Electronic Supplementary Information (ESI)

Bandgap Engineering of Covalent Organic Frameworks for Boosting Photocatalytic Hydrogen Evolution from Water

Yuxiang Chen\textsuperscript{a,\#}, Xiao Luo\textsuperscript{b,\#}, Jiejie Zhang\textsuperscript{a}, Lu Hu\textsuperscript{a}, Ting Xu\textsuperscript{a}, Wei Li\textsuperscript{a}, Lei Chen\textsuperscript{a}, Mao Shen\textsuperscript{a}, Shi-Bin Ren\textsuperscript{a,*}, De-Man Han\textsuperscript{a,*}, Guo-Hong Ning\textsuperscript{b,*}, Dan Li\textsuperscript{b}

\textsuperscript{a} Department of Chemistry, School of Pharmaceutical and Chemical Engineering, Taizhou University, 1139 Shifu Avenue, Taizhou 318000, Zhejiang Province, PR China
\textsuperscript{b} College of Chemistry and Materials Science, Jinan University, Guangzhou, Guangdong 510632, PR China.

\#These authors contributed equally to this work.

E-mail: renshibin@126.com, hdm@tzc.edu.cn, guohongning@jnu.edu.cn
Fig. S1. PXRD patterns with corresponding powder photo for COF-OH-0 in experimental (a), simulated with AA stacking mode (b) and for simulated with AB stacking mode (c).
Fig. S2. PXRD patterns with corresponding powder photo for COF-OH-1 in experimental (a), simulated with AA stacking mode (b) and for simulated with AB stacking mode (c).
Fig. S3. PXRD patterns with corresponding powder photo for COF-OH-2 in experimental (a), simulated with AA stacking mode (b) and for simulated with AB stacking mode (c).
**Fig. S4.** PXRD patterns with corresponding powder photo for COF-OH-3 in experimental (a), simulated with AA stacking mode (b) and for simulated with AB stacking mode (c).
**Fig. S5.** Simulated packing structures (O: red; N: blue; C: white; hydrogen were omitted for clarity) for COF-OH-0 (a), COF-OH-1 (b), COF-OH-2 (c), COF-OH-3 (d), respectively.
Fig. S6. N₂ adsorption (filled symbols) and desorption (open symbols) isotherm with the pore size distribution (inset) for COF-OH-0 (a), COF-OH-1 (b), COF-OH-2 (c), COF-OH-3 (d), respectively.
Fig. S7. Experimental PXRD patterns after 3-day exposure to various solvents for COF-OH-0 (a), COF-OH-1 (b), COF-OH-2 (c), COF-OH-3 (d), respectively.
Fig. S8. The thermogravimetric analysis (TGA) plot of COF-OH-0 (a), COF-OH-1 (b), COF-OH-2 (c), COF-OH-3 (d), respectively.
Fig. S9. FT-IR spectra of the four COFs with their corresponding precursors COF-OH-0 (a), COF-OH-1 (b), COF-OH-2 (c), COF-OH-3 (d), respectively.
Fig. S10. CP/MAS $^{13}$C solid-state NMR spectra of COF-OH-0 (a), COF-OH-1 (b), COF-OH-2 (c), COF-OH-3 (d), respectively.
Fig. S11. SEM images of COF-OH-0 (a, b), COF-OH-1 (c, d), COF-OH-2 (e, f), COF-OH-3 (g, h), respectively.
Fig. S12. TEM images with the lattice fringes (inset of the right one) for COF-OH-0 (a, b), COF-OH-1 (c, d), COF-OH-2 (e, f), COF-OH-3 (g, h), respectively.
Fig. S13. The Tauc plots for the band gaps of COF-OH-0 (a), COF-OH-1 (b), COF-OH-2 (c), COF-OH-3 (d), respectively.
Fig. S14. Mott-Schottky plots for COF-OH-0 (a), COF-OH-1 (b), COF-OH-2 (c), COF-OH-3 (d), respectively.
Fig. S15. Hydrogen evolution plots for COF-OH-3 with 1% Pt using different sacrificial electron donor reagents (AA: ascorbic acid; TEOA: triethanolamine; EDTA: ethylenediaminetetraacetic acid disodium salt dihydrate).

Fig. S16. Hydrogen evolution plots for COF-OH-3 using ascorbic acid as sacrificial electron donor reagents with different platinum contents.
Fig. S17. Time course for photocatalytic H₂ production of COF-OH-3 (50 mg of catalyst with 1 wt % Pt in 50 mL 0.1 M ascorbic acid aqueous solution) under λ = 420 nm light (300 W Xe lamp equipped with a band-pass filter λ = 420 nm).
Fig. S18. PXRD patterns for COF-OH-3 before (red line) and after (black line) the 30 hours irradiation reaction.

Fig. S19. FT-IR spectrum for COF-OH-3 before (red line) and after (black line) the 30 hours irradiation reaction.
Table S1. Experiment PXRD data for COF-OH-0–3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>COF-OH-0</th>
<th>COF-OH-1</th>
<th>COF-OH-2</th>
<th>COF-OH-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>5.58°</td>
<td>5.54°</td>
<td>5.58°</td>
<td>5.64°</td>
</tr>
<tr>
<td>(110)</td>
<td>9.72°</td>
<td>9.70°</td>
<td>9.74°</td>
<td>9.86°</td>
</tr>
<tr>
<td>(200)</td>
<td>11.26°</td>
<td>11.16°</td>
<td>11.24°</td>
<td>–</td>
</tr>
<tr>
<td>(210)</td>
<td>14.98°</td>
<td>14.92°</td>
<td>14.74°</td>
<td>14.88°</td>
</tr>
<tr>
<td>(220)</td>
<td>19.62°</td>
<td>19.61°</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(001)</td>
<td>25.68°</td>
<td>26.28°</td>
<td>26.60°</td>
<td>26.32°</td>
</tr>
</tbody>
</table>
Table S2. The crystal structure and refinement data for COF-OH-0–3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a, b, c (Å)</th>
<th>α, β, γ (°)</th>
<th>V (Å³)</th>
<th>Space group</th>
<th>R_p, R_wp</th>
</tr>
</thead>
<tbody>
<tr>
<td>COF-OH-0</td>
<td>18.7121</td>
<td>90</td>
<td>1043.6</td>
<td>P-6</td>
<td>12.47%, 9.39%</td>
</tr>
<tr>
<td></td>
<td>18.7121</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.4416</td>
<td>120</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COF-OH-1</td>
<td>3.4131</td>
<td>120</td>
<td>1034.4</td>
<td>P 1</td>
<td>5.11%, 4.04%</td>
</tr>
<tr>
<td></td>
<td>18.7075</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.7075</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COF-OH-2</td>
<td>3.4566</td>
<td>120</td>
<td>1034.8</td>
<td>P 1</td>
<td>5.03%, 3.99%</td>
</tr>
<tr>
<td></td>
<td>18.5924</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.5924</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COF-OH-3</td>
<td>18.7251</td>
<td>90</td>
<td>1044.5</td>
<td>P-6</td>
<td>6.86%, 5.49%</td>
</tr>
<tr>
<td></td>
<td>18.7251</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.4397</td>
<td>120</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table S3. The flat band and band gap data for COF-OH-0–3a.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flat band (V)</th>
<th>Calculated valence band (V)</th>
<th>Band gap (eV)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>COF-OH-0</td>
<td>–0.51</td>
<td>2.17</td>
<td>2.68</td>
</tr>
<tr>
<td>COF-OH-1</td>
<td>–0.24</td>
<td>1.66</td>
<td>1.90</td>
</tr>
<tr>
<td>COF-OH-2</td>
<td>–0.55</td>
<td>1.47</td>
<td>2.02</td>
</tr>
<tr>
<td>COF-OH-3</td>
<td>–0.62</td>
<td>1.66</td>
<td>2.28</td>
</tr>
</tbody>
</table>

[a] All the potentials (V) have been calculated vs. SHE; [b] Calculated from the solid UV–vis diffuse reflectance spectra.
Table S4. Summary of the representative COFs as photocatalysts for photocatalytic hydrogen evolution under visible-light irradiation\textsuperscript{a}.

<table>
<thead>
<tr>
<th>COFs</th>
<th>Sacrificial agent</th>
<th>HER (mmol·g\textsuperscript{-1}·h\textsuperscript{-1})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>COF-JLU100</td>
<td>AA</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>CYANO-COF</td>
<td>AA</td>
<td>60.85</td>
<td>2</td>
</tr>
<tr>
<td>Tp-2C/BPy\textsuperscript{2+}-COF</td>
<td>AA</td>
<td>34.6</td>
<td>3</td>
</tr>
<tr>
<td>COF TtaTf\textalpha</td>
<td>AA</td>
<td>20.7</td>
<td>4</td>
</tr>
<tr>
<td>SonoCOF-3</td>
<td>AA</td>
<td>16.6</td>
<td>5</td>
</tr>
<tr>
<td>BTH-3</td>
<td>AA</td>
<td>15.1</td>
<td>6</td>
</tr>
<tr>
<td>COF TpaTf\textalpha</td>
<td>AA</td>
<td>14.9</td>
<td>4</td>
</tr>
<tr>
<td>NKCOF-108</td>
<td>AA</td>
<td>11.6</td>
<td>7</td>
</tr>
<tr>
<td>COF TtaTpa</td>
<td>AA</td>
<td>10.8</td>
<td>4</td>
</tr>
<tr>
<td>BTH-1</td>
<td>AA</td>
<td>10.5</td>
<td>6</td>
</tr>
<tr>
<td>FS-COF</td>
<td>AA</td>
<td>10.1</td>
<td>8</td>
</tr>
<tr>
<td>COF-OH-3</td>
<td>AA</td>
<td>9.89</td>
<td>This work</td>
</tr>
<tr>
<td>TF-HUST-A1</td>
<td>TEOA</td>
<td>9.2</td>
<td>9</td>
</tr>
<tr>
<td>Py-CITP-BT-COF</td>
<td>AA</td>
<td>8.875</td>
<td>10</td>
</tr>
<tr>
<td>TP-COF</td>
<td>AA</td>
<td>8.42</td>
<td>11</td>
</tr>
<tr>
<td>TpPa-COF-(CH\textsubscript{3})\textsubscript{2}</td>
<td>SA</td>
<td>8.33</td>
<td>12</td>
</tr>
<tr>
<td>TpPa-Cl\textsubscript{2}</td>
<td>SA</td>
<td>7.6</td>
<td>13</td>
</tr>
<tr>
<td>TpPa-1-COF\textsuperscript{b}</td>
<td>AA</td>
<td>5.585</td>
<td>14</td>
</tr>
<tr>
<td>TpPa-1</td>
<td>AA</td>
<td>5.479</td>
<td>14</td>
</tr>
<tr>
<td>CTF-HUST-C1</td>
<td>TEOA</td>
<td>5.1</td>
<td>15</td>
</tr>
<tr>
<td>S-COF</td>
<td>AA</td>
<td>4.44</td>
<td>8</td>
</tr>
<tr>
<td>TpPa-COF-CH\textsubscript{3}</td>
<td>SA</td>
<td>3.07</td>
<td>12</td>
</tr>
<tr>
<td>COF-OH-2</td>
<td>AA</td>
<td>2.91</td>
<td>This work</td>
</tr>
<tr>
<td>Py-FTP-BT-COF</td>
<td>AA</td>
<td>2.875</td>
<td>10</td>
</tr>
<tr>
<td>sp\textsuperscript{2}c-COF\textsubscript{ERDN}</td>
<td>TEOA</td>
<td>2.12</td>
<td>16</td>
</tr>
<tr>
<td>PyTz-COF</td>
<td>AA</td>
<td>2.0724</td>
<td>17</td>
</tr>
<tr>
<td>TFPT-COF</td>
<td>TEOA</td>
<td>1.97</td>
<td>18</td>
</tr>
<tr>
<td>N\textsubscript{2}-COF</td>
<td>TEOA</td>
<td>1.703</td>
<td>19</td>
</tr>
<tr>
<td>TP-COF (Ref.\textsuperscript{3})</td>
<td>AA</td>
<td>1.6</td>
<td>8</td>
</tr>
<tr>
<td>TpPa-COF</td>
<td>SA</td>
<td>1.56</td>
<td>12</td>
</tr>
<tr>
<td>sp\textsuperscript{2}c-COF</td>
<td>TEOA</td>
<td>1.36</td>
<td>16</td>
</tr>
<tr>
<td>TpPa-1-COF\textsuperscript{b}</td>
<td>SA</td>
<td>1.223</td>
<td>20</td>
</tr>
<tr>
<td>BTH-2</td>
<td>AA</td>
<td>1.2</td>
<td>6</td>
</tr>
<tr>
<td>NTU-BDA-THTA</td>
<td>AA</td>
<td>1.127</td>
<td>21</td>
</tr>
<tr>
<td>Py-HTP-BT-COF</td>
<td>AA</td>
<td>1.078</td>
<td>10</td>
</tr>
<tr>
<td>BT-TAPT-COF</td>
<td>AA</td>
<td>0.949</td>
<td>22</td>
</tr>
<tr>
<td>N\textsubscript{2}-COF\textsuperscript{c}</td>
<td>TEOA</td>
<td>0.782</td>
<td>23</td>
</tr>
<tr>
<td>BtCOF150</td>
<td>TEOA</td>
<td>0.75</td>
<td>24</td>
</tr>
<tr>
<td>N\textsubscript{2}-COF</td>
<td>TEOA</td>
<td>0.438</td>
<td>19</td>
</tr>
<tr>
<td>N\textsubscript{2}-COF\textsuperscript{d}</td>
<td>TEOA</td>
<td>0.414</td>
<td>23</td>
</tr>
<tr>
<td>ZnPor-DETH-COF</td>
<td>TEOA</td>
<td>0.413</td>
<td>25</td>
</tr>
<tr>
<td>Material</td>
<td>Catalyst</td>
<td>Conversion (%)</td>
<td>Reaction Type</td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------</td>
<td>----------------</td>
<td>---------------</td>
</tr>
<tr>
<td>TP-BDDA</td>
<td>TEOA</td>
<td>0.324</td>
<td>26</td>
</tr>
<tr>
<td>COF-42</td>
<td>TEOA</td>
<td>0.233</td>
<td>23</td>
</tr>
<tr>
<td>TpPa-COF-NO₂</td>
<td>SA</td>
<td>0.22</td>
<td>12</td>
</tr>
<tr>
<td>COF(ERDN)</td>
<td>TEOA</td>
<td>0.212</td>
<td>16</td>
</tr>
<tr>
<td>N₃-COFᶜ</td>
<td>TEOA</td>
<td>0.163</td>
<td>23</td>
</tr>
<tr>
<td>COF-OH-0</td>
<td>AA</td>
<td>0.11</td>
<td>This work</td>
</tr>
<tr>
<td>N₁-COFᶜ</td>
<td>TEOA</td>
<td>0.1</td>
<td>23</td>
</tr>
<tr>
<td>A-TEBPY-COF</td>
<td>TEOA</td>
<td>0.098</td>
<td>27</td>
</tr>
<tr>
<td>N₁-COF</td>
<td>TEOA</td>
<td>0.09</td>
<td>19</td>
</tr>
<tr>
<td>BT-COF</td>
<td>AA</td>
<td>0.076</td>
<td>11</td>
</tr>
<tr>
<td>N₀-COF</td>
<td>TEOA</td>
<td>0.023</td>
<td>19</td>
</tr>
</tbody>
</table>

[a] The reactions were performed with Pt as co-catalyst; [b] The co-catalyst is MoS₂; [c] The co-catalyst is [Co(dmgH₂pyCl); [d] The co-catalyst is [Co(dmgBF₂)₂(OH₂)₂]; AA: Ascorbic acid; SA: Sodium ascorbate; TEOA: triethanolamine.
References


