Supplementary information

Bifunctional porphyrin based metal-organic polymers for enhanced electrochemical water splitting

Neidy Ocuane, Yulu Ge, Christian Sandoval-Pauker, Dino Villágran

*Dino Villagrán

Email: dino@utep.edu
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Scheme S2. Synthesis of 5,10,15, 20 tetrakis (4-aminophenylporphyrin) - H₂TAPP.
Scheme S3. Synthesis of metalloporphyrin (M-TAPP).
**Figure S1**: SEM images of carbon paper coated with cobalt polymer 2 ink. A) carbon paper before bulk electrolysis; B) carbon paper electrode after bulk electrolysis.

**Figure S2**: TEM images of cobalt polymer 2, at different magnifications.
Figure S3: TEM images of polymer 2 after 10h electrolysis experiment in 1M KOH electrolyte solution
Figure S4. EDX of A) Fe polymer (1), B) Co polymer (2), C) Ni polymer (3), and D) Cu polymer (4).
Figure S5. Elemental mapping of Fe polymer (1), Co polymer (2), Ni polymer (3), and Cu polymer (4).
Figure S7: pXRD of the carbon paper electrode coated with cobalt polymer 2. Bottom diffraction pattern corresponds to the coated electrode before electrolysis and top diffraction pattern corresponds to the spectra after bulk electrolysis experiment.
Figure S8: UV-vis spectra of free base porphyrin, metallated porphyrin and metal polymers in DMF. A) H₂TAPP, iron porphyrin and iron polymer (1); B) H₂TAPP, cobalt porphyrin and cobalt polymer (2); C) H₂TAPP, nickel porphyrin and nickel polymer (3); D) H₂TAPP, copper porphyrin and copper polymer (4).
Figure S9. Infrared spectra of the different synthetic stages from meta free to polymerization A) H₂TAPP, iron porphyrin and iron polymer (1); B) H₂TAPP, cobalt porphyrin and cobalt polymer (2); C) H₂TAPP, nickel porphyrin and nickel polymer (3); D) H₂TAPP, copper porphyrin and copper polymer (4).
**Figure S10.** Linear sweep voltammogram of metal porphyrin monomers A) OER and B) HER of co-porphylar, Ni-porphylar and Cu-porphylar voltammogram of metal porphyrin monomers A) OER of co-TAPP, Ni-TAPP and Cu-TAPP B) HER of Co-TAPP, Ni-TAPP and Cu-TAPP and C) and D) respective tafel slopes

**Table S1.** Over potential values of metalloporphyrins

<table>
<thead>
<tr>
<th>M-TAPP</th>
<th>$\eta_1$</th>
<th>$\eta_{10}$</th>
<th>$j_{max}$</th>
<th>$\eta_1$</th>
<th>$\eta_{10}$</th>
<th>$j_{max}$</th>
</tr>
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<tbody>
<tr>
<td>Fe-TAPP</td>
<td>357</td>
<td>506</td>
<td>-44.6</td>
<td>153</td>
<td>754</td>
<td>9.06</td>
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<tr>
<td>Co-TAPP</td>
<td>357</td>
<td>436</td>
<td>-75.6</td>
<td>229</td>
<td>695</td>
<td>16.3</td>
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<td>Ni-TAPP</td>
<td>326</td>
<td>441</td>
<td>-37.4</td>
<td>556</td>
<td>754</td>
<td>5.01</td>
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<tr>
<td>Cu-TAPP</td>
<td>481</td>
<td>693</td>
<td>-5.39</td>
<td>230</td>
<td>754</td>
<td>9.96</td>
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</table>
Figure S11: Cathodic linear sweep voltammogram measured in 0.5 M H$_2$SO$_4$ solution using copper polymer 4 as HER cathode and cobalt polymer 2 as OER anode pairs in a full cell device experiment.
Figure S12. Double layer capacitance of the non-faradaic region in basic conditions.
Figure S13. Double layer capacitance of the non-faradaic region in acidic conditions.
Figure S14. Computed electronic structure of CoTPP at the TPSSH-D3/def2-TZVP level of theory. Molecular orbitals are plotted at an isosurface of 0.02 a.u. Hydrogen atoms are omitted for clarity.
Figure S15. Computed electronic structure of the monomer model of Co-polymer (2) at the TPSSh-D3/def2-TZVP level of theory. Molecular orbitals are plotted at an isosurface of 0.02 a.u. Hydrogen atoms are omitted for clarity.
**Figure S16.** Computed equilibrium structure of CoTPP and the monomer model of Co-polymer (2) at the PBE0-D3/def2-TZVP(-f) level. Calculated metrics are provided in Å. Hydrogen atoms are omitted for clarity.

**Table S4.** Calculated Mulliken and atomic dipole corrected Hirshfeld atomic charges (TPSSh-D3/def2-TZVP)

<table>
<thead>
<tr>
<th></th>
<th>CoTPP</th>
<th>Mulliken</th>
<th>Hirshfeld (ADCH)</th>
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<tbody>
<tr>
<td>Co</td>
<td>0.004</td>
<td>0.216</td>
<td></td>
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<tr>
<td>N</td>
<td>-0.177</td>
<td>-0.145</td>
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<tr>
<td>N</td>
<td>-0.177</td>
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<tr>
<td>N</td>
<td>-0.179</td>
<td>-0.139</td>
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<tr>
<td>N</td>
<td>-0.178</td>
<td>-0.142</td>
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<tr>
<td>Co(II) monomer model</td>
<td>0.001</td>
<td>0.202</td>
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<tr>
<td>N</td>
<td>-0.175</td>
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<tr>
<td>N</td>
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<td>N</td>
<td>-0.174</td>
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<tr>
<td>N</td>
<td>-0.176</td>
<td>-0.131</td>
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Figure S17. Electrochemical impedance spectroscopy (EIS) of oxygen evolution reaction (OER) in basic condition (1.0 M KOH solution) and respective simulation catalyzed by A) Co-porphyrin B) Fe-porphyrin C) Ni-porphyrin and D) Cu-porphyrin. E) the equivalent circuit from simulated impedance spectra. Bode plots of OER in 1.0 M KOH (1) Co-porphyrin (2) Fe-porphyrin (3) Ni-porphyrin and (4) Cu-porphyrin.
Figure S18 Electrochemical impedance spectroscopy (EIS) of hydrogen evolution reaction (OER) in basic condition (0.5 M H$_2$SO$_4$ solution) and respective simulation catalyzed by A) Co-porphvlar B) Fe-porphvlar C) Ni-porphvlar and D) Cu-porphvlar. E) the equivalent circuit from simulated impedance spectra. Bode plots of OER in 1.0 M KOH (1) Co-porphvlar (2) Fe-porphvlar (3) Ni-porphvlar and (4) Cu-porphvlar.
Table S2. Equivalent circuits parameters for the oxygen evolution reaction.

<table>
<thead>
<tr>
<th></th>
<th>OER</th>
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<tbody>
<tr>
<td></td>
<td>Fe-porphylar</td>
<td>Co-porphylar</td>
<td>Ni-porphylar</td>
<td>Cu-porphylar</td>
</tr>
<tr>
<td>R1 (Ohm)</td>
<td>62.76e-15</td>
<td>47.33e-15</td>
<td>0.109e-12</td>
<td>15.81e-15</td>
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<tr>
<td>CPE1 (F_s(a-1))</td>
<td>6.529e-6</td>
<td>8.08e-6</td>
<td>4.84e-6</td>
<td>18.52e-6</td>
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<tr>
<td>A1</td>
<td>0.767</td>
<td>0.742</td>
<td>0.772</td>
<td>0.671</td>
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<tr>
<td>R2 (Ohm)</td>
<td>4.721</td>
<td>7.626</td>
<td>7.238</td>
<td>7.709</td>
</tr>
<tr>
<td>CPE3 (F_s(a-1))</td>
<td>0.396e-3</td>
<td>0.589e-3</td>
<td>82.13e-6</td>
<td>0.876e-3</td>
</tr>
<tr>
<td>A3</td>
<td>0.747</td>
<td>0.863</td>
<td>0.893</td>
<td>0.854</td>
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<tr>
<td>R3 (Ohm)</td>
<td>107.2</td>
<td>16.69</td>
<td>99.7</td>
<td>224.5</td>
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<tr>
<td>(\chi/N^{1/2})</td>
<td>1.641</td>
<td>0.166</td>
<td>1.425</td>
<td>2.866</td>
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<tr>
<td>(\chi^2)</td>
<td>0.02891</td>
<td>0.01577</td>
<td>0.0263</td>
<td>0.09729</td>
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Table S3. Equivalent circuits parameters for the hydrogen evolution reaction.

<table>
<thead>
<tr>
<th></th>
<th>HER</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Fe-porphylar</td>
<td>Co-porphylar</td>
<td>Ni-porphylar</td>
<td>Cu-porphylar</td>
</tr>
<tr>
<td>R1 (Ohm)</td>
<td>5.024</td>
<td>7.71</td>
<td>5.567</td>
<td>21.56e-12</td>
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<tr>
<td>R2 (Ohm)</td>
<td>303.8</td>
<td>1.847</td>
<td>222.4</td>
<td>86.58</td>
</tr>
<tr>
<td>CPE2 (Ohm)</td>
<td>0.33e-3</td>
<td>0.234e-3</td>
<td>49.95e-6</td>
<td>80.7e-6</td>
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<tr>
<td>A2</td>
<td>0.8627</td>
<td>0.8974</td>
<td>0.9041</td>
<td>0.8474</td>
</tr>
<tr>
<td>CPE3 (F_s(a-1))</td>
<td>0.0558</td>
<td>0.3215</td>
<td>0.0667</td>
<td>0.1217</td>
</tr>
<tr>
<td>A3</td>
<td>0.253</td>
<td>0.798</td>
<td>0.1913</td>
<td>0.02612</td>
</tr>
<tr>
<td>(\chi/N^{1/2})</td>
<td>5.004</td>
<td>0.2873</td>
<td>1.52</td>
<td>0.9102</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>0.04413</td>
<td>0.01818</td>
<td>0.01624</td>
<td>0.02052</td>
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</tbody>
</table>
Figure S19. NMR of free base porphyrin (H$_2$TAPP) in dimethylsulfoxide (DMSO).
Table S5. Comparison of porphyrin material for electrochemical OER

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\eta_{10}$ (mV)</th>
<th>Tafel slope mV/dec</th>
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</thead>
<tbody>
<tr>
<td>Fe-porphvlar *</td>
<td>506</td>
<td>195.7</td>
</tr>
<tr>
<td>Co-porphvlar *</td>
<td>435</td>
<td>69.2</td>
</tr>
<tr>
<td>Ni-porphvlar *</td>
<td>424</td>
<td>96</td>
</tr>
<tr>
<td>CoTcPP/ZrP$^1$</td>
<td>476</td>
<td>76.4</td>
</tr>
<tr>
<td>FeTAPP-NiTCPP-POP$^2$</td>
<td>338</td>
<td>52</td>
</tr>
<tr>
<td>CoP-2ph-CMP-800$^3$</td>
<td>370</td>
<td>86</td>
</tr>
<tr>
<td>Fe(Salen)@PIZA-1-400$^4$</td>
<td>340</td>
<td>56</td>
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<tr>
<td>TiCP-PCP$^5$</td>
<td>310</td>
<td>117</td>
</tr>
<tr>
<td>Mn$_2$DP-a</td>
<td>ITO$^6$</td>
<td>470</td>
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<tr>
<td>(CoP)n-MWCNTs$^7$</td>
<td>430</td>
<td>60.8</td>
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<tr>
<td>PCOF-1-Co$^8$</td>
<td>386</td>
<td>89</td>
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Table S6. Comparison of porphyrin material for electrochemical OER

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\eta_{10}$ mV</th>
<th>tafel slope mV/dec</th>
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</thead>
<tbody>
<tr>
<td>Fe-porphvlar *</td>
<td>678</td>
<td>363</td>
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<tr>
<td>Co-porphvlar *</td>
<td>437</td>
<td>195</td>
</tr>
<tr>
<td>Ni-porphvlar *</td>
<td>644</td>
<td>345</td>
</tr>
<tr>
<td>Cu-porphvlar *</td>
<td>436</td>
<td>236</td>
</tr>
<tr>
<td>CoCOP$^9$</td>
<td>310</td>
<td>161</td>
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<tr>
<td>NiTIPP@CNT$^{10}$</td>
<td>450</td>
<td>104</td>
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<td>FeTPP@NiTPP/NF$^{11}$</td>
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<td>CoPor-GDY$^{12}$</td>
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<td>CuPor-based CMPs$^{13}$</td>
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<td>TiCP-PCP$^5$</td>
<td>339</td>
<td>142</td>
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*This work
References


