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Supporting Information

High-throughput Screening of Mechanically Interlocked Catenane Metal Complexes for Enhanced Electrocatalytic Activity

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DFT calculations

Table S1. Formation energies and dissolution potentials of metal complexes.

Metal complex	E_M (eV)*	Ne, ref.[1]	U_{diso} (V), ref.[1]	$E_{formation}$ (eV)	U_{dis} (V)
$Cu(I)_{CN2}$	-3.72	2	0.34	-0.43	0.56
$Cu(I)_{CN3}$	-3.72	2	0.34	-1.25	0.97
$Cu(II)_{CN2}$	-3.72	2	0.34	-0.59	0.63
$Cu(II)_{CN3}$	-3.72	2	0.34	-1.96	1.32
$Cu(I)_{CN4}$	-3.72	2	0.34	-2.85	1.76
$Cu(I)_{CN5}$	-3.72	2	0.34	-2.93	1.80
$Cu(I)_{CN6}$	-3.72	2	0.34	-3.39	2.04
$Cu(II)_{CN4}$	-3.72	2	0.34	-3.15	1.92
$Cu(II)_{CN5}$	-3.72	2	0.34	-4.03	2.35
$Cu(II)_{CN6}$	-3.72	2	0.34	-4.61	2.64
$Fe(II)_{CN4}$	-8.23	2	-0.45	-3.66	1.38
$Fe(II)_{CN5}$	-8.23	2	-0.45	-4.47	1.79
$Fe(II)_{CN6}$	-8.23	2	-0.45	-5.42	2.26
$Co(II)_{CN4}$	-7.02	2	-0.28	-3.50	1.47
$Co(II)_{CN5}$	-7.02	2	-0.28	-4.09	1.76
$Co(II)_{CN6}$	-7.02	2	-0.28	-5.11	2.27
$Ni(II)_{CN4}$	-5.47	2	-0.26	-3.36	1.42
$Ni(II)_{CN5}$	-5.47	2	-0.26	-4.73	2.11
$Ni(II)_{CN6}$	-5.47	2	-0.26	-5.44	2.46
$Zn(II)_{CN4}$	-1.11	2	-0.76	-5.10	1.79
$Zn(II)_{CN5}$	-1.11	2	-0.76	-5.58	2.03
$Zn(II)_{CN6}$	-1.11	2	-0.76	-6.37	2.42
$Cr(II)_{CN4}$	-9.51	2	-0.91	-4.17	1.18
$Cr(II)_{CN5}$	-9.51	2	-0.91	-5.43	1.80
$Cr(II)_{CN6}$	-9.51	2	-0.91	-6.96	2.57
$Mn(II)_{CN4}$	-8.01	2	-1.19	-5.61	1.62
$Mn(II)_{CN5}$	-8.01	2	-1.19	-6.24	1.93
$Mn(II)_{CN6}$	-8.01	2	-1.19	-7.67	2.64
$Ti(II)_{CN4}$	-7.84	2	-1.63	-5.25	1.00
$Ti(II)_{CN5}$	-7.84	2	-1.63	-6.60	1.67
$Ti(II)_{CN6}$	-7.84	2	-1.63	-8.19	2.47
$V(II)_{CN4}$	-8.99	2	-1.18	-4.56	1.10
$V(II)_{CN5}$	-8.99	2	-1.18	-5.95	1.79
$V(II)_{CN6}$	-8.99	2	-1.18	-7.77	2.70

* Obtained in this work using PBE functional

Table S2. Linear relationship coefficients between the Gibbs free energy of reaction intermediates with the Gibbs free energy of OH*.

Intermediate	Scaling relationship	R^2 value
OH	$\Delta G_{OH} = 1.000\Delta G_{OH} + 0.000$	1.0000
O	$\Delta G_{O} = 1.470\Delta G_{OH} + 0.228$	0.7752
OOH	$\Delta G_{OOH} = 0.589\Delta G_{OH} + 0.844$	0.8435
OO	$\Delta G_{OO} = 0.028\Delta G_{OH} + 4.719$	0.0155
H	$\Delta G_{H} = -0.369\Delta G_{OH} + 1.335$	0.3502
CO_2	$\Delta G_{CO_2} = -0.015\Delta G_{OH} + 0.450$	0.0139
COOH	$\Delta G_{COOH} = 0.214\Delta G_{OH} + 1.781$	0.1804
CO	$\Delta G_{CO} = 0.009\Delta G_{OH} + 1.221$	0.005
COH	$\Delta G_{CHO} = 0.303\Delta G_{OH} + 2.314$	0.0674

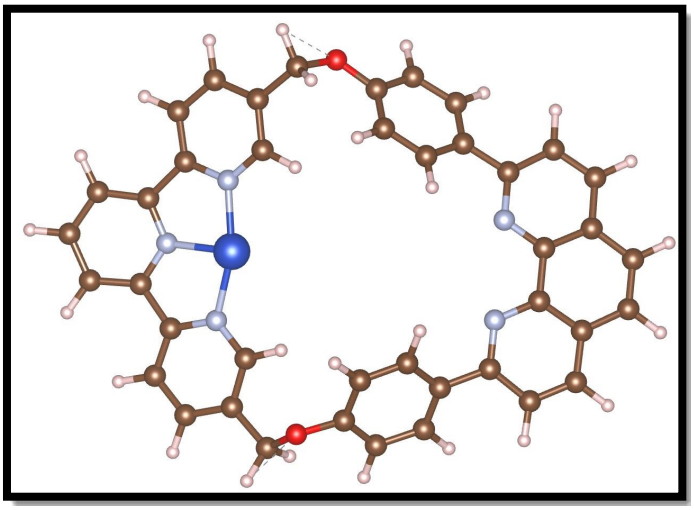

Figure S1. The structure of one individual macrocycle denoted as M(I or II)$_{CNx=2,3}$ where M indicates the 3d transition metals.

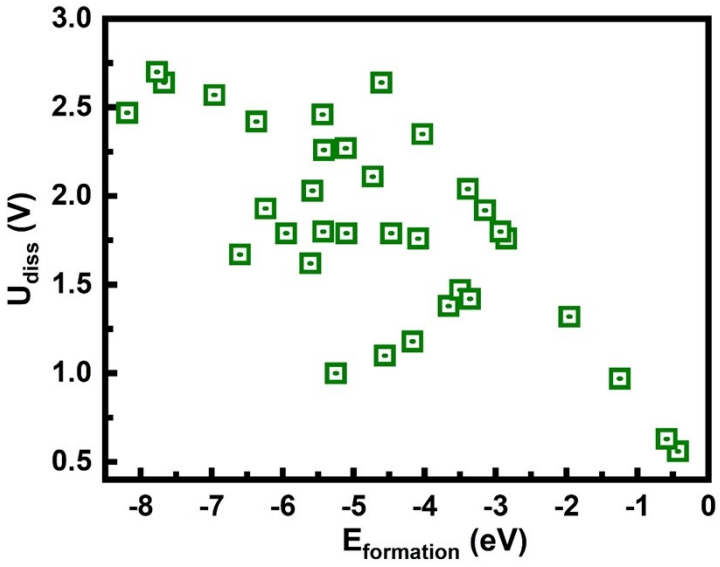

Figure S2. Dissolution potential versus formation energies of M(I or II)$_{CNx=2,3,4,5,6}$, indicating that all candidates meet the stability criteria (U_{diss}>0 and $E_{formation}$<0).

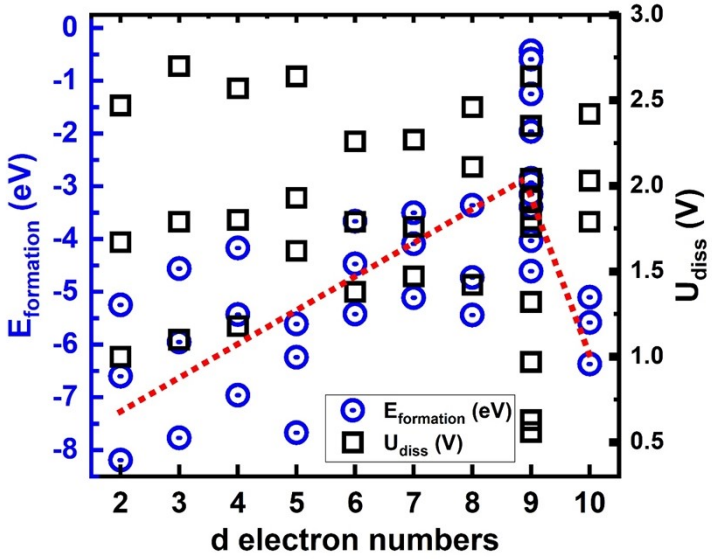

Figure S3. DFT-calculated formation energies and dissociation potentials versus the d electron numbers.

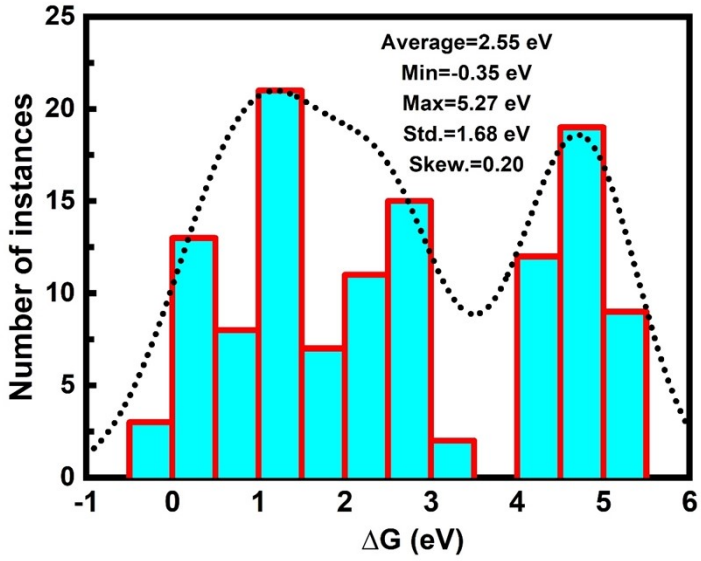

Figure S4. The histogram of Gibbs free energies variation obtained from DFT-D3 calculations, containing 108 data points with an average of 2.55 eV and a standard deviation (std.) of 1.68 eV.

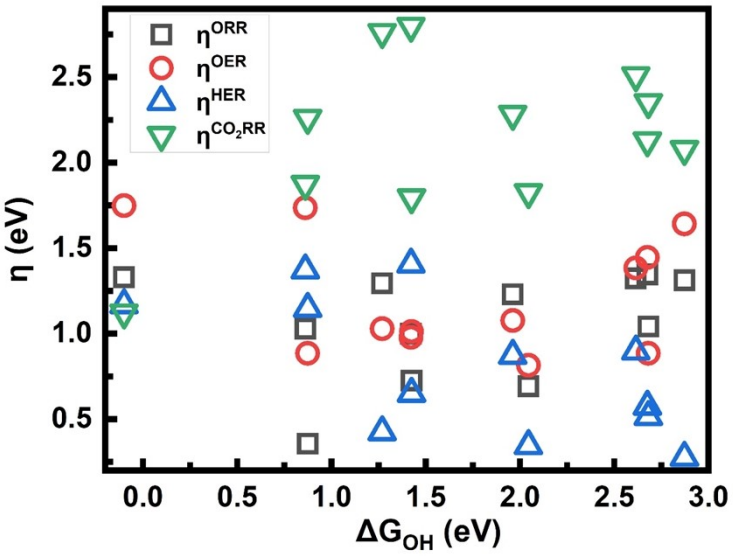

Figure S5. DFT-calculated CO_2RR, HER, ORR, and OER overpotentials versus ΔG_{OH}.

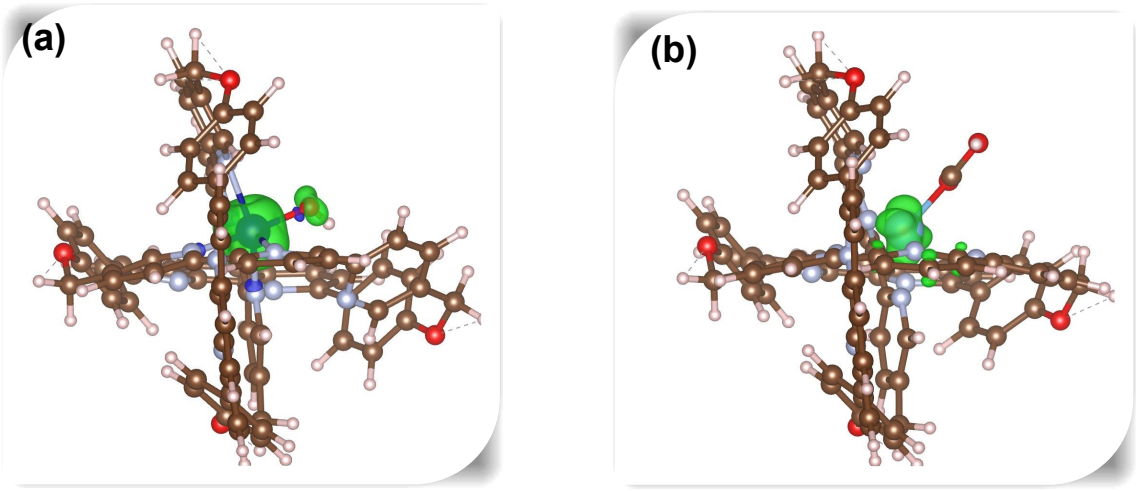

Figure S6. The spin density of (a) $Cr(II)_{CN6}$ with OH intermediate and (b) $Ti(II)_{CN6}$ with COOH intermediate (Isosurface value = 0.01 e/Å^3).

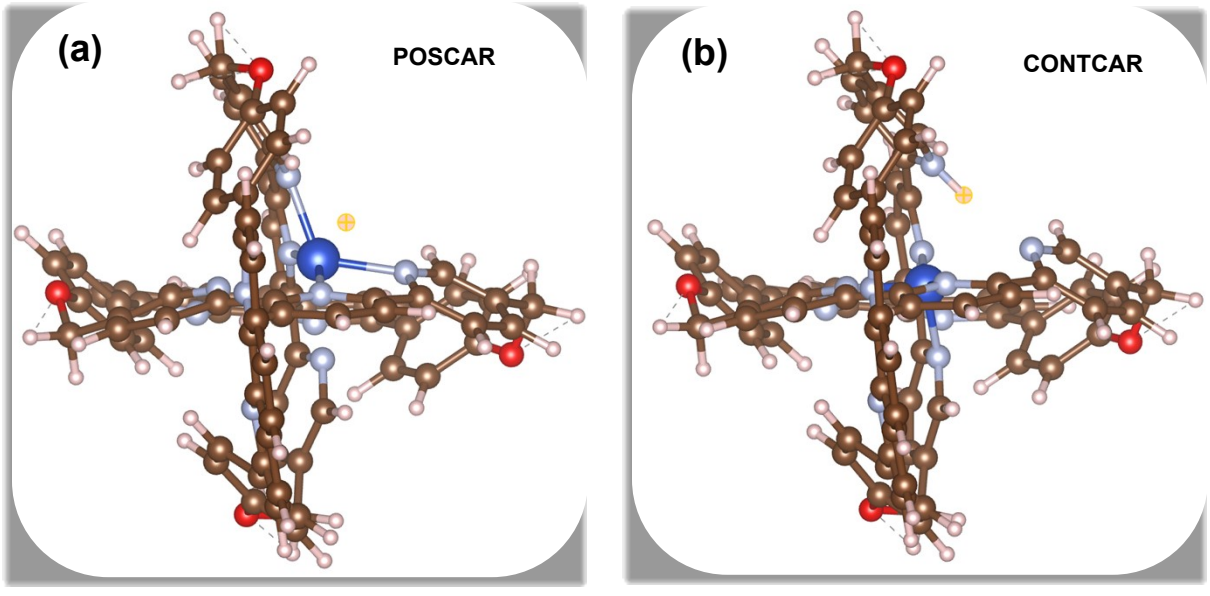

Figure S7. (a) Initial structure (POSCAR file) and (b) final structure (CONTCAR file) for the adsorption of H intermediate on $Cu(II)_{CN6}$ catalyst.

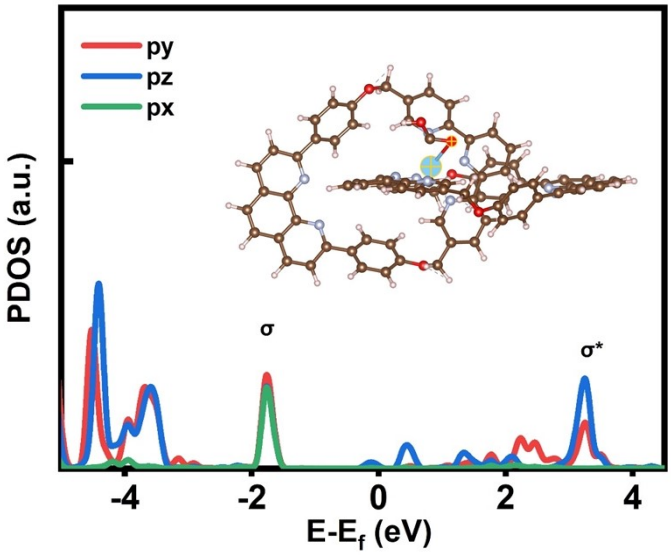

Figure S8. Partial density of states (PDOS) of p_y, p_z, and p_x orbitals of O atom in COOH intermediate adsorbed on $Ti(II)_{CN6}$.

CONTCAR file of $Co(II)_{CN6}$

Co(II)CN6
1.00000000000000
27.9549999237100018 0.0000000000000000 0.0000000000000000
0.0000000000000000 21.5499992370999998 0.0000000000000000
0.0000000000000000 0.0000000000000000 21.5499992370999998
C H N O Co
82 54 10 4 1
Direct
0.2551397081870034 0.4319639195553442 0.6592268169937268
0.2070414883848525 0.4456554799842708 0.6593401952858627
0.1918091312758141 0.5073090601659493 0.6489316214814486
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0.2884070481097165 0.4800918997512013 0.6467543551271584
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0.1855160687610566 0.7404152722248415 0.6283224948149386
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0.2726338583623110 0.7689424723725943 0.6287713385845460
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0.3511240169287922 0.8065319905574838 0.5969213949766677
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