Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information of "Cobalt-porphine Catalyzed CO_2 Electroreduction: A Novel Protonation Mechanism"

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Table S1. The free energy change (ΔG) of proposed steps from CO_2 to CO, and that of the formation of CoP-proton adduct and CoP-water adduct, each constituting part of ΔG is listed. $\Delta G = \Delta E - T \cdot \Delta S + \Delta ZPVE$, in which ΔE is the change of total energy, ΔS is the change of (vibrational) entropy, T is temperature (298 K), $\Delta ZPVE$ is the change of zero point vibrational energy. All energy data are in eV. Required reduction potentials of potential dependent steps are given in the parenthesis (V vs NHE).

Step	ΔE	$-T \cdot \Delta S$	$\Delta ZPVE$	ΔG
$CoP + e^- \rightarrow CoP^-$	-3.07	0.005	-0.06	-3.13 (-1.15)
$CoP^- + e^- \rightarrow CoP^{2-}$	-2.28	-0.02	-0.17	-2.47 (-1.81)
$CoP + H^+ \rightarrow [CoP \cdot H^+]$	-0.82	0.05	0.36	-0.41
$[CoP \cdot H^+] + e^- \rightarrow [CoP \cdot H]$	-2.92	-0.07	-0.06	-3.05 (-1.23)
$[CoP \cdot H] + e^- \rightarrow [CoP \cdot H]^-$	-3.32	-0.04	-0.03	-3.39 (-0.89)
$[CoP \cdot H]^- + CO_2 \rightarrow [CoP \cdot COOH]^-$	-0.95	0.38	0.09	-0.48
$[CoP \cdot COOH]^- + H^+ \rightarrow [CoP \cdot CO] + H_2O$	-0.36	-0.62	0.04	-0.94
$CoP + H_2O \rightarrow [CoP \cdot H_2O]$	-0.78	0.36	0.10	-0.32
$[CoP \cdot 4H_2O] \rightarrow CoP + 4H_2O$	-0.04	-0.49	-0.06	-0.59

Table S2. The free energy change (ΔG) of proposed steps from CO to hydrocarbons, each constituting part of ΔG is listed. $\Delta G = \Delta E - T \cdot \Delta S + \Delta ZPVE$, in which ΔE is the change of total energy, ΔS is the change of (vibrational) entropy, T is temperature (298 K), $\Delta ZPVE$ is the change of zero point vibrational energy. All energy data are in eV. Required reduction potentials of potential dependent steps are given in the parenthesis (V vs NHE).

Step	ΔE	$-T \cdot \Delta S$	$\Delta ZPVE$	ΔG
$*CO + e^- \rightarrow *CO^-$	-2.97	-0.01	-0.02	-3.00 (-1.28)
$*CO^- + H^+ \rightarrow *CHO$	-1.63	0.04	0.37	-1.22
$*CHO + e^- \rightarrow *CHO^-$	-3.04	-0.08	-0.10	-3.22 (-1.06)
$*CHO^- + H^+ \rightarrow *CHOH$	-0.37	0.03	0.41	0.07
$*CHOH + e^- \rightarrow *CHOH^-$	-3.15	-0.01	-0.09	-3.25 (-1.03)
$*CHOH^- + H^+ \rightarrow *CH_2OH$	-3.44	-0.01	0.43	-3.02
$*CH_2OH + e^- \rightarrow *CH_2OH^-$	-3.00	0.02	-0.08	-3.06 (-1.23)
$*CH_2OH^- + H^+ \rightarrow CH_3OH$	-2.27	-0.51	0.32	-2.46
$*CH_3OH + H^+ + e^- \rightarrow CH_4 + *OH$	-0.27	0.20	-0.18	-0.25
$*CH_3OH + H^+ + e^- \rightarrow *CH_3 + H_2O$	0.30	0.20	0.01	0.51
$*OH + H^+ + e^- \rightarrow H_2O$	-0.57	-0.29	0.28	-0.58
$*CO^- + H^+ \rightarrow *COH$	-0.11	0.02	0.30	0.21
$*CHO^- + H^+ \rightarrow *OCH_2$	-1.94	-0.08	0.37	-1.65
$*OCH_2 + e^- \rightarrow *OCH_2^-$	-3.12	-0.02	-0.31	-3.45 (-1.03)
$*OCH_2^- + H^+ \rightarrow *OCH_3$	-1.28	0.14	0.40	-0.74
$*OCH_3 + e^- \rightarrow *OCH_3^-$	-4.05	0.02	0.10	-3.93 (-0.35)
$*OCH_3^- + H^+ \rightarrow *O + CH_4$	1.41	-0.54	0.24	1.11
$*OCH_3^- + e^- \rightarrow CH_3OH$	-1.63	-0.54	0.43	-1.74
$*CHOH^- + H^+ \rightarrow *CH + H_2O$	0.49	-0.45	0.15	0.19
$*CH_2OH^- + H^+ \rightarrow *CH_2 + H_2O$	0.32	-0.60	0.08	-0.20

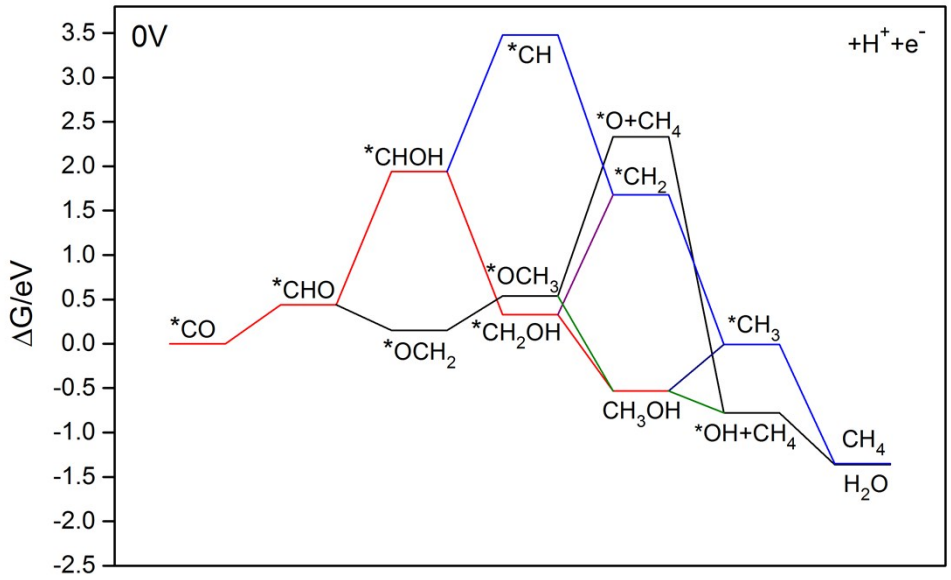

Figure S1. Reduction pathway from CO to methanol/methane with CPET (concerted proton and electron transferring) scheme.