Electronic Supplementary Information for

Efficient Water Oxidation by Cerium Ammonium Nitrate with [Ir^{III}(Cp^*)(4,4’-bishydroxy-2,2’-bipyridine)(H_2O)]^{2+} as a Precatalyst

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Synthesis of Ir containing compounds

**[Ir^{III}(Cp^*)(4,4’-(OH)2-2,2’-bpy)(H_2O)]SO_4 (1)** An aqueous solution (30 mL) of [Ir(Cp^*)(H_2O)_3]SO_4 (400 mg, 0.84 mmol) and 4,4’-dihydroxy-2,2’-bipyridine (158 mg, 0.84 mmol) was stirred at 40 °C for 12 h. The formed yellow crystals were collected by filtration to yield 1 (400 mg, 75%). ^1H NMR (300 MHz, D_2O): δ = 1.64 ppm (s, 15H), 7.13 (dd, J = 6.4, 2.6 Hz, 2 H), 7.66 (d, J = 2.6 Hz, 2H), 8.70 (d, J = 6.4 Hz, 2H); ESI-MS: m/z = 515 [M–SO_4–H_2O–H]^+.

**[Ir^{III}(Cp^*)(4,4’-(OMe)2-2,2’-bpy)(H_2O)]SO_4 (2)** An aqueous solution (30 mL) of [Ir(Cp^*)(H_2O)_3]SO_4 (192 mg, 0.40 mmol) and 4,4’-dimethoxyl-2,2’-bipyridine (86 mg, 0.40 mmol) was stirred at 40 °C for 12 h. The formed yellow crystals were collected by filtration to yield 2 (223 mg, 85%). ^1H NMR (300 MHz, D_2O): δ = 1.67 (s, 15H), 4.11 (s, 6H), 7.41 (dd, J = 6.6, 2.2 Hz, 2H), 7.98 (d, J = 2.2 Hz, 2H), 8.90 (d, J = 6.6 Hz, 2H).

**[Ir^{III}(Cp^*)(4,4’-Me2-2,2’-bpy)(H_2O)]SO_4 (3)** An aqueous solution (30 mL) of [Ir(Cp^*)(H_2O)_3]SO_4 (192 mg, 0.40 mmol) and 4,4’-dimethyl-2,2’-bipyridine (74 mg, 0.40 mmol) was stirred at 40 °C for 12 h. The formed yellow crystals were collected by filtration to yield 3 (202 mg, 81%). ^1H NMR (300 MHz, D_2O): δ = 1.67 (s, 15 H), 2.65 (s, 6H), 7.71 (dd, J = 5.9, 1.0 Hz, 2H), 8.36 (br, 2H), 8.93 (d, J = 5.9 Hz, 2H).

**[Ir^{III}(Cp^*)(4,4’-(COOH)2-2,2’-bpy)(H_2O)]SO_4 (4)** An aqueous solution (30 mL) of [Ir(Cp^*)(H_2O)_3]SO_4 (192 mg, 0.40 mmol) and 2,2’-bipyridine-4,4’-dicarboxylic acid (98 mg, 0.40 mmol) was stirred at 40 °C for 12 h. The formed yellow crystals were collected by filtration to yield 4 (205 mg, 75%). ^1H NMR (300 MHz, D_2O): δ = 1.70 (s, 15H), 3.7–3.4 (br, 2H), 8.29 (dd, J = 5.9, 1.7 Hz, 2H), 9.01 (d, J = 1.5 Hz, 2H), 9.27 (d, J = 5.9 Hz, 2H).

**Iridium hydroxide (5) and iridium oxide (5’)** The pH of an aqueous solution of H_2IrCl_6 was adjusted to ~10 by adding 5.0 M NaOH solution with vigorous stirring at 100 °C. After 1.0 h stirring, precipitates appeared were collected by a centrifugation. Then, the precipitates were washed by water three times and dried in vacuo at room temperature and kept at 65 °C for 10 h (5). Iridium oxide (5’) was obtained by calcination of iridium hydroxide (5) at 600 °C for 3 h.
Fig. S1 Time course of concentration of CAN determined from the absorbance change at 420 nm in the catalytic water oxidation by CAN with the precatalyst 1 for repeated 4 cycles. The reaction solution (2.0 mL) contained 5.0 μM of 1, 10 mM CAN and 0.10 M HNO₃.

Fig. S2 ¹H NMR spectra (bpy region) of 1 (5.0 mM) in 0.1 M DNO₃ with 0 (black), 1 (blue), 2 (green), 4 (red) and 10 (pink) equiv. of CAN. TSP sealed in a glass capillary was used as an external standard.
**Fig. S3** TEM images at different magnifications (a-d) of iridium hydroxide (5) prepared by a conventional method.

**Fig. S4** TEM images at different magnifications (a-d) of iridium oxide (5') prepared by a conventional method.
**Fig. S5** TG/DTA data for (a) the Ir complex 1, (b) iridium hydroxide (5), (c) iridium oxide (5'); TG curve (black) and DTA curve (red). The temperature increased from 25 °C to 100 °C (held at 100 °C for 10 min) and from 100 °C to 600 °C with a ramp rate of 2 °C/min.

**Fig. S6** TEM images at different magnifications (a-d) of the particles from [IrCp*(H₂O)₃]SO₄ prepared by adding 10 equivalents of CAN to 2.0 mM of [IrCp*(H₂O)₃]SO₄ in 0.10 M HNO₃.
Calculation of the numbers of Ir atoms on the particles surfaces

The numbers of surface Ir atoms were calculated by following equation.

\[ N_s = \left[ N_A \times \left( \frac{d}{f_w} \right) \right]^{2/3} \times \text{(number of Ir atoms in chemical formula)} \times \text{(catalyst weight)} \times \text{(SA)} \]

- \( N_s \): number of surface Ir atoms
- \( N_A \): the Avogadro’s number
- \( d \): density of Ir-based metal oxide (IrO₂ for 11.7 g cm⁻³)
- \( f_w \): formula weight of Ir-based metal oxide
- \( \text{SA} \): BET surface area

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<tr>
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<th>BET surface area (m² g⁻¹)</th>
<th>number of surface Ir atoms in the reaction solution</th>
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<tbody>
<tr>
<td>Iridium hydroxide (5)</td>
<td>88</td>
<td>( 8.1 \times 10^{17} )</td>
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<tr>
<td>Iridium oxide (5′)</td>
<td>51</td>
<td>( 4.6 \times 10^{17} )</td>
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