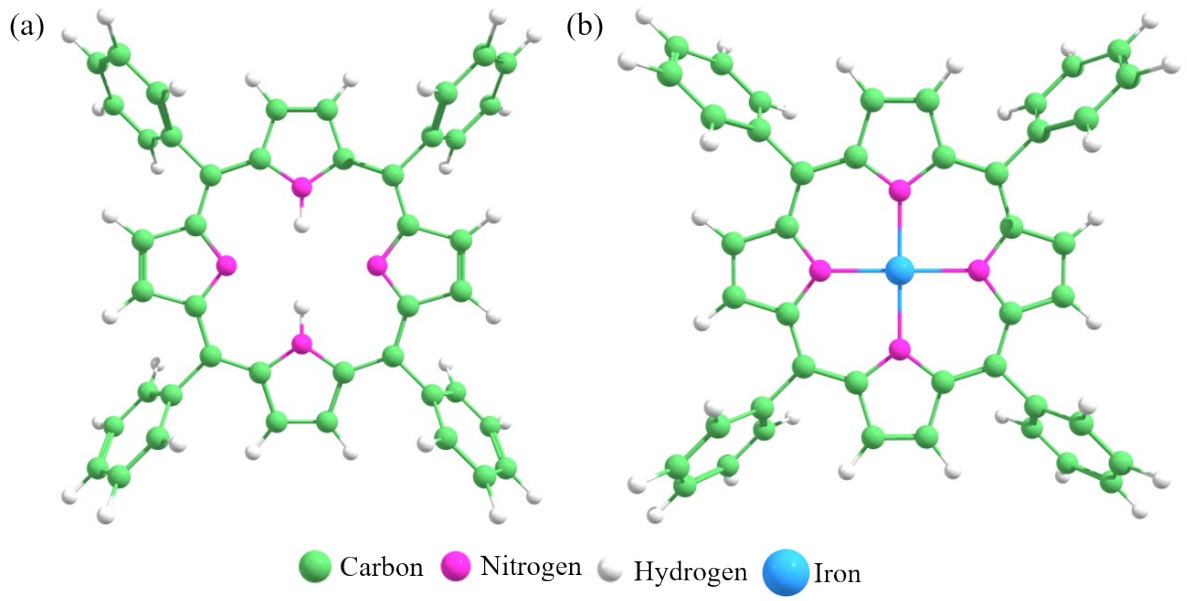

Fig. S1. Optimized geometries of (a) Tetraphenylporphyrin (TPP) and (b) iron-doped tetraphenylporphyrin (Fe-TPP) surfaces. The structures illustrate the atomic arrangements and coordination environments after full geometry optimization. These optimized configurations serve as the basis for analyzing their structural stability, electronic properties, and catalytic reactivity.

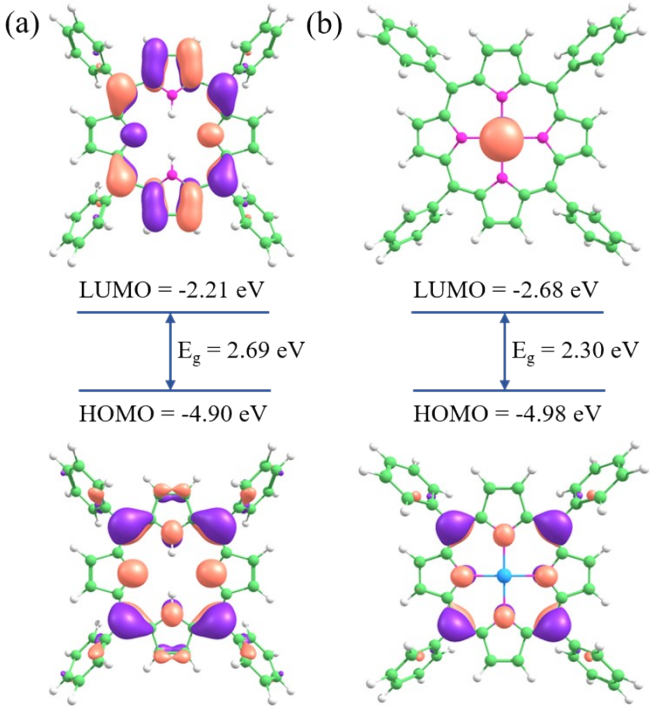

Fig. S2. HOMO-LUMO plots of (a) TPP and (b) Fe-TPP surfaces. The violet and orange regions represent the negative and positive lobes of the molecular orbitals, respectively, illustrating the spatial distribution of electron density in the frontier orbitals.

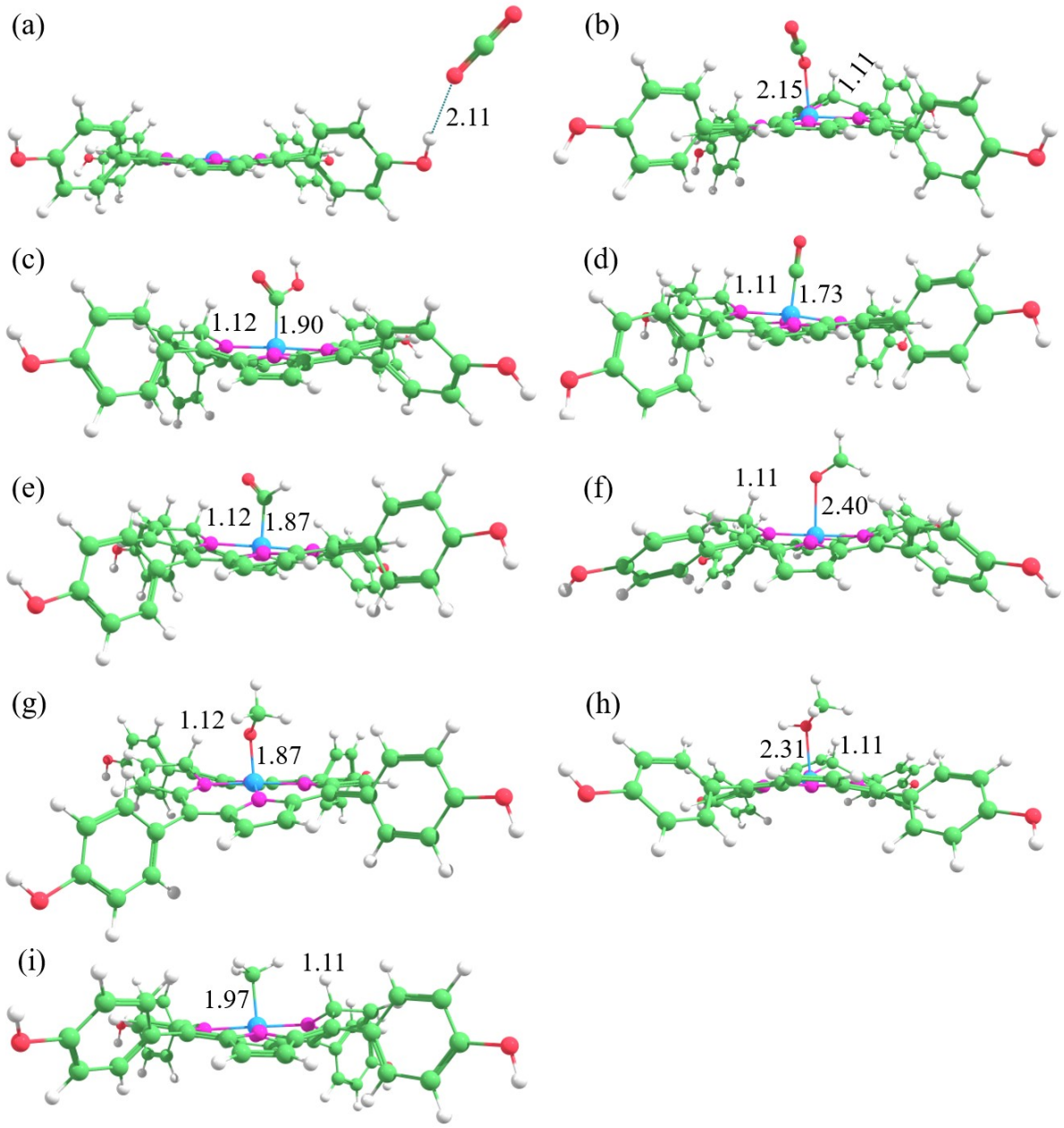

Fig. S3. The optimized geometries of reactants (CO_2 reduction to C_1 products): (a) *+CO_2, (b) *CO_2+H, (c) *COOH+H, (d) *CO+H, (e) *CHO+H, (f) *OCH_2+H, (g) *OCH_3+H, (h) *CH_3OH+H, and (i) *CH_3+H. The * indicates the adsorbed on the Fe-OHTPP surface. The unit of bond lengths are indicated in Å. The green, red, pink, white, and blue represents the carbon, oxygen, nitrogen, hydrogen atoms, and iron transition metal.

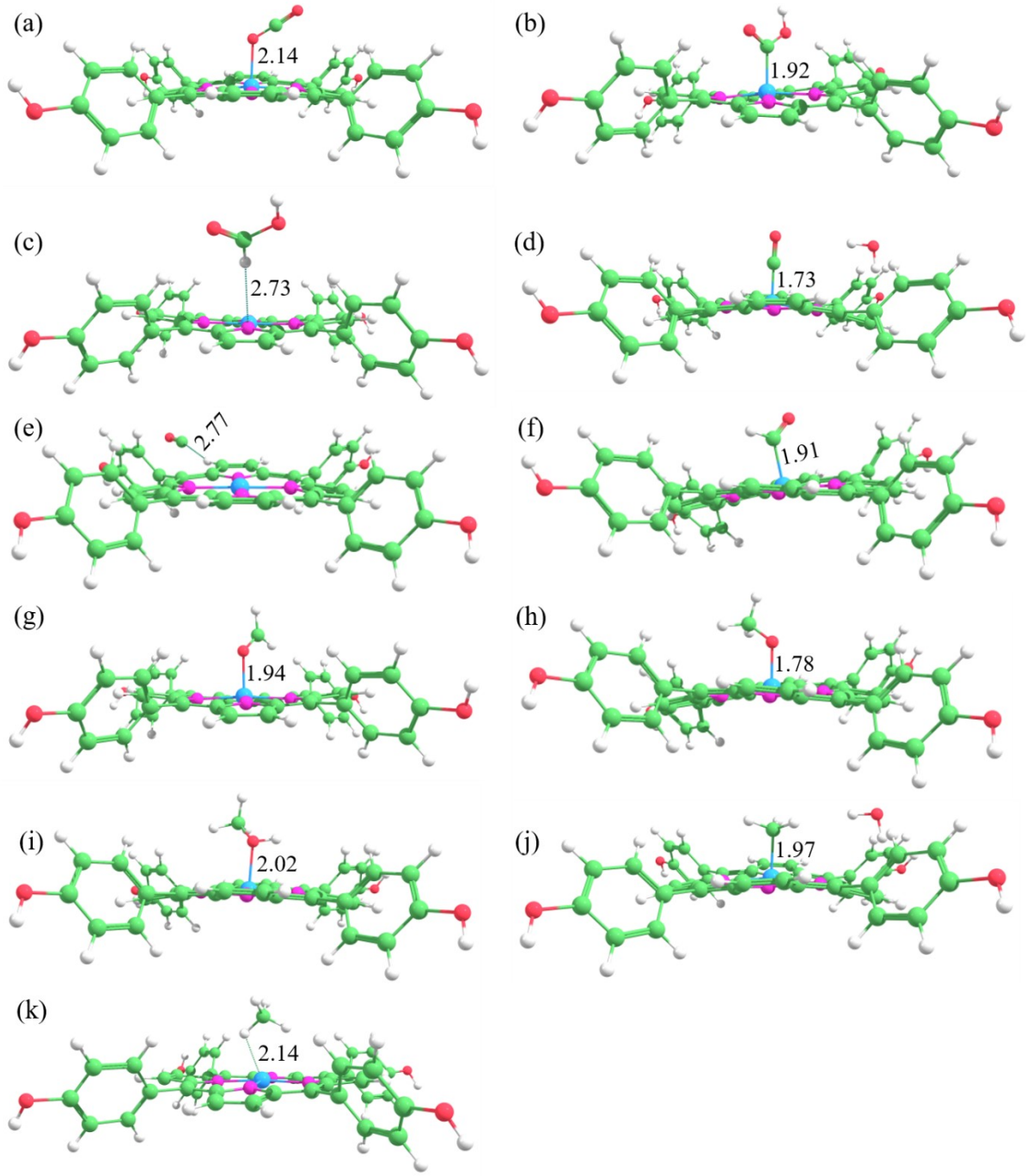

Fig. S4. The optimized geometries of products (CO_2 reduction to C_1 products): (a) *CO_2, (b) *COOH, (c) *+HCOOH, (d) *CO+H_2O, (e) *+CO, (f) *CHO, (g) *OCH_2, (h) *OCH_3 (i) *CH_3OH, (j) *CH_3+H_2O, and (k) *+CH_4. The * indicates the adsorbed on the Fe-OHTPP surface. The unit of bond lengths are indicated in Å. The green, red, pink, white, and blue represents the carbon, oxygen, nitrogen, hydrogen atoms, and iron transition metal.

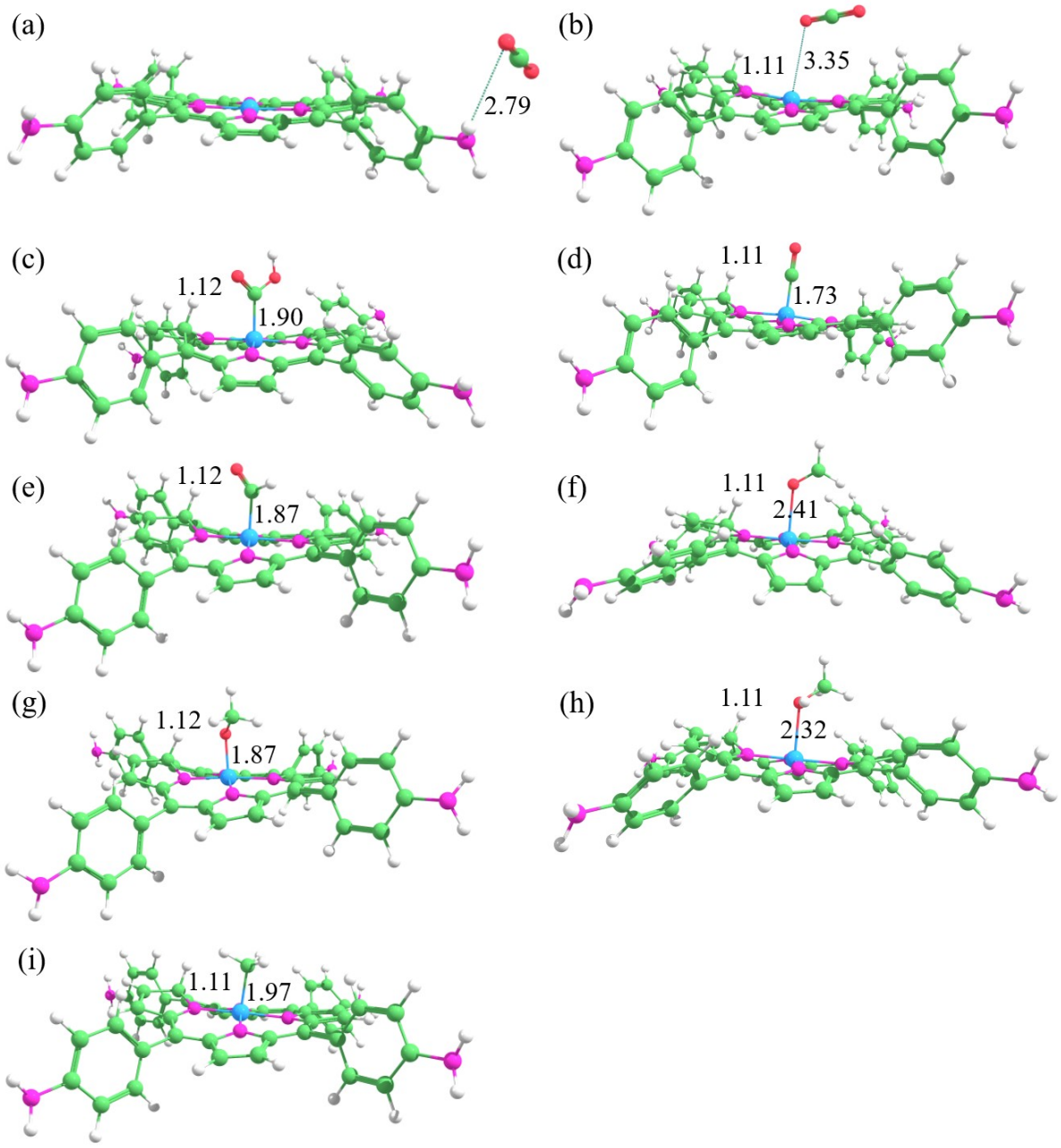

Fig. S5. The optimized geometries of reactants (CO_2 reduction to C_1 products): (a) *+CO_2, (b) *CO_2+H, (c) *COOH+H, (d) *CO+H, (e) *CHO+H, (f) *OCH_2+H, (g) *OCH_3+H, (h) *CH_3OH+H, and (i) *CH_3+H. The * indicates the adsorbed on the Fe-NH_2TPP surface. The unit of bond lengths are indicated in Å. The green, red, pink, white, and blue represents the carbon, oxygen, nitrogen, hydrogen atoms, and iron transition metal.

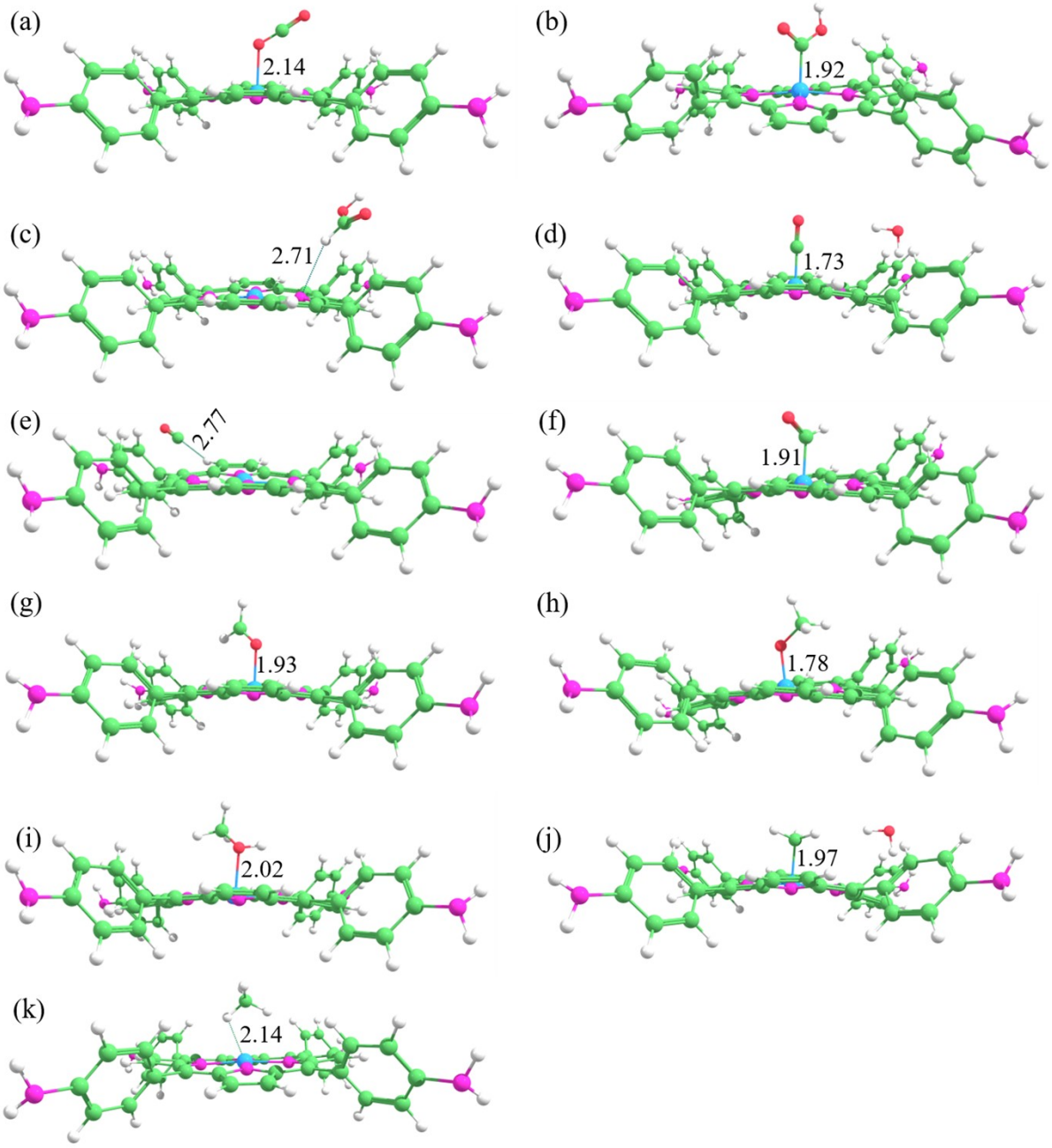

Fig. S6. The optimized geometries of products (CO_2 reduction to C_1 products): (a) *CO_2, (b) *COOH, (c) *+HCOOH, (d) *CO+H_2O, (e) *+CO, (f) *CHO, (g) *OCH_2, (h) *OCH_3 (i) *CH_3OH, (j) *CH_3+H_2O, and (k) *+CH_4. The * indicates the adsorbed on the Fe-NH_2TPP surface. The unit of bond lengths are indicated in Å. The green, red, pink, white, and blue represents the carbon, oxygen, nitrogen, hydrogen atoms, and iron transition metal.

Table S1. Calculated electronic parameters of the investigated systems, including the HOMO-LUMO energy gap (E_{H-L} gap), ionization potential (IP), electron affinity (EA), and chemical hardness (η), presented in electron volts (eV).

Structure	**HOMO**	**LUMO**	**E_{H-L} gap**	**IP**	**EA**	**η**
TPP	-4.90	-2.21	2.69	4.90	2.21	1.35
Fe-TPP	-4.98	-2.68	2.30	4.98	2.68	1.15
OHTPP	-4.74	-2.12	2.62	4.74	2.12	1.31
Fe-OHTPP	-4.82	-2.59	2.23	4.82	2.59	1.12
NH_2TPP	-4.41	-1.86	2.55	4.41	1.86	1.28
Fe-NH_2TPP	-4.50	-2.35	2.15	4.50	2.35	1.08