Supporting Information

Iron/Cobalt/Nickel Regulation for Efficient Photocatalytic Carbon Dioxide Reduction over Phthalocyanine Covalent Organic Frameworks

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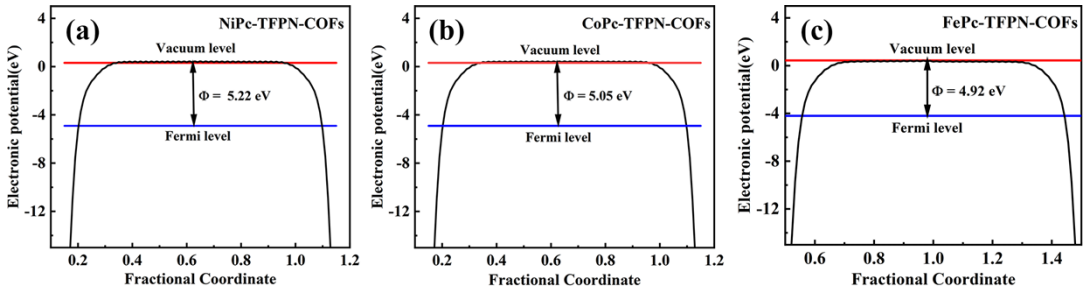

Figure S1: The work function of MPc-TFPN-COFs (a) NiPc-TFPN-COFs, (b) CoPc-TFPN-COFs, (c) FePc-TFPN-COFs

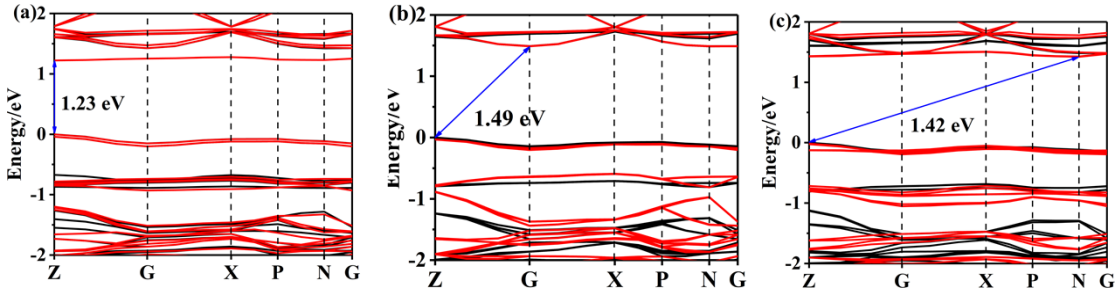

Figure S2: Band structure NiPC-TFPN-CoFs (a), CoPC-TFPN-CoFs (b), FePC-TFPN-CoFs (c).

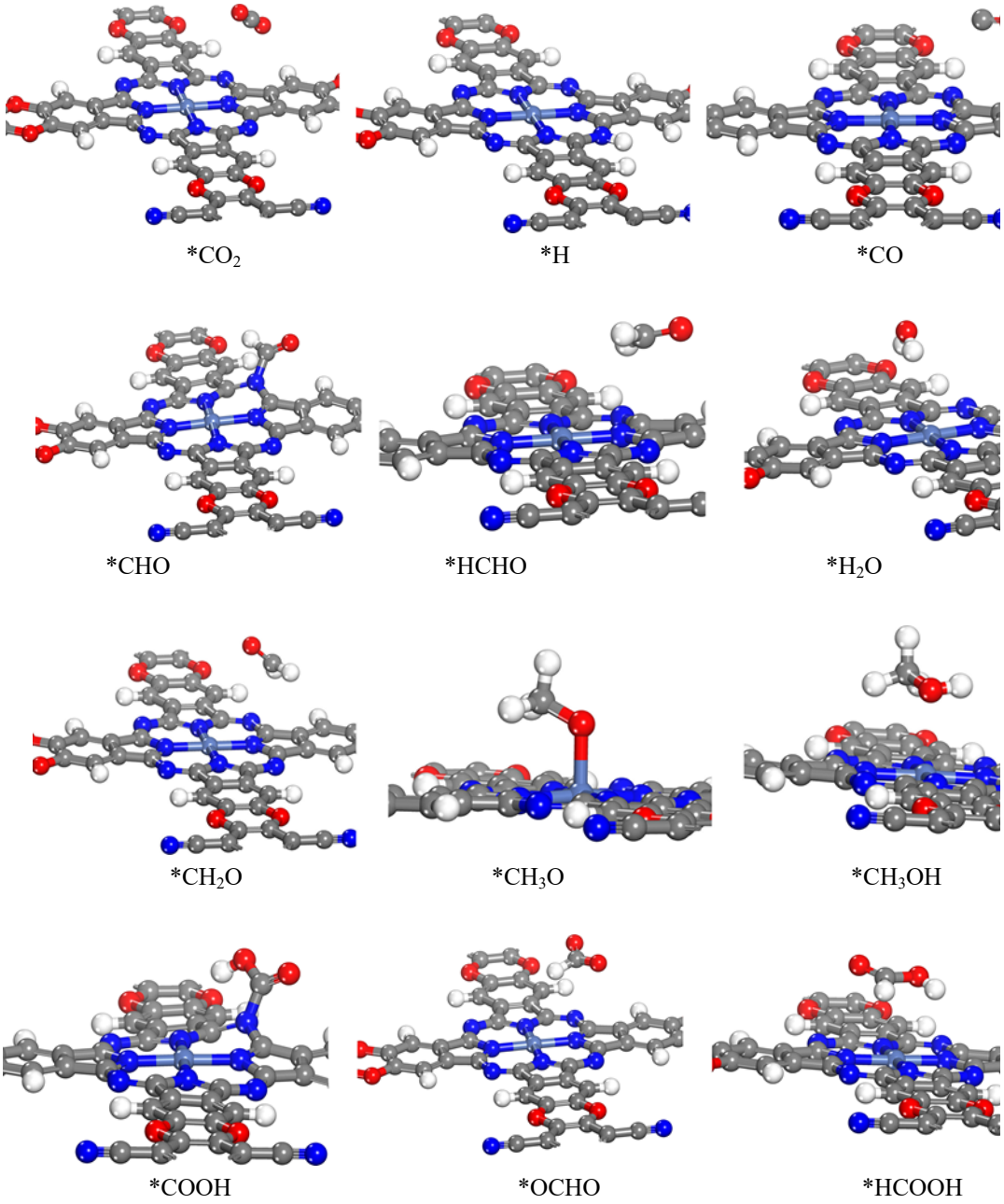

Figure S3: Stable adsorption configurations of adsorbents on NiPc-TFPN-CoFs

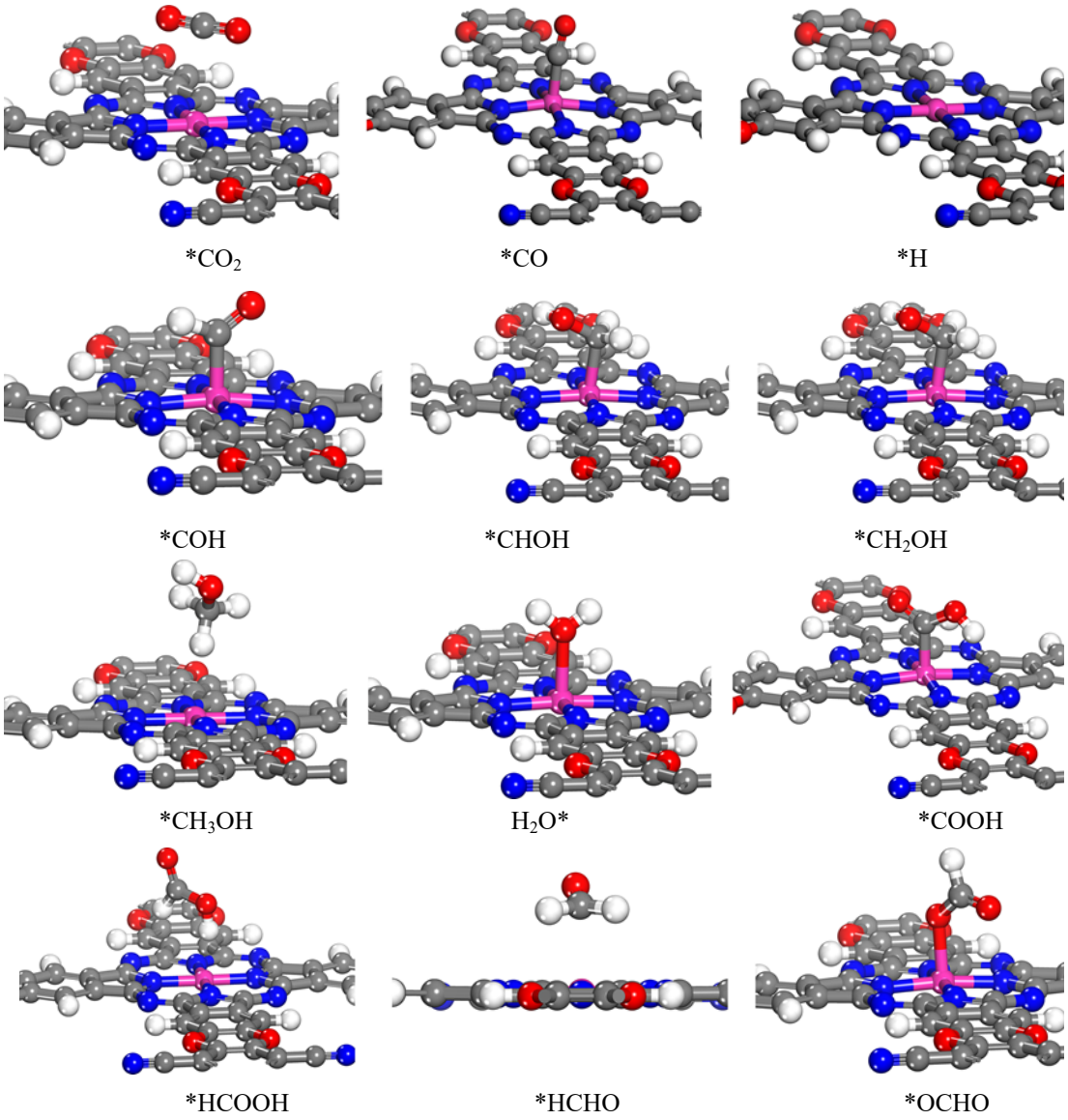

Figure S4: Stable adsorption configurations of adsorbents on CoPc-TFPN-COFs

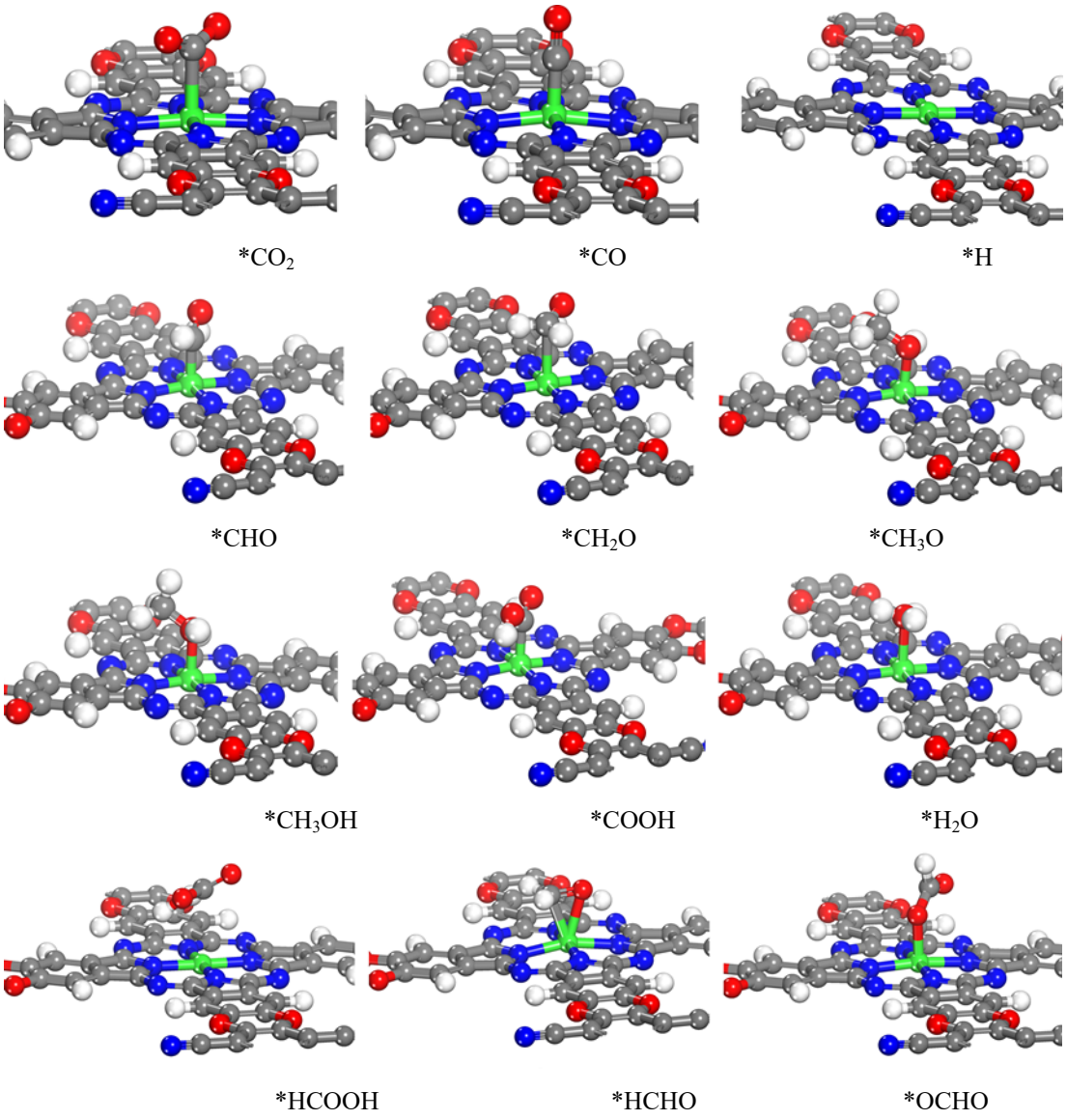

Figure S5: Stable adsorption configurations of adsorbents on FePc-TFPN-COFs

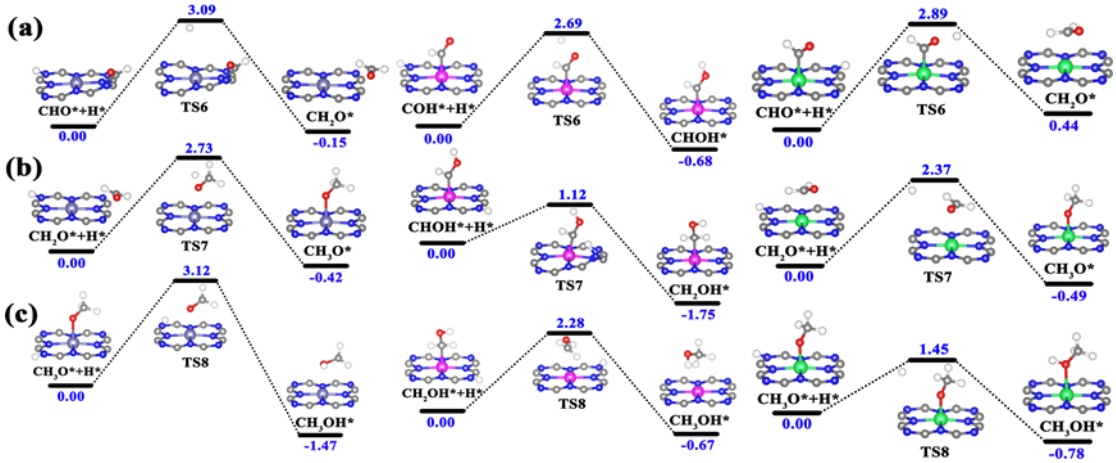

Figure S6: The energy barrier of CO_2 reduction reaction to CH_3OH catalyzed by (a) NiPc-TFPN-COFs, (b) CoPc-TFPN-COFs and (c) FePc-TFPN-COFs.

M	adsorbates	E_{ads}	d(M-CO_2)
Ni	*CO_2	-0.67	3.02
	*COOH	-1.55	1.42
	*OCHO	-2.12	2.51
	*HCOOH	-0.51	3.06
	*CO	-0.48	3.16
	*CHO	-1.85	1.40
	*COH	-1.39	1.53
	*CH_2O	-0.50	2.68
	*CH_3O	-1.12	2.06
	*CHOH	-2.17	1.33
	*CH_2OH	-1.72	1.49
	*H	-1.33	1.02
	*H_2O	-1.54	2.64
	*CH_3OH	-1.63	2.77
	*HCHO	-0.50	2.75
Co	*CO_2	-0.76	3.11
	*COOH	-3.97	1.90
	*OCHO	-2.21	1.74
	*HCOOH	-0.69	3.52
	*CO	-0.67	1.99
	*CHO	-2.26	1.87
	*COH	-2.26	1.84
	*CH_2O	-0.65	2.48
	*CH_3O	-1.61	1.96
	*CHOH	-1.84	1.80
	*CH_2OH	-2.21	1.20
	*H	-0.11	1.02
	*H_2O	-0.42	3.12
	*CH_3OH	-0.56	3.19
	*HCHO	-0.64	2.46
Fe	*CO_2	-0.77	2.11
	*COOH	-3.14	1.95
	*OCHO	-2.97	1.91
	*HCOOH	-0.58	3.04
	*CO	-2.84	1.70
	*CHO	-3.09	1.87
	*COH	-3.06	1.77
	*CH_2O	-0.67	2.43
	*CH_3O	-2.56	1.86
	*CHOH	-3.38	1.75
	*CH_2OH	-2.86	2.00
	*H	-1.15	1.02
	*H_2O	-0.92	2.30
	*CH_3OH	-0.48	3.04
	*HCHO	-0.62	2.08

Table S1. The adsorption energy on the surface of MPc-TFPN-COFs and the distance of adsorbates to the surface.

Elementary steps	TS	$E_{(b)}$NiPc-TFPN-COFs	$E_{(b)}$CoPc-TFPN-COFs	$E_{(b)}$FePc-TFPN-COFs
$*CO_2 + *H \rightarrow *COOH$	TS1-a	2.82	2.42	1.33
$*CO_2 + *H \rightarrow *OCHO$	TS1-b	2.95	2.81	1.76

Table 2 Energies of the transition states of the first protonation reaction of CRR on the surface of MPc-TFPN-COFs (eV). $E_{(b)}$ is the energy barrier of the reaction.

Elementary steps	TS	$E_{(b)}$NiPc-TFPN-COFs	$E_{(b)}$CoPc-TFPN-COFs	$E_{(b)}$FePc-TFPN-COFs
$*CO + *H \rightarrow *CHO$	TS3-a	1.56	2.86	1.77
$*CO + *H \rightarrow *COH$	TS3-b	2.95	1.80	3.08

Table 3 Energies of the transition states of the third protonation reaction of CRR on the surface of MPc-TFPN-COFs (eV). $E_{(b)}$ is the energy barrier of the reaction.