

Supporting Information

for

Preparation of Bispyridine based Porous Organic Polymer as a New Platform for Cu(II) Catalyst and Its Use in Heterogeneous Olefin Epoxidation

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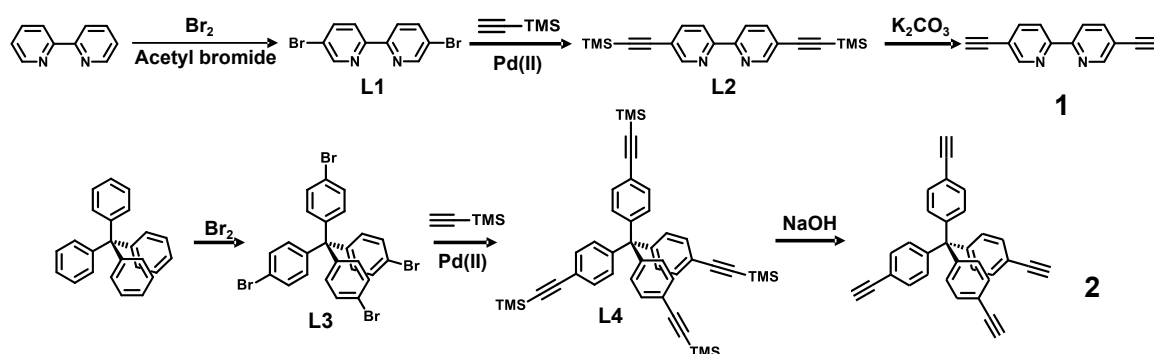
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I. General information.

¹H-NMR spectra were recorded on a Varian AS400 (399.937 MHz for ¹H and 100.573 MHz for ¹³C) and Bruker 500 MHz Ascend spectrometer. ¹H chemical shifts were referenced to the proton resonance resulting from protic residue in deuterated solvent and ¹³C chemical shift recorded downfield in ppm relative to the carbon resonance of the deuterated solvents. Solid-state MAS-NMR experiments were acquired on a Bruker AVANCE II⁺ 400MHz NMR system (400 MHz for ¹H, 100.4 MHz for ¹³C) in KBSI Seoul Western Center, Korea. The spinning rate was 12 kHz. Spectra were acquired using a ¹H-¹³C CP contact time of 2 ms and a recycle delay of 3 s between scans. ¹³C NMR chemical shifts were calibrated using tetramethylsilane (TMS) as zero ppm. Fourier-transformed infrared (FTIR) spectroscopy was performed on an ALPHA FT-IR Spectrometer (Bruker Optics) equipped with a single-reflection diamond ATR accessory for all samples. Frequencies are given in reciprocal centimeters (cm⁻¹). Thermogravimetric analyses were carried out at a ramp rate of 10 °C/min under a N₂ flow (30 mL/min) using a Scinco TGA N-1000 instrument. N₂ adsorption and desorption isotherms were measured on BELSORP–mini II (MicrotracBEL Corp., Japan) instrument at 77 K. Before each run, samples were activated at 80 °C for 2 h under high vacuum on a BELSORP Prep II (MicrotracBEL Corp., Japan) or critical point dry on a SAMDRI-PVT-3D (Tousimis, USA). Around 50–90 mg of sample was used in each measurement. All gas chromatography (GC) analyses using an Agilent Technologies 6890N Network GC system (Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with an FID detector and HP-5 capillary column (50 m × 320 μm × 0.17 μm film thickness).

Scanning electron microscopy (SEM) images were collected on a JSM-7001F (JEOL, Japan) microscope. Samples were activated and coated with Pt using a Sputter Coater 108 Auto (Cressington, Watford, UK) before imaging. Copper contents were measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, JY Ultima2C, Jobin Yvon, France) in KBSI Seoul Center. Cu-POP catalysts (ca. 40 mg) were heated in HNO₃ 5 mL at 190 °C and acid was evaporated. Evaporating until 1-5 % of concentration of acid, then 1 % HNO₃ was added until 15 mL. Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM/EDX) measurements were carried out using a Hitachi SU-70 ESM equipped with a silicon draft EDX detector (50 mm², Horiba, Japan) in KBSI Seoul Center. The accelerating beam voltage was 15 kV.



Scheme S1. Preparation of **1** and **2**.

II. Materials and synthesis

All reagents and solvents were purchased from commercial sources and were used without further purification, unless otherwise indicated. All the reactions and manipulations were carried out under N₂ atmosphere. Distilled solvents used in inert-atmosphere reactions were dried using standard procedures. All Flash column chromatography was carried out using silica gel 60 (230-400 mesh, Merck, Germany) using wet-packing method and TLC was performed on pre-coated silica gel plates (0.25 mm thick, 60 F254, Merck, Germany). All deuterated solvents were purchased from Cambridge Isotope Laboratories and Aldrich.

5,5'-dibromo-2,2'-bipyridine (L1). To a solution of 2,2'-bipyridine (10 g) in methanol (75 mL) was added acetyl bromide (12 mL) dropwise with vigorous stirring at 0 °C. After adding, the cooling bath was removed and the reaction mixture was stirred for an additional 30 min at room temperature. After removal of volatiles, the residue was dried under high vacuum for 24

h. This dried solid (3.2 g) was charged in a mortar and 3.3 mL of bromine was added slowly. Make sure that the tip of the needle is digging into the dried solid. From time to time, the mixture was mixed well and ground using the pestle and spoon. After the addition, the reaction mixture was ground until a homogenous orange powder was obtained and the resulting mixture was transferred into a 20 mL vial. This vial was then transferred into a stainless steel bomb and the steel bomb was sealed. The steel bomb was placed in an oven at 185 °C for 72 h. After cooling to room temperature, the bomb was opened and the resulting reaction mixture was placed into a mortar and carefully smashed. After removal of pieces of glass with the tweezers, the reaction mixture was ground until a fine powder was obtained. The crude product was transferred into a large Erlenmeyer flask and 2 M NaOH solution (120 mL), EDTA tetrasodium salt (6 g), Na₂SO₃ (6 g) and CH₂Cl₂ (60 mL) were added. After stirring the reaction mixture for 2 h at room temperature, the organic phase was separated and extracted from the aqueous phase five times with CH₂Cl₂. The organic was and dried over anhydrous Na₂SO₄ and recrystallized from CH₂Cl₂ to afford **L1** as a white solid (1.3 g, 39 %). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.70 (d, *J* = 2.0 Hz, 2H), 8.28(d, *J* = 8.6 Hz, 2H), 7.94 (dd, *J* = 8.6 Hz, 2H).

5,5'-Trimethylsilylacetylene-2,2'-bipyridine (L2). In a two-necked round-bottomed flask, **L1** (2 g), PdCl₂(PPh₃)₂ (0.21 g) and CuI (0.1 g) were suspended in THF (100 mL) and NEt₃ (20 mL). Then, N₂ was bubbled through the solution for 5 min. Trimethylsilylacetylene (3.6 mL) was added to the resulting mixture, and then allowed to stir at 60 °C overnight under nitrogen. After cooling down, the reaction mixture was filtered and concentrated under reduced pressure, and the residue dissolved in CH₂Cl₂ and extracted with an aqueous saturated solution of NH₄Cl, then brine and dried over anhydrous MgSO₄. After filtration, the solvent was removed under reduced pressure and purified by column chromatography (CH₂Cl₂:Hex, 1:1 v/v) to afford **L2** as a pale yellow solid (1.8 g, 80 %). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.75 (s, 2H), 8.39 (d, *J* = 8.2 Hz, 2H), 7.89 (dd, *J* = 8.2 Hz, 2H), 0.31 (s, 18H), ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 154.2, 152.1, 139.8, 120.5, 101.8, 99.5, -0.1.

Tetrakis(4-bromophenyl)methane (L3). Tetraphenylmethane (0.5 g) was added in portions under vigorous stirring to a two necked round bottomed flask equipped with condenser and containing bromine (1.59 mL) at room temperature. After portions were completed, the resulting mixture was stirred for 20 min and then cooled down to -78 °C keeping vigorous

stirring. Ethanol (25 mL) was added slowly through condenser and the resulting suspension was allowed to warm to room temperature under stirring overnight. The precipitate was filtered off and washed subsequently with an aqueous solution of sodium hydrogen sulfite and ethanol. After drying, tetrakis(4-bromophenyl)methane (0.76 g, 76 %) was obtained as yellowish solid. ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.41 (d, 8H, $J = 8.9$ Hz), 7.03 (d, 8H, $J = 8.9$ Hz).

Tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane (L4). In a two neck round bottomed flask tetrakis(4-bromophenyl)methane (0.5 g), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.099 g), CuI (0.018 g) and PPh_3 (0.025 g) were suspended in anhydrous THF (5.6 mL) and $i\text{-Pr}_2\text{NH}$ (1.9 mL) under nitrogen atmosphere. After degassing this solution 3 min, trimethylsilylacetylene (1.5 mL) were added and resulting mixture was allowed to stir 80 °C for 24 h. Then, the mixture was cooled down to room temperature, filtered and removed under reduced pressure. The residue was extracted with CH_2Cl_2 and aqueous solution of NH_4Cl . The organic solution was dried over anhydrous MgSO_4 . After removing of the solvent and purified by column chromatography (CH_2Cl_2 :Hex, 1:9 v/v). Pure tetrakis(4-(ethynyl)phenyl)methane was obtained as a yellow solid (0.39 g, 70 %). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.35 (d, $J=8.5$ Hz, 8H), 7.07 (d, $J=8.5$ Hz, 8H), 0.26 (s, 32H), ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 146.0, 131.4, 130.7, 121.2, 104.6, 94.8, 64.8, -0.1.

5,5'-Diethynyl-2,2'-bipyridine (1). L2 (0.50 g) was dissolved in a mixture of methanol and THF (1:1, 26 mL) and powdered K_2CO_3 (0.2 g) was added. The mixture was stirred for 3h at room temperature and the solvent was reduced pressure. The residue dissolved in CH_2Cl_2 and extracted with brine. The organic fraction was dried over anhydrous MgSO_4 and the solvent was removed under reduced pressure. After column chromatography (CH_2Cl_2 :Hex, 1:1 v/v) pure **1** was obtained as a brown solid (0.28 g, 96 %). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.78 (d, $J = 1.8$ Hz, 2H), 8.41 (d, $J = 8.2$ Hz, 2H), 7.89 (dd, $J = 8.2, 2.1$ Hz, 2H), 3.33 (s, 2H), ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 154.5, 152.3, 140.1, 120.6, 119.4, 81.9, 80.6.

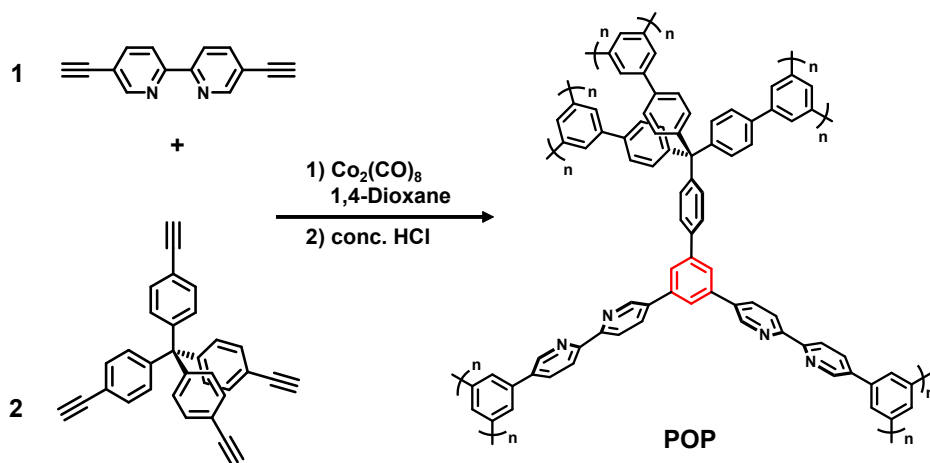
Tetrakis(4-ethynylphenyl)methane (2). The solution NaOH (0.28 g) in MeOH (5 mL) was added to a solution tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane (0.50 g) in CH_2Cl_2 . The mixture was stirred for 6 h at room temperature and the solvent was removed. Then, solution was washed with water and extracted with CH_2Cl_2 and dried over MgSO_4 . The

solution was concentrated, purified by column chromatography (CH₂Cl₂:Hex, 1:1.5 v/v) pure tetrakis(4-ethynylphenyl)methane was obtained as a white solid (0.25 g, 84 %). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.41 (d, *J*=8.5 Hz, 8H), 7.14 (d, *J*=8.5 Hz, 8H), 3.09 (s, 4H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 146.2, 131.7, 130.8, 120.3, 83.2, 77.3, 64.8.

Preparation of POP-1. **1** (69 mg) and **2** (70 mg) were charged into a flame-dried round bottom flask. Distilled 1,4-dioxane (15 mL) was added and the mixture was stirred for 5 min. After the solid was dissolved, Co₂(CO)₈ (0.114 g) was added under the protection of N₂, and the mixture was stirred for 5 min. The reaction flask was put in a preheated oil bath at 115 °C and allowed to stir 1.5 h. After that, the flask was lifted above the oil bath to cool to room temperature. The solid was collected by filtration and washed with water. The solid was shanked in conc. HCl for 2h. The product was obtained by filtration and washed with water, acetone, DMF, and MeOH. The resulting solid was soaked in EtOH for 48 h and dried under supercritical CO₂. The **POP-1** was obtained as brown solid (134 mg, 96 %).

Metalation of POP-1. CuCl₂·2H₂O (0.413 g) was dissolved in distilled DMF (50 mL) and **POP-1** (0.1 g) was added. The mixture was placed in 110 °C oven for 48 h. After cooling down to room temperature, the mixture was centrifuged. The resulting solid was washed with DMF for 5 times followed by washing with acetone for 3 times. Then solid was soaked in acetone for overnight. And the solid was soaked in EtOH for 48 h. After drying, **POP-Cu(II)** was obtained as dark green solid (0.11 g, 83 %).

General procedure of oxidation. Catalytic olefin oxidation was carried out in liquid phase in a vial at 85 °C. **POP-Cu(II)** (2 mg) was combined with olefin (1.2 mmol) and acetonitrile (1 mL). After stirring for 10 min, TBHP (0.17 mL, 1.2 mmol, 70% in H₂O) was added. Reaction mixture was stirred at 80 °C. After 24 h, internal standard dodecane was added and analyzed by GC-FID.



Scheme S2. Preparation of POP.

Table S1. Summary of the preparation of POP-1, POP-2 and POP-3.

POPs	1	2	Solvent amount	Reaction time	Yield
POP-1	69 mg	70 mg	15 mL	1.5 h	96 %
POP-2	69 mg	70 mg	7.5 mL	> 5 min	92 %
POP-3	69 mg	70 mg	45 mL	~ 72 h	5 %

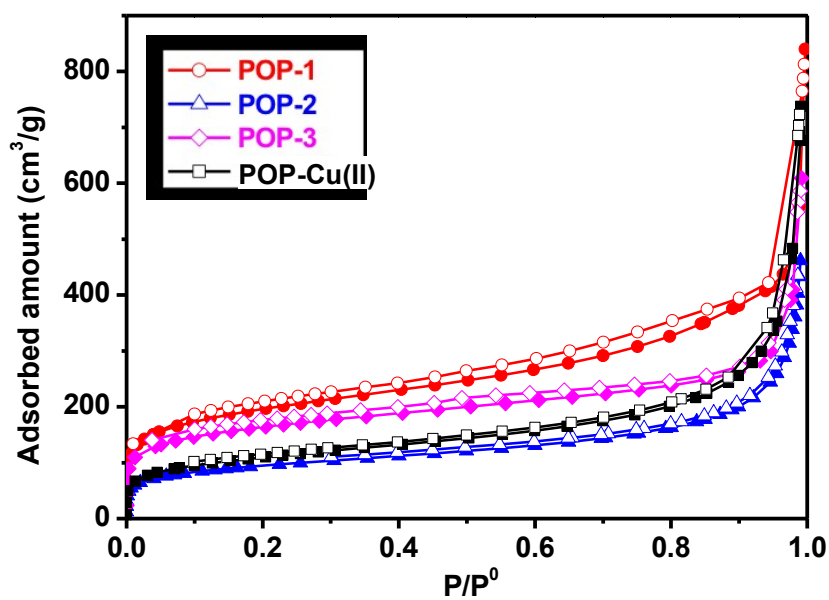


Fig. S1. N_2 isotherms of the polymers POP-1, POP-2, POP-3 and POP-Cu(II).

Table S2. Cu loading, surface areas and pore sizes of **POP-1**, **POP-2**, **POP-3** and **POP-Cu(II)**.

Compound	Cu loading ^a (%)	SA _{BET} ^b [m ² g ⁻¹]	Pore size [nm]	Yield
POP-1	-	812	5.3	96 %
POP-2	-	659	6.1	97 %
POP-3	-	760	4.9	5 %
POP-Cu(II)	8.3	462	11.2	83 %

^aDetermined from analysis of ICP-AES.

^bSA_{BET} = Brunauer-Emmet-Teller (BET) surface area.

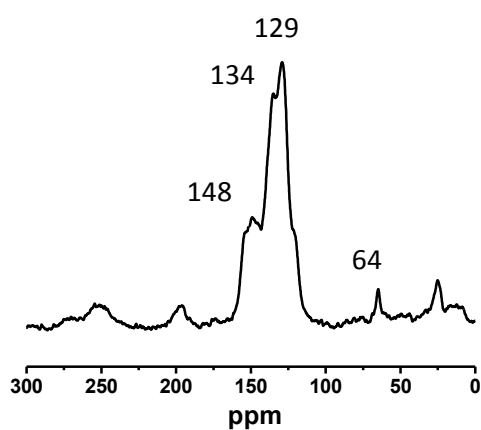


Fig. S2. ¹³C CPMAS NMR spectra of the **POP-1**. The peaks between 129-148 ppm are assigned to aromatic carbons. The peak at 64 ppm is assigned to a quaternary carbon of tetraphenylmethane moiety.

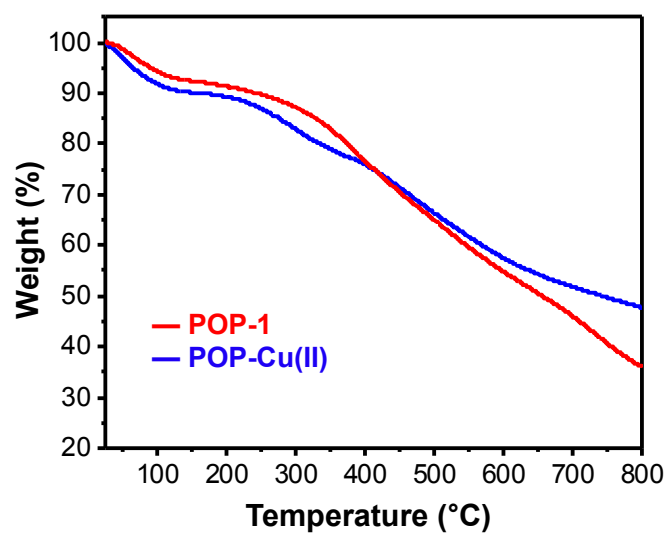


Fig. S3. Thermal characteristics of **POP-1** and **POP-Cu(II)** analyzed by TGA.

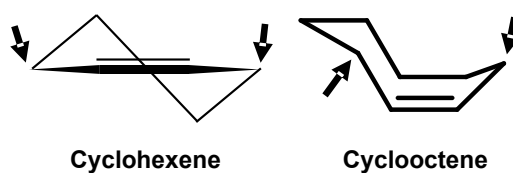


Fig. S4. Conformation of cyclohexene and cyclooctene (arrows indicate the allylic carbons).

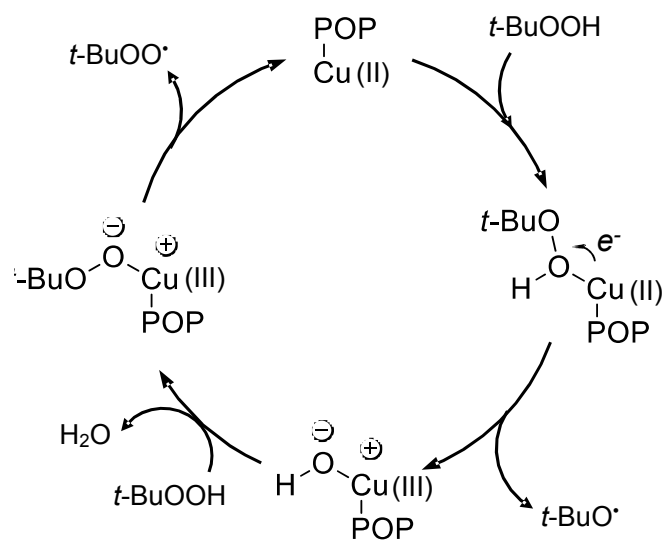


Fig. S5. Proposed catalytic cycle of [**POP-Cu(II)** + TBHP].

Table S3. Olefin epoxidation with the addition of diphenylamine as a radical inhibitor.^{a,b}

Entry	Substrate	Conversion (%) ^c
1	cyclooctene	5.8
2	cyclohexene	35.3
3	1-octene	12.4
4	styrene	18.7

^aReaction conditions; Olefin (1.2 mmol), **POP-Cu(II)** 2 mg (2.6 μ mol of Cu), TBHP 0.17 mL (70 % in H₂O), acetonitrile 1 mL, diphenylamine 0.02g (1.2 mmol).
^bConversions were quantified by GC-FID and dodecane was used as internal standard. ^cConversion is based on olefin consumption towards products.

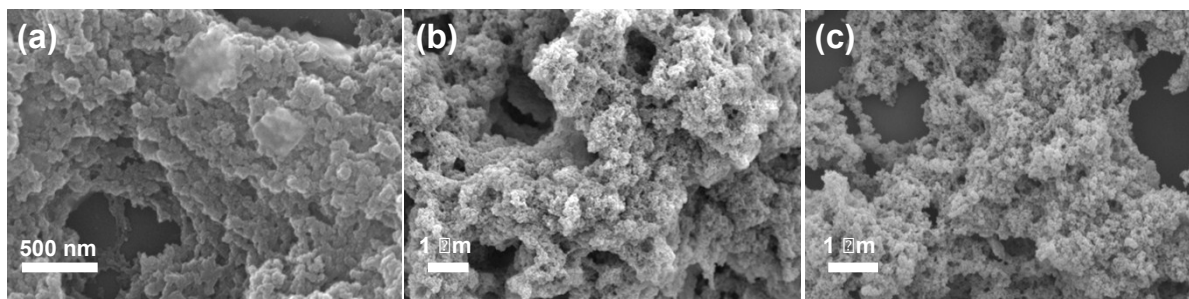


Fig. S6. SEM images of (a) **POP-1**, (b) **POP-Cu(II)**, and (c) **POP-Cu(II)** recovered after the catalytic reaction showing no significant changes in the morphology.

III. References

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