Supporting Information

Theoretical investigation of tandem catalysts utilizing S-modified metalloporphyrin two-dimensional carbon-rich conjugated frameworks for the electrocatalytic reduction synthesis of L-erythrulose

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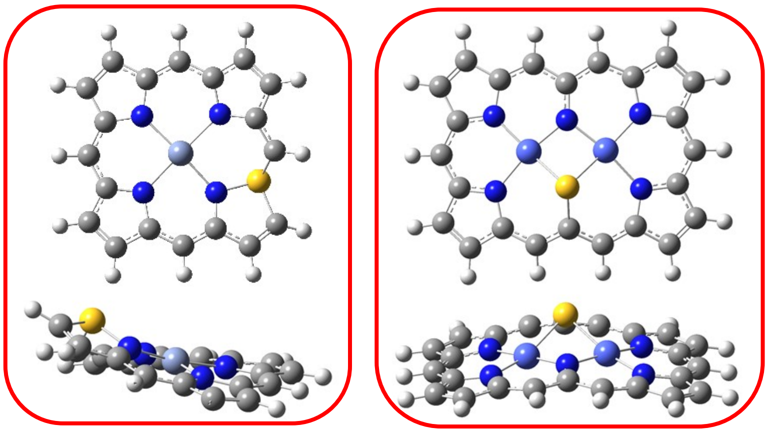

Fig. S1. Optimized M-SPor and CoM-SN_5TPor structures.

Fig. S2. Three key adsorption intermediates over TM-SPor and CoTM-SN_5TPor catalysts.

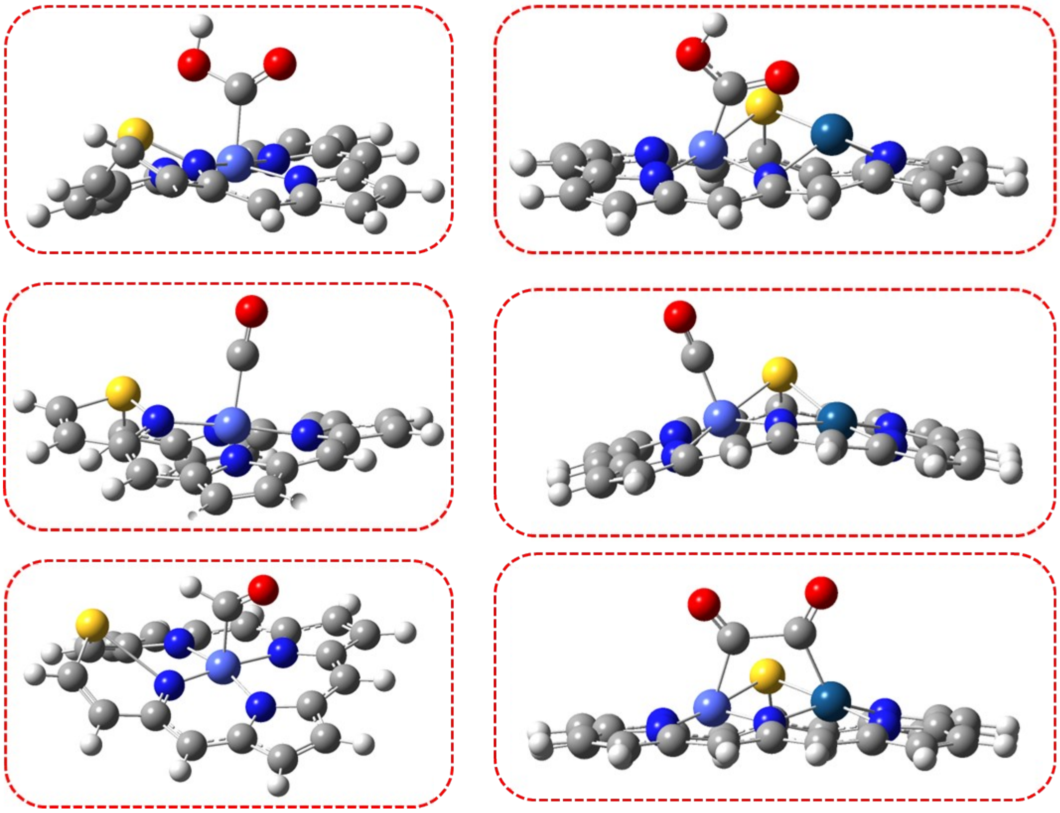

Fig. S3. Schematic representation of the structural optimisation for L-erythrulose synthesis via C-C coupling on the CoRh-SN_5TPor catalyst.

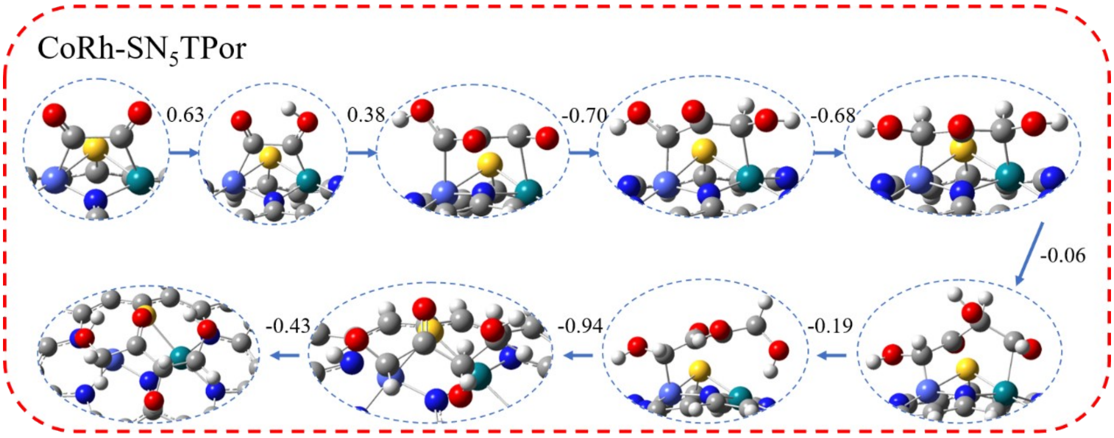

Fig. S4. Schematic representation of the structural optimisation for L-erythrulose synthesis via C-C coupling on the CoIr-SN_5TPor catalyst.

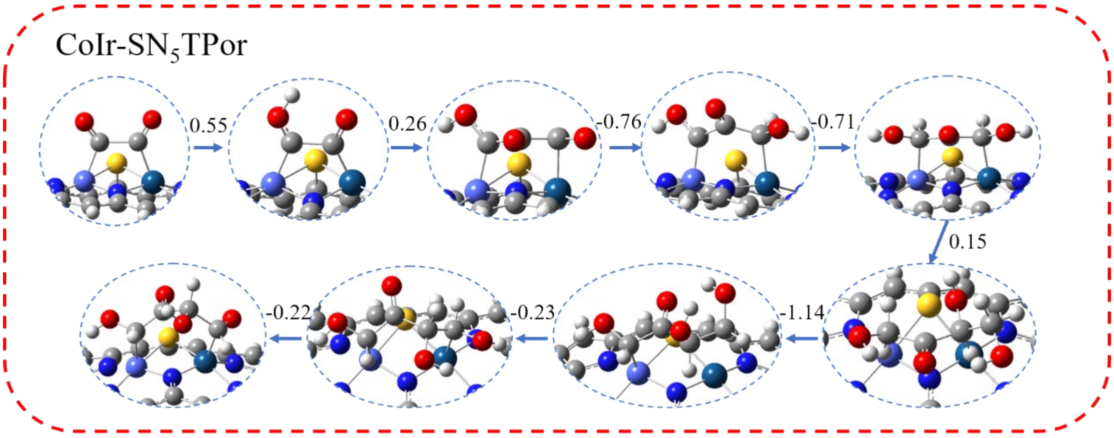

Table S1. Computed formation energy (E_f) and dissolution potential (U_{diss}) of TM-SPor, U_{diss}^{0} and n are the standard dissolution potential of bulk metal and the number of transferred electrons involved in the dissolution.

M-Spor	***n***	$U_{diss}^{0}(V)$	E_f ***(eV)***	$U_{diss}(V)$
Ti-SPor	*2*	*-1.63*	*-16.09*	*6.42*
V-SPor	*2*	*-1.18*	*-10.48*	*4.06*
Cr-SPor	*2*	*-0.91*	*-19.77*	*8.97*
Mn-SPor	*2*	*-0.19*	*-10.95*	*5.29*
Fe-SPor	*2*	*-0.45*	*-18.60*	*8.85*
Co-SPor	*2*	*-0.28*	*-8.29*	*3.87*
Ni-SPor	*2*	*-0.26*	*-16.08*	*7.78*
Zr-SPor	*4*	*-1.45*	*-13.32*	*1.88*
Nb-SPor	*3*	*-1.1*	*-12.14*	*2.95*
Mo-SPor	*3*	*-0.2*	*-15.44*	*4.95*
Ru-SPor	*2*	*0.46*	*-11.90*	*6.41*
Rh-SPor	*2*	*0.6*	*-8.41*	*4.81*
Hf-SPor	*4*	*-1.55*	*-12.17*	*1.49*
Ta-SPor	*3*	*-0.6*	*-12.88*	*3.69*
W-SPor	*3*	*0.1*	*-17.35*	*5.88*
Re-SPor	*3*	*0.3*	*-12.18*	*4.36*
Os-SPor	*8*	*0.84*	*-16.02*	*2.84*
Ir-SPor	*3*	*1.16*	*-10.29*	*4.59*
Pt-SPor	*2*	*1.18*	*-10.95*	*6.66*

Table S2. The calculated Gibbs free energy changes for CO_2 adsorption (ΔG_{*CO2}) on various TM-SPor candidates. (E in eV).

M-Spor	ΔG_{*CO2}	***M-Spor***	ΔG_{*CO2}
Ti-SPor	*0.05*	*Ru-SPor*	*-0.13*
V-SPor	*-0.50*	*Rh-SPor*	*-0.16*
Cr-SPor	*0.32*	*Hf-SPor*	*-1.72*
Mn-SPor	*-0.15*	*Ta-SPor*	*-0.83*
Fe-SPor	*-0.03*	*W-SPor*	*-1.17*
Co-SPor	*-0.13*	*Re-SPor*	*-0.52*
Ni-SPor	*-0.61*	*Os-SPor*	*0.52*
Zr-SPor	*-0.05*	*Ir-SPor*	*-0.16*
Nb-SPor	*0.96*	*Pt-SPor*	*-0.43*
Mo-SPor	*0.58*		

Table S3. The calculated Gibbs free energy changes for *COOH to *CO on M-SPor candidates(E in eV).

M-Spor	$\Delta G_{*COOH \rightarrow *CO}$	***M-Spor***	$\Delta G_{*COOH \rightarrow *CO}$
V-SPor	*0.40*	*Rh-SPor*	*1.04*
Mn-SPor	*0.28*	*Hf-SPor*	*0.92*
Fe-SPor	*-0.06*	*Ta-SPor*	*1.02*
Co-SPor	*-0.21*	*W-SPor*	*0.64*
Ni-SPor	*0.33*	*Re-SPor*	*0.21*
Zr-SPor	*0.81*	*Ir-SPor*	*1.15*
Ru-SPor	*0.00*	*Pt-SPor*	*-0.61*

Table S4. The clculaated Gibbs free energy changes for the first hydrogenation step in CO_2RR (ΔG_{*COOH}) and HER ($\Delta G*_H$) on various M-SPor candidates. (E in eV).

M-Spor	$\Delta G_{*CO2\rightarrow *COOH}$	ΔG_{*H}	***M-Spor***	$\Delta G_{*CO2\rightarrow *COOH}$	ΔG_{*H}
V-SPor	*0.09*	*-0.21*	*Rh-SPor*	*0.00*	*-0.19*
Mn-SPor	*0.35*	*0.31*	*Hf-SPor*	*-0.25*	*-1.17*
Fe-SPor	*-0.28*	*-0.15*	*Ta-SPor*	*-0.63*	*-1.15*
Co-SPor	*0.34*	*0.42*	*W-SPor*	*0.34*	*-0.89*
Ni-SPor	*1.29*	*0.84*	*Re-SPor*	*-0.54*	*-0.99*
Zr-SPor	*-0.54*	*-0.33*	*Ir-SPor*	*-0.19*	*-0.37*
Ru-SPor	*-0.28*	*-0.39*	*Pt-SPor*	*2.00*	*0.25*

Table S5. Computed formation energy (E_f) and dissolution potential (U_{diss}) of FeTMs@Pc, U_{diss}^{0} and *n* are the standard dissolution potential of bulk metal and the number of transferred electrons involved in the dissolution, respectively. $n = [n(Fe) + n(TM)]/2$, $U_{diss}^{0} = [U_{diss}^{0}(Fe) + U_{diss}^{0}(TM)]/2$.

M-Spor	***n***	$U_{diss}^{0}(V)$	***E_f (eV)***	$U_{diss}(V)$
CoTi-SN_5TPor	*2*	*-0.96*	*-20.85*	*9.47*
CoV- SN_5TPor	*2*	*-0.73*	*-16.16*	*7.35*
CoCr- SN_5TPor	*2*	*-0.60*	*-23.58*	*11.19*
CoMn- SN_5TPor	*2*	*-0.24*	*-16.17*	*7.85*
CoFe- SN_5TPor	*2*	*-0.37*	*-24.22*	*11.74*
CoCo- SN_5TPor	*2*	*-0.28*	*-13.61*	*6.52*
CoZr- SN_5TPor	*4*	*-0.87*	*-17.73*	*5.05*
CoNb SN_5TPor	*3*	*-0.69*	*-16.53*	*5.92*
CoMo- SN_5TPor	*3*	*-0.24*	*-19.32*	*7.49*
CoRu- SN_5TPor	*2*	*0.09*	*-16.78*	*8.48*
CoRh- SN_5TPor	*2*	*0.16*	*-13.50*	*6.91*
CoPd- SN_5TPor	*2*	*0.34*	*-11.95*	*6.31*
CoHf- SN_5TPor	*4*	*-0.92*	*-18.21*	*5.15*
CoTa- SN_5TPor	*3*	*-0.44*	*-17.35*	*6.50*
CoW- SN_5TPor	*3*	*-0.09*	*-21.30*	*8.43*
CoRe- SN_5TPor	*3*	*0.01*	*-16.41*	*6.58*
CoOs- SN_5TPor	*8*	*0.28*	*-20.50*	*4.38*
CoIr- SN_5TPor	*3*	*0.44*	*-15.35*	*6.58*
CoPt- SN_5TPor	*2*	*0.45*	*-16.07*	*8.48*

Table S6. The calculated Gibbs free energy changes for *COOH to *CO on CoTM-SN_5TPor candidates. (E in eV).

CoTM-SN_5TPor	***$\Delta G_{*COOH\rightarrow *CO}$***	***CoTM-SN_5TPor***	***$\Delta G_{*COOH\rightarrow *CO}$***
CoV-SN_5TPor	*0.75*	*CoRh-SN_5TPor*	*-0.46*
CoCr-SN_5TPor	*1.36*	*CoPd-SN_5TPor*	*0.15*
CoMn-SN_5TPor	*-0.82*	*CoAg-SN_5TPor*	*0.40*
CoFe-SN_5TPor	*-0.59*	*CoHf-SN_5TPor*	*1.57*
CoCo-SN_5TPor	*0.09*	*CoTa-SN_5TPor*	*0.80*
CoNi-SN_5TPor	*0.21*	*CoW-SN_5TPor*	*0.62*
CoCu-SN_5TPor	*0.13*	*CoRe-SN_5TPor*	*0.26*
CoY-SN_5TPor	*1.20*	*CoOs-SN_5TPor*	*-0.11*
CoZr-SN_5TPor	*0.88*	*CoIr-SN_5TPor*	*-0.58*
CoNb-SN_5TPor	*0.41*	*CoPt-SN_5TPor*	*0.14*
CoMo-SN_5TPor	*1.49*	*CoAu-SN_5TPor*	*0.47*
CoRu-SN_5TPor	*0.09*		

Table S7. The calculated Gibbs free energy changes for the first hydrogenation step in CO_2RR (ΔG_{*COOH}) and HER (ΔG_{*H}) on various CoTM-SN_5TPor candidates. (E in eV).

CoTM-SN_5TPor	***ΔG_{*H}***	***$\Delta G_{*CO2 \rightarrow *COOH}$***	***CoTM-SN_5TPor***	***$\Delta G_{*CO2 \rightarrow *COOH}$***	***ΔG_{*H}***
CoTi-SN_5TPor	*0.46*	*0.47*	*CoRu-SN_5TPor*	*0.49*	*-0.02*
CoV-SN_5TPor	*0.49*	*0.33*	*CoRh-SN_5TPor*	*0.40*	*-0.08*
CoCr-SN_5TPor	*-0.39*	*0.51*	*CoPd-SN_5TPor*	*0.40*	*0.05*
CoMn-SN_5TPor	*1.61*	*0.65*	*CoHf-SN_5TPor*	*0.79*	*0.48*
CoFe-SN_5TPor	*0.17*	*-0.30*	*CoTa-SN_5TPor*	*-0.72*	*0.84*
CoCo-SN_5TPor	*0.21*	*0.25*	*CoW-SN_5TPor*	*0.40*	*0.36*
CoZr-SN_5TPor	*0.29*	*0.49*	*CoRe-SN_5TPor*	*0.73*	*0.55*
CoNb-SN_5TPor	*0.64*	*0.83*	*CoOs-SN_5TPor*	*0.48*	*0.11*
CoMo-SN_5TPor	*0.30*	*0.28*	*CoIr-SN_5TPor*	*0.39*	*0.01*

Table S8. Summary of valence-electron number Sv_1, Sv_2 and Sv_3 of transition metal dopant and nitrogen atom, the electronegativity χ_1, χ_2, χ_3 and χ_4 of transition metal element and nitrogen atoms and descriptor ψ for $CoTM\text{-}SN_5TPor$.

$CoTM\text{-}SN_5TPor$	Sv_1	Sv_2	Sv_3	Sv_4	χ_1	χ_2	χ_3	χ_4	ψ
$CoTi\text{-}SN_5TPor$	4	9	6	5	1.54	1.88	2.58	3.04	15.05
$CoV\text{-} N_5TPor$	5	9	6	5	1.63	1.88	2.58	3.04	16.59
$CoCr\text{-}SN_5TPor$	6	9	6	5	1.66	1.88	2.58	3.04	18.10
$CoMn\text{-}SN_5TPor$	7	9	6	5	1.55	1.88	2.58	3.04	19.88
$CoFe\text{-}SN_5TPor$	8	9	6	5	1.83	1.88	2.58	3.04	20.39
$CoCo\text{-}SN_5TPor$	9	9	6	5	1.88	1.88	2.58	3.04	21.48
$CoCu\text{-}SN_5TPor$	11	9	6	5	1.9	1.88	2.58	3.04	23.69
$CoZr\text{-}SN_5TPor$	4	9	6	5	1.33	1.88	2.58	3.04	15.62
$CoNb\text{-}SN_5TPor$	5	9	6	5	1.6	1.88	2.58	3.04	16.67
$CoMo\text{-}SN_5TPor$	6	9	6	5	2.16	1.88	2.58	3.04	16.94
$CoRu\text{-}SN_5TPor$	8	9	6	5	2.2	1.88	2.58	3.04	19.47
$CoRh\text{-}SN_5TPor$	9	9	6	5	2.28	1.88	2.58	3.04	20.47
$CoPd\text{-}SN_5TPor$	10	9	6	5	2.2	1.88	2.58	3.04	21.77
$CoAg\text{-}SN_5TPor$	11	9	6	5	1.93	1.88	2.58	3.04	23.60
$CoHf\text{-}SN_5TPor$	4	9	6	5	1.3	1.88	2.58	3.04	15.71
$CoTa\text{-}SN_5TPor$	5	9	6	5	1.5	1.88	2.58	3.04	16.94
$CoW\text{-}SN_5TPor$	6	9	6	5	2.36	1.88	2.58	3.04	16.57
$CoRe\text{-}SN_5TPor$	7	9	6	5	1.9	1.88	2.58	3.04	18.90
$CoOs\text{-}SN_5TPor$	8	9	6	5	2.2	1.88	2.58	3.04	19.47
$CoIr\text{-}SN_5TPor$	9	9	6	5	2.2	1.88	2.58	3.04	20.66
$CoPt\text{-}SN_5TPor$	10	9	6	5	2.28	1.88	2.58	3.04	21.58
$CoAu\text{-}SN_5TPor$	11	9	6	5	2.54	1.88	2.58	3.04	22.03

TableS9. The adsorption energy of *CO,*COOH and *HCOO on CoTM-SN_5TPor.

CoTM-SN_5TPor	E_{*CO}	E_{*COOH}	E_{*HCOO}
CoTi-SN_5TPor	-0.43	-2.54	-4.12
CoV- N_5TPor	-0.58	-2.16	-3.54
CoCr-SN_5TPor	-0.75	-2.94	-4.49
CoMn-SN_5TPor	-0.64	-0.64	-1.57
CoFe-SN_5TPor	-1.25	-1.49	-2.32
CoCo-SN_5TPor	-0.96	-1.02	-1.84
CoCu-SN_5TPor	-0.85	-1.81	-1.79
CoZr-SN_5TPor	-1.26	-2.98	-4.60
CoNb-SN_5TPor	-0.89	-2.13	-4.02
CoMo-SN_5TPor	-0.09	-2.41	-3.93
CoRu-SN_5TPor	-0.85	-1.77	-2.83
CoRh-SN_5TPor	-0.84	-1.21	-1.93
CoPd-SN_5TPor	-0.92	-1.90	-1.78
CoAg-SN_5TPor	-0.82	-2.05	-1.85
CoHf-SN_5TPor	-0.31	-2.72	-4.87
CoTa-SN_5TPor	-0.40	-2.03	-4.11
CoW-SN_5TPor	-0.75	-2.21	-3.87
CoRe-SN_5TPor	-0.55	-1.64	-3.20
CoOs-SN_5TPor	-0.76	-1.48	-2.77
CoIr-SN_5TPor	-0.83	-1.08	-1.91
CoPt-SN_5TPor	-1.35	-2.32	-2.21
CoAu-SN_5TPor	-0.83	-2.13	-2.01