

Supporting Information

for

Cu(II)Cl₂ Containing Bispyridine-based Porous Organic Polymer Support Prepared via Alkyne-Azide Cycloaddition as a Heterogeneous Catalyst for Oxidation of Various Olefins

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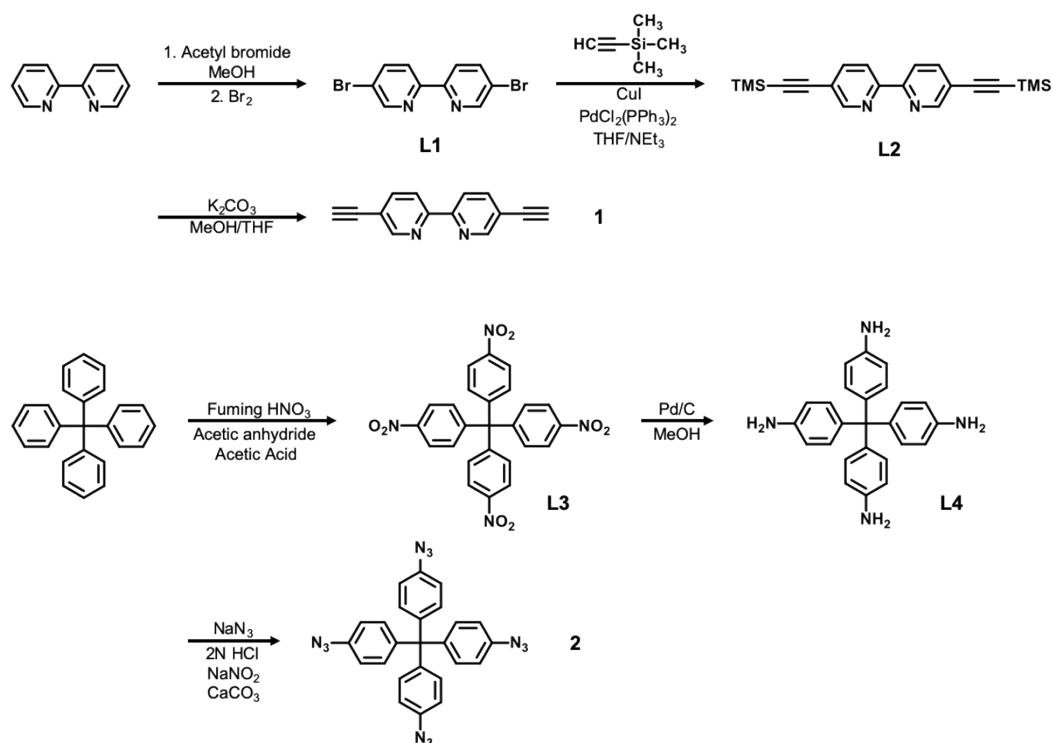
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I. General information.

Nuclear magnetic resonance (NMR) spectra for the synthesized materials were recorded on a Varian AS400 (399.937 MHz for ¹H and 100.573 MHz for ¹³C) and a Bruker 500 MHz Ascend spectrometer. Chemical shifts of ¹H NMR spectra were referenced to the proton resonance resulting from protic residue in deuterated solvent and chemical shift of ¹³C were recorded downfield in ppm relative to the carbon resonance of the deuterated solvents. Solid-state NMR experiments were conducted on a Bruker AVANCE II+ 400MHz NMR system (400 MHz for ¹H, 100.4 MHz for ¹³C) in Korea Basic Science Institute (Seoul Western Center). The spectra were acquired using a ¹H-¹³C CP contact time of 2 ms and a recycle delay of 3 s between scans and spinning rate was 12 kHz. NMR chemical shifts of ¹³C were calibrated using tetramethylsilane (TMS) as zero ppm. Fourier-transformed infrared (FT-IR) spectroscopy of the samples were collected on an ALPHA FT-IR Spectrometer (Bruker Optics) equipped with a single-reflection diamond ATR accessory. Frequencies are given in reciprocal centimeters (cm⁻¹). The thermal properties of the all samples were evaluated using a thermogravimetric analyses (TGA) instrument Scinco TGA N-1000 at a rate of 10 °C/min under a N₂ flow (30 mL/min). N₂ adsorption–desorption measurements were measured using the 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 50-80 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 conducted 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. Energy dispersive spectrometry (EDS) analyzing was carried out using a Hitachi SU-70 SEM equipped with a silicon drift EDX detector (50 mm², Horiba, Japan) in KBSI Seoul Center. The accelerating beam voltage was fixed to 15 kV. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES, OPTIMA 8300, Perkin-Elmer(USA)) for copper contents was conducted in Seoul National University National Center for inter-university facilities.

Scheme S1



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. 2,2'-Bipyridine, PdCl₂(PPh₃)₂, CuI, trimethylsilylacetylene, tetraphenylmethane and NaNO₂ were purchased from Aldrich.

5,5'-dibromo-2,2'-bipyridine (L1).¹ To a solution of 2,2'-bipyridine (10 g) in methanol (75 mL) was added acetyl bromide (12 mL) dropwise with vigorous stirring using a disposable plastic syringe at 0 °C. Upon complete addition, the cooling bath was removed, and the reaction mixture was stirred for an additional 30 min at room temperature. After removal of volatiles using a rotary evaporator, the residue was dried under high vacuum for 24h. This dried solid (3.2 g) was charged in a mortar and 3.3 mL of bromine was added slowly. 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 combined and dried over anhydrous Na₂SO₄. After recrystallization from CH₂Cl₂, L1 was obtained as a white solid (1.3 g, 39 %). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.70 (d, 2H, J = 2.1 Hz), 8.28 (d, 2H, J = 8.5 Hz), 7.94 (dd, 2H, J = 8.5 Hz, J = 2.4 Hz).

5,5'-Trimethylsilylacetylene-2,2'-bipyridine (L2).² In a two-necked round-bottomed flask, L1 (0.5 g), PdCl₂(PPh₃)₂ (0.11 g) and CuI (0.05 g) were suspended in THF (33.5 mL) and NEt₃ (12.5 mL). Then, N₂ was bubbled through the solution for 5 min. Trimethylsilylacetylene (0.65mL) 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, 1:2

v/v) to afford **L5** as a pale yellow solid (0.55 g, 95.6 %). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.72 (s, 2H), 8.36 (d, J = 8.2 Hz, 2H), 7.86 (dd, J = 8.2, 2.1 Hz, 2H), 0.28 (s, 18H), ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 154.3, 151.8, 139.7, 121.1, 121.0, 101.4, 99.2, -0.2.

Tetra-(4-nitrophenyl)-methane (L3).³ Tetraphenylmethane (2 g) was added in portions to 10 mL of fuming nitric acid (96%) at -10 °C with vigorous stirring. To this mixture 3.3 mL of acetic anhydride and 6.6 mL of glacial acetic acid was slowly added and stirred for ~15 min. Finally, the reaction mixture was diluted with 32 mL of glacial acetic acid and the resulting yellow solid was filtered on a glass frit, washed with acetic acid, methanol, chilled THF and dried under dynamic vacuum to obtain **L3** as a yellow crystalline solid (1.6 g, 51.2 %). ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 8.23 (d, 8H, J = 9.2 Hz), 7.60 (d, 8H, J = 9.2 Hz), ¹³C NMR (100 MHz, DMSO-d₆): δ (ppm) 151.1, 145.8, 131.7, 123.6.

Tetrakis(4-aminophenyl)methane (L4).⁴ In a two-necked round-bottomed flask, **L3** (0.5 g) and Pd/C (10 %, 0.01 g) were suspended in degassed methanol (20 mL) under nitrogen. The reaction mixture was degassed and backfilled with hydrogen for five times. The resulting reaction mixture was vigorously stirred under hydrogen atmosphere for 48 h at room temperature. Then, the resulting mixture was filtered on a glass frit, washed with methanol and THF, and evaporated to afford pure **L4** as a light yellow solid (0.94 g, 96 %). ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 6.67 (d, 8H, J = 8.9 Hz), 6.38 (d, 8H, J = 8.9 Hz), 4.85 (s, 8H), ¹³C NMR (100 MHz, DMSO-d₆): δ (ppm) 145.4, 135.5, 130.8, 112.3, 61.4.

5,5'-Diethynyl-2,2'-bipyridine (1).² **L2** (0.10 g) was dissolved in a mixture of methanol and THF (1:1, 5 mL) and powdered K₂CO₃ (0.04 g) was added. The mixture was stirred for 3 h at room temperature and the solution was filtered and concentrated under reduced pressure. The residue dissolved in CH₂Cl₂ and extracted with brine. The organic fraction was treated with activated charcoal, dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. After column chromatography (CH₂Cl₂:Hex, 1:2 v/v) pure **1** was obtained as a beige solid (0.05 g, 89 %). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.77 (d, J = 2.1 Hz, 2H), 8.42 (d, J = 8.2 Hz, 2H), 7.91 (dd, J = 8.2, 2.14 Hz, 2H), 3.31 (s, 2H), ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 154.4, 152.1, 140.2, 120.3, 119.2, 81.5, 80.5.

Tetra(4-azidophenyl)methane (2).⁵ **L4** (0.4 g) was dissolved in 2N aqueous HCl (21 mL) in a 500-mL round-bottom flask and cooled down to 0 °C. A solution of NaNO₂ (0.45 g) in H₂O (2 mL) was then added drop-wise into the cooled reaction flask with vigorous stirring. The reaction mixture was kept at 0 °C for 30 min before being neutralized with CaCO₃ (0.65 g). To this mixture was then added a solution of NaN₃ (0.5 g) in H₂O (2 mL) at 0 °C. The resulting mixture was allowed to stir at 0 °C for an additional 20 min and then filtered. The collected solid was washed with excess H₂O and dried under dynamic vacuum to afford **2** as a white solid (0.5 g, 95 %). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.13 (d, 8H, J = 8.9 Hz), 6.93 (d, 8H, J = 8.9 Hz), ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 142.7, 138.1, 132.2, 118.6, 63.4.

Preparation of Free-POP.⁵ A solution of **1** (168.6 mg) and **2** (200 mg) in DMF (82.4 mL) was added into a 250-mL flask equipped with a magnetic stir bar and a reflux condenser. Then, resulting mixture heated up to 60 °C to make clear solution. After then, CuSO₄·5H₂O (41.2 mg, 0.1 equiv. per acetylene functional group) and sodium ascorbate (32.7 mg, 0.1 equiv. per acetylene functional group) were added subsequently. The reaction mixture was heated at 100 °C for 24 h. After cooling, the reaction mixture was filtered over a fine fritted funnel and successively washed with water (2 × 50 mL), methanol (2 × 50 mL), and THF (2 × 50 mL). The resulting brown solid was shaken in water (10 mL) for 5 h at room temperature before being filtered through a fine fritted funnel. After drying under vacuum, the **Free-POP** was obtained as yellow to brown solid (357 mg, 91 % yield).

Preparation of Cu-POP.⁶ CuCl₂·6H₂O (100 mg) was dissolved in distilled DMF (23 mL) and powdered **Free-POP** (0.1 g) was added. The mixture was placed in 110 °C oven for 24 h. After cooling down to room temperature, the mixture was centrifuged. The liquid was decanted and the remaining solid washed with fresh DMF for three times. The solid was soaked in acetone overnight and washed with acetone twice thereafter. After drying, **Cu-POP** was obtained as a green solid.

General procedure of catalytic reaction of Cu-POP. Catalyst (2 mg) and olefin (1.2 mmol) were dispersed in 1 mL of acetonitrile placed in a vial. Then TBHP (0.17 mL, 1.2 mmol, 70% in H₂O) was added slowly and the reaction mixture was stirred at 50 °C for 24 h. At the stated time, internal standard dodecane was added and analyzed by GC-FID.

III. Additional analyses

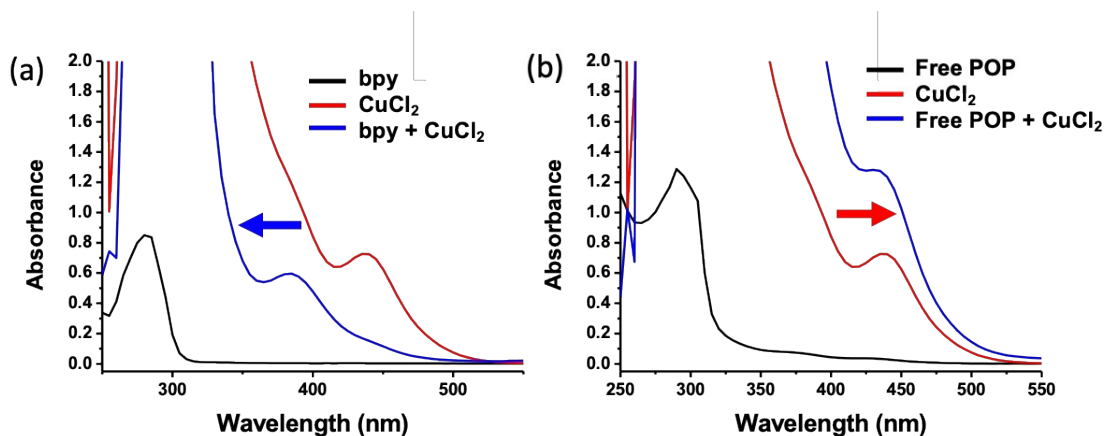


Figure S1. UV-Vis adsorption study of (a) bipyridine ligand (bpy) and CuCl₂, and (b) Free-POP and CuCl₂.

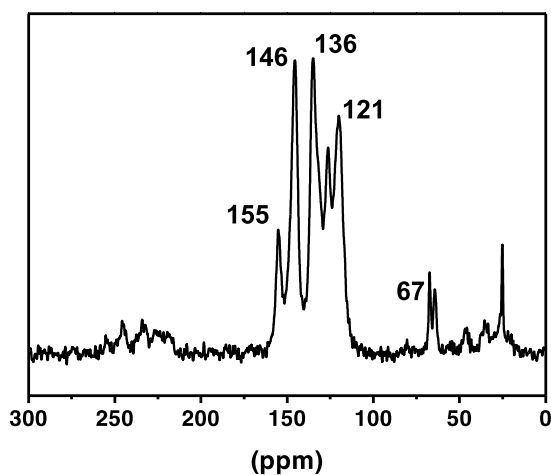


Figure S2. ¹³C CPMAS NMR spectra of the POP-1. The peaks between 121-155 ppm are assigned to aromatic carbons. The peak at 67 ppm is assigned to a quaternary carbon of tetraphenylmethane moiety.

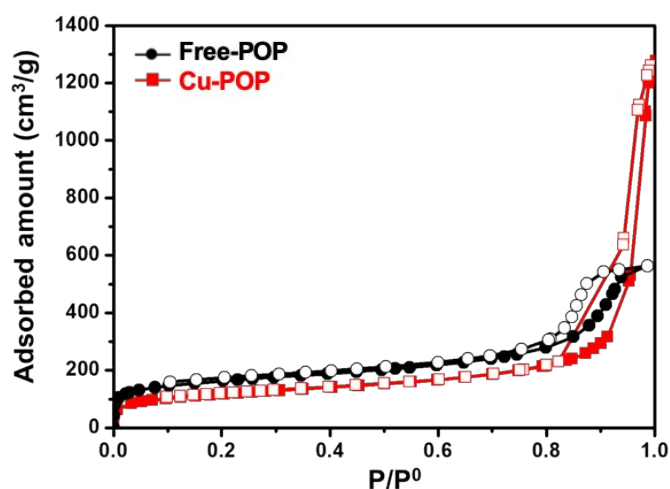


Figure S3. N₂ isotherms of the polymers. Free-POP (black) and Cu-POP (red).

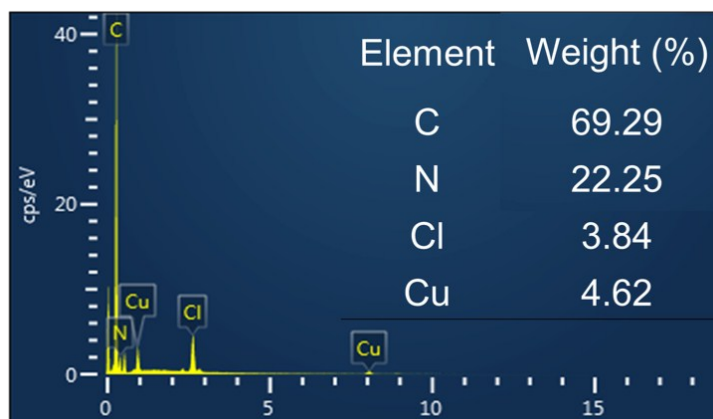


Fig. S4. EDX analysis of **Cu-POP**.

Table S1. Cu loading, surface areas and pore sizes of **Free-POP** and **Cu-POP**.

Compound	Cu loading (%) ^a	SA _{BET} [m ² g ⁻¹] ^b	Pore size [nm]
Free-POP	0.01	594	11.6
Cu-POP	6.3	421	17.8

^aDetermined from analysis of ICP-AES.
^bSA_{BET} = Brunauer–Emmet–Teller (BET) surface area.

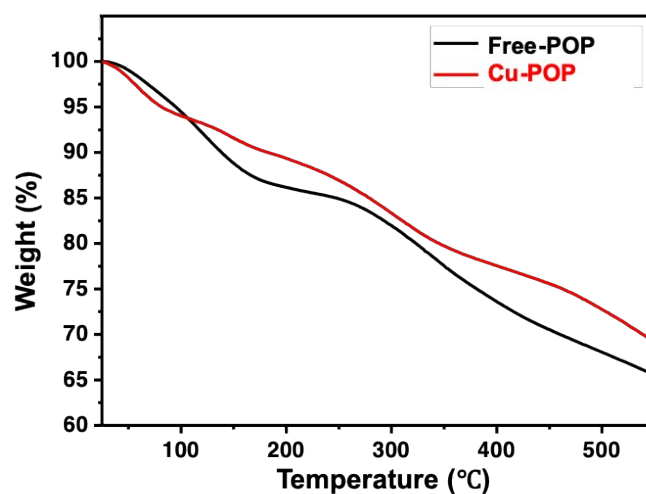


Figure S5. Thermal characteristics of **Free-POP** and **Cu-POP** analyzed by TGA.

Table S2. Recycling experiment of styrene oxidation by **Cu-POP** with TBHP in AcCN at room temperature.^{a,b}

Cycle	Conversion (%) ^c	TON ^d
1	87.4	524
2	85.8	514
3	86.4	517
4	86.1	516
5	85.5	513

^aReaction conditions; Olefins (1.2 mmol), **Cu-POP** 2 mg (2.0 μmol of Cu), TBHP 0.17 mL (70% in H₂O, 1.2 mmol), acetonitrile 1 mL, 85 °C, 24 h. ^bConversions were quantified by GC-FID and toluene was used as an internal standard. ^cConversion is based on olefin consumption towards product. ^dTON (turnover number): moles of substrate converted per mole metal ion.

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

Entry	Substrate	Conversion (%) ^{c,d}
1	styrene	14.8
2	cyclooctene	4.7

^aReaction conditions; Olefin (1.2 mmol), **Cu-POP** 2 mg (2.0 μmol of Cu), TBHP 0.17 mL (70% in H₂O, 1.2 mmol), acetonitrile 1 mL, 85 °C, 24 h, diphenylamine 0.02g (1.2 mmol). ^bConversions were quantified by GC-FID and toluene was used as internal standard. ^cConversion is based on olefin consumption towards products.

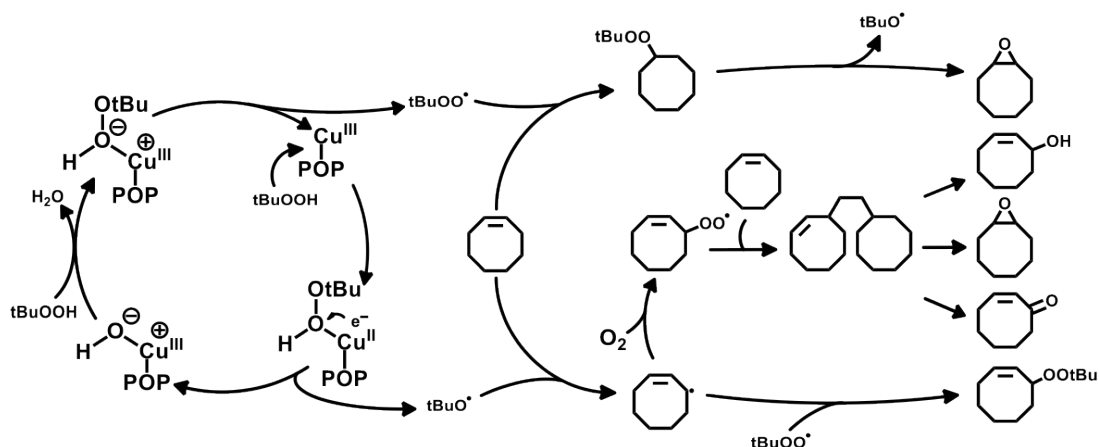


Figure S6. Proposed mechanism of the generation of *t*-BuO• and *t*-BuOO• from copper-peroxo species.

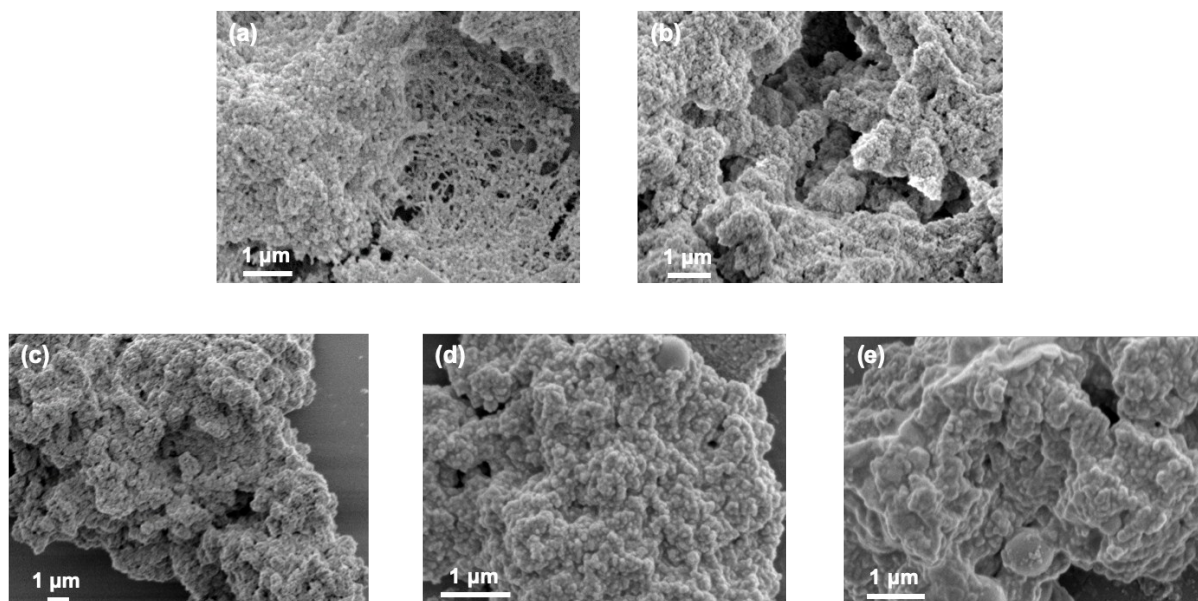


Figure S7. SEM images of (a) **Free-POP**, (b) **Cu-POP**, and (c) **Cu-POP** recovered after 1 cycle, (d) 3 cycles and (e) 5 cycles catalytic reaction showing no significant changes in the morphology.

IV. References

1. D. M. D'Souza, D. A. Leigh, M. Pappmeyer, S. L. Woltering, *Nat. Protoc.* 7 (2012) 2022-2028.
2. J. F. Ayme, J. E. Beves, D. A. Leigh, R. T. McBurney, K. Rissanen, D. Schultz, *Nat. Chem.* 4 (2012) 15-20.
3. P. Ganesan, X. Yang, J. Loos, T. J. Savenije, R. D. Abellon, H. Zuilhof, E. J. R. Sudholter, *J. Am. Chem. Soc.*, 127 (2005) 14530–14531.
4. O. Plietzsch, C. I. Schilling, M. Tolev, M. Nieger, C. Richert, T. Muller, S. Brase, *Org. Biomol. Chem.*, 7 (2009) 4734–4743.
5. P. Pandey, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, M. G. Kanatzidis, J. T. Hupp, S. T. A. Nguyen, *J. Mater. Chem.*, 21 (2011) 1700–1703.
6. D. Feng, W.-C. Chung, Z. Wei, Z.-Y. Gu, H.-L. Jiang, Y.-P. Chen, D. J. Darensbourg, H.-C. Zhou, *J. Am. Chem. Soc.* 135 (2013) 17105–17110.