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

Supporting Information

The synergetic effect of aqua ligand and metal site on performance of single-atom catalysts in H_2O_2 synthesis: a Density Functional Theory Study

Xin-cheng Zhu[#1,2], Wei Zhang[#2], Qian Xia[#1], An-Fu Hu[1], Jian Jiang*[1], Qiao-jun Fang,[2] Gui-lin Zhuang*[2]

[1]China Tobacco Zhejiang Industrial Co., Ltd.
[2]Institute of Industrial Catalysis, State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, P.R. China.
*Email: jiangj@zjtobacco.com(J. Jiang)， glzhuang@zjut.edu.cn (G. L. Zhuang)

Author Contributions

# These authors contributed equally.

Table of contents

Computational Details

The adsorption energy of adsorbate on the catalyst is computed as following:

$$E_{ads} = E_{tot} - E_{TM@substrate} - E_{adsorbate} \quad \text{(SI-1)}$$

where E_{tot}, $E_{TM@substrate}$, and $E_{adsorbate}$ are the total energies of the catalyst with adsorbate, TM@substrate, and isolated adsorbed pieces in vacuum, respectively.

In this work, the computational hydrogen electrode (CHE) model, proposed by Nørskov et al.[1] was adopted to evaluate the Gibbs free energy (ΔG) for elementary steps of the ORR. And in line with the standard hydrogen electrode (SHE) model developed by Nørskov and co-worker[2] the chemical potential of the H^+ / e^- pair is equal to half of a hydrogen molecule in gas phase ($H^+ + e^- \leftrightarrow 1/2H_2$). The reaction free energy is defined as the following equation:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} \quad \text{(SI-2)}$$

where ΔE stands for the change of electronic energy obtained from the DFT calculations, ZPE is the zero-point energy, $T\Delta S$ represents for the entropy contributions, of which T is the temperature (298.15K) and ΔS is the entropy change. The bias effect on the free energy is considered in the parameter (ΔG_U),

$$\Delta G_U = -neU \quad \text{(SI-3)}$$

where n is the number of H^+ / e^- pairs transferred in the reaction, e is the transferred charge and the U is the potential applied at the electrode.

The pH effect is considered in the parameter (ΔG_{pH}),

$$\Delta G_{pH} = -k_B T \ln H^+ = pH \times k_B T \ln 10 \quad \text{(SI-4)}$$

where k_B is the Boltzmann constant, the value of pH is set to be 0 and T is set to 298.15 K.

The overpotentials (η) of $2e^-$ ORR and $4e^-$ ORR can be determined as following:

$$G_{2e^- ORR} = U_L = \max \{ \Delta G_1, \Delta G_2 \} \quad \text{(SI-5)}$$

$$\eta_{2e^- ORR} = G_{2e^- ORR} / e - 0.70 \text{ V} \quad \text{(SI-6)}$$

$$G_{4e^- ORR} = U_L = \max \{ \Delta G_3, \Delta G_4, \Delta G_5, \Delta G_6 \} \quad \text{(SI-7)}$$

$$\eta_{4e^- ORR} = G_{4e^- ORR} / e - 1.23 \text{ V} \quad \text{(SI-8)}$$

where ΔG_1, ΔG_2, ΔG_3, ΔG_4 , ΔG_5, ΔG_6 are the free energy of reactions in $2e^-$ ORR and $4e^-$ ORR, the 0.70 V and 1.23 V are the equilibrium potential of $2e^-$ and $4e^-$ mechanism,respectively.

The evaluating method of $2e^-$ ORR selectivity

The selectivity of $2e^-$ ORR can be simply estimated according to the Boltzmann distribution at corresponding the reaction temperature, which is the $f_{2e^-\ ORR} = 1 / (1 + \exp\{ -\delta G / k_B T \})^3$, where the δG is the free energy barrier difference between the energy barrier of the potential-limiting step for $2e^-$ ORR and the active barrier of the corresponding reaction step for $4e^-$ ORR, calculated by the $G_{4e^-\ ORR} - G_{2e\text{-}ORR}$. k_B is the Boltzmann constant, the value of T is temperature, set to 298.15 K.

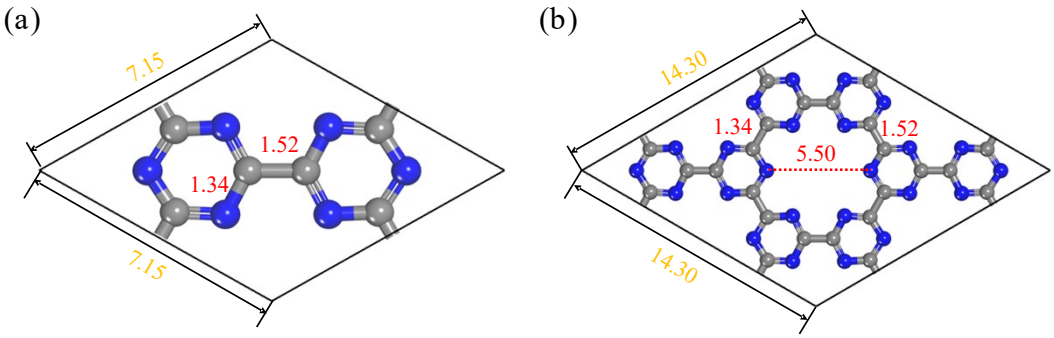

Figure S1. The optimized (a) C_6N_6 primitive cell structure (top view), the lattice parameter and the bond length of C-N and C-C bond, (b) C_6N_6 supercell structure (2 × 2 × 1, top view), the lattice parameter and the bond length of C-N bond, C-C bond and N-N bond (in hole, symmetry). C atom: brown, N atom: blue.

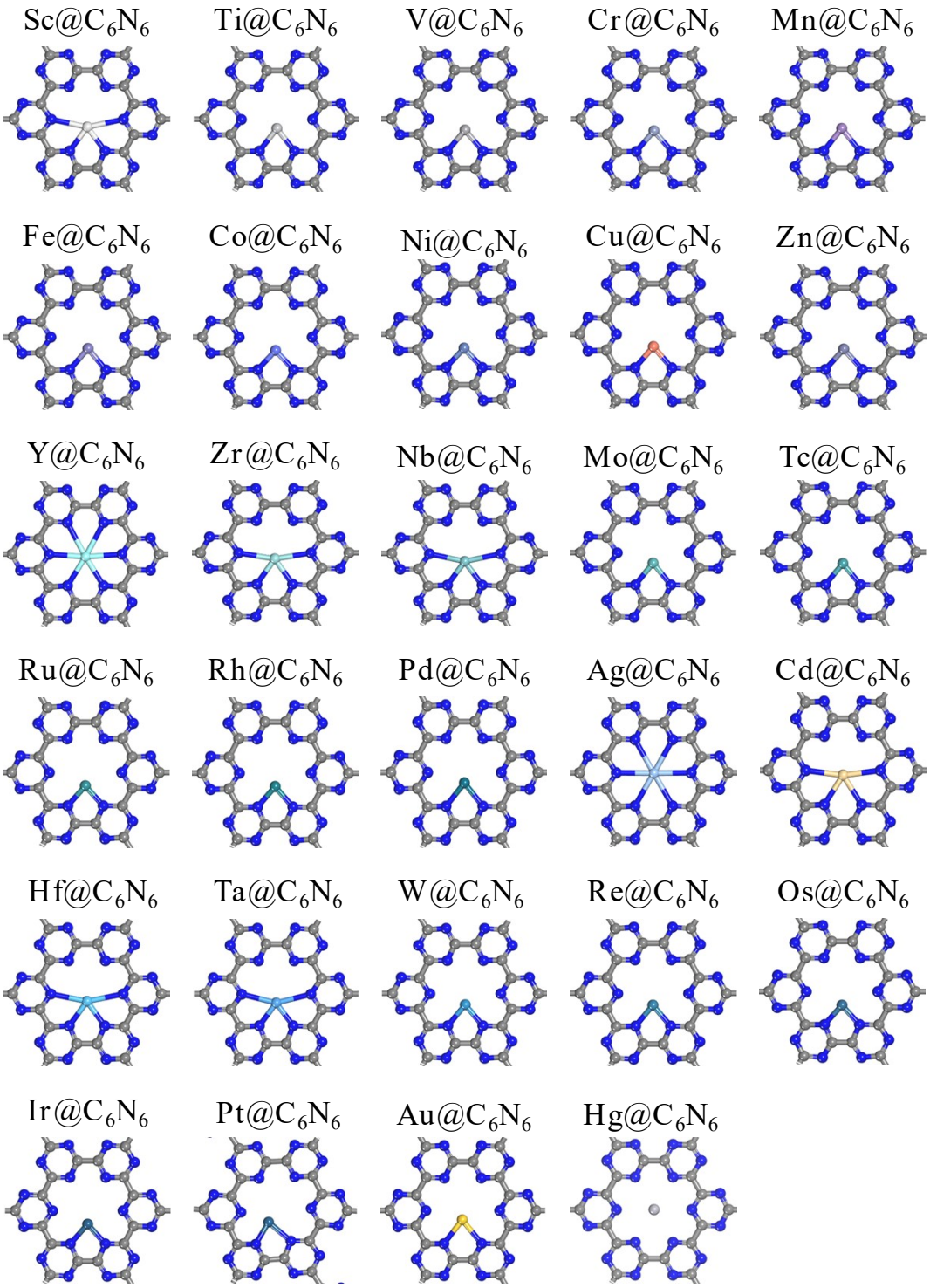

Figure S2. The optimized structures of 29 TM@C_6N_6 in top view (TM = 3*d* (Sc - Zn), 4*d* (Y - Cd) and 5*d* (Hf - Hg)). C atom: brown, N atom: blue, TM single atom (colorful) in the hole of C_6N_6.

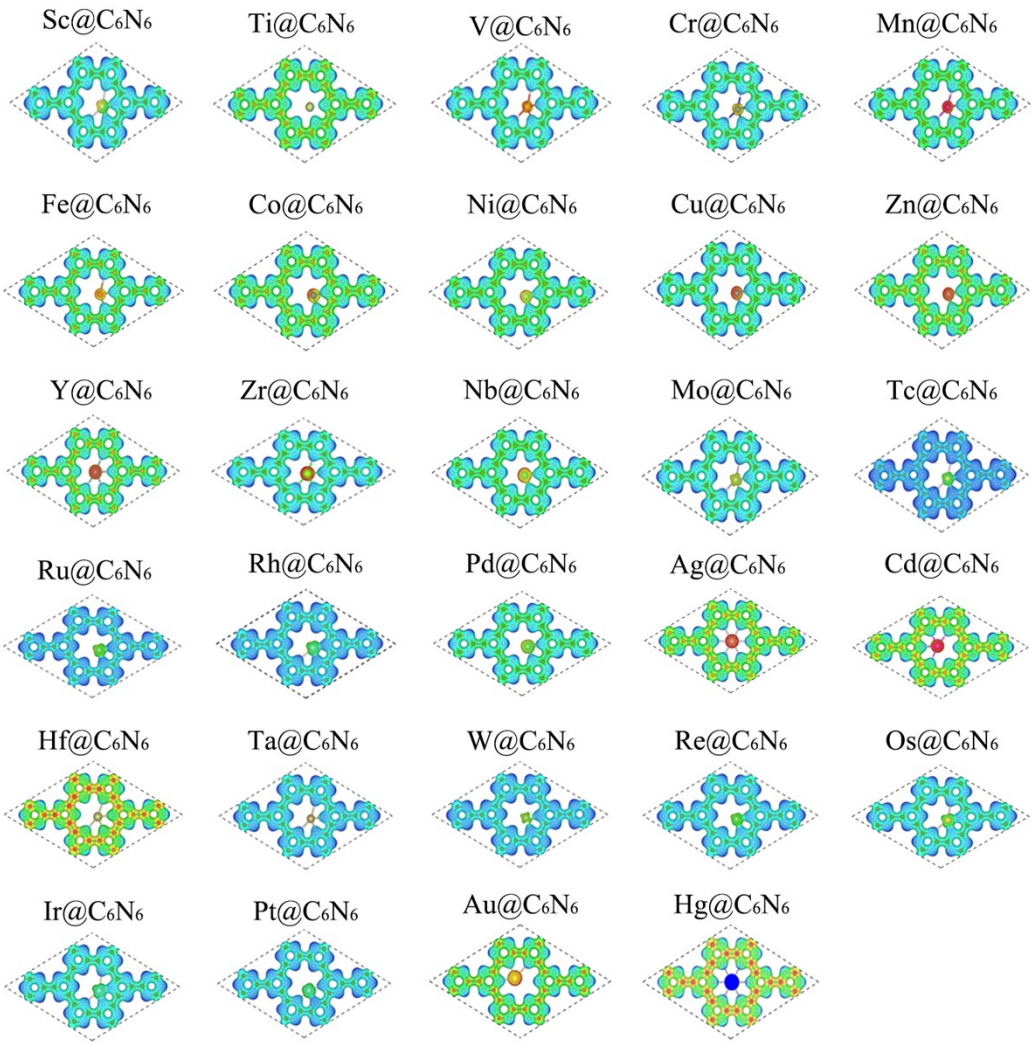

Figure S3. The electrostatic potential of 29 TM@C_6N_6. (TM = 3*d* (Sc - Zn), 4*d* (Y - Cd) and 5*d* (Hf - Hg)).

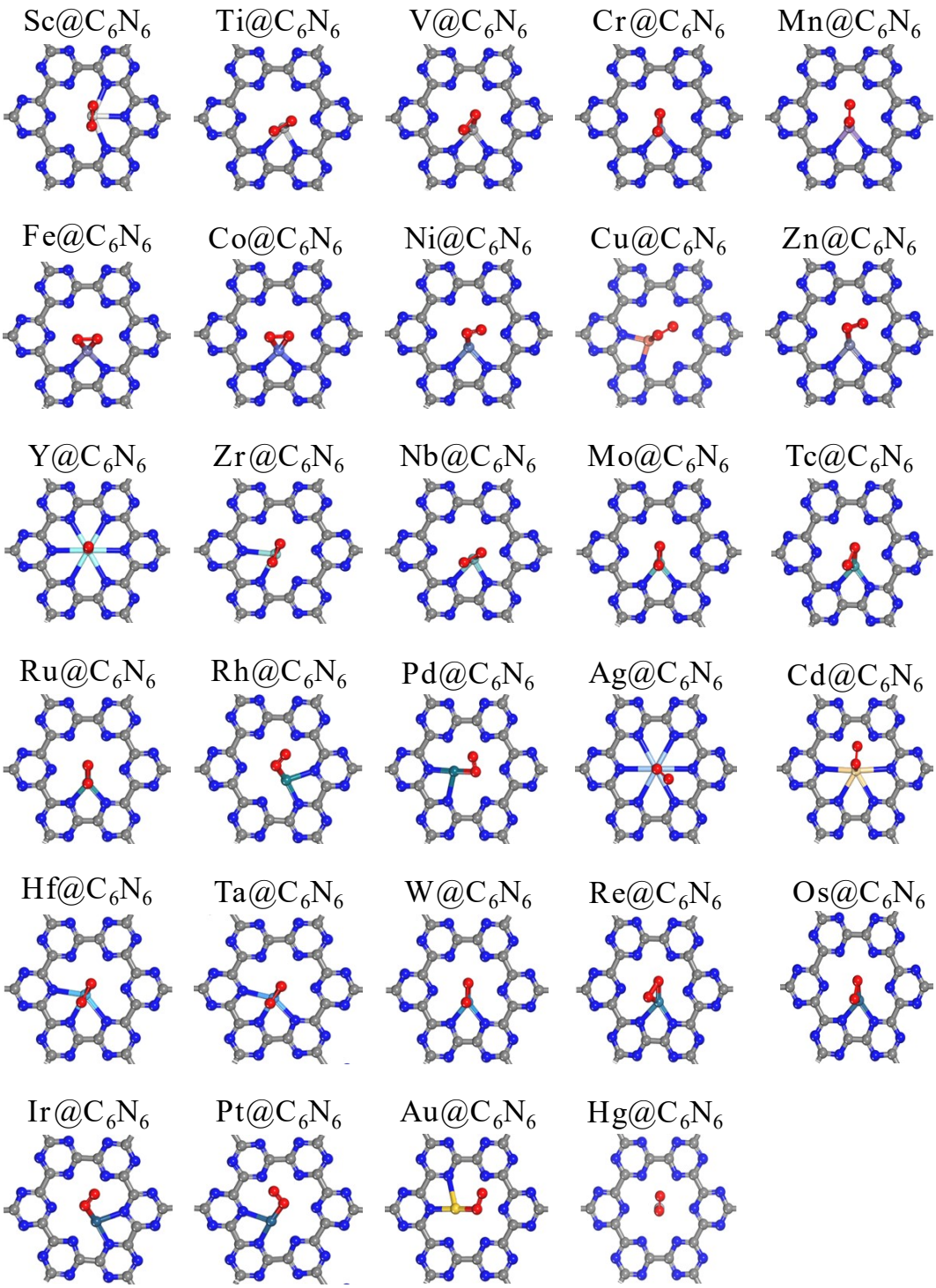

Figure S4. The adsorption configuration relaxed of O_2 molecule on TM@C_6N_6 in top view (TM = 3*d* (Sc - Zn), 4*d* (Y - Cd) and 5*d* (Hf - Hg)). C atom: brown, N atom: blue, O atom: red, TM single atom (colorful) in the hole of C_6N_6.

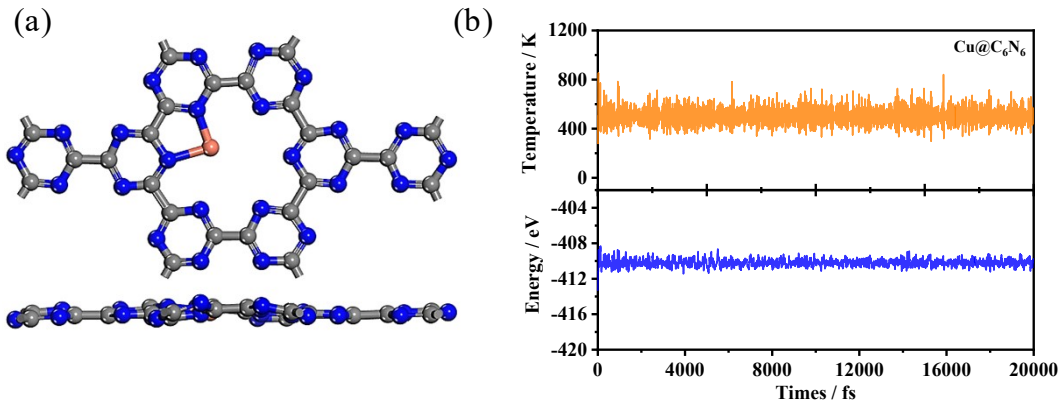

Figure S5. The structure (top view and side view) (a) and the temperature and system energy variations (b) of $Cu@C_6N_6$ catalyst through AIMD simulation under 500 K for 10 ps with a time step of 0.5 fs. C atom: brown, N atom: blue, Cu atom: orange.

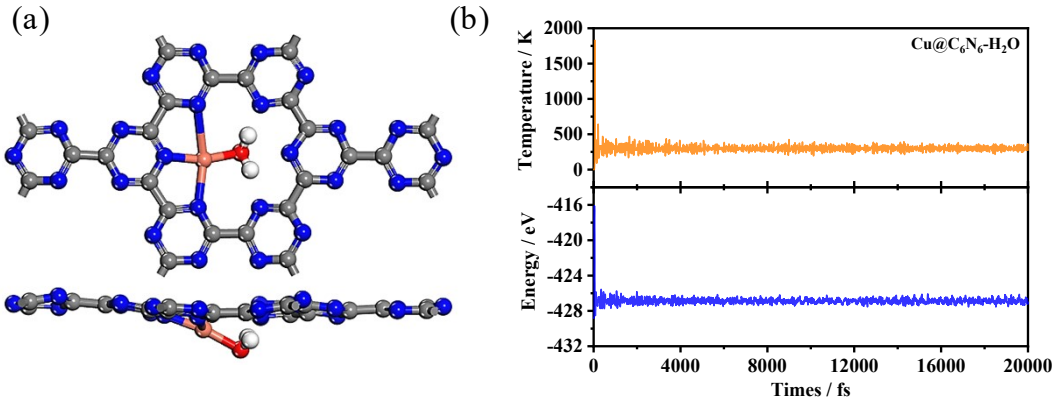

Figure S6. The structure (top view and side view) (a) and the temperature and system energy variations (b) of $Cu@C_6N_6$ with an aqua ligand through AIMD simulation under 298.15 K for 10 ps with a time step of 0.5 fs. C atom: brown, N atom: blue, O atom: red, H atom: white, Cu atom: orange.

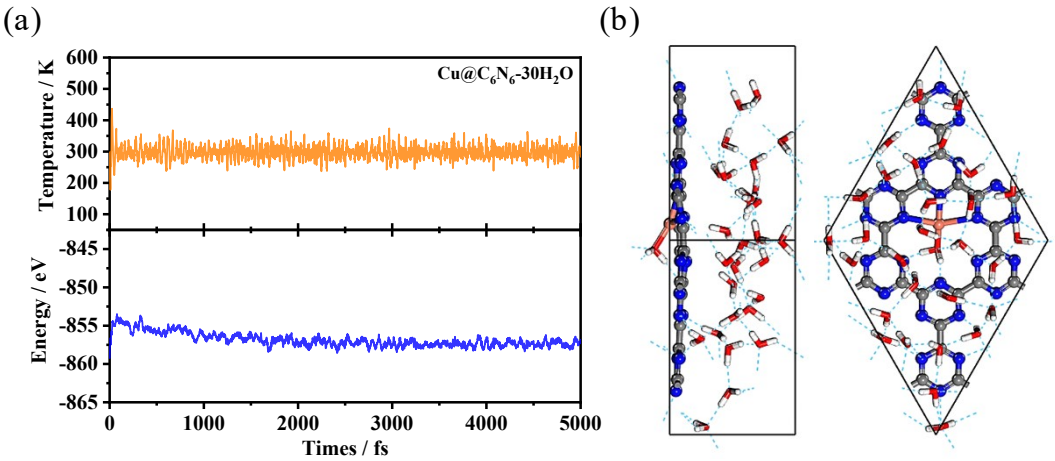

Figure S7. (a) Variations of temperature and system energy against the time via AIMD simulation of 5 ps under 298.15 K with a time step of 1.0 fs, and (b) The fully relaxed structure (side and top views) for Cu@C_6N_6 system with 30 H_2O explicit molecules. C atom: brown, N atom: blue, O atom: red, H atom: white, Cu atom: orange.

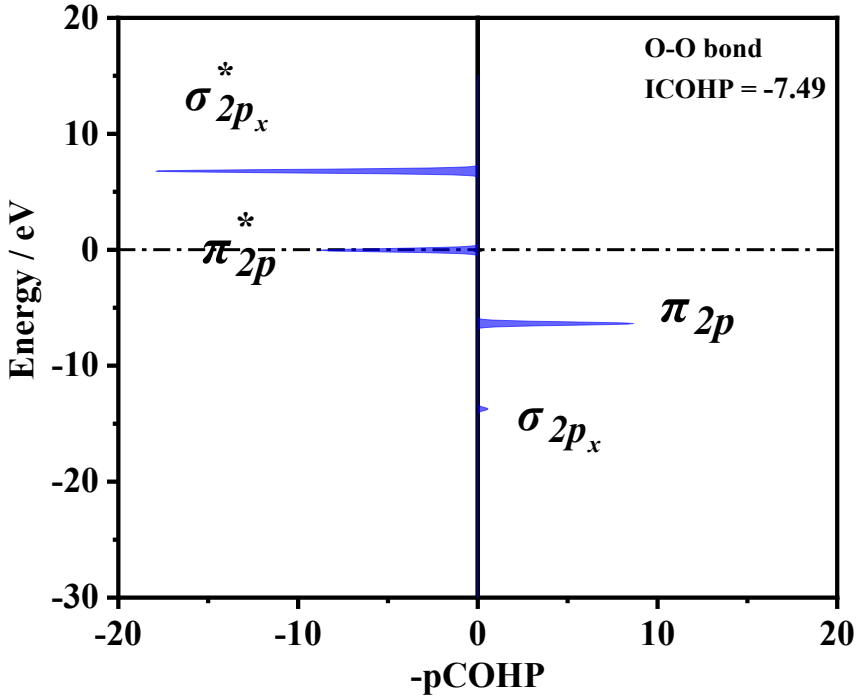

Figure S8. The -pCOHP curve of O-O bond for free O_2 molecule.

Table S1. The binding energy (E_b) between TM single atom and C_6N_6, the cohesive energy (E_{coh}) of TM bulk structure and the difference (E_f) between them for TM single atom embedded in the C_6N_6, the diffusion energy (E_{diff}) of TM single atom from TM@C_6N_6 and the difference (E_{diff} - E_f) between E_{diff} and E_f. (unit: eV)

TM	$E_{TM\ (single)}$	E_b	$E_{TM\ (bulk)}$	N	E_{coh}	E_f	E_{diff}	E_{diff} - E_f
Sc	-1.95	-7.54	-12.39	2	-4.24	-3.30	7.38	/
Ti	-2.38	-6.99	-15.51	2	-5.38	-1.62	6.75	/
V	-3.69	-5.93	-17.85	2	-5.23	-0.70	5.82	/
Cr	-5.44	-4.53	-18.93	2	-4.03	-0.51	7.59	/
Mn	-5.10	-4.37	-35.59	4	-3.79	-0.57	7.35	/
Fe	-3.38	-3.76	-16.45	2	-4.85	1.09	5.70	4.60
Co	-1.57	-4.81	-14.07	2	-5.47	0.66	5.46	4.80
Ni	-0.29	-4.89	-21.87	4	-5.17	0.29	4.83	4.54
Cu	-0.29	-3.29	-14.91	4	-3.43	0.14	3.32	3.18
Zn	-0.01	-1.28	-2.19	2	-1.09	-0.19	1.26	/
Y	-2.44	-8.39	-12.86	2	-3.99	-4.40	8.40	/
Zr	-2.54	-8.28	-17.04	2	-5.98	-2.31	8.55	/
Nb	-3.66	-6.89	-20.42	2	-6.55	-0.35	7.22	/
Mo	-4.59	-5.40	-21.89	2	-6.36	0.96	5.39	4.43
Tc	-3.42	-5.60	-20.75	2	-6.96	1.36	5.46	4.10
Ru	-1.24	-6.57	-18.50	2	-8.01	1.44	6.40	4.97
Rh	-1.29	-5.33	-29.09	4	-5.99	0.65	5.31	4.66
Pd	-1.46	-3.29	-20.81	4	-3.74	0.45	3.23	2.78
Ag	-0.20	-2.96	-10.84	4	-2.51	-0.45	2.95	/
Cd	-0.01	-1.35	-1.44	2	-0.71	-0.65	1.35	/
Hf	-3.37	-8.45	-19.92	2	-6.59	-1.86	8.20	/
Ta	-3.61	-7.90	-23.73	2	-8.25	0.35	8.38	8.03
W	-4.54	-6.26	-26.03	2	-8.47	2.22	7.80	5.58
Re	-4.61	-5.03	-24.85	2	-7.82	2.79	6.21	3.42
Os	-2.89	-5.72	-24.18	2	-9.20	3.47	6.82	3.35
Ir	-1.43	-5.84	-35.33	4	-7.40	1.57	5.66	4.09
Pt	-0.55	-4.38	-24.34	4	-5.53	1.15	4.30	3.15
Au	-0.18	-2.10	-12.78	4	-3.01	0.91	2.09	1.18
Hg	-0.01	-0.39	-0.38	2	-0.18	-0.21	0.38	/

Table S2. The number of charge transfer from TM single atom to C_6N_6 substrate via Bader charge analysis for 29 TM@C_6N_6. (unit: *e*)

TM	Charge transfer
Sc	1.67
Ti	1.38
V	1.21
Cr	1.23
Mn	1.26
Fe	1.11
Co	0.85
Ni	0.77
Cu	0.72
Zn	1.06
Y	2.08
Zr	1.68
Nb	1.52
Mo	1.19
Tc	1.09
Ru	0.70
Rh	0.63
Pd	0.57
Ag	0.68
Cd	1.16
Hf	1.62
Ta	1.54
W	1.29
Re	1.16
Os	0.91
Ir	0.64
Pt	0.60
Au	0.48
Hg	0.10

Table S3. The adsorption energy (ΔE_{O2*}) of O_2 molecule on the surface of 29 TM@C_6N_6. (unit: eV)

TM	ΔE_{O2*}
Sc	-3.37
Ti	-3.81
V	-2.96
Cr	-2.16
Mn	-1.26
Fe	-2.65
Co	-1.90
Ni	-0.87
Cu	-0.68
Zn	-1.16
Y	-2.22
Zr	-4.38
Nb	-3.72
Mo	-2.84
Tc	-2.28
Ru	-1.79
Rh	-0.85
Pd	-1.06
Ag	-0.13
Cd	-0.36
Hf	-4.54
Ta	-4.19
W	-3.70
Re	-2.88
Os	-1.97
Ir	-1.09
Pt	-1.08
Au	-0.30
Hg	0.82

Table S4. The O-O bond length of O_2*, OOH* and H_2O_2* on 11 TM@C_6N_6 (O-O bond lengths of O_2, OOH, H_2O_2 are 1.23 Å, 1.35 Å and 1.48 Å in vacuum, respectively. (unit: Å)

TM	O-O bond length		
	O_2*	OOH*	H_2O_2*
Mn	1.31	1.46	/
Co	1.37	1.45	/
Ni	1.29	1.42	1.51
Cu	1.29	1.40	1.49
Zn	1.32	1.46	1.48
Ru	1.41	/	/
Rh	1.29	1.42	1.49
Pd	1.30	1.43	1.46
Os	1.44	/	/
Ir	1.31	1.44	1.50
Pt	1.30	1.43	/

Table S5. The O-O bond length of O_2*, OOH* and H_2O_2* on $Cu@C_6N_6$ with a adsorbed H_2O. (unit: Å)

O-O bond length		
O_2*	OOH*	H_2O_2*
1.28	1.40	1.47

Table S6. The adsorption strengths (ΔE_{O2*}, ΔG_{OOH*}, ΔG_{O*}, ΔG_{OH*}) of reaction (O_2) and intermediates (OOH, O, OH). (unit: eV)

TM	ΔE_{O2*} / eV	ΔG_{OOH} / eV	ΔG_{O} / eV	ΔG_{OH} / eV
Sc	-3.37	1.97	-0.29	-1.28
Ti	-3.81	-0.70	-0.94	-0.81
V	-2.96	-0.84	-0.38	-0.38
Cr	-2.16	3.04	0.70	0.03
Mn	-1.26	3.46	1.33	1.52
Fe	-2.65	2.59	0.68	-0.55
Co	-1.90	3.16	1.62	0.49
Ni	-0.87	3.85	2.35	0.80
Cu	-0.68	4.20	3.08	1.16
Zn	-1.16	3.41	2.66	0.02
Y	-2.22	2.24	0.27	-1.40
Zr	-4.38	-1.02	-1.89	-1.51
Nb	-3.72	-1.92	-1.34	-0.80
Mo	-2.84	-0.75	-0.20	-0.07
Tc	-2.28	3.07	0.13	0.07
Ru	-1.79	1.58	1.14	0.55
Rh	-0.85	3.71	2.16	0.91
Pd	-1.06	3.90	3.16	1.30
Ag	-0.13	5.26	4.46	2.22
Cd	-0.36	3.92	3.42	0.67
Hf	-4.54	-1.26	-1.83	-1.72
Ta	-4.19	-2.54	-1.67	-1.07
W	-3.70	-2.49	-1.06	-1.00
Re	-2.88	-1.11	-0.41	-0.50
Os	-1.97	0.69	0.65	0.22
Ir	-1.09	3.32	1.55	0.42
Pt	-1.08	3.69	2.06	0.62
Au	-0.30	4.27	3.15	0.99

Table S7. The number of positive charge (N_{pc}) for 29 active metals. (unit: *e*)

TM	N_{pc}
Sc	1.67
Ti	1.38
V	1.21
Cr	1.23
Mn	1.26
Fe	1.11
Co	0.85
Ni	0.77
Cu	0.72
Zn	1.06
Y	2.08
Zr	1.68
Nb	1.52
Mo	1.19
Tc	1.09
Ru	0.70
Rh	0.63
Pd	0.57
Ag	0.68
Cd	1.16
Hf	1.62
Ta	1.54
W	1.29
Re	1.16
Os	0.91
Ir	0.64
Pt	0.60
Au	0.48
Hg	0.10

Table S8. The obtained electron (Q_{O2}) of adsorbed O_2 possessed by 29 TM@C_6N_6. (unit: *e*)

TM	Q_{O2}
Sc	0.93
Ti	0.77
V	0.74
Cr	0.78
Mn	0.50
Fe	0.75
Co	0.62
Ni	0.41
Cu	0.38
Zn	0.54
Y	0.74
Zr	1.02
Nb	0.86
Mo	0.79
Tc	0.70
Ru	0.67
Rh	0.43
Pd	0.37
Ag	0.20
Cd	0.47
Hf	0.95
Ta	0.84
W	0.85
Re	0.77
Os	0.73
Ir	0.47
Pt	0.45
Au	0.39
Hg	0.06

Table S9. The *d*-band center (ε_d) of TM for 29 TM@C_6N_6. (unit: eV)

TM	ε_d
Sc	0.45
Ti	0.53
V	0.72
Cr	-1.04
Mn	-1.83
Fe	-0.32
Co	-1.39
Ni	-2.02
Cu	-1.55
Zn	-7.33
Y	2.37
Zr	1.00
Nb	0.22
Mo	-0.69
Tc	-1.88
Ru	-1.25
Rh	-2.46
Pd	-1.70
Ag	-2.62
Cd	-9.15
Hf	1.59
Ta	-0.49
W	-0.72
Re	-1.71
Os	-1.94
Ir	-2.48
Pt	-2.36
Au	-2.79
Hg	-3.54

Table S10. The integrater crystal orbit Hamilton population (ICOHP) between TM and O_2 for TM@C_6N_6.

TM	ICOHP
Sc	-2.17
Ti	-2.20
V	-2.19
Cr	-1.88
Mn	-1.07
Fe	-1.24
Co	-1.24
Ni	-0.87
Cu	-0.83
Zn	-0.85
Y	-2.55
Zr	-2.54
Nb	-2.34
Mo	-2.01
Tc	-1.82
Ru	-0.21
Rh	-1.95
Pd	-1.46
Ag	-0.26
Cd	-0.50
Hf	-3.03
Ta	-2.86
W	-2.44
Re	-1.89
Os	-2.06
Ir	-2.10
Pt	-2.01
Au	-1.33
Hg	-0.02

Reference

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