Supporting Information

Incorporation of a Molecular [Ru(dcbpy)(bpy)$_2$]$^{2+}$ Photosensitizer and a Pt(dcbpy)Cl$_2$ Catalyst into Metal-Organic Frameworks for Photocatalytic Hydrogen Evolution from Aqueous Solution

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Figure S1. (A) The UV-vis absorption spectra of RuDCBPY at various concentrations in aqueous solution. (B) The absorbance of RuDCBPY at 448 nm as a function of concentration.
Figure S2. $N_2$ absorption (filled symbols) and desorption (open symbols) isotherms for Pt-UIO-67 (red) and Ru-Pt@UIO-67 (black).

Figure S3. Pore size distribution of Pt-UIO-67 (left) and Ru-Pt@UIO-67 (right) obtained from $N_2$ gas sorption experiments by DFT calculation.
Table S1. Surface area, pore volume and main pore size of Pt@UIO-67 and Ru-Pt@UIO-67.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$</th>
<th>Pore volume</th>
<th>Main Pore Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>UIO-67</td>
<td>3000 m$^2$/g</td>
<td>1.05 cm$^3$/g</td>
<td>8 Å</td>
</tr>
<tr>
<td>Pt@-UIO-67</td>
<td>2053.713 m$^2$/g</td>
<td>0.9083 cm$^3$/g</td>
<td>8-10 Å</td>
</tr>
<tr>
<td>Ru-Pt@UIO-67</td>
<td>1886.130 m$^2$/g</td>
<td>0.8286 cm$^3$/g</td>
<td>8-10 Å</td>
</tr>
</tbody>
</table>

Figure S4. SEM images of (a) UIO-67, (b) Pt@UIO-67 and (c,d) Ru-Pt@UIO-67. Scale bar: 1 μm.
Figure S5. SEM-Energy disperses X-ray (EDX) analysis in random areas of UIO-67, Pt@UIO-67, and Ru-Pt@UIO-67 (from top to bottom).
Figure S6. Photographs of Pt@UIO-67 and Ru-Pt@UIO-67 MOFs with various doping concentrations under natural light.

Figure S7. The XRD patterns of Ru-Pt@UIO-67 MOFs.
**Figure S8.** The XRD patterns of Pt@UIO-67 MOFs.

**Figure S9.** Photocatalytic hydrogen production after 5 h of irradiation from an acetate buffer solution (pH = 5.0) of EDTA-2Na and Ru-Pt@UIO-67 (5 mg). Light source: LED $\lambda > 420$ nm, $30 \times 1$ W.
Figure S10. Photocatalytic hydrogen production from an acetate buffer solution (pH = 5.0) of EDTA-2Na and Pt@UIO-67 (~1.47 μmol Pt). Light source: LED λ > 420 nm, 30 × 1 W.

Figure S11. Emission spectra of Pt@UIO-67 MOFs with various doping concentrations at 77 K (λ_{ex} = 365 nm). Inset: The emission spectrum of Pt(dcbpy)Cl₂ in glassy MeOH/EtOH (1:4) solution at 77 K (λ_{ex} = 365 nm).
Figure S12. The diameters of RuDCBPY and PtDCBPY molecules.

Figure S13. The cyclic voltammograms (CV) and linear sweep voltammograms (LSV) of 0.1 mM PtDCBPY (top) and 0.1 mM RuDCBPY (bottom) in DMF solution.
Table S2. Spectral data and electrochemical potentials \((E_{1/2} \text{ vs Ag/AgCl})^a\) of RuDCBPY and PtDCBPY.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{em}}) (nm)</th>
<th>(\lambda_{\text{em}}) (nm)</th>
<th>(E_{1/2}^\text{ir}(\Delta E))</th>
<th>(E_{1/2}^\text{eq}(\Delta E))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2O</td>
<td>DMF</td>
<td>H_2O</td>
<td>DMF</td>
<td>0.97 (169)</td>
</tr>
<tr>
<td>Ru-DCBPY</td>
<td>448</td>
<td>462</td>
<td>650</td>
<td>625</td>
</tr>
<tr>
<td>Pt-DCBPY</td>
<td>415</td>
<td></td>
<td>1.13 (^a)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Measured with a glassy carbon working electrode, a Ag/AgCl reference electrode, and a platinum plate counter electrode in DMF solution containing \(\text{Bu}_4\text{NPF}_6\) (0.1 M) at a scan rate of 100 mV/s; ir = irreversible. \(E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2\) in volts, and \(\Delta E = E_{\text{pa}} - E_{\text{pc}}\) in mV.

Figure S14. The emission spectra of RuDCBPY in DMF and in water.
Figure S15. Emission lifetime decays obtained at room temperature for Ru-Pt@UIO-67.

Figure S16. The nanosecond transient absorption spectra and the corresponding nanosecond recovery kinetics of transient bleaching recovery (monitored at 400 nm upon laser excitation at 355 nm) for EDTA-2Na (30 mM) + [Ru(dcbpy)(bpy)]^{2+} (1.5×10^{-4} M) in pH 5.0 solution.
Figure S17. TEM images of Ru-Pt@UIO-67 obtained at different reaction time.

Figure S18. TEM images of Pt@UIO-67 obtained at different reaction time.