[Supporting Information]

Porous Organic Frameworks with Mesopores and [Ru(bpy)₃]²⁺

Ligand Built-in as Highly Efficient Visible-Light Heterogeneous

Photocatalyst

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A. General information

Chemicals and solvents were purchased from commercial suppliers. All equipment was thoroughly oven-dried. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light. Flash column chromatography (FCC) was carried out with silica gel (200–300 mesh). ¹H and ¹³C liquid NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer. N₂ adsorption and desorption isotherms were measured at 77 K using a Quantachrome autosorb IQ-2. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDPT) method. Solid-state NMR experiments were performed on a Bruker Avance II WB 400 MHz NMR spectrometer. The ¹³C CP/MAS NMR spectra were recorded with the contact time of 3 ms (ramp 100) and the recycle delay of 2 s on a 2.5 mm double resonance probe. FT-IR spectra were collected on a Nicolet 6700 instrument. Thermal properties of the synthesized materials were evaluated on a STA PT1600 Linseis thermogravimetric analysis (TGA) instrument in the temperature range of 25 to 800 °C under nitrogen atmosphere with a heating rate of 10 °C/min. Surface morphologies and microstructures of the synthesized materials were examined with a ZEISS Gemini-500 scanning electron microscope (SEM). The UV-Visible absorption spectra of the [Ru(bpy)₃]²⁺ Ligand and the Ru-POPs were recorded on UV-Vis spectrometer (U-4100) in solid state powder at room temperature. A Agilent 7700ce Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) was used to determine Ru content. Powder X-ray diffraction (PXRD) was performed by a Rigaku D/MAX-2400 diffractometer using Cu-Ka radiation, 40 kV, 100 mA with a scanning rate of 15° min⁻¹. Cyclic voltammetry (CV) experiment was carried out using CHI 760E in a three-electrode electrochemical cell with a scan rate of 0.1 V/s. The experiment was conducted in anhydrous acetonitrile with tertrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte.

The auxiliary electrode was a platinum wire. The reference electrode was based on the calomel electrode. The working electrode was a glassy carbon electrode.

B. Materials and experimental procedures

Materials: All reagents were purchased from commercial sources and used as received without further purification. $RuCl_3 H_2O$ and 1,2-diaminobenzene were received from J&K. All the substrates were purchased from Energy Chemical (Shanghai, China) and used as received. DMF was dried by calcium hydride and used after distillation. [Pd(PPh_3)_2Cl_2] and 1,3,5-tri(4-ethynylphenyl)benzene were prepared and purified according to the literature procedures. All anhydrous reactions were carried out under dry nitrogen by using Schlenk tube techniques. All catalytic reactions were performed in a 10 mL glass tube.

Experimental procedures:

(I) Synthesis of 1,3,5-tri(4-ethynylphenyl)benzene¹



4-iodooacetophenone (500 mg, 2.03 mmol) was dissolved in ethanol (5 mL) and silicon tetrachloride (575 mg, 3.39 mmol) was quickly added at 0 °C (a tube is needed to release hydrogen chloride into the fume hood) and the resulting orange solution was stirred at room temperature for 3 d. The mixture was quenched with water (5 mL) and the solution was concentrated to 6 mL. CH_2Cl_2 (5 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on aluminum oxide (hexane/ethyl acetate = 10:1) to give 1,3,5-tris(4-iodophenyl)benzene (396 mg, 85%) as a yellow solid.

A mixture of 1,3,5-tris(4-iodophenyl)benzene (350 mg, 512 μ mol), ethynyltrimethylsilane (201 mg, 2.05 mmol), PdCl₂(PPh₃)₂ (60 mg), and CuI (10 mg) in THF (2.5 mL) and triethylamine (2.5 mL) was heated to 80 °C for 16 h under N₂ atmosphere. The volatile components were removed under reduced pressure and the residue was diluted with CH₂Cl₂ (10 mL). Satd. aq. NH₄Cl solution (10 mL) was added, the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to give **3** (211 mg, 70%) as a pale brownish solid.

A solution of **3** (200 mg, 336 µmol) and TBAF (1.2 ml, 1.18 mmol, 1 M in THF) in THF (2 mL) was stirred at room temperature for 30 min. The mixture was quenched with satd. aq. NH₄Cl solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried with Na₂SO₄ and concentrated to dryness. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 10:1) to give 1,3,5-tri(4-ethynylphenyl)benzene (102 mg, 80%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.77 (s, 3H); 7.67-7.61 (m, 12H); 3.17 (s, 3H). ¹³CNMR (100 MHz, CDCl₃): δ (ppm) 141.6, 141.2, 132.7, 127.2, 125.3, 121.5, 83.4, 78.2.

(II) Synthesis of the photoactive functional building block (FBB-Ru(bpy)₃²⁺)²



In a typical procedure, a solution of ruthenium trichloride monohydrate (22.5 mg, 0.1mmol) and 4,4'-dibromo-2,2'-bipyridyl (157 mg, 0.5 mmol) in 95% ethanol (10 mL) was heated under reflux for 7 days. The deep orange-red solution was filtered hot and evaporated to a small volume. The residue was purified by column chromatography on silica gel (MeOH/CH₂Cl₂ = 1:10) to give **FBB-Ru(bpy)**₃²⁺ (67.7 mg, 65%) as a orange-red solid. ¹H NMR (400 MHz, MeOD): δ (ppm) 9.08 (d, *J* = 1.8 Hz, 6 H), 7.75 (dd, *J* = 6.1, 2.0 Hz, 6 H), 7.74–7.67 (m, 6 H). ¹³C NMR (101 MHz,

MeOD) δ (ppm) 158.4, 153.53, 136.2, 132.8, 129.9. HRMS m/z calcd for $C_{30}H_{18}Br_6N_6Ru^{2+}$: 521.7838, found: 521.7832.

(III) Synthesis of Ru(bpy)₃²⁺-based porous organic polymer (**Ru-POP**)³



SBB (67.3 mg, 0.18 mmol), **FBB-Ru(bpy)**₃²⁺ (92.7 mg, 0.089 mmol), bis-(triphenylphosphine)palladium(II) dichloride (30 mg), and copper iodide (15 mg) were dissolved in a mixture of dried dimethylformamide (5 mL) and Et₃N (5 mL). The reaction mixture was heated to 80 °C and stirred for 72 h under nitrogen atmosphere. The mixture was then cooled to room temperature, and the precipitated **Ru-POP** frameworks was filtered and washed four times (once each) with chloroform, water, methanol, and acetone to remove any unreacted substrates or catalyst residues. Further purification of the **Ru-POP** frameworks was carried out by Soxhlet extraction with methanol for 48 h. The product was dried in vacuum for 24 h at 80 °C (108 mg, yield: 92%). Anal. calcd for C₉₀H₆₄N₆Ru: C 87.5; H 5.21; N 6.84. Elemental analysis (%) Found: C 78.59; H 4.72; N 3.25. The Ru content in **Ru-POP** frameworks was 3.26% as determined by ICP.

C. Powder X-ray diffraction for Ru-POP



Figure S1. Powder X-ray diffraction pattern of Ru-POP. No intensive diffraction peaks were observable.

D. Band gap of Ru-POP



Figure S2. Band gap of Ru-POP obtained from the UV/Vis spectrum according to the Kubelka-Munk theory.

E. CV measurement of Ru-POP



Figure S3. CV measurement of Ru-POP

F. The geometries of the reactants and product

The geometries of reactants and product were fully optimized with the Gaussian 09 package ⁴ at B3LYP/6-31G(d) level in combination with frequency calculations. Then, using Monte-Carlo method embedded in Gaussian 09, the Volume=Tight keyword was employed to carry out single-point calculations at the same basis set level to obtain molecular volumes based on 0.001 e/bohr³ density envelope, with the IOp(6/45=2000) keyword to define the number of points per bohr³ as 2000. In the structural optimizations and volume calculations, the solvent effect was evaluated with the polarizable continuum model (PCM) to simulate the ethanol environments. Our theoretical results predicted the molecular volumes of 1,2-phenylenediamine, benzaldehyde and 2-phenyl-benzimidazole to be 144.89, 138.94 and 239.43 Å³, respectively. Considering the optimized structures, molecular volumes and electron dispersions, the three dimensional sizes of1,2-phenylenediamine, benzaldehyde and 2-phenyl-benzimidazole to be 7.8 Å × 7.4 Å × 2.5 Å, 8.5 Å × 6.7 Å × 2.4 Å, and 13.3 Å × 7.4 Å × 2.4 Å, as depicted in Figure S2.



Figure S4. The geometries of the reactants and products

G. FT-IR spectra for fresh and recycled Ru-POP



Figure S5. FT-IR spectra of Ru-POP as the fresh catalyst (in black) and as recycled catalyst after 12 run (in red)



H. N₂ adsorption-desorption isotherms of the recycled Ru-POP

Figure S6. N_2 adsorption-desorption isotherms of the recycled Ru-POP after the 6th run and the 12th run. The BET surface area of Ru-POP decreased to 349 m²g⁻¹ after the 6th recycled used and decreased to 169 m²g⁻¹ after the 12th recycled used. We believe that the substrates or the products have blocked the partial micropores of Ru-POP lead to the decrease in BET surface area.

I. SEM image of the recycled Ru-POP



Figure S7. SEM images of Ru-POP after the 12th run of catalysis. The unchanged SEM images indicated that Ru-POP is stable after photocatalytic cycles.

J. EDX elemental mapping of the recycled Ru-POP



Figure S8. EDX elemental mapping of Ru-POP after the 12th run of catalysis. The EDX elemental mapping showed that the elements C, N, and Ru were also well-dispersed in the Ru-POP frameworks after the 12th of catalysis, which indicated that Ru-POP is stable after photocatalytic cycles.

K. General experimental procedure for the synthesis of 2-substituted benzimidazole catalyzed by Ru-POP⁵

To a stirred solution of Ru-POP catalyst (3 mg, 0.4 mol%) in ethanol (1.0 mL) in 10 mL glass tube, aldehyde (0.25 mmol, 1 equiv) and *o*-Phenylenediamine (0.25 mmol, 1 equiv) were added and the mixture was stirred at room temperature under irradiation with visible light using a cool fluorescent bulb (24 W) until all starting substrates had been consumed. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was centrifugated and the solid catalyst was washed with EtOH (3 x 5.0 mL). The combined organic phase was evaporated at reduced pressure and the residue was purified by flash column chromatography using silica gel with petroleum ether/ethanol or petroleum ether/ethyl acetate mixture as eluent to give the desired product as white solid.

2-phenyl-1H-benzo[d]imidazole (Table 2, Entry 1)

Prepared according to the general procedure with *o*-Phenylenediamine and benzaldehyde. The product was collected as white solid in 99% yield after silica gel chromatography (petroleum ether/ethanol = 10:1). ¹H NMR (400 MHz, DMSO- d_6) δ 12.91 (s, 1H), 8.19 (d, J = 7.1 Hz, 2H), 7.81 – 7.40 (m, 5H), 7.21 (s, 2H). ¹³C NMR (101 MHz, DMSO- d_6) δ 151.19, 143.79, 134.98, 130.15, 129.80, 128.92, 126.40, 122.49, 121.63, 118.85, 111.29.

2-(4-bromophenyl)-1H-benzo[d]imidazole (Table 2, Entry 2)

Prepared according to the general procedure with *o*-Phenylenediamine and 4-bromobenzaldehyde. The product was collected as white solid in 98% yield after silica gel chromatography (petroleum ether/ethanol = 10:1). ¹H NMR (400 MHz, DMSO- d_6) δ 13.00 (s, 1H), 8.12 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H), 7.66 (s, 1H), 7.54 (d, J = 5.5 Hz, 1H), 7.22 (s, 2H).¹³C NMR (101 MHz, DMSO-*d*₆) δ 150.19, 143.72, 134.99, 131.95, 129.37, 128.33, 123.22, 122.77, 121.82, 118.94, 111.40.

2-(2-chlorophenyl)-1H-benzo[d]imidazole (Table 2, Entry 3)

Prepared according to the general procedure with *o*-Phenylenediamine and 2-chlorobenzaldehyde. The product was collected as white solid in 92% yield after silica gel chromatography (petroleum ether/ethanol = 10:1). ¹H NMR (400 MHz, DMSO- d_6) δ 12.72 (s, 1H), 7.99 – 7.80 (m, 1H), 7.65 (dd, J = 7.5, 1.5 Hz, 2H), 7.61 – 7.46 (m, 3H), 7.24 (d, J = 3.9 Hz, 2H). ¹³C NMR (101 MHz, DMSO- d_6) δ 149.06, 143.18, 134.64, 132.06, 131.61, 131.17, 130.32, 129.95, 127.40, 122.70, 121.65, 121.00, 119.05, 111.67.

2-(3,5-dimethylphenyl)-1H-benzo[d]imidazole (Table 2, Entry 4)



 CH_3 Prepared according to the general procedure with *o*-Phenylenediamine and 3,5-dimethylbenzaldehyde. The product was collected as white solid in 93% yield after silica gel chromatography (petroleum ether/ethanol = 10:1). ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.82 (s, 1H), 7.81 (s, 2H), 7.76 – 7.44 (m, 2H), 7.21 (dd, *J* = 20.7, 6.7 Hz, 2H), 7.12 (s, 1H), 2.37 (s, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 151.40, 143.78, 137.96, 137.67, 134.93, 131.19, 130.01, 126.96, 124.20, 122.29, 121.56, 118.71, 111.21.

2-(4-nitrophenyl)-1H-benzo[d]imidazole (Table 2, Entry 5)

Prepared according to the general procedure with *o*-Phenylenediamine and 4-nitrobenzaldehyde. The product was collected as white solid in 88% yield after silica gel chromatography (petroleum ether/ethanol = 6:1). ¹H NMR (400 MHz, DMSO- d_6) δ 13.29 (s, 1H), 8.65 – 8.31 (m, 4H), 7.72 (s, 1H), 7.60 (s, 1H), 7.43 (dd, J = 5.7, 3.2 Hz, 1H), 7.27 (s, 2H), 7.09 (dd, J = 5.8, 3.1 Hz, 1H). ¹³C

NMR (101 MHz, DMSO-*d*₆) δ 151.19, 148.98, 147.78, 143.82, 136.02, 135.22, 127.37, 124.27, 123.56, 122.29, 121.00, 119.44, 111.79.

4-(1H-benzo[d]imidazol-2-yl)benzonitrile (Table 2, Entry 6)

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in 84% yield after silica gel chromatography (petroleum ether/ethanol = 6:1). ¹H NMR (400 MHz, DMSO- d_6) δ 13.19 (s, 1H), 8.34 (d, J = 8.3 Hz, 2H), 8.02 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 7.3 Hz, 1H), 7.58 (d, J = 7.3 Hz, 1H), 7.35 – 7.15 (m, 2H). ¹³C NMR (101 MHz, DMSO- d_6) δ 149.34, 143.73, 135.09, 134.25, 132.95, 126.95, 123.39, 122.18, 119.34, 118.60, 111.86, 111.70.

2-(naphthalen-2-yl)-1H-benzo[d]imidazole (Table 2, Entry 7)

Prepared according to the general procedure with *o*-Phenylenediamine and 2-naphthaldehyde. The product was collected as white solid in 93% yield after silica gel chromatography (petroleum ether/ethanol = 10:1). ¹H NMR (400 MHz, DMSO- d_6) δ 13.08 (s, 1H), 8.75 (s, 1H), 8.42 – 8.25 (m, 1H), 8.04 (ddd, J = 23.1, 11.3, 6.2 Hz, 3H), 7.80 – 7.51 (m, 4H), 7.23 (s, 2H). ¹³C NMR (101 MHz, DMSO- d_6) δ 151.22, 143.91, 135.13, 133.44, 132.79, 128.52, 128.42, 127.77, 127.60, 127.08, 126.89, 125.79, 123.92, 122.64, 121.73, 118.88, 111.34. 2-(naphthalen-1-yl)-1H-benzo[d]imidazole (Table 2, Entry 8)



Prepared according to the general procedure with *o*-Phenylenediamine and 1-naphthaldehyde. The product was collected as white solid in 94% yield after silica gel chromatography (petroleum ether/ethanol = 10:1). ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.95 (s, 1H), 9.12 (d, *J* = 8.2 Hz, 1H), 8.05 (dt, *J* = 20.4, 10.7 Hz, 3H), 7.86 – 7.49 (m, 6H), 7.26 (d, *J* = 4.2 Hz, 2H). ¹³C NMR (101 MHz,

DMSO-*d*₆) δ 151.33, 133.59, 130.48, 130.12, 128.36, 127.84, 127.50, 127.04, 126.31, 125.25, 122.60, 121.58, 119.05, 111.33.

4-(1H-benzo[d]imidazol-2-yl)phenol (Table 2, Entry 9)

Prepared according to the general procedure with *o*-Phenylenediamine and 4-hydroxybenzaldehyde. The product was collected as white solid in 92% yield after silica gel chromatography (petroleum ether/ethanol = 6:1). ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.63 (s, 1H), 9.95 (s, 1H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.53 (s, 2H), 7.15 (dd, *J* = 5.9, 3.1 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 163.30, 159.09, 151.75, 132.09, 128.12, 121.56, 121.14, 118.28, 115.83, 115.65, 111.15.

2-butyl-1H-benzo[d]imidazole (Table 2, Entry 10)



Prepared according to the general procedure with *o*-Phenylenediamine and n-pentanal. The product was collected as colorless oil in 98% yield after silica gel chromatography (petroleum ether/ ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.61 (m, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.28 – 7.08 (m, 2H), 5.32 (t, *J* = 6.8 Hz, 1H), 3.41 – 3.14 (m, 2H), 2.94 – 2.78 (m, 2H), 2.21 – 2.07 (m, 1H), 1.98 (ddd, *J* = 32.9, 16.8, 9.4 Hz, 1H), 1.46 – 1.33 (m, 3H), 1.09 (t, *J* = 7.0 Hz, 2H), 0.82 (t, *J* = 7.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 154.70, 142.79, 133.38, 122.08, 122.92, 119.10, 111.89, 110.37, 30.00, 27.37, 22.68, 14.78.

2-phenethyl-1H-benzo[d]imidazole (Table 2, Entry 11)



Prepared according to the general procedure with *o*-Phenylenediamine and 3-phenylpropanal. The product was collected as colorless oil in 89% yield after silica gel chromatography (petroleum ether/ ethyl acetate = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 6.94 (m, 1H), 3.95 – 3.83 (m, 1H), 3.20 – 3.07 (m, 1H), 3.05 – 2.87 (m, 1H), 2.70 – 2.48 (m, 1H), 1.97 (dt, *J* = 15.1, 7.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 153.95, 140.78, 140.21, 134.72, 128.64, 128.59, 128.38, 128.25, 126.40, 122.21, 122.02, 119.14, 109.29, 34.11, 29.51.

L. Recyclability of Ru-POP catalyst

The recycling experiment was performed by recovering the **Ru-POP** catalyst using the centrifugation method. The recovered **Ru-POP** catalyst was washed with EtOH (3 x 5mL) to remove the residual product and simply dried before reuse. We chose the photocatalytic synthesis of 2-phenyl-1H-benzo[d]imidazole with *o*-Phenylenediamine and benzaldehyde to investigate the recyclability of **Ru-POP** catalyst, and the results are summarized in Table S2.

Table S2. Recycling of **Ru-POP** catalyst for the photocatalytic synthesis of 2-phenyl-1H-benzo[d]imidazole. ^[a]

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NH ₂ NH ₂	+ OHC·		I-POP (3.0 m EtOH, r.t., fluorescent l	g)	
0.25 mmol	0.25 mmol				
Cycle	Time (h)	Yield (%) ^[b]	Cycle	Time (h)	Yield (%) ^[b]
1	2	99	7	5	96
2	2	96	8	5	95
3	2	96	9	6	95
4	3	96	10	6	95
5	3	96	11	6	95
6	5	96	12	8	93

[a] General condition: *o*-Phenylenediamine (27.0 mg, 0.25 mmol), benzaldehyde
(26.5 mg, 0.25 mmol), and **Ru-POP** (3.0 mg), r.t., 24 W fluorescent bulb, EtOH (1.0 mL), in air . [b] Isolated yield after silica gel column chromatography.

M. General procedure for the photocatalytic Aza-Henry reaction by Ru-

POP⁶



N-phenyl-tetradroisoquinolines (0.2 mmol), nitroalkane (1.0 mL), and **Ru-POP** (1.0 mg) were added into a 10-mL glass tube. The tube was sealed with a rubber stopper and the reaction mixture was connected to the air through a needle in the stopper. The tube was subsequently stirred at room temperature under irradiation with visible light using a cool daylight energy-saving bulb (24 W) until all starting material had been consumed. After the reaction was completed (monitored by TLC), the mixture was centrifugated and the solid was washed with EtOAc (3 x 5 mL). The combined organic phase was then concentrated and purified by flash column chromatography with petroleum ether/EtOAc = 10:1 as the eluent to give the pure product.



1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **EY-POP-1** (10 mg), 2-phenyl-1,2,3,4-tetrahydroisoquinoline (41.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (52.6 mg, 98%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.28–7.16 (m, 5 H), 7.11 (d, *J* = 7.0 Hz, 1 H), 6.97 (d, *J* = 8.2 Hz, 2 H), 6.83 (t, *J* = 7.3 Hz, 1 H), 5.53 (t, *J* = 7.2 Hz, 1 H), 4.85 (dd, *J* = 11.8, 7.8 Hz, 1 H), 4.54 (dd, *J* = 11.8, 6.6 Hz, 1 H), 3.65–3.59 (m, 2 H), 3.09–3.03 (m, 1 H), 2.77 (dt, *J* = 16.3, 4.9 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 148.37, 135.22, 132.86, 129.45, 129.14, 128.06, 126.94, 126.64, 119.36, 115.04, 78.71, 58.14, 42.00, 26.39.

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