Supporting Information

A polypyridyl Co(II) complex-based water reduction catalyst with double H₂ evolution sites

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Materials
Cobalt (II) chloride hexahydrate, di-(2-picolyl)amine, sodium triacetoxyborohydride, 6-methyl-2-pyridinecarboxaldehyde, 2-pyridinecarboxaldehyde, 6-bromo-2-pyridine carboxaldehyde and 6-chloro-2-pyridinecarboxaldehyde were purchased from Adamas. Triethylamine (TEA) and tetrabutylammonium hexafluorophosphate were obtained from Alfa. All solvents were of analytical purity and used without further treatment. Distilled water was used in all experiments.

Determination of Faradaic Efficiency
A solution of 1 mM 1 and 20 mM acetic acid in 10 mL of Ar-saturated CH$_3$CN was electrolyzed at an applied potential of ~2.0 V vs. SCE for 2 h in a gas-tight electrolysis cell. After electrolysis, the gas components in the headspace were analyzed by gas chromatography. The amount of hydrogen generated was determined by the external standard method and the hydrogen dissolved in the solution was neglected. The Faradaic efficiency were calculated by the equation: (the moles of H$_2$ evolved during the CPE process) / (the moles of H$_2$ calculated based on consumed charges) × 100%.

Scheme S1. Schematic presentation of the photocatalytic reaction setup.

Figure S1. Absorption spectra of 4 (1 mM) in CH$_3$CN in the presence of various concentrations of acetic acid.
**Figure S2.** Absorption spectra of 2 (1 mM) in CH$_3$CN in the presence of various concentrations of acetic acid.

**Figure S3.** $^1$H NMR spectra of 1-4 in CD$_3$CN.
**Figure S4.** $^1$H NMR of 2 (1.0 mM) in CD$_3$CN in the absence (bottom) or presence (top) of 1 equivalent of deuterated trifluoroacetic acid.

**Figure S5.** $^1$H NMR of 3 (1.0 mM) in CD$_3$CN in the absence (bottom) or presence (top) of 1 equivalent of deuterated trifluoroacetic acid.
Figure S6. $^1$H NMR of 4 (1.0 mM) in CD$_3$CN in the absence (bottom) or presence (top) of 1 equivalent of deuterated trifluoroacetic acid.

Figure S7. Cyclic voltammograms of blank CH$_3$CN (black), 15 mM acetic acid in CH$_3$CN (red), and 15 mM acetic acid and 1 mM 1 in CH$_3$CN (blue). Condition: 0.1 M $n$-Bu$_4$NPF$_6$, scan rate 100 mV/s.
Figure S8. Absorption spectra of 1-4 before and after 100 cycles of CV scan in the range of 0 and -2.0 V vs SCE in Ar-saturated CH₃CN.

Figure S9. (a) Photocatalytic H₂ production profiles of the AP systems containing 0.1 mM [Ir(ppy)₂(dtbpyp)]Cl, 0.01 mM 2, 0.6 M TEA in CH₃CN/H₂O of varied compositions. (b) H₂ production amounts of the AP systems after 6 h irradiation.

Figure S10. (a) Photocatalytic H₂ production profiles of the AP systems containing 0.1 mM [Ir(ppy)₂(dtbpyp)]Cl, 0.01 mM 2, and varied concentrations of TEA in CH₃CN/H₂O (9:1). (b) H₂ production amounts of the AP systems after 6 h irradiation.
Figure S11. (a) Photocatalytic H\₂ production profiles of the AP systems containing 0.01 mM 2, 0.45 M TEA, and varied concentrations of [Ir(ppy)₂(dtbbpy)]Cl in CH₂CN/H₂O (9:1); (b) H₂ production amounts of the AP systems after 6 h irradiation.

Figure S12. (a) Photocatalytic H₂ production profiles of the AP systems containing 0.2 mM [Ir(ppy)₂(dtbbpy)]Cl, 0.45 M TEA, and varied concentrations of 2 in CH₂CN/H₂O (9:1). (b) H₂ production amounts of the AP systems after 5 h irradiation.

Figure 13. Photocatalytic H₂ production profiles of the AP systems containing 0.2 mM Ir-based PS, 10 µM 1 and 0.45 M TEA in Ar-saturated CH₂CN/H₂O (9:1). After 2 h of irradiation (as shown by a red arrow), 1 equiv of PS, 1, or TEA was added, and H₂ evolution recovery was only found in the case of the addition of 1. H₂ production profiles of the free ligands in the conditions similar to their Co complexes are also included.
Figure S14. Stern-Volmer plot of the luminescence quenching of [Ir(ppy)$_2$(dtbpy)]Cl by 1 in CH$_3$CN/H$_2$O (9:1).

Figure S15. Stern-Volmer plot of the luminescence quenching of [Ir(ppy)$_2$(dtbpy)]Cl by 2 in CH$_3$CN/H$_2$O (9:1).

Figure S16. Stern-Volmer plot of the luminescence quenching of [Ir(ppy)$_2$(dtbpy)]Cl by 3 in
CH$_3$CN/H$_2$O (9:1).

Figure S17. Stern-Volmer plot of the luminescence quenching of [Ir(ppy)$_2$(dtbpy)]Cl by 4 in CH$_3$CN/H$_2$O (9:1).

Figure S18. Stern-Volmer plot of the luminescence quenching of [Ir(ppy)$_2$(dtbpy)]Cl by TEA in CH$_3$CN/H$_2$O (9:1).

Table S1. Selected bond lengths (Å) and angles (deg) of 2.

<table>
<thead>
<tr>
<th>Complex 2</th>
<th>[Co(Br-TMPA)Cl$_2$]</th>
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<tbody>
<tr>
<td>Co(1)-N(3)</td>
<td>2.078(5)</td>
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<tr>
<td>Co(1)-N(2)</td>
<td>2.095(5)</td>
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<tr>
<td>Co(1)-N(1)</td>
<td>2.296(4)</td>
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<tr>
<td>Co(1)-Cl(1)</td>
<td>2.3163(16)</td>
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<tr>
<td>Co(1)-Cl(2)</td>
<td>2.3191(17)</td>
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<tr>
<td>N(3)-Co(1)-N(2)</td>
<td>110.52(17)</td>
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<tr>
<td>N(3)-Co(1)-N(1)</td>
<td>77.15(17)</td>
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<td>N(2)-Co(1)-N(1)</td>
<td>76.60(17)</td>
</tr>
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<td>N(3)-Co(1)-Cl(1)</td>
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<tr>
<td>N(2)-Co(1)-Cl(1)</td>
<td>135.61(13)</td>
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<td>Bond</td>
<td>Value</td>
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<tr>
<td>------</td>
<td>-------</td>
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<td>Cl(2)</td>
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Table S2. Selected bond lengths (Å) and angles (deg) of 4.

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<td>Co(1)-N(2)</td>
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<td>Co(1)-N(1)</td>
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<td>Co(1)-N(4)</td>
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<td>Co(1)-Cl(2)</td>
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<td>N(1)</td>
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<td>N(4)</td>
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<td>N(1)-Co(1)-Cl(1)</td>
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<td>N(2)-Co(1)-Cl(1)</td>
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<td>N(1)-Co(1)-Cl(2)</td>
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<td>171.78(10)</td>
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<td>N(1)-Co(1)-Cl(2)</td>
<td>95.57(9)</td>
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<td>N(4)-Co(1)-Cl(2)</td>
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<td>Cl(1)</td>
<td>90.99(9)</td>
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<td>Co(1)-Cl(1)</td>
<td>95.16(4)</td>
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Table S3. Crystallographic data and processing parameters of 2.

<table>
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<tr>
<th>Complex</th>
<th>Co(Br-TMPA)Cl₂</th>
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</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₁₈H₁₇Cl₂BrCoN₄</td>
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<td>Temperature</td>
<td>153k</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<td>Crystal system, space group</td>
<td>Monoclinic, P2(1)/n</td>
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<td>Unit cell dimensions</td>
<td>a = 14.188(7) Å, alpha = 90 deg</td>
</tr>
<tr>
<td></td>
<td>b = 6.883(3) Å, beta = 107.131(9) deg.</td>
</tr>
<tr>
<td></td>
<td>c = 21.321(11) Å, gamma = 90 deg.</td>
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<td>Volume</td>
<td>1989.6(16) Å³</td>
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<td>Z, Calculated density</td>
<td>4, 1.666 Kg/m³</td>
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<tr>
<td>Absorption coefficient</td>
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<td>F(000)</td>
<td>996</td>
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<td>Crystal size</td>
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<tr>
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<td>--------------------------------</td>
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<tr>
<td>Theta range for data collection</td>
<td>2.93 to 29.07 deg</td>
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<tr>
<td>Limiting indices</td>
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</tr>
<tr>
<td>Reflections collected / unique</td>
<td>16990 / 5235 [R(int) = 0.0778]</td>
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<td>Completeness to theta = 29.07</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Max. and min. transmission</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F^2</td>
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<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on F^2</td>
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<td>Final R indices [I&gt;2sigma(I)]</td>
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<td>R indices (all data)</td>
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<tr>
<td>Extinction coefficient</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>1.837 and -1.565 e.Å^-3</td>
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</table>

**Table S4.** Crystallographic data and processing parameters of 4.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Co(CH₃-TMPA)Cl₂</th>
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<tbody>
<tr>
<td>Formula</td>
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<td>Wavelength</td>
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<td>Crystal system, space group</td>
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<tr>
<td>Unit cell dimensions</td>
<td>a = 9.0440(16) Å, alpha = 90 deg</td>
</tr>
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<td></td>
<td>b = 9.0440(16) Å, beta = 90 deg.</td>
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<td></td>
<td>c = 40.737(10) Å, gamma = 120 deg.</td>
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<td>Volume</td>
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<td>Z, Calculated density</td>
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<td>Absorption coefficient</td>
<td>1.181 mm⁻¹</td>
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<td>F(000)</td>
<td>1345</td>
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<tr>
<td>Crystal size</td>
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<td>Theta range for data collection</td>
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<tr>
<td>Limiting indices</td>
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</tr>
<tr>
<td>Reflections collected / unique</td>
<td>13031 / 4738 [R(int) = 0.0475]</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F^2</td>
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<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on F^2</td>
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<td>Extinction coefficient</td>
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<td>Largest diff. peak and hole</td>
<td>0.884 and -0.394 e.Å⁻³</td>
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