Supplementary Information

{[Ru(bda)]_xL_y}_n Cross-linked Coordination Polymers: Toward Efficient Heterogeneous Catalysis for Water Oxidation in Organic Solvent-free System

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Preparation of multi-pyridyl ligands via Suzuki coupling

1,4-dibromobenzene (1.0 g, 4.24 mmol), 4-pyridylboronic acid (1.563 g, 12.71 mmol) and tetrakis(triphenylphosphine)-palladium(0) (293.0 mg, 0.26 mmol), were dissolved in a mixture of anhydrous 1,4-dioxane (60 mL) and K$_2$CO$_3$ solution (15 mL, 2M). The reaction mixture was heated to 110 °C and stirred for 24 hours under a nitrogen atmosphere. The mixture was cooled to room temperature, evaporated to remove 1,4-dioxane and dissolved in dichloromethane. The mixture was purified by silica gel column chromatography (eluent: ethyl acetate/methanol/triethylamine, 100/5/1, v/v/v). The product was evaporated to remove dichloromethane and dried in vacuum for 12 h at room temperature to give 1,4-bis(4-pyridyl)benzene (Yield:80%).

1,3,5-tribromo-benzen (1.0 g, 3.17 mmol), 4-pyridylboronic acid (2.342 g, 19.05 mmol) and tetrakis(triphenylphosphine)-palladium(0) (550.0 mg, 0.48 mmol), were dissolved in a mixture of anhydrous 1,4-dioxane (60 mL) and K$_2$CO$_3$ solution (15 mL, 2M). The reaction mixture was heated to 110 °C and stirred for 24 hours under a nitrogen atmosphere. The mixture was cooled to room
temperature, evaporated to remove 1,4-dioxane and dissolved in dichloromethane. The mixture was purified by silica gel column chromatography (eluent: ethyl acetate/methanol/triethylamine, 100/5/1, v/v/v). The product was evaporated to remove dichloromethane and dried in vacuum for 12 h at room temperature to give 1,3,5-tri(4-pyridyl)benzene (Yield:75%).

2,2',7,7'-tetrabromo-9,9'-spirobifluorene (1.0 g, 1.54 mmol), 4-pyridylboronic acid (1.167 g, 9.21 mmol) and tetrakis(triphenylphosphine)-palladium(0) (215.1 mg, 0.19 mmol), were dissolved in a mixture of anhydrous 1,4-dioxane (60 mL) and Na$_2$CO$_3$ solution (15 mL, 2M). The reaction mixture was heated to 110 °C and stirred for 24 hours under a nitrogen atmosphere. The mixture was cooled to room temperature, evaporated to remove 1,4-dioxane and give solid mixture. The mixture was dissolved in dichloromethane, filtered to get filtrate and the filtrate was evaporated to get product. The product was washed by ice methanol and dried in vacuum for 12 h at room temperature to give 2,2',7,7'-tetra(4-pyridyl)-9,9'-spirobifluorene (Yield:67%).
Table S1. Experimental conditions of CCP water suspensions used for kinetics study.

<table>
<thead>
<tr>
<th></th>
<th>[Ru(bda)pic$_2$]</th>
<th>LCP</th>
<th>CCP1</th>
<th>CCP2</th>
<th>CCP3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection concentration/($\mu$g/mL)</td>
<td>25, 50, 100, 200</td>
<td>200, 400, 1000</td>
<td>200, 400, 1000</td>
<td>200, 400, 1000</td>
<td>50, 100, 200, 400</td>
</tr>
<tr>
<td>b$m_{Ru}/\mu$g</td>
<td>4.8, 9.6, 19.2, 38.4</td>
<td>31.6, 63.2, 158</td>
<td>34.4, 68.8, 172</td>
<td>32.2, 64.4, 161</td>
<td>9.9, 17.8, 35.6, 71.2</td>
</tr>
<tr>
<td>c$C_{Ru}/\mu$M</td>
<td>4.75, 9.50, 19.0, 38.0</td>
<td>31.3, 62.6, 156.4</td>
<td>34.1, 68.1, 170.5</td>
<td>31.9, 63.8, 159.5</td>
<td>8.82, 17.63, 35.25, 70.5</td>
</tr>
</tbody>
</table>

a: Injection concentration represents the mass concentration of CCP in the injected water suspension (0.5 mL).
b: $m_{Ru}$ represents the calculated absolute mass of Ru element in the injected water suspension (0.5 mL) based on ICP-MS results.
c: $C_{Ru}$ represents the calculated molar concentration of Ru in the final water suspension (10 mL) used in catalysis.

Figure S1. Schematic synthesis of intermediate products, ligands L0-L3 and [Ru(bda)(pic)$_2$].
Figure S2. NMR spectra of multi-pyridyl ligands and other intermediate products.

Reaction mixture at t = 1 h

Reaction mixture at t = 24 h

Before centrifugation

After centrifugation

Figure S3. (a) and (b) Digital photographs of reaction mixture (CCP3) at t = 1 h and t = 24 h. (c) and (d) Digital photographs of reaction mixture (CCP3) before and after centrifugation.
**Figure S4.** (a) Digital photograph of reaction vials containing CAN for catalysis study. (b) Digital photograph of CCP water suspensions with a polymer concentration of 1.0 g/L.

**Figure S5.** (a) Digital photographs of reaction vial and oxygen sensor system. (b) Calibration curves monitored by oxygen sensor for kinetics study. (c) Digital photograph of GC system (Shidadzu).

**Figure S6.** Plot of oxygen evolution versus time by using the filtrate of CCP3 suspension (1.0 mg/mL) as catalyst solution.
Figure S7. Reaction time (t) dependence of oxygen concentration ([O2]) by using the reference [Ru(bda)(pic)2] as WOCs ([CeIV] = 100 mM, pH = 1.0).

Figure S8. (a) and (b) Reaction time (t) dependence of CeIV absorbance decay at 360 nm for CCP1 and CCP3, where [CeIV] = 1.12 mM. (c) and (d) Catalyst concentration (C_Ru) dependence of initial reaction rate (dA/dt) for CCP1 and CCP3, where [CeIV] = 1.12 mM.
**Figure S9.** Linear fitting of experimental data obtained within the first few seconds in Figures S8.

Mechanism 1: single-site water nucleophilic attack

\[
[Ru^V=O] + H_2O \xrightarrow{^-H^+} [Ru^{III}-OOH] \xrightarrow{e^-+H^+} [Ru^{IV}-O=O] \xrightarrow{} [Ru^{II}] + O=O
\]

Mechanism 2: interaction of two metal oxide units

\[
[Ru^V=O] + [Ru^{V}=O] \xrightarrow{} [Ru^{IV}-O-O-Ru^{IV}] \xrightarrow{+H_2O} [Ru^{III}-O-H_2] + O=O
\]

**Figure S10.** Potential mechanistic pathways for water oxidation catalysis: 1) single-site water nucleophilic attack; 2) interaction of two metal oxide units.

**Figure S11.** (a) and (b) Reaction time (t) dependence of CeIV absorbance decay at 360 nm for CCP1 and CCP3, where \(C_{Ru} = 20 \, \mu M\) (CCP1) and 10 \(\mu M\) (CCP3). (c) and (d) Oxidant concentration ([CeIV]) dependence of initial reaction rate (dA/dt) for CCP1 and CCP3, where \(C_{Ru} = 20 \, \mu M\) (CCP1) and 10 \(\mu M\) (CCP3).
Figure S12. Linear fitting of experimental data obtained within the first few seconds in Figures S11.

Figure S13. Reaction time ($t$) dependence of oxygen concentration ([O$_2$]) by using CCP3 as WOCs in H$_2$O and D$_2$O, where [Ce$^{IV}$] = 100 mM and pH = 1.0 (HNO$_3$).

Figure S14. (a) UV-vis spectra of [Ru(bda)(pic)$_2$] stock solution before and after stirring for 5 h. (b) Diffusion reflectance UV-vis spectra of CCP3 before and after stirring for 24 h.
Based on the SEM result, the morphology of CCP catalysts showed irregular nanoparticle morphologies. To simplify the model, spherical particle structure was assumed for theoretical calculation. Thus, we define the following parameters:

Particle parameter:
- $R$: the average radius for each CCP spherical particle
- $S$: the average total surface area of each CCP spherical particle
- $V$: the average volume of each CCP spherical particle

Ru center parameter:
- $A_{s,Ru}$: surface area occupied by a single Ru site, $A_{s,Ru} = 4.76 \text{ nm}^2$.
- $\rho$: the packing density of CCP catalyst
- $m_{s,Ru}$: the real mass of a single Ru site, and $m_{s,Ru} = M_{s,Ru}/N_A$, where $M_{s,Ru} (548 \text{ g/mol})$ and $N_A$ represents the molar mass of a single Ru-site and Avogadro constant.

Thus, the number of Ru-sites on the surface of a spherical particle ($N_s$) and the total number of Ru-sites in the whole space of a spherical particle ($N_t$) can be expressed as follows:

$$N_s = \frac{S}{A_{s,Ru}}$$
$$N_t = \frac{V \rho}{m_{s,Ru}}$$

The molar percentage of active Ru-sites can be calculated as

$$\frac{N_s}{N_t} = \frac{m_{s,Ru}}{\rho A_{s,Ru}} = \frac{4 \pi R^2 m_{s,Ru}}{(4/3 \pi R^3) \rho} = \frac{3 M_{s,Ru}}{N_A \rho R A_{s,Ru}}$$

Assuming $\rho \sim 0.6 \text{ g/cm}^3$ and $R \sim 50 \text{ nm}$, $N_s/N_t$ is calculated to be $2.0\%$.

**Figure S15.** Calculation of the number densities of active Ru sites located at the outermost layer of porous framework for CCP3.

**Figure S16.** Catalyst concentration ($C_{Ru}$) dependence of initial oxygen evolution rate ($v$) in log-scale coordinate for CCP3 and CCP3m, where $C_{Ru}$ represents the molar concentration of Ru in suspension used in catalysis reaction.
Figure S17. FTIR spectra of CCP3 and CCP3M.

Figure S18. (b) Diffusion reflectance UV-vis spectra of CCP3 and CCP3M.
Figure S19. (a) Repetitive cyclic voltammograms (CVs) for CCP/Nafion/ITO electrodes at pH = 8.0 up to 1.50 V (100 mV/s), where mass ratio of CCP/Nafion was varied.
Figure S20. (a) and (b) Repetitive cyclic voltammograms (CVs) for CCP3/Nafion/ITO electrodes at pH = 8.0 up to 1.50 V (100 mV/s) for 27 cycles.