Supporting Information for

Topology-Guided Design of An Anionic bor-Network to for Photocatalytic [Ru(bpy)]$_2^{2+}$ Encapsulation

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1. General Information

Materials

N,N-dimethylformamide (DMF), ethanol, InCl₃·xH₂O, tetrafluoroboric acid, and tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate were purchased from either Alfa Aesar or Sigma Aldrich. Unless otherwise noted, all chemicals were used without further purification.

Instrumentation

Synchrotron powder X-ray diffraction (PXRD) was carried out with Bruker D8-Discover diffractometer equipped with a Mo sealed tube (λ = 0.72768Å) on the beamline 17-BM at the Advanced Photon Source, Argonne National Laboratory. In-house powder X-ray diffraction (PXRD) was carried out on a Bruker D8-Focus Bragg-Brentano X-ray powder Diffractometer equipped with a Cu sealed tube (λ = 1.54178) at 40 kV and 40 mA. UV-Vis spectra were recorded on Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were recorded on Horiba Fluorolog spectrofluorometer. Thermogravimetric analyses (TGA) were carried out on a Shimadzu TGA-50 thermal analyzer from room temperature to 800 °C at a ramp rate of 2 °C/min in a flowing air atmosphere. Nuclear magnetic resonance (NMR) data were collected on a Mercury 300 spectrometer. Single Crystal XRD data were collected with a Bruker APEX II diffractometer and processed using the program SAINT routine. The structure was solved by direct methods of SHELXL¹ program and refined by full-matrix least squares techniques using the SHELXL² program and WINGX³. Contributions to scattering due to these solvent molecules were corrected with the SQUEEZE⁴, part of the PLATON package, and the structures were then refined again using the data generated. Solvent molecules are not represented in the unit cell contents (chemical formula) in the crystal data. The topology was calculated using the TOPOS⁵ software.

2. Synthesis of linker

2.1 Synthesis of trimethyl 4,4',4''-(benzene-1,3,5-triyltris(azanediyl))tribenzoate (c)

![Scheme S1. Synthesis of triethyl 4,4',4''-(benzene-1,3,5-triyltris(azanediyl))tribenzoate(c)](image)
Synthetic procedure of \( \mathbf{c} \) was followed according to the literature.\(^6\)

### 2.2 Synthesis of \( 10,15\)-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole-3,8,13-tricarboxylic acid (\( \text{H}_3\text{DCTA} \))

**Scheme S2.** Synthesis of \( \text{H}_3\text{DCTA} \).

Synthesis of \( \mathbf{d} \): 0.03 g (0.09 mmol) \( \text{Pd(CF}_3\text{COO)}_2 \), 1 g \( \mathbf{c} \) and 20 mL acetic acid in 50 mL round bottom flask with the eliminator. Temperature up was carried out to 100 degree, blowing and agitating air in the system of reaction with an air pump for 7 hours. An exception carries out the crystal which deposits after cooling, washed with acetic acid and obtained the compound \( \mathbf{d} \) (0.63 g, 74%) \(^1\)H-NMR (DMSO-\(d_6\)) 1.44(9H, t), 4.45 (6H, dd) 7.84(3H, d), 8.07(3H, dd), 9.38(3H, s), 12.67(3H, s),
Synthesis of H$_3$DCTA: Compound d (1g) and 1.5g KOH were suspended in 20 mL EtOH, and refluxed for 2 Hours. After cooling, the pH value was adjusted to approximately 2 using hydrochloric acid. The resulting precipitate was collected by centrifugal, washed with water, and dried under vacuum to give H$_3$DCTA (0.63 g, 74\%). $^1$H-NMR (DMSO-$d_6$): 7.81(3H, d), 8.07(3H, dd), 9.37(3H, s), 12.61(3H, s).


InCl$_3$·xH$_2$O (20 mg) and H$_3$DCTA (5 mg, 0.010 mmol) was immersed in 1.8 mL 4, 4’-dimethylformamide (DMF), 0.2 mL ethanol and 2 drop HBF$_4$(40% min v/v aq solution) in a 4 mL Pyrex vial. After sonication for 5 min, the mixture was moved to a pre-heated 120 °C oven for 4 days. After cooling down under room temperature and DMF wash, colorless cubic crystals was harvested (33% yield based on ligand).
4. Single Crystal X-ray Analysis

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>( \text{C}<em>{108}\text{H}</em>{48}\text{In}<em>3\text{N}</em>{12}\text{O}_{24} )</td>
</tr>
<tr>
<td>( \text{FW} )</td>
<td>2242.04</td>
</tr>
<tr>
<td>Color/Shape</td>
<td>Colorless/Cube</td>
</tr>
<tr>
<td>Crystal size (mm(^3))</td>
<td>0.05 x 0.05 x 0.05</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>( Fm\bar{3}m )</td>
</tr>
<tr>
<td>( a, b, c (\text{Å}) )</td>
<td>43.645(3)</td>
</tr>
<tr>
<td>( \alpha, \beta, \gamma(°) )</td>
<td>90</td>
</tr>
<tr>
<td>( V (\text{Å}^3) )</td>
<td>83137(10)</td>
</tr>
<tr>
<td>( Z )</td>
<td>8</td>
</tr>
<tr>
<td>( d_{\text{calc.}} (\text{g/cm}^3) )</td>
<td>0.358</td>
</tr>
<tr>
<td>( \mu (\text{mm}^{-1}) )</td>
<td>0.185</td>
</tr>
<tr>
<td>( T (\text{K}) )</td>
<td>110(2)</td>
</tr>
<tr>
<td>( F(000) )</td>
<td>8952</td>
</tr>
<tr>
<td>Reflxs collected</td>
<td>194999</td>
</tr>
<tr>
<td>Independent reflxs</td>
<td>3422</td>
</tr>
<tr>
<td>Obsd data [I&gt;2\sigma(I)]</td>
<td>2143</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3422/80/64</td>
</tr>
<tr>
<td>Completeness</td>
<td>99.6 %</td>
</tr>
<tr>
<td>GOF on ( F_2 )</td>
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</tr>
<tr>
<td>( R_{\text{int}} )</td>
<td>0.1229</td>
</tr>
<tr>
<td>( R_u, wR_2 \ [I &gt; 2\sigma(I)] )</td>
<td>0.0987, 0.2798</td>
</tr>
<tr>
<td>( R_u, wR_2 ) (all data)</td>
<td>0.1597, 0.3309</td>
</tr>
<tr>
<td>( \Delta \rho_{\text{max}}/\Delta \rho_{\text{min}} \ [\text{e} \cdot \text{Å}^{-3}] )</td>
<td>0.626/-3.032</td>
</tr>
</tbody>
</table>

5. Loading process for PCN-99

Part a. The congo red solution and \( \text{Ru(bpy)}_3\text{Cl}_2\cdot\text{6H}_2\text{O} \) were prepared as 1mmol/L in DMF solution, respectively. One vial of PCN-99 were treated with 200 µL those stock solution before the UV-absorption measurement.

Note: \( \text{[Ru(bpy)}_3\text{]}^{2+} \), has a dimension of 1.15 X 1.15 X 1.15 nm, while congo red is 0.7 X 2.5 nm. The channel size of 2.2 nm is capable to accommodate the diffusion of the congo red solution and \( \text{Ru(bpy)}_3\text{Cl}_2\cdot\text{6H}_2\text{O} \).
Part b. The Ru(bpy)$_3$Cl$_2$·6H$_2$O (10 mg, 0.021 mmol) was dissolved in 10 mL DMF as the stock solution. This stock solution was incubated with as-synthesized PCN-99 (5 mg) at room temperature and gently shaken for 40 min. The resulted Ru(bpy)$_3$@PCN-99 was then centrifuged and the supernatant was carefully removed for UV-vis measurement. According to the Beer-Lambert Law, the absorption of the band (454 nm for [Ru(bpy)$_3$]$^{2+}$) was proportional to the concentration of [Ru(bpy)$_3$]$^{2+}$. Therefore, the loading amount was calculated by subtracting the concentration of [Ru(bpy)$_3$]$^{2+}$ in the supernatant from the free-MOF amount. The uptake reached the saturation in 6 hr until the band of 454 nm no longer changed any more. The mole absorption coefficient was determined by preparing four different concentrations to derive a standard curve which gave $\varepsilon = 13372$ M$^{-1}$ cm$^{-1}$. After wash with DMF several times, Ru(bpy)$_3$@PCN-99 was ready to use for further analysis.

6. TGA data for PCN-99 and Ru(bpy)$_3$@PCN-99

![Figure S1. Thermogravimetric analysis data for PCN-99 and Ru(bpy)$_3$@PCN-99.](image)

The Ru(bpy)$_3$@PCN-99 has more decomposition residue compare to that of PCN-99, which indicated the
entrapment of Ru cation in PCN-99.

7. **General Procedure and NMR Spectral Data of Products**

According to the literature, a mixture of 4-methoxycarbonylphenylboronic acid 1a (90 mg, 0.50 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mol%) in 5mL DMF with iPr$_2$EtN (1 mmol) was stirred at room temperature under visible light radiation in open air. After 48 hr, the reaction and evaporated to remove the dryness. The residue was purified with column (EtOAc :Hexanes = 3:7) to give the pure product 2a (109.2 mg, 71.8%) as a white solid. Similar procedure was performed with 2 mmol % Ru(bpy)$_3$@PCN-99.

$^1$H NMR spectra

4-methoxycarbonylphenol (2a)

Reaction was prepared based on general procedure. Product 2a yield 109.2 mg for Ru salt (71.9%) and 45 mg for Ru(bpy)$_3$@PCN-99 (59%).

![Figure S2. $^1$H NMR spectra of 2a catalyzed by Ru(bpy)$_3$Cl$_2$·6H$_2$O in CDCl$_3$.](image-url)
Figure S3. $^1$H NMR spectra of 2a catalyzed by Ru(bpy)$_3$@PCN-99 in CDCl$_3$

**4-methylphenol (2b)**

\[
\text{Me} \quad \text{B} \quad \text{OH} \quad \text{OH} \quad \text{Me} \quad \text{OH}
\]

\[
\begin{align*}
\text{visible light,} & \\
[Ru(bpy)$_3$Cl$_2$.6H$_2$O (2mol\%)] & \\
iPr$_2$NEt (2 equiv), & \\
DMF (5mL), air & \\
\rightarrow & \\
\text{Me} & \\
\text{B} & \\
\text{OH} & \\
\text{OH} & \\
\text{Me} & \\
\text{OH}
\end{align*}
\]

Similar reaction was prepared based on general procedure with the 4-methylphenyl boronic acid (68 mg, 0.50 mmol). Product 2b yield 48.3 mg for Ru salt (89.4%) and 35.3 mg for Ru(bpy)$_3$@PCN-99 (65.4%).
Figure S4. $^1$H NMR spectra of $2b$ catalyzed by Ru(bpy)$_3$Cl$_2$:6H$_2$O in CDCl$_3$.

Figure S5. $^1$H NMR spectra of $2b$ catalyzed by Ru(bpy)$_3$@PCN-99 in CDCl$_3$.

4-Hydroxybenzaldehyde (2c).

\[
\text{OH} = \text{C} - \text{OH} \quad \text{visible light,} \quad [\text{Ru(bpy)}_3\text{Cl}_2] \cdot 6\text{H}_2\text{O} (2\text{mol}\%) \\
\text{iPr}_2\text{NEt (2 equiv),} \quad \text{DMF (5mL), air} \quad \text{OH} \quad \text{OH} \\
\text{1c} \quad \text{2c}
\]
Similar reaction was prepared based on general procedure with the (4-formylphenyl)boronic acid (75mg, 0.50 mmol). Product 2c yield 50.2 mg for Ru salt (82%) and 28 mg for Ru(bpy)$_3$@PCN-99 (45.9%).

**Figure S6.** $^1$H NMR spectra of 2c catalyzed by Ru(bpy)$_3$Cl$_2$·6H$_2$O in CDCl$_3$.

**Figure S7.** $^1$H NMR spectra of 2c catalyzed by Ru(bpy)$_3$@PCN-99 in CDCl$_3$. 
Figure S8. PXRD after the catalysis.

Powder XRD (collected from X-ray powder diffractometer with a Cu sealed tube (λ = 1.54178) at 40 kV and 40 mA) before and after catalysis approved that the crystallinity was maintained.

SEM images of Ru(bpy)$_3$@PCN-99 before the catalysis
SEM images of Ru(bpy)$_3$@PCN-99 after the catalysis

The SEM images indicated there was not much change of the crystals before and after the catalysis.

8. Screening and Control experiments of catalytic activity of Ru(bpy)$_3$@PCN-99 in oxidation of 4-(methoxycarbonyl)phenyl)boronic acid.

First, screening and control experiments is demonstrated using 4-(methoxycarbonyl)phenyl)boronic acid as the substrate according to the general procedure as Section 9. The absence of product 2a excluded the influences from the interference of the H$_3$DCTA (Table S1, Entry 2), the Lewis acidity of indium (III) (Table S1, Entry 3), and the framework itself (Table S1, Entry 4). Thus, all the catalytic behaviour were dedicated solely to the [Ru(bpy)$_3$]$^{2+}$ components in Ru(bpy)$_3$@PCN-99. (Table S1, Entry 1). In addition, no significant effect was observed caused by the electron-rich ligand on the photocatalysis of [Ru(bpy)$_3$]$^{2+}$ (Table S1, Entry 5 vs 71.9% for just [Ru(bpy)$_3$]$^{2+}$).

**Table. S1** Screening and control experiments of Ru(bpy)$_3$@PCN-99 as catalyst$^{[a]}$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ru(bpy)$_3$@PCN99</th>
<th>H$_3$DCTA</th>
<th>In(NO$_3$)$_3$</th>
<th>PCN-99</th>
<th>[Ru(bpy)$_3$]Cl$_2$·6H$_2$O (2mol%)</th>
<th>Yield %$^{[b]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>59%</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>No Reaction</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>No Reaction</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>No Reaction</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>70.2%</td>
</tr>
</tbody>
</table>
[a]Reaction Condition: 1a (0.5mmol), catalyst (2 mol%), iPr$_2$NET (2.0 equiv), DMF (5mL), 36 W fluorescence lamp irradiation, and open to air for 48 hr. [b] yield based on the isolated structure. “+” means including, while “-” means excluding.

9. Recyclability of Ru(bpy)$_3$@PCN-99

Comparing the Ru complex content before and after the first catalysis, 9.48% Ru(bpy)$_3^{2+}$ was found in the solution after the first use of Ru(bpy)$_3$@PCN-99 system, which could be from partial decomposition of MOFs under basic conditions. A separate control experiment (R=COOMe) with leached Ru(bpy)$_3^{2+}$ ended up with 13% product yield. However, most of the Ru(bpy)$_3^{2+}$ was still preserved in PCN-99. The second use of Ru(bpy)$_3$@PCN-99 for second use end with only greatly decreased leaching of 4.76% but comparable product yields.

Table. S2. Recyclability of Ru(bpy)$_3$@PCN-99 as catalysis in hydroxylation of arylboronic acid.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R-</th>
<th>Catalyst</th>
<th>1st Conversion</th>
<th>2nd Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>COOMe</td>
<td>Ru(bpy)$_3$@PCN-99</td>
<td>59.0%</td>
<td>60.0%</td>
</tr>
<tr>
<td>2</td>
<td>Me</td>
<td>Ru(bpy)$_3$@PCN-99</td>
<td>65.4%</td>
<td>65.0%</td>
</tr>
<tr>
<td>3</td>
<td>CHO</td>
<td>Ru(bpy)$_3$@PCN-99</td>
<td>45.9%</td>
<td>45.0%</td>
</tr>
</tbody>
</table>

10. Acknowledgements

The organic synthesis and structural studies of this research was supported as part of the Hydrogen and Fuel Cell Program under Award Number DE-EE-0007049. The UV study and catalysis study were supported as part of the U.S. Department of Energy, ARPA-e (DE-AR0000249) program, the Office of Naval Research (N00014-14-1-0720), and the Welch Foundation through a Robert A. Welch chair in Chemistry to HCZ. The authors also acknowledge the financial supports of Texas A&M University. The X-ray diffractometers in the X-ray Diffraction Laboratory at Department of Chemistry, Texas A&M University were purchased with funds provided by the National Science Foundation (CHE-9807975, CHE-0079822, and CHE-0215838). Use of the Advanced Photon Source, an Office of Science User
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11. References