Electronic Supplementary Information for

Computational screening of two-dimensional metal-benzenehexathial for the oxygen reduction reaction

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Additional computational details

Reaction-free energy calculations

The free energy diagram of the ORR was obtained by using the computational hydrogen electrode (CHE) model proposed by Nørskov and co-workers.[1,2] According to the CHE model, the Gibbs free energy change (ΔG) can be defined as follows:

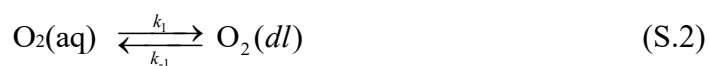$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + G_U + \Delta G_{PH}$$

(S.1)

where ΔE is the electronic energy difference, ΔZPE is the difference of zero-point energy, T is the temperature, and ΔS is defined as the change of entropy correction. The terms ΔG_U and ΔG_{PH} are the free energy contributions related to the electrode potential U and pH, respectively. All the intermediates' ZPE and entropies were obtained from the vibrational frequencies, in which the chemical absorption was accurately calculated, while the surface was fixed. The vibrational frequencies and entropies of molecules, such as H_2; H_2O, can be referenced in the NIST database. Owing to the restriction of the triplet state, the Gibbs free energy of the O_2 molecule was derived by: $G_{O_2} = 4.92 + 2G_{H_2O} - 2G_{H_2}$. For the electr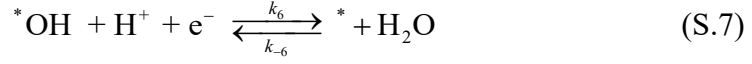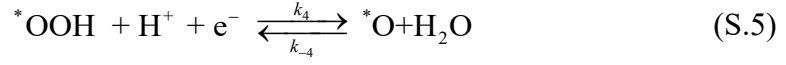ochemical process, limiting potential was defined as $U_L = -\dfrac{\left|\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\right| \max}{e}$, and the value of overpotential was $\eta = 1.23 - U_L$.

Because of the strong correlation that existed on oxide transitional metal, we systemically the intermediates of Co-BHT during ORR via the PBE+U method and PBE functional. The results demonstrate that the free energies of the three intermediates are consistent (Table S2).

Microkinetic analysis

During the whole ORR, O_2 diffusion, adsorption, and four electrochemical reduction steps are considered.

$$O_2(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2(dl) \qquad (S.2)$$

$$O_2(dl) + {}^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} {}^*O_2 \tag{S.3}$$

$$^*O_2 + H^+ + e^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} {}^*OOH \tag{S.4}$$

$$^*OOH + H^+ + e^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} {}^*O + H_2O \tag{S.5}$$

$$^*O + H^+ + e^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} {}^*OH \tag{S.6}$$

$$^*OH + H^+ + e^- \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} {}^* + H_2O \tag{S.7}$$

where k_i is the rate constant and k_{-i} is the reverse reaction's rate constant.

Based on the above steps, the rate equation can be described respectively. There are as follows:

$$\frac{\partial x_{O_2}}{\partial t} = k_1 x_{O_2} - k_{-1}\theta_{O_2(dl)} - k_1\theta_{O_2(dl)}\theta^* + k_{-2}x_{*O_2} \tag{S.8}$$

$$\frac{\partial \theta_*}{\partial t} = k_6\theta_{*OH} - k_{-6}x_{H_2O}\theta_* - k_2\theta_{O_2(dl)}\theta_* + k_{-2}\theta_{*O_2} \tag{S.9}$$

$$\frac{\partial \theta_{*O_2}}{\partial t} = -k_3\theta_{*O_2} + k_{-3}\theta_{*OOH} + k_2\theta_{O_2(dl)}\theta_* - k_{-2}\theta_{*O_2} \tag{S.10}$$

$$\frac{\partial \theta_{*OOH}}{\partial t} = -k_4\theta_{*OOH} + k_{-4}\theta_{*O}x_{H_2O} + k_3\theta_{*O_2} - k_{-3}\theta_{*OOH} \tag{S.11}$$

$$\frac{\partial \theta_{*O}}{\partial t} = -k_5\theta_{*O} + k_{-5}\theta_{*OH} + k_4\theta_{*OOH} - k_{-4}\theta_O x_{H_2O} \tag{S.12}$$

$$\frac{\partial x_{O2}}{\partial t} = k_1 x_{O2} + k_{-1}\theta_{O2} + k_2\theta_{O2} - k_{-2}x_{O2} \tag{S.13}$$

where θ is the coverage of the intermediate species, t is the reaction time and x is the mole fraction. There exists a quantitative relationship among the coverage of these intermediate species

$$\theta_* + \theta_{O_2} + \theta_{*OOH} + \theta_{*O} + \theta_{*OH} = 1$$

(S.14)

For non-electrochemical step i, the equilibrium constant (K_i) and the rate constant k_i are calculated using:

$$K_i = \exp\left(\frac{-\Delta G_i}{k_B T}\right)$$

(S.15)

$$k_i = \gamma_i \exp\left(\frac{-E_{a,i}}{k_B T}\right)$$

(S.16)

where ΔG_i is the free energy change, and is k_B the Boltzmann constant, $E_{a,i}$ and γ_i are the activation energy and pre-exponential factor, respectively.

For electrochemical step i, ΔG_i and k_i are related to the electrode potential (U), which are defined as:

$$K_i = \exp\left(\frac{-e\beta(U - U_i)}{k_B T}\right)$$

(S.17)

$$k_i = A_i \exp\left(\frac{-E_{a,i}}{k_B T}\right)\exp\left(\frac{-e\beta_i(U - U_i)}{k_B T}\right)$$

(S.18)

where U_i is the reversible potential of step i calculated by the equation: $U_i = -\dfrac{\Delta G_i}{e}$, a previous calculation has obtained that $\beta = 0.5$, $E_{a,i} \approx 0.26$ and $A_i = 10^9$.[3] Therefore, we calculated $A_i e^{-\frac{E_{a,i}}{k_B T}}$ to be about 5×10^4, the rate constant can be simplified as $k_i = 5 \times 10^4 e^{-\frac{0.5e(U - U_i)}{k_B T}}$. For all the reverse reactions, the rate constant is $k_{-i} = \dfrac{k_i}{K_i}$, which can be simplified as $k_{-i} = 5 \times 10^4 e^{\frac{0.5e(U - U_i)}{k_B T}}$.[4]

The turnover frequency (TOF) values were calculated by solving the rate equations at steady state.

Finally, the partial current density j is expressed by:

$$j = -2e\rho\text{TOF}_{H2O}$$

(S.19)

Where ρ is the surface density of active sites, it can be defined by:

$$\rho_n = \rho_1/n$$

(S.20)

Because 2D M-BHT is SACs, $n = 1$.

Constant-Potential Calculations

The Poisson–Boltzmann implicit solvation model was used to establish the relationship between charge (adding or removing extra electrons into the slab) and electrode potential (U).[6,7] Considering the high computational cost, we used 5 points to fit quadratic function relations of U and E. In Constant-Potential Calculations, for each species, five independent calculations with system charge from -0.75 to 0.25 in a step of 0.25 were performed. The electric potential of the electrochemical interface is changed by adjusting the work function. It could be calculated by:

$$U = (W_f - 4.60) + 0.0592 \times pH \tag{S.21}$$

where U is electrode potential referenced to SHE, W_f is the work function and 4.60 is the work function of $H_2/H+$ at standard conditions.[6,8,9] The work function could be controlled by adjusting the number of charges. When the electrode potential is at a fixed potential on the RHE scale, the electric potential referenced to the SHE scale is also changed by changing the pH values. It was given by:

$$U_{RHE} = U_{SHE} + 0.0592pH \tag{S.22}$$

According to Neurock methods,[10] the potential-dependent energy can be calculated by:

$$E_{free}(U) = E_{DFT} + \int_0^q \langle V_{tot} \rangle dQ + qW_f \tag{S.23}$$

The electrode potential (U) and energy (E) can be fitted to a function of quadratic form in Figure S5, and this quadratic form is consistent with a capacitor created by charged-slab and background-charge system, which could be written as:

$$E(U) = -\frac{1}{2}C(U - U_{PZC})^2 + E_0 \tag{S.24}$$
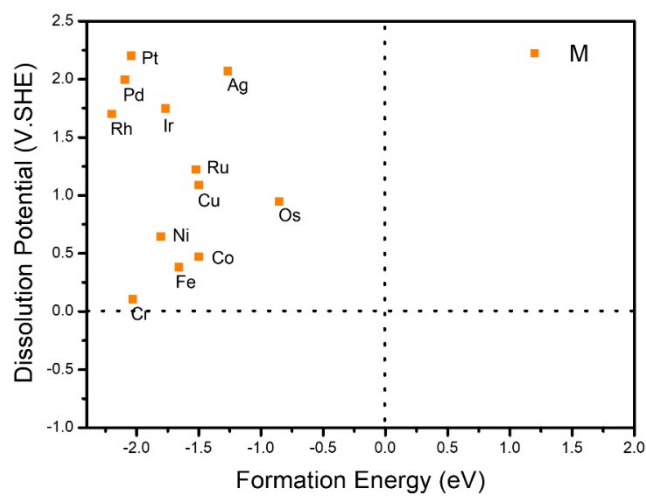
Supporting Figure S1-S7

Fig. S1 Computed formation energy and dissolution potential of metal atoms in M-BHT monolayers.
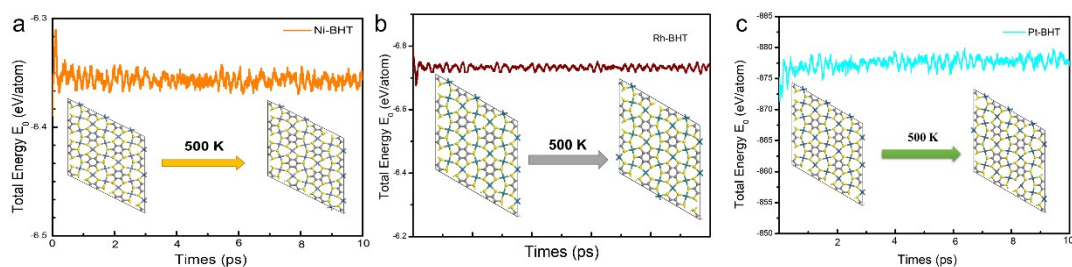

Fig. S2 Evolution of the total energy of ab initio molecular dynamics (AIMD) simulations for (a) the Ni-BHT monolayer, (b) the Rh-BHT monolayer, and (c) Pt-BHT monolayer at 500 K.
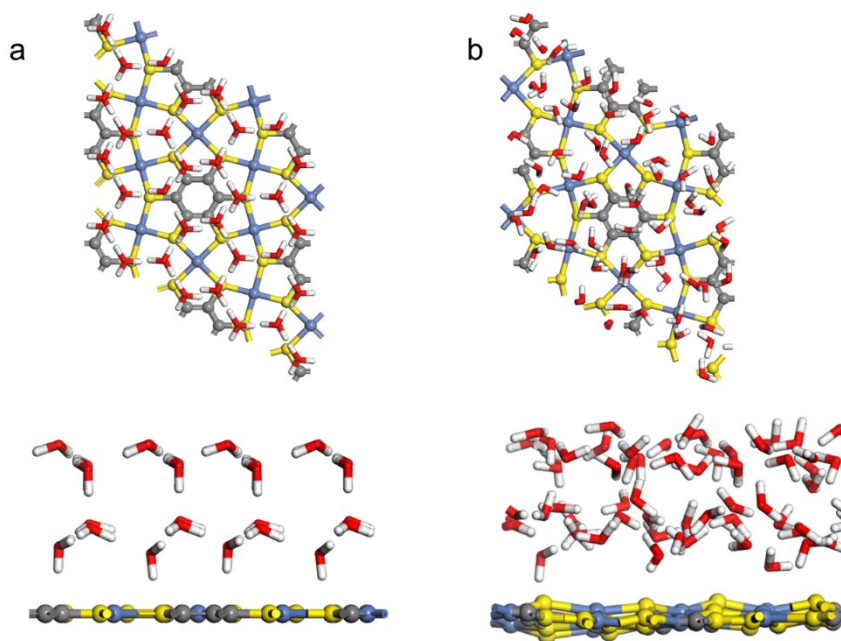
Fig. S3 Snapshots of equilibrium of (a) the initial and (b) final structure of Ni-BHT monolayer in an aqueous environment at 300 K after 10 ps AIMD simulation.
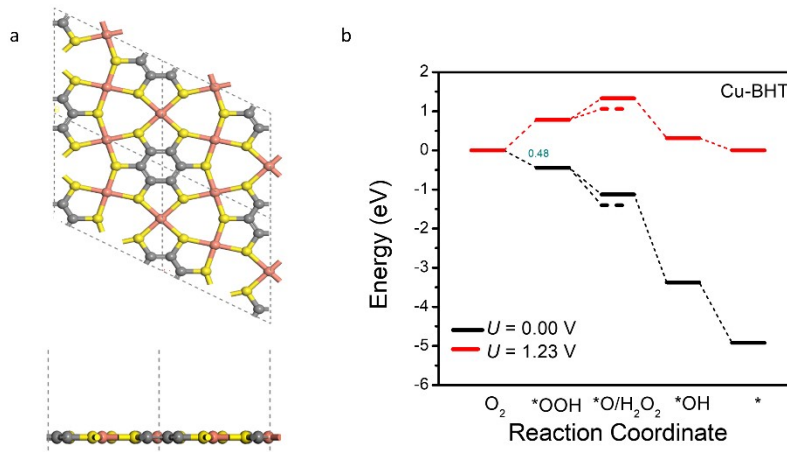

Fig. S4 (a) Top and side views of the Cu-BHT monolayer. (b) Free energy diagrams of the 4e ORR (solid lines) and the 2e ORR (dashed lines) proceeded on the Cu-BHT monolayer at $U = 0$ V and $U = 1.23$ V.
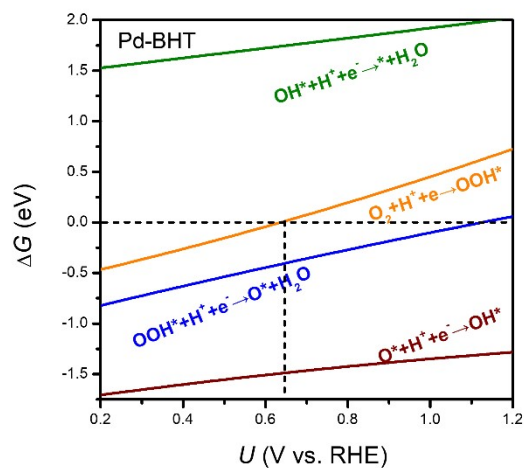
Fig. S5 Free energy change of the Pd-BHT monolayer as a function of potential at pH = 1.
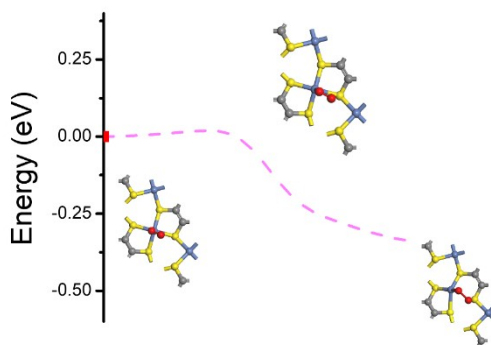

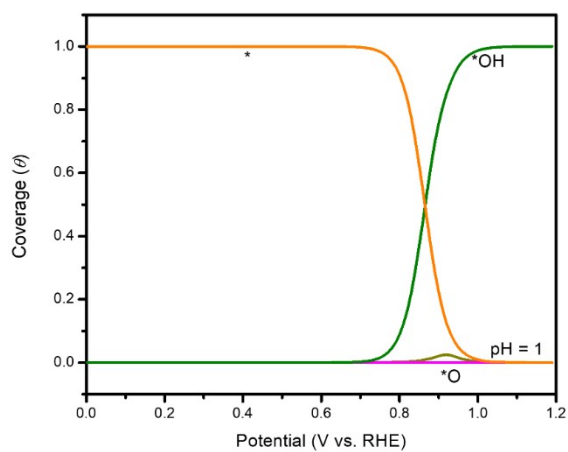**Fig. S6** The O_2 adsorption process on Ni-BHT by CI-NEB.

Fig. S7 The coverage curves of the major ORR species on the Ni-BHT at pH = 1.

Table S1 Optimized lattice parameters of M-BHT and their O_2 adsorption configurations.

Metal	Lattice constant (Å)	O–O bond length (Å)	Adsorption model
Fe	8.61	1.29	side-on
Co	8.47	1.29	side-on
Ni	8.56	1.29	end-on
Cu	8.76	1.29	end-on
Ru	8.67	1.30	end-on
Rh	8.70	1.29	end-on
Pd	8.90	1.27	side-on
Os	8.67	1.31	end-on
Ir	8.69	1.29	end-on
Pt	8.82	1.29	end-on

Table S2 Free Energy of intermediates of Co-BHT calculated by PBE and PBE+U. The effective Hubbard-U parameter (U_{eff}) for Co was set to be 2.0 eV.

	ΔG_{*OOH}	ΔG_{*O}	ΔG_{*OH}
PBE	3.51	1.63	0.60
PBE+U	3.53	1.62	0.56

References

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