

Supporting Information for

**Topology-Guided Design of An Anionic bor-Network to for Photocatalytic [Ru(bpy)<sub>3</sub>]<sup>2+</sup> Encapsulation**

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## 1. General Information

### Materials

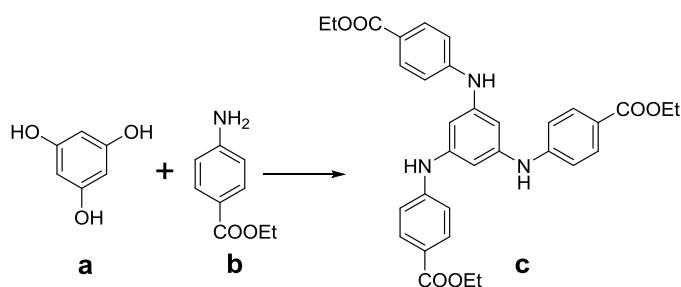
N,N-dimethylformamide (DMF), ethanol,  $\text{InCl}_3 \cdot x\text{H}_2\text{O}$ , tetrafluoroboric acid, and tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate were purchased from either Alfa Aesar or Sigma Aldrich. Unless otherwise noted, all chemicals were used without further purification.

### Instrumentation

Synchrotron powder X-ray diffraction (PXRD) was carried out with Bruker D8-Discover diffractometer equipped with a Mo sealed tube ( $\lambda = 0.72768\text{\AA}$ ) 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 ( $\lambda = 1.54178$ ) 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 SHELXL<sup>1</sup> program and refined by full-matrix least squares techniques using the SHEXL<sup>2</sup> program and WINGX<sup>3</sup>. Contributions to scattering due to these solvent molecules were corrected with the SQUEEZE<sup>4</sup>, 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 TOPOS<sup>5</sup> software.

## 2. Synthesis of linker

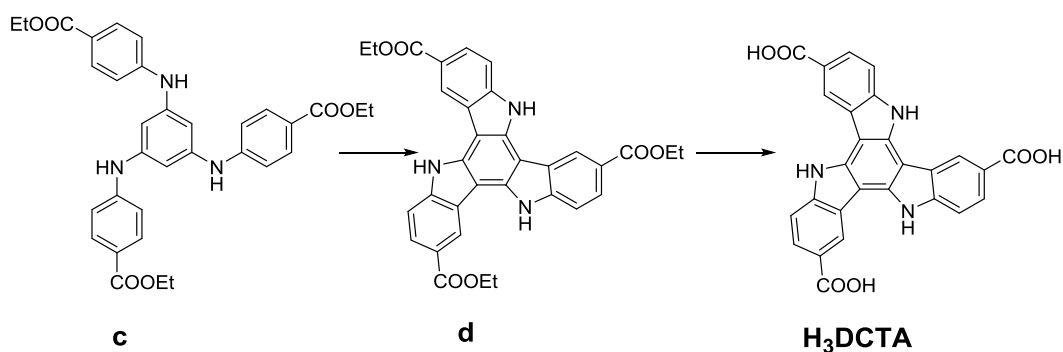
### 2.1 Synthesis of triethyl 4,4',4''-(benzene-1,3,5-triyltris(azanediyl))tribenzoate (c)



**Scheme S1.** Synthesis of triethyl 4,4',4''-(benzene-1,3,5-triyltris(azanediyl))tribenzoate(c)

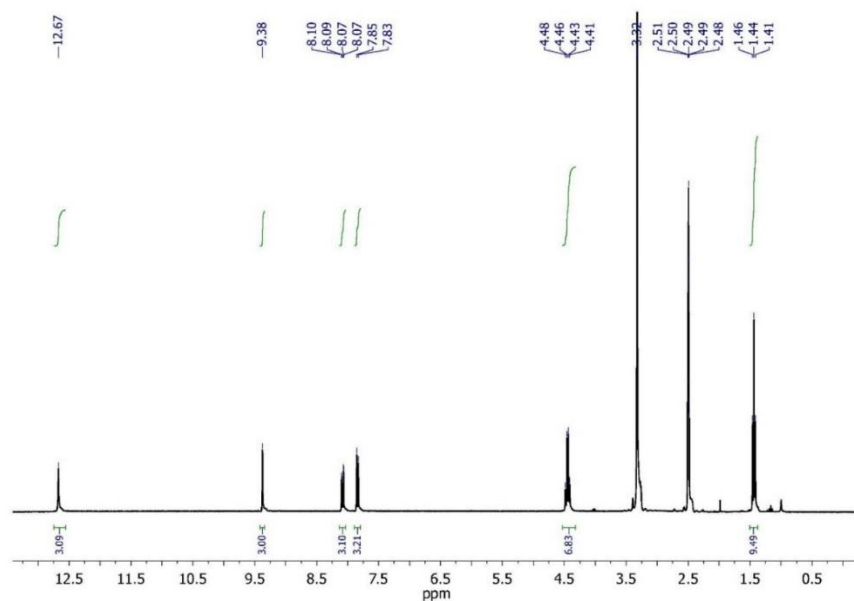
Synthetic procedure of **c** was followed according to the literature.<sup>6</sup>

## 2.2 Synthesis of 10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole-3,8,13-tricarboxylic acid (**H<sub>3</sub>DCTA**)

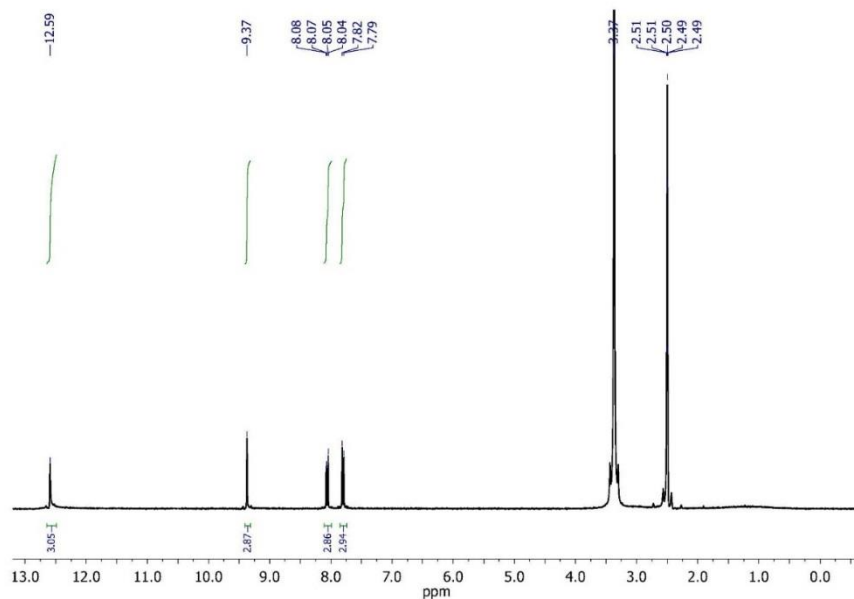


**Scheme S2.** Synthesis of **H<sub>3</sub>DCTA**.

Synthesis of **d**: 0.03 g (0.09 mmol)  $\text{Pd}(\text{CF}_3\text{COO})_2$ , 1 g **c** and 20 mL acetic acid in 50mL 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 **d** (0.63 g, 74%)  $^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ ) 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<sub>3</sub>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<sub>3</sub>DCTA (0.63 g, 74%). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>): 7.81(3H, d), 8.07(3H, dd), 9.37(3H, s), 12.61(3H, s).



### 3. Synthesis of PCN-99

InCl<sub>3</sub>·xH<sub>2</sub>O (20 mg) and H<sub>3</sub>DCTA (5 mg, 0.010 mmol) was immersed in 1.8 mL 4, 4'-dimethylformamide (DMF), 0.2 mL ethanol and 2 drop HBF<sub>4</sub>(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

Formula	C <sub>108</sub> H <sub>48</sub> In <sub>3</sub> N <sub>12</sub> O <sub>24</sub>
Fw	2242.04
Color/Shape	Colorless/Cube
Crystal size (mm <sup>3</sup> )	0.05 x 0.05 x 0.05
Crystal system	Cubic
Space group	<i>Fm-3m</i>
a, b, c (Å)	43.645(3)
α, β, γ(°)	90
V (Å <sup>3</sup> )	83137(10)
Z	8
d <sub>calc.</sub> (g/cm <sup>3</sup> )	0.358
μ(mm <sup>-1</sup> )	0.185
T (K)	110(2)
F(000)	8952
Reflns collected	194999
Independent reflns	3422
Obsd data [ <i>I</i> >2σ( <i>I</i> )]	2143
Data/restraints/parameters	3422/80/64
Completeness	99.6 %
GOF on F <sub>2</sub>	1.117
R <sub>int</sub>	0.1229
R <sub>1</sub> , wR <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0987, 0.2798
R <sub>1</sub> , wR <sub>2</sub> (all data)	0.1597, 0.3309
Δρ <sub>max</sub> /Δρ <sub>min</sub> [e·Å <sup>-3</sup> ]	0.626/-3.032

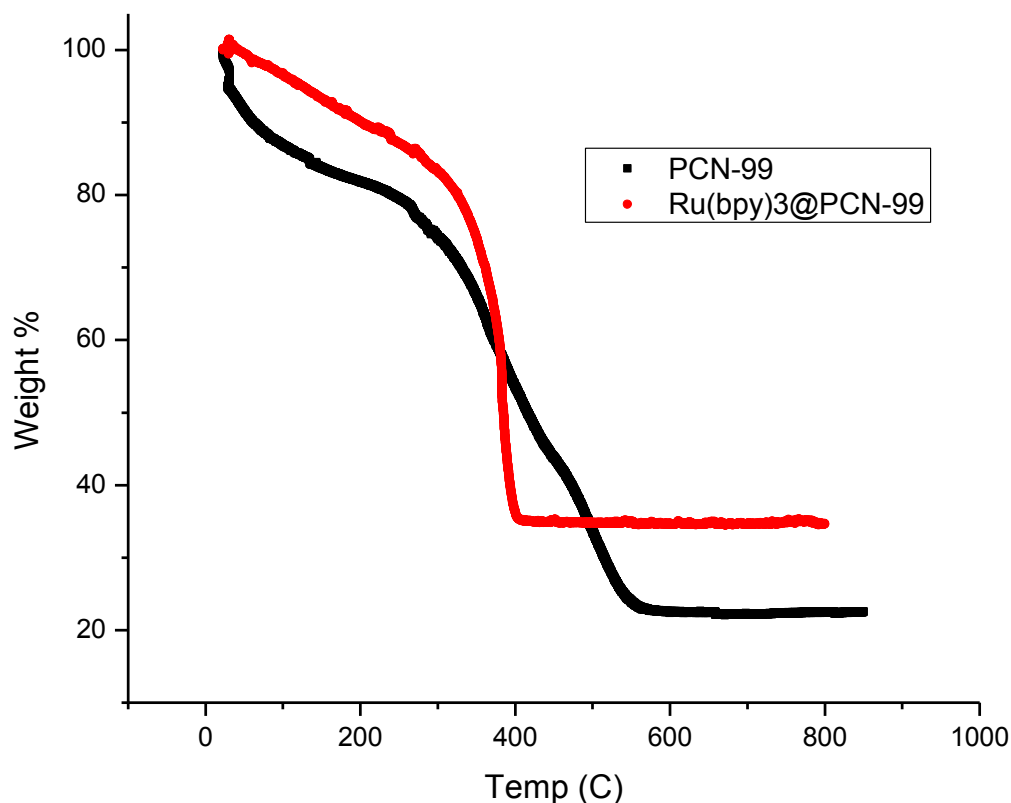
#### 5. Loading process for PCN-99

Part a. The congo red solution and Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>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: [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, 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 Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O. <sup>7</sup>

Part b. The  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (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  $\text{Ru}(\text{bpy})_3@PCN-99$  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  $[\text{Ru}(\text{bpy})_3]^{2+}$ ) was proportional to the concentration of  $[\text{Ru}(\text{bpy})_3]^{2+}$ . Therefore, the loading amount was calculated by subtracting the concentration of  $[\text{Ru}(\text{bpy})_3]^{2+}$  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  $\epsilon = 13372 \text{ M}^{-1} \text{ cm}^{-1}$ . After wash with DMF several times,  $\text{Ru}(\text{bpy})_3@PCN-99$  was ready to use for further analysis.

#### 6. TGA data for PCN-99 and $\text{Ru}(\text{bpy})_3@PCN-99$

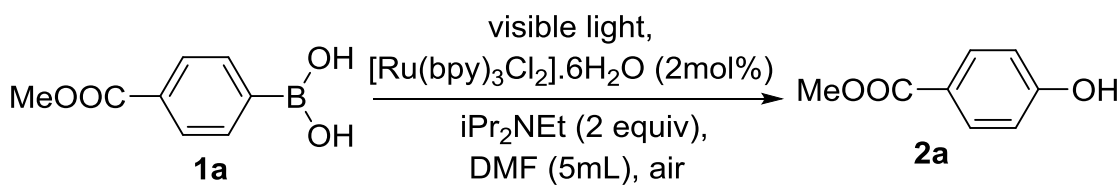


**Figure S1.** Thermogravimetric analysis data for PCN-99 and  $\text{Ru}(\text{bpy})_3@PCN-99$ .

The  $\text{Ru}(\text{bpy})_3@PCN-99$  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<sup>8</sup>, a mixture of 4-methoxycarbonylphenylboronic acid **1a** (90 mg, 0.50 mmol),  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (2 mol%) in 5 mL DMF with  $i\text{Pr}_2\text{NEt}$  (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 %  $\text{Ru}(\text{bpy})_3@PCN-99$ .

### <sup>1</sup>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  $\text{Ru}(\text{bpy})_3@PCN-99$  (59%).

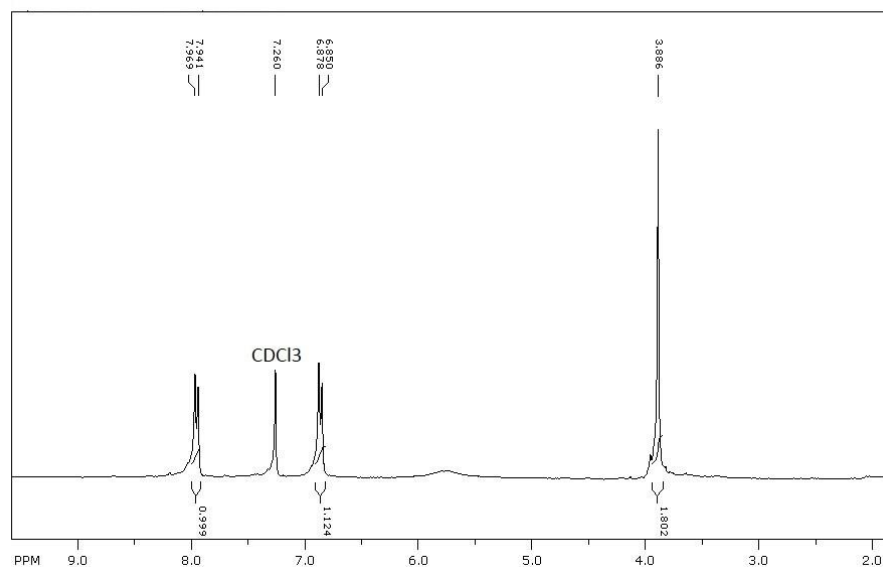
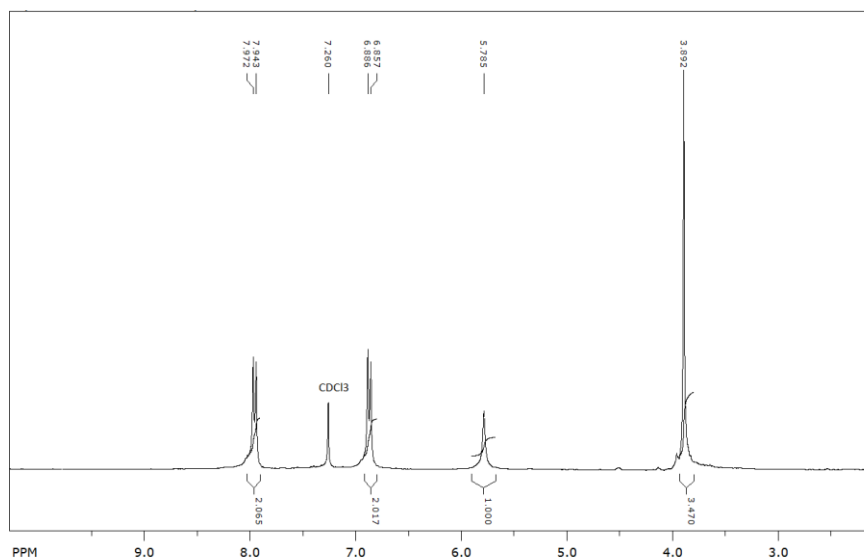
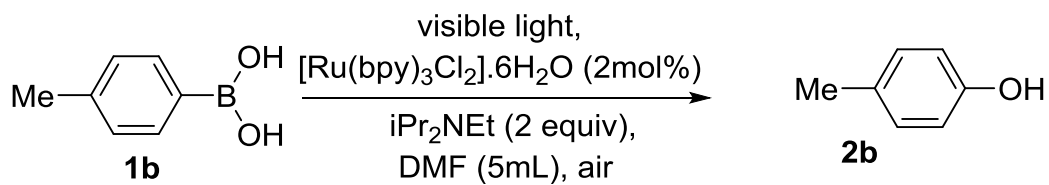


Figure S2. <sup>1</sup>H NMR spectra of **2a** catalyzed by  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  in  $\text{CDCl}_3$ .



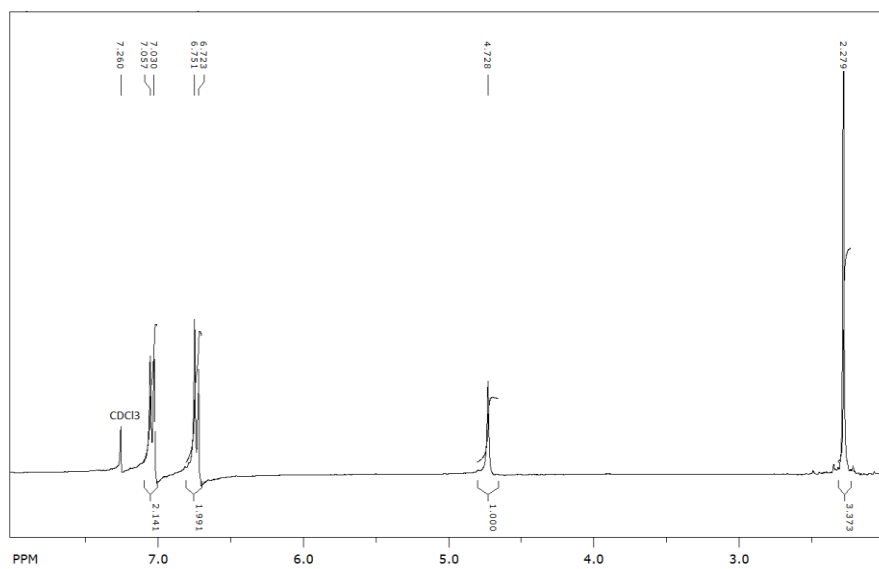
**Figure S3.**  $^1\text{H}$  NMR spectra of **2a** catalyzed by  $\text{Ru}(\text{bpy})_3@ \text{PCN-99}$  in  $\text{CDCl}_3$

#### 4-methylphenol (**2b**)

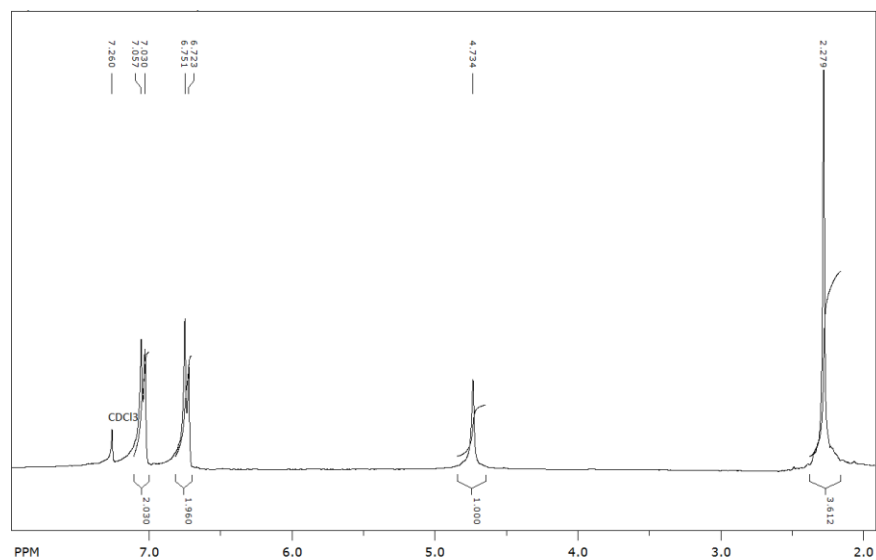


Similar reaction was prepared based on general procedure with the 4-methylphenyl boronic acid (68 mg, 0.50 mmol). Product **2b** yield 48.3 mg for Ru salt (89.4%) and 35.3 mg for  $\text{Ru}(\text{bpy})_3@ \text{PCN-99}$  (65.4%).



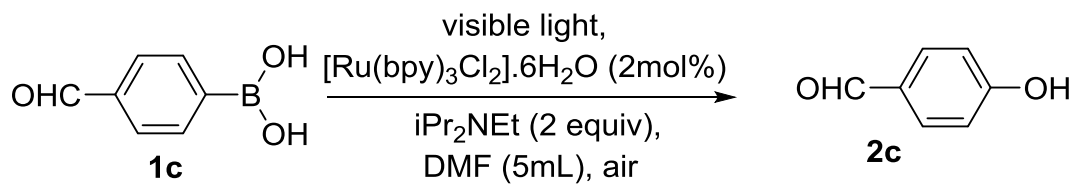


**Figure S4.**  $^1\text{H}$  NMR spectra of **2b** catalyzed by  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  in  $\text{CDCl}_3$ .

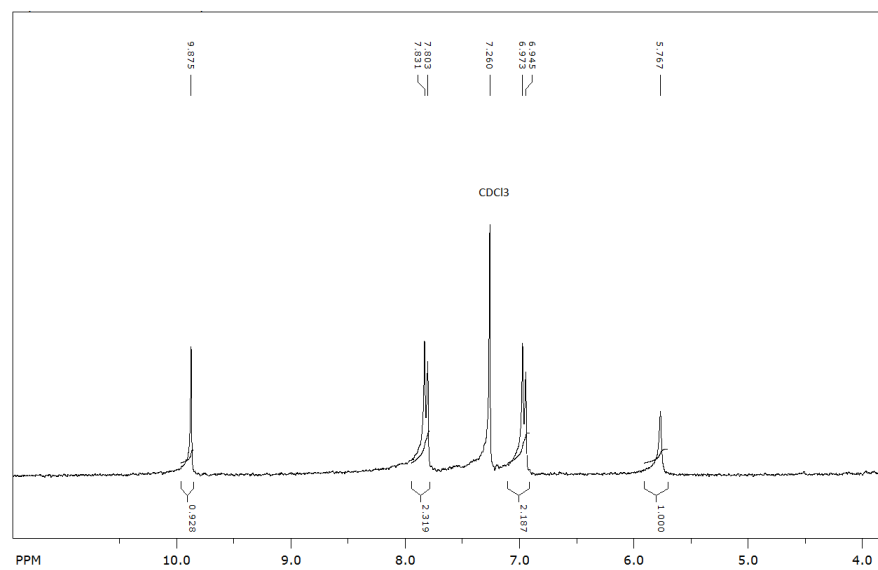


**Figure S5.**  $^1\text{H}$  NMR spectra of **2b** catalyzed by  $\text{Ru}(\text{bpy})_3@PCN-99$  in  $\text{CDCl}_3$ .

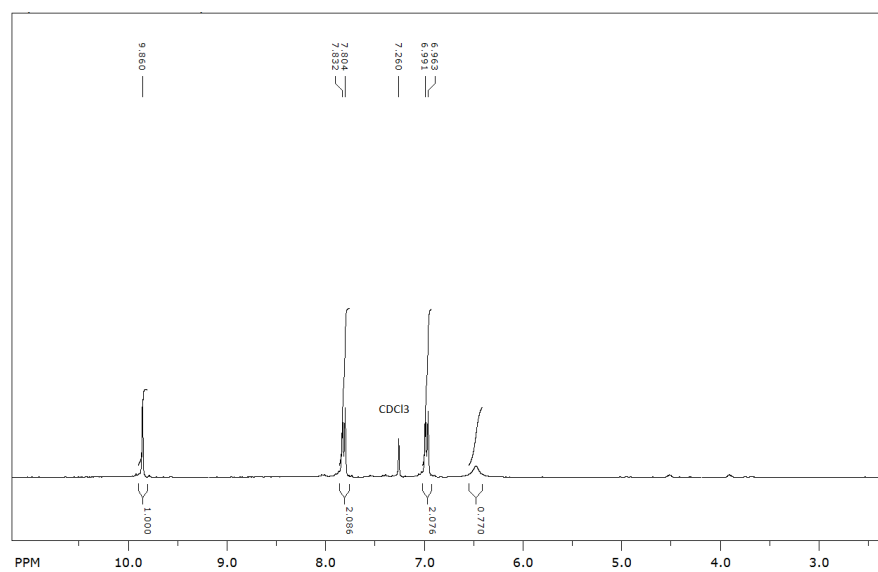
#### 4-Hydroxybenzaldehyde (**2c**).



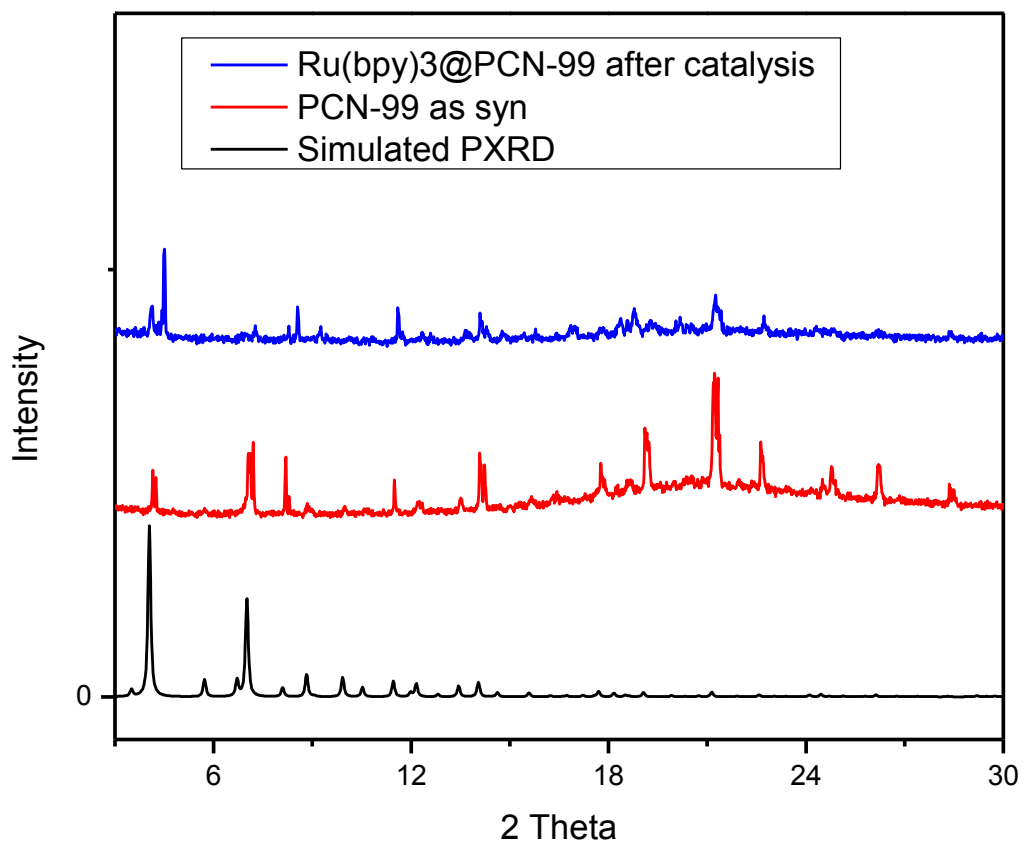
Similar reaction was prepared based on general procedure with the (4-formylphenyl)boronic acid (75mg, 0.50 mmol). Product **2c** yield 50.2 mg for Ru salt (82%) and 28 mg for Ru(bpy)<sub>3</sub>@PCN-99 (45.9%).



**Figure S6.** <sup>1</sup>H NMR spectra of **2c** catalyzed by Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O in CDCl<sub>3</sub>.



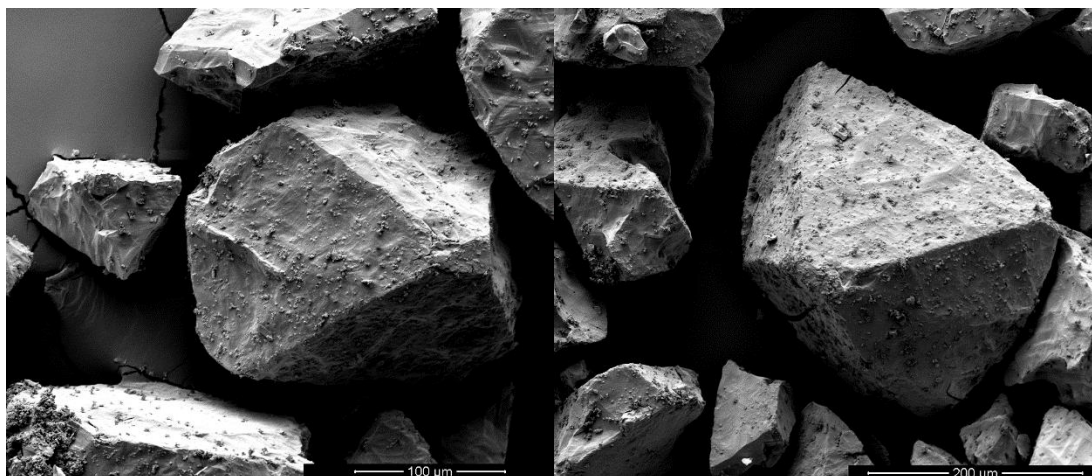
**Figure S7.** <sup>1</sup>H NMR spectra of **2c** catalyzed by Ru(bpy)<sub>3</sub>@PCN-99 in CDCl<sub>3</sub>.



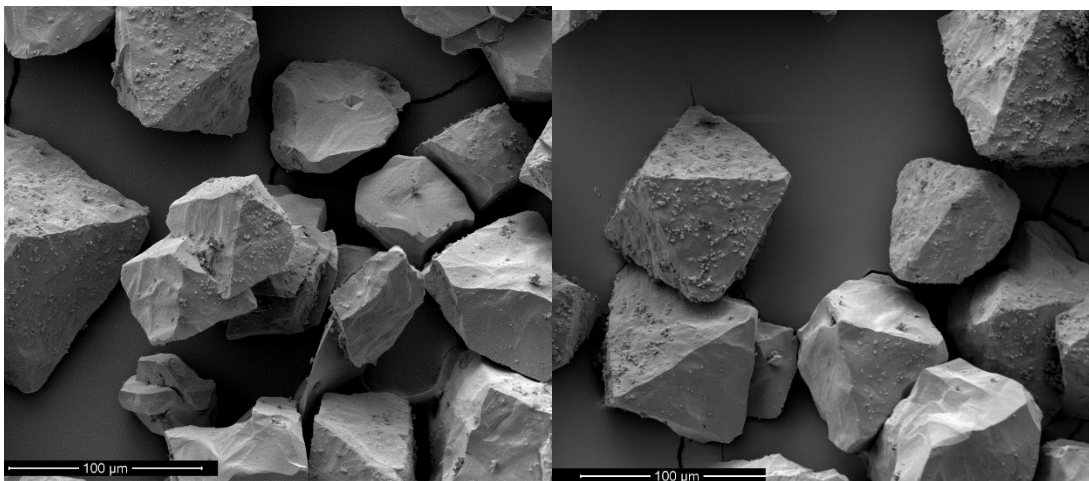
**Figure S8.** PXRD after the catalysis.

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

SEM images of  $\text{Ru}(\text{bpy})_3@$ PCN-99 before the catalysis



### SEM images of Ru(bpy)<sub>3</sub>@PCN-99 after the catalysis

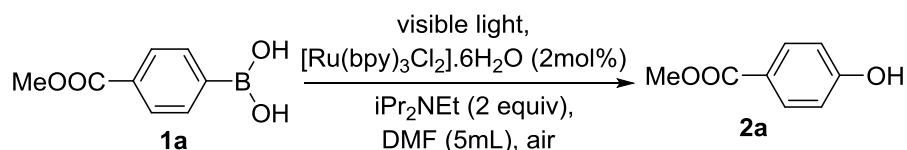


The SEM images indicated there was not much change of the crystals before and after the catalysis.

### 8. Screening and Control experiments of catalytic activity of Ru(bpy)<sub>3</sub>@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<sub>3</sub>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)<sub>3</sub>]<sup>2+</sup> components in Ru(bpy)<sub>3</sub>@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)<sub>3</sub>]<sup>2+</sup> (Table S1, Entry 5 vs 71.9% for just [Ru(bpy)<sub>3</sub>]<sup>2+</sup>).

**Table. S1** Screening and control experiments of Ru(bpy)<sub>3</sub>@PCN-99 as catalysis <sup>[a]</sup>.



Entry	Ru(bpy) <sub>3</sub> @PCN99	H <sub>3</sub> DCTA	In (NO <sub>3</sub> ) <sub>3</sub>	PCN-99	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> ·6H <sub>2</sub> O	Yield % <sup>[b]</sup>
1	+	-	-	-	-	59%
2	-	+	-	-	-	No Reaction
3	-	-	+	-	-	No Reaction
4	-	-	-	+	-	No Reaction
5	-	+	-	-	+	70.2%

[a]Reaction Condition: **1a** (0.5mmol), catalyst (2 mol%),  $i\text{Pr}_2\text{NEt}$  (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 $\text{Ru}(\text{bpy})_3@ \text{PCN-99}$

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

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

$\text{R}-\text{C}_6\text{H}_4-\text{B}(\text{OH})_2$  (**1a**)  $\xrightarrow[\text{DMF (5mL), air}]{\text{Ru}(\text{bpy})_3@ \text{PCN-99 (2mol\%)}, \text{visible light}, i\text{Pr}_2\text{NEt (2 equiv)}}$   $\text{R}-\text{C}_6\text{H}_4-\text{OH}$  (**2a**)

Entry	R-	Catalyst	1 <sup>st</sup> Conversion	2 <sup>nd</sup> Conversion
1	COOMe	$\text{Ru}(\text{bpy})_3@ \text{PCN-99}$	59.0%	60.0%
2	Me	$\text{Ru}(\text{bpy})_3@ \text{PCN-99}$	65.4%	65.0%
3	CHO	$\text{Ru}(\text{bpy})_3@ \text{PCN-99}$	45.9%	45.0%

### 10. Acknowledgements

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