Supplementary Information

Design of Iron Atom Modified Thiophene-Linked Metalloporphyrin 2D Conjugated Microporous Polymer as CO$_2$ Reduction Photocatalyst

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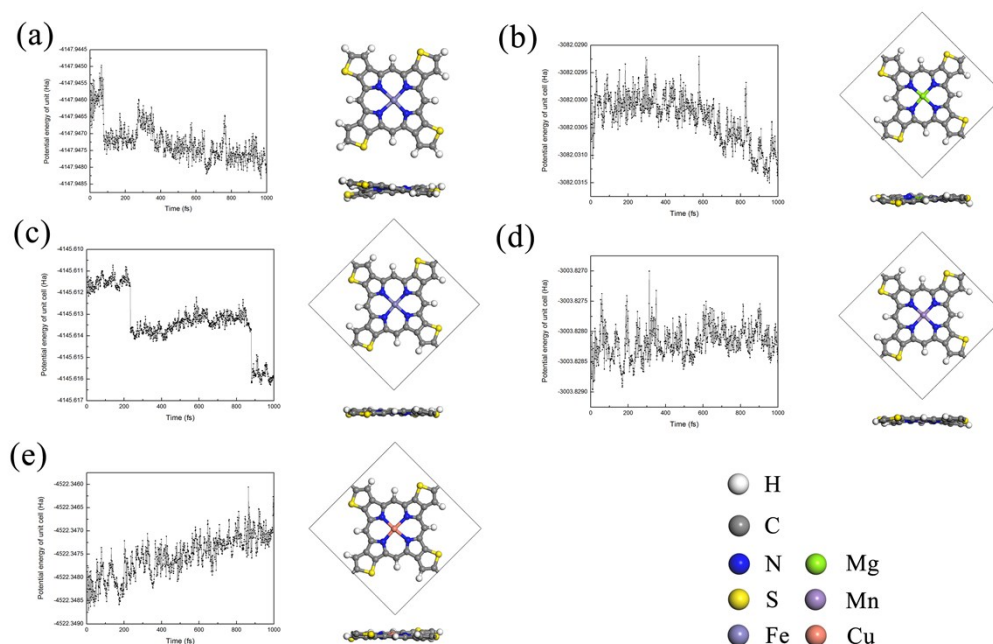
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Fig. S1 Diagram and structures of molecular dynamic (MD) calculations at 300 K with 1 ps: (a) Fe modified thiopene-linked porphin (TP) unit; (b) Mg modified thiopene-linked metalloporphyrin (TMP) unit cell; (c) Fe-TMP unit cell; (d) Mn-TMP unit cell; (e) Cu-TMP unit cell.
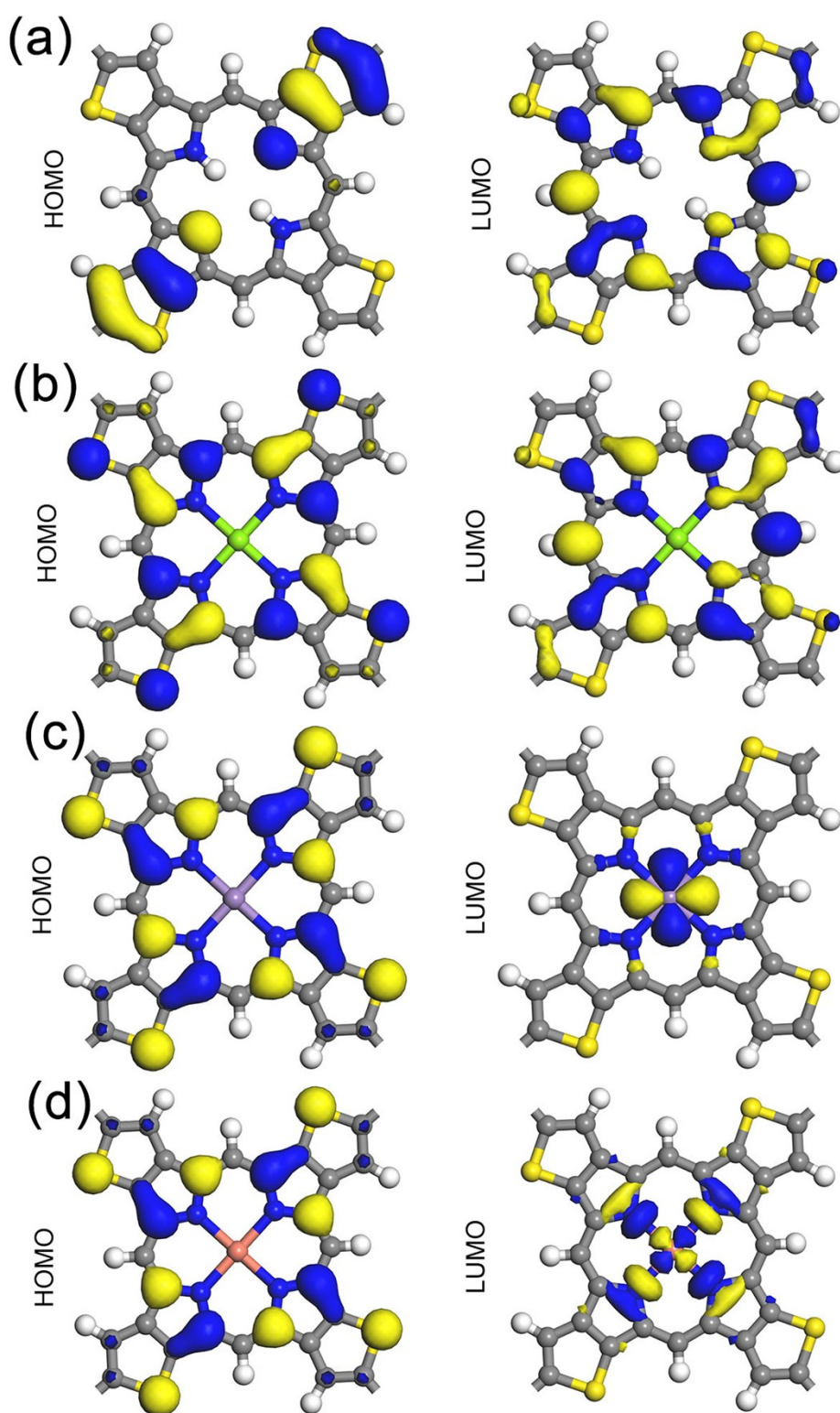
Fig. S2 The HOMO and LUMO of pure CMP (a), Mg-CMP (b), Mn-CMP (c) and Cu-CMP (d) with an isosurface of 0.03 e Å^{-3}.
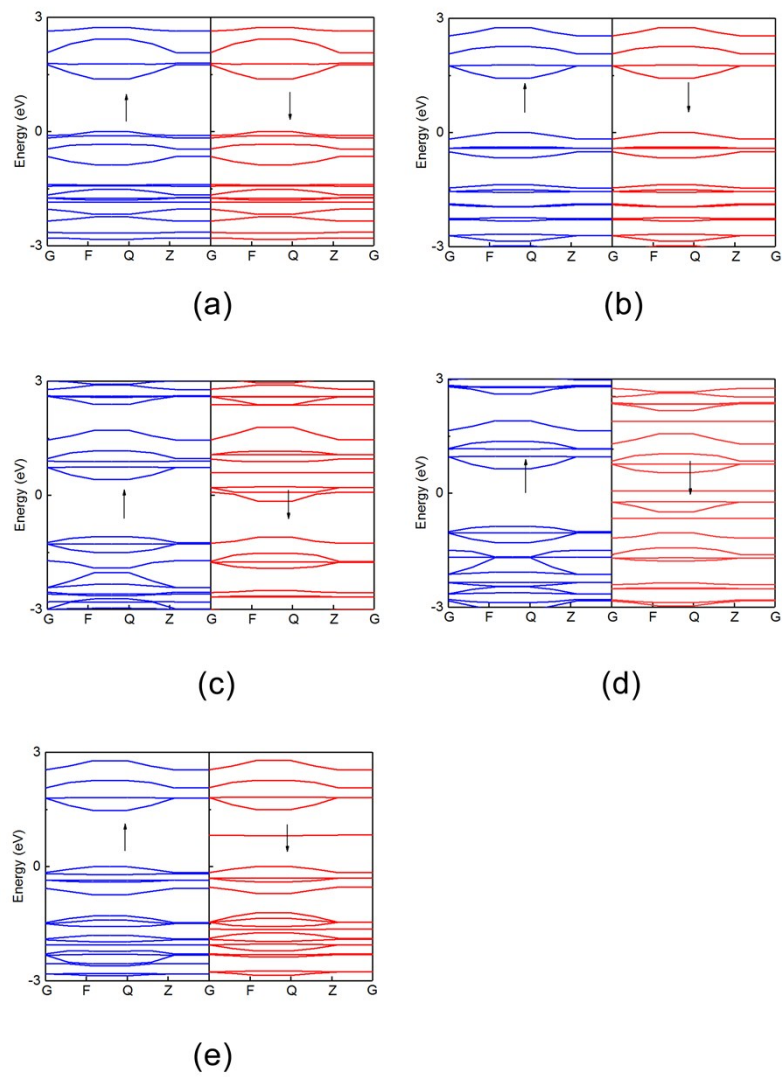
Fig. S3 The calculated band structures of TP or various metal modified TMP unit cell: (a) pure TP; (b) Mg-TMP; (c) Mn-TMP; (d) Fe-TMP; (e) Cu-TMP. The fermi level was set to zero.

Table S1. Fermi level, valance band edge, conduction band edge position and band gap of various 2D monolayer slabs

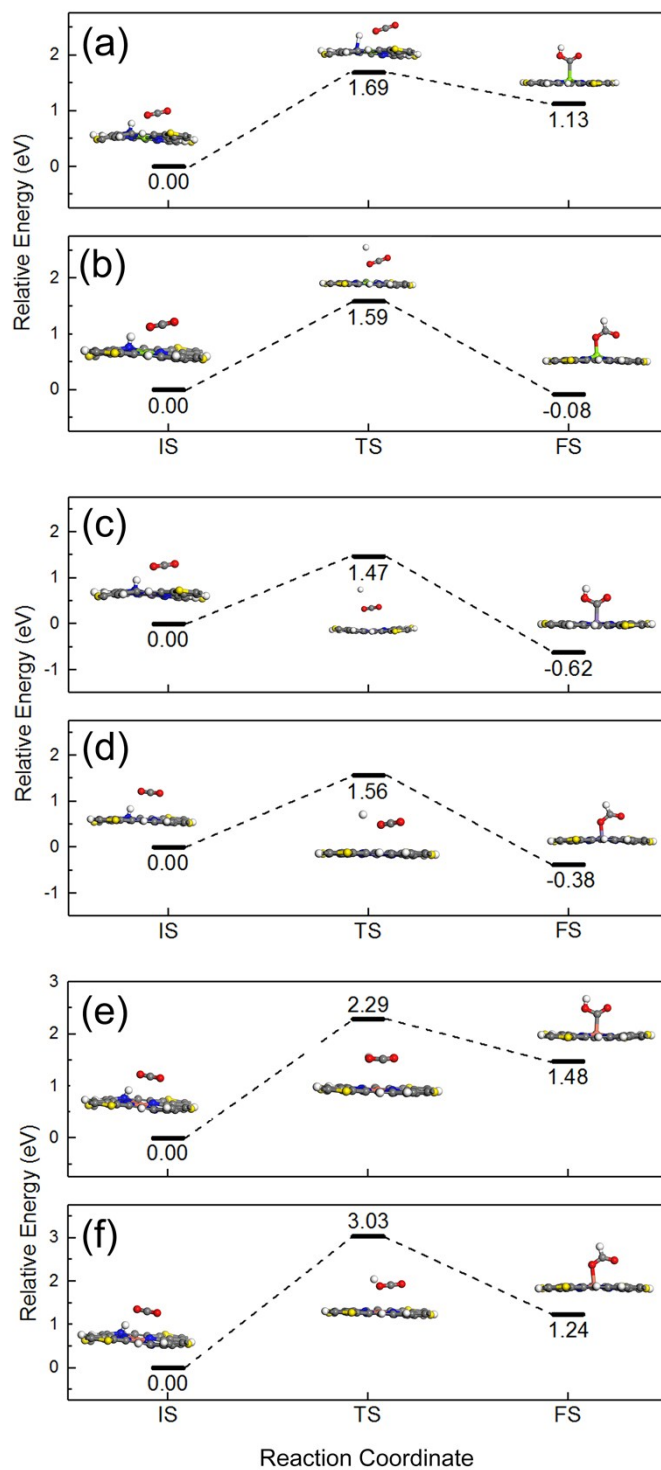|	Fermi Level Position (eV)	Valence Band Edge Position (eV)	Conduction Band Edge Position (eV)	Band Gap (eV)
Pure	-4.34	-4.95	-3.72	1.22
Mg-CMP	-4.04	-4.99	-3.65	1.34
Mn-CMP	-4.07	—	—	—
Fe-CMP	-4.30	—	—	—
Cu-CMP	-4.50	-5.02	-4.25	0.77

Fig. S4 The optimized structures of the initial (IS), transition (TS), final (FS) states of the first reduction step and the corresponding activation barriers: CO_2* + H* →

COOH* catalysised by Mg-CMP (a), Mn-CMP (c), and Cu-CMP (e); CO_2* + H* → HCOO* catalysised by Mg-CMP (b), Mn-CMP (d), and Cu-CMP (f).