Electronic supplementary information

Application of a Ni mercaptopyrimidine MOF as a highly efficient catalyst for sunlight-driven hydrogen generation

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Figure S1. The amount of hydrogen photogenerated in the presence of [Ni₂(PymS)₄]ₙ (15 μmol), Fl (2 mM) and TEA (15%) in water at pH = 10 (black); (b) the amount of hydrogen photogenerated by the filtrate of the aqueous solution containing [Ni₂(PymS)₄]ₙ (15 μmol), TEA (15%) and Fl (2 mM) after stirring for 5 minutes.

Figure S2. FT-IR spectra (left) and powder PXRD patterns (right) of [Ni₂(PymS)₄]ₙ before (black line) and after photocatalytic reactions (blue).
Figure S3. The amount of hydrogen photogenerated by [Ni$_2$(PymS)$_4$]$^\text{n-}$ (10 μmol) with Fl (2 mM) and TEA (15%, v/v) in water with varied pH values from 7 to 10.

Figure S4. The amount of hydrogen photogenerated by [Ni$_2$(PymS)$_4$]$^\text{n-}$ (10 μmol) with Fl (2 mM) in water when TEA changes from 5% to 15% (v/v).
Figure S5. The amount of hydrogen photogenerated by \([Ni_2(PymS)_4]_n\) (10 μmol) with TEA (15%) in water when Fl changes from 2 to 10 mM at pH = 10.

Figure S6. The amount of hydrogen photogenerated by \([Ni_2(PymS)_4]_n\) (5 μmol) with different particle sizes: (a) 20 × 10 × 20 μm; (b) 11 × 4 × 10 μm; (c) 4 × 1 × 4 μm in the presence of Fl (2 mM) and TEA (15%) in an hour.
Figure S7. Emission quenching (left) and Stern-Volmer plot (right) of Fl (0.01 mM) by TEA in water at pH =10.

Figure S8. UV-vis spectrum of Fl (0.002 mM) in aqueous NaOH solution (pH = 10).
### Table S1 TON of the catalyst in different cycles

<table>
<thead>
<tr>
<th></th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
<th>Cycle 4</th>
</tr>
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<td>TON</td>
<td>2.5</td>
<td>2.5</td>
<td>2.2</td>
<td>2.0</td>
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</table>

All data was calculated from the photocatalytic experiments in the presence of [Ni$_2$(PymS)$_4$]$_n$ (15 μmol) Fl (2 mM) and TEA (15%, v/v) at pH = 10.

### Table S2 TOF of different amounts of catalyst for hydrogen production

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<th>$m_{\text{cat}}$ / mg</th>
<th>1.4</th>
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<th>2.8</th>
<th>5.6</th>
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<td>TOF / h$^{-1}$</td>
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<td>9.0</td>
<td>6.5</td>
<td>3.5</td>
<td>2.5</td>
<td>1.7</td>
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</table>

All data was calculated from the photocatalytic experiments in the presence of Fl (2 mM) and TEA (15%, v/v) at pH = 10.