## **Supporting Information**

Theoretical insights on the catalytic mechanism for the oxygen reduction reaction on  $M_3$ (hexaiminotriphenylene)<sub>2</sub> (M = Ni, Cu)

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		E	ads
	$U_{\rm eff}(ev)$	ООН	0
GGA	_	-0.44	-1.64
GGA + U	2	-0.40	-1.60
	3	-0.38	-1.56
	4	-0.36	-1.53
	5	-0.34	-1.49

**Table S1.** The adsorption energies ( $E_{ads}$ , eV) for OOH and O atom on the top site of monolayers Ni<sub>3</sub>(HITP)<sub>2</sub> calculated (with VASP) using GGA and GGA + U methods.

**Table S2.** The Mulliken charge transfer (Q, e) values of ORR intermediates on  $M_3(HITP)_2$  (M=Cu, Ni).

	OOH	0	ОН	H <sub>2</sub> O	$H_2O_2$
Ni <sub>3</sub> (HITP) <sub>2</sub>	-0.24	-0.42	-0.39	-0.02	-0.04
Cu <sub>3</sub> (HITP) <sub>2</sub>	-0.36	-0.42	-0.48	-0.02	-0.04



Fig. S1. The spin density contour plot of  $Cu_3(HITP)_2$  in (a) doublet, (b) triplet and (c) quartet. The isosurface value is set to be 0.005. The spin density average value of Cu, N, and C are listed under the three plots. The H atoms spin density distributions are ignored.



Fig. S2. The optimized structures of ORR intermediates of (a) O<sub>2</sub>, (b) OOH, (c) OH,(d) O (bridge site), (e) O (top site), (f) H<sub>2</sub>O on Cu<sub>3</sub>(HITP)<sub>2</sub>.



Fig. S3. The configurations of the initial state (left panel), transition state (middle panel), and final state (right panel) for  $a_6$  and  $a_6$ .



Fig. S4. The configurations of the initial states (left panel), transition states (middle panel), and final states (right panel) for all the reaction pathways on  $Cu_3(HITP)_2$ .  $E_{bar}$  represents the energy barrier and  $\Delta E$  represents the reaction energy (in units of eV).



Fig. S4. (continued).



Fig. S5. The optimized structures of OOH (a, d), O (b, e), and OH (c, f) on  $Ni_3(HITP)_2$  (a, b, c) and  $Cu_3(HITP)_2$  (d, e, f), respectively.



**Fig. S6.** The optimized structures of various ORR intermediates inside the pore of the  $Ni_3(HITP)_2$ . (a)  $O_2$ , (b) OOH, (c) O, (d) OH, (e)  $H_2O$ , (f)  $H_2O_2$ .  $E_{ads}$  is the absorption energy.



Fig. S7. The relative energy diagram of ORR inside the pore of the  $Ni_3(HITP)_2$ .



Fig. S8. The optimized (with VASP) eclipsed structures of Ni<sub>3</sub>(HITP)<sub>2</sub>.



Fig. S9. The optimized structures of ORR intermediates of (a) OOH, (b) O, and (c) OH on bilayer  $Ni_3(HITP)_2$ .

## **Computational details I:**

Further calculations were performed using the Vienna ab initio Simulation Package (VASP)<sup>1-3</sup>. During the calculations, the ion cores were represented by the projector–augmented wave (PAW) potentials. The generalized gradient approximation (GGA) for the exchange–correlation potential prescribed by Perdew–Burke–Ernzerhof (PBE) was used to handle the exchange and correlations. Spin–polarized GGA + U calculations were also performed with a  $U_{eff}$  $(U_{eff} = 2-5)$  value for the Ni ions. The hybrid Heyd–Scuseria–Ernzerhof (HSE06)<sup>4-6</sup> functional was used for calculation the electronic band gap. For geometry optimization, the total energy change is set to less than 10<sup>-4</sup> eV and the magnitude of the largest force acting on the atoms is set to less than 0.02 eV Å<sup>-1</sup>. A kinetic energy cutoff of 420 eV was employed. The Brillouin zone integration was performed with 5 × 5 × 1 k–points for geometry optimizations, and the 2 × 2 × 1 k–mesh for calculations of band structures using the HSE06 functional.

## **Computational details II:**

The 4e<sup>-</sup> ORR in an acidic medium proceeds via the following reactions:<sup>7</sup>

 $O_{2} + (H^{+} + e^{-}) \rightarrow \cdot OOH (aq)$ (1a)  $\cdot OOH (aq) \rightarrow OOH^{*}$ (1b)  $OOH^{*} + (H^{+} + e^{-}) \rightarrow O^{*} + H_{2}O$ (2)  $O^{*} + (H^{+} + e^{-}) \rightarrow OH^{*}$ (3)

 $OH^* + H^+ + e^- \rightarrow H_2O + *$  (4)

The  $\Delta G$  of each step is calculation by (where  $G_{(\mathrm{H}^+ + \mathrm{e}^-)} = 1/2G_{\mathrm{H}_2}$ )<sup>8</sup>:

$$\Delta G_1 = G_{\rm OOH^*} - G_{*+O_2 + 1/2H_2}$$

 $\Delta G_2 = G_{\rm O^* + H_2O} - G_{\rm OOH^* + 1/2H_2}$ 

$$\Delta G_3 = G_{\rm OH^*} - G_{\rm O^* + 1/2H_2}$$

$$\Delta G_4 = G_{* + H_2O} - G_{OH^* + 1/2H_2}$$

The overpotential of ORR ( $\eta^{\text{ORR}}$ ) is calculated by:

$$G^{\text{ORR}} = \min(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)$$

 $\eta^{\text{ORR}} = 1.23 \text{ V} - G^{\text{ORR}/\text{e}}$ 

## References

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