Electronic Supplementary Information

Two-Dimensional Conductive Metal-Organic Frameworks with Dual Metal Sites toward Electrochemical Oxygen Evolution Reaction

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1. Experimental Section

**TOF calculation:** The TOF values were estimated according to the following formula:

\[
\text{TOF} = \frac{\text{number of total oxygen turnovers / cm}^2}{\text{number of active sites / cm}^2}
\]

The number of total oxygen turnovers was calculated from the current density by the following equation:

\[
\text{Number of O}_2 = \left(\frac{1 \text{ mA/cm}^2}{1000 \text{ mA}}\right) \left(\frac{1 \text{ mol e}^-}{96485.3 \text{ e}^-}\right) \left(\frac{1 \text{ mol O}_2}{4 \text{ mol e}^-}\right) \left(\frac{6.022 \times 10^{23} \text{ O}_2 \text{ molecules}}{1 \text{ mol O}_2}\right) = 1.56 \times 10^{15} \frac{\text{O}_2/s \text{ per mA}}{\text{cm}^2}
\]

The number of active sites was regarded as the number of surface sites (Ni atoms are regarded as possible active sites), and calculated by the following formula:

\[
\text{Number of active sites} = \left(\frac{\text{number of Ni atoms / unit cell}}{\text{Volume / unit cell}}\right)^3
\]

Finally, the plot of current density can be converted into a TOF plot according to the following formula:

\[
\text{TOF} = \frac{1.56 \times 10^{15} \frac{\text{O}_2}{\text{cm}^2 \text{ per mA}} \times |J|}{\text{Number of active sites} \times A_{\text{ECSA}}}
\]

The \(A_{\text{ECSA}}\) is the electrochemical active surface area, which can be calculated from the following formula, where specific capacitance is \(C_{\text{dl}}\), and 40 μF is a constant to convert capacitance to \(A_{\text{ECSA}}\):

\[
A_{\text{ECSA}} = \frac{\text{specific capacitance}}{40 \text{ μF cm}^{-2} \text{ per cm}^2_{\text{ECSA}}}
\]

**D-band center Analysis:** The d-band center (\(\varepsilon_d\)) was calculated according to following equation:

\[
\varepsilon_d = \frac{\int N(\varepsilon)\varepsilon \, d\varepsilon}{N(\varepsilon) \, d\varepsilon}
\]

Where \(N(\varepsilon)\) is the d-band DOS, \(\varepsilon\) is the energy. The integration was set in the whole range of d-band DOS.
2. $^1$H NMR and MALDI-TOF MS

**Figure S1.** $^1$H NMR spectra of NiPc.

**Figure S2.** MALDI-TOF MS spectra of ZnPc.
3. FT-IR Spectra

Figure S3. FT-IR spectra of NiPc, NiPc-Ni and NiPc-Zn.
4. PXRD Measurements

Table S1. Lattice parameters of MPc-M' MOFs

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>NiPc-Ni</th>
<th>NiPc-Zn</th>
<th>ZnPc-Ni</th>
<th>ZnPc-Zn</th>
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<tbody>
<tr>
<td>a (Å)</td>
<td>17.8963</td>
<td>17.9504</td>
<td>17.9396</td>
<td>17.9936</td>
</tr>
<tr>
<td>b (Å)</td>
<td>17.8963</td>
<td>17.9504</td>
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<td>17.9936</td>
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<tr>
<td>c (Å)</td>
<td>3.4372</td>
<td>3.4317</td>
<td>3.4337</td>
<td>3.4283</td>
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<td>α (°)</td>
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<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

Figure S4. PXRD patterns of NiPc-Ni, NiPc-Zn, ZnPc-Ni and ZnPc-Zn.
5. SEM Images

Figure S5. SEM images of NiPc-Ni (a, b), NiPc-Zn (c, d), ZnPc-Ni (e, f), ZnPc-Zn (g, h).
6. TEM Images

Figure S6. TEM images of NiPc-Ni (a-c), NiPc-Zn (d-f), ZnPc-Ni (g-i), ZnPc-Zn (j-l).
Figure S7. EDX mapping images of NiPc-Ni (a), NiPc-Zn (b), ZnPc-Ni (c), ZnPc-Zn (d).
7. XPS Spectra

Figure S8. XPS survey spectra of NiPc-Ni

Figure S9. XPS spectra of NiPc-Zn: a) survey, b) C 1s, c) N 1s, d) O 1s, e) Ni 2p, f) Zn 2p. There is a integral ratio of 58:42 for C=O : C-O.
Figure S10. XPS spectra of ZnPc-Ni: a) survey, b) C 1s, c) N 1s, d) O 1s, e) Ni 2p, f) Zn 2p. There is an integral ratio of 54:46 for C=O : C-O.

Figure S11. XPS spectra of ZnPc-Zn: a) survey, b) C 1s, c) N 1s, d) O 1s, e) Zn 2p. There is an integral ratio of 53:47 for C=O : C-O.
8. ECSA Measurements

Figure S12. CVs in non-faradaic region of four MOFs.
9. TOF calculation

Figure S13. TOF of NiPc-Ni, NiPc-Zn and ZnPc-Ni based on LSV tests.
10. Band Structure Calculations

Figure S14. a) Brillouin zone and K-path selection for MOFs. b-e) Band structure and indirect band-gap of NiPc-Ni, NiPc-Zn, ZnPc-Ni, and ZnPc-Zn, respectively.
11. Stability Test

Figure S15. a) Chronoamperometry test of NiPc-Ni @Carbon Cloth. b) Ni 2p XPS spectra before and after chronoamperometry test.
12. Comparison Table

Table S2. Comparisons of the OER activity of MOF-based catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>onset overpotential (mV)</th>
<th>overpotential @ j=10 mA/cm² (mV)</th>
<th>Tafel slope (mV/dec)</th>
<th>Substrate</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>NiPc-Ni</td>
<td>1.0 M KOH</td>
<td>319</td>
<td>427</td>
<td>83</td>
<td>GC</td>
<td>This work</td>
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<td>Pb-TCPP</td>
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<td>470</td>
<td>106.2</td>
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<td>Dalton Trans., 2016, 45, 61-65</td>
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<td>UTSA-16</td>
<td>1.0 M KOH</td>
<td>320</td>
<td>408</td>
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<td>GC</td>
<td>ACS Appl. Mater. Interfaces, 2017, 9, 7193-7201</td>
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<td>Fe-MOF</td>
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<td>443</td>
<td>74</td>
<td>GC</td>
<td>J. Mater. Chem. A., 2020, 8, 3658-3666</td>
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<td>Ni-Cu(BDC)</td>
<td>1.0 M KOH</td>
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<td>375</td>
<td>179.7</td>
<td>GC</td>
<td>New J. Chem., 2020, 44, 2459-2464</td>
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<td>Ni₅Ru₆(HHT₃P)₃</td>
<td>0.1 M KOH</td>
<td>290</td>
<td>390</td>
<td>61</td>
<td>GC</td>
<td>Chem. Commun., 2020, 56, 13615-13618</td>
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<td>Co-AIM NU-1000</td>
<td>pH 11</td>
<td>400</td>
<td>-</td>
<td>90</td>
<td>FTO</td>
<td>ACS Appl. Mater. Interfaces., 2015, 7, 28223-28230</td>
</tr>
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<td>[Co₃(HHTP)₂]₆</td>
<td>0.1 M KOH</td>
<td>340</td>
<td>490</td>
<td>83</td>
<td>FTO</td>
<td>Chem. Commun., 2018, 54, 13579-13582</td>
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<tr>
<td>NNU-23</td>
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<td>-</td>
<td>365</td>
<td>81.8</td>
<td>Carbon Cloth</td>
<td>Angew. Chem. Int. Ed., 2018, 57, 9660-9664</td>
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</table>

References: