

Supporting Information

Molecular copper complexes embedded within porous polymer macroligands for the heterogeneously catalyzed aerobic oxidative formation of N–N bonds

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Materials and methods

Materials

Copper bromine (98%), di-*p*-tolylamine (97%), Divinylbenzene (DVB, 80%), 1,1'-azobis(cyclohexanecarbonitrile) (ACHN, 98%), cesium carbonate (Cs₂CO₃, 99%), palladium (II) acetate (98%), acetonitrile (anhydrous, 99.8%), tetrahydrofuran (THF) (anhydrous, ≥99.9%), 1,1',2,2'-tetrachloro-ethane (98%) were purchased from Sigma-Aldrich.

5-bromo-2,2'-bipyridine (98%) and potassium vinyltrifluoroborate (97%) were purchased from TCI.

FLUKA: 2,2'-bipyridine (97%)

BLD pharm : 4,4'-divinyl-2,2'-bipyridine (98%)

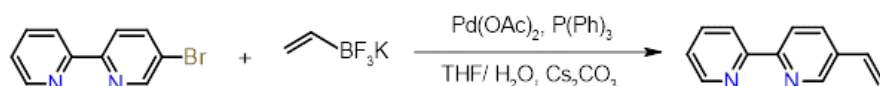
All the chemicals were used without any further purification.

Analysis

The liquid-state NMR spectra were recorded at room temperature on a Bruker AVANCE HD 400 WB spectrometer which is equipped with a gradient BBFO 5mm automatic probe. Samples were previously diluted in CDCl₃ (purchased from Eurisotop). The solid-state NMR spectra were recorded at room temperature on a Bruker AVANCE III 500 WB spectrometer which is equipped with a 2.5 mm MAS (magic angle spinning) probe. Copper measurements were performed by X-ray fluorescence using an Epsilon 4 Panalytical with 50kV power and 3mA intensity. Prior to analysis, samples were dissolved in a glass bead to homogenize matrix effects. Nitrogen physisorption experiments of all the solids were performed at 77 K by using BELSORP-mini II and prior to measurements the samples were degassed at 80°C for overnight. IR spectra were recorded using a Nicolet Magna IR 550 FT-IR spectrometer (Thermo Fisher Scientific) in diffuse reflection (resolution 2 cm⁻¹, 128 scans, Praying Mantis Diffuse Reflection Accessory, Harrick Scientific).

Synthesis of the 5-monovinyl-2,2'-bipyridine

Synthesis has been done according to a modified literature procedure.^[1] In a glovebox, 850 mg of potassium vinyltrifluoroborate (6.35 mmol), 375 mg of 5-bromo-2,2'-bipyridine (1.60 mmol), 7 mg of palladium (II) acetate (0.03 mmol), 25 mg of triphenylphosphine (0.1 mmol) and 1,5 g of cesium carbonate (4.77 mmol) were added in a quartz tube. 25mL of THF/water (24:1) was added in the sealed tube. The suspension was heated at 85°C for 48h under Ar atmosphere. After coming back to room temperature, the mixture was diluted with H₂O (25 mL) and extracted with CH₂Cl₂ (20 mL x 3). The organic phases were combined and extracted with brine (50 mL), and dried over Na₂SO₄. The solvent was removed under vacuum, using a rotating evaporator. The light orange solid was purified by column chromatography using a mixture of petroleum ether/dichloromethane/trimethylamine (35/70/01 v/v/v). (Yield: 143.5 mg)



Synthesis of bipyridine porous polymer

Synthesis has been done according to a modified literature procedure.^[2] In a Teflon vessel, the divinylbenzene (80%, passed through a column of basic Al₂O₃ in order to remove dissolved oxygen in the solution), the 4,4'-divinyl-2,2'-bipyridine and/or the 5-vinyl-2,2'-bipyridine were dissolved in 6.6 ml of a deaerated THF:H₂O mixture (10:1). The amount of the different monomers is dependant of the ratio of monovinyl and divinyl bipyridine targeted in the final material with a total amount set

to 2mmol. 13.6 mg (0.06 mmol) of ACHN was added then the reaction mixture was stirred for 30 min and bubbled with Ar. Afterwards, the solution was transferred into a Teflon lined stainless-steel autoclave and placed in a preheated oven at 100 °C for 48 h. The polymer (monolith) was transferred into a Soxhlet thimble and purified by Soxhlet extraction using THF for one night. The white solid was dried at 80 °C under vacuum.

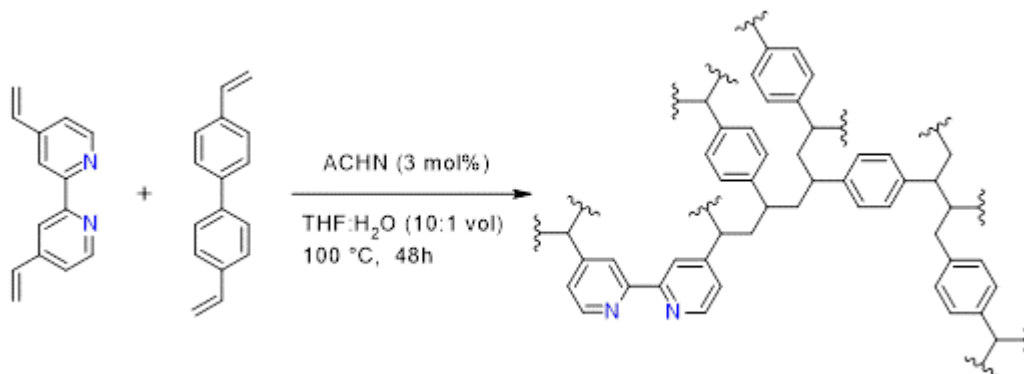
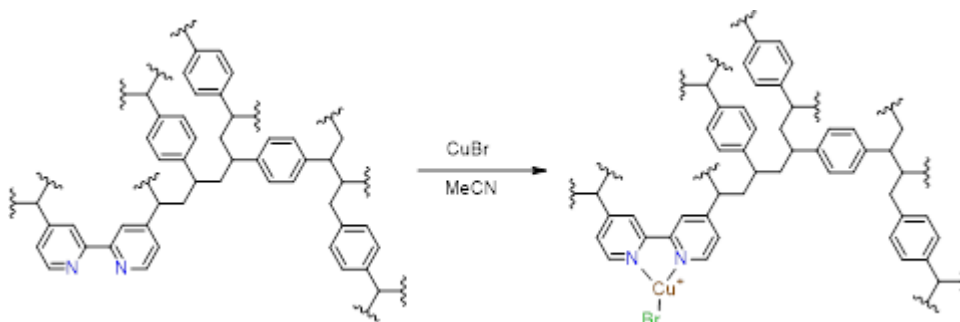


Table S1. Amount of monomer for porous polymer synthesis

Sample	divinylbenzene (mg)	4,4' divinyl-2,2'-bipyridine (mg)	5-vinyl-2,2'-bipyridine (mg)
05-N-POP-1	390	35	-
20-N-POP-1	242	75.2	-
50-N-POP-1	135	206	-
75-N-POP-1	73	312	-
N-POP-2	-	353	-
50N-POP-3	136	110	107

Copper deposition on bipyridine porous polymer

100 mg of dry porous polymer (N-POP) was added into a 10mL vial under Ar atmosphere. 8 mg of CuBr was dissolved in 10 mL of dry acetonitrile. The resultant solution is added in the vial changing the color of the polymer from white to brown. The suspension was stirred at room temperature for one night. The solid was separated from the solution by centrifugation and washed three times with 10 mL of acetonitrile. Finally the solid was dried at 80°C under vacuum overnight and stored in a glovebox.



NMR spectra of the 5-vinyl-2,2'-bipyridine

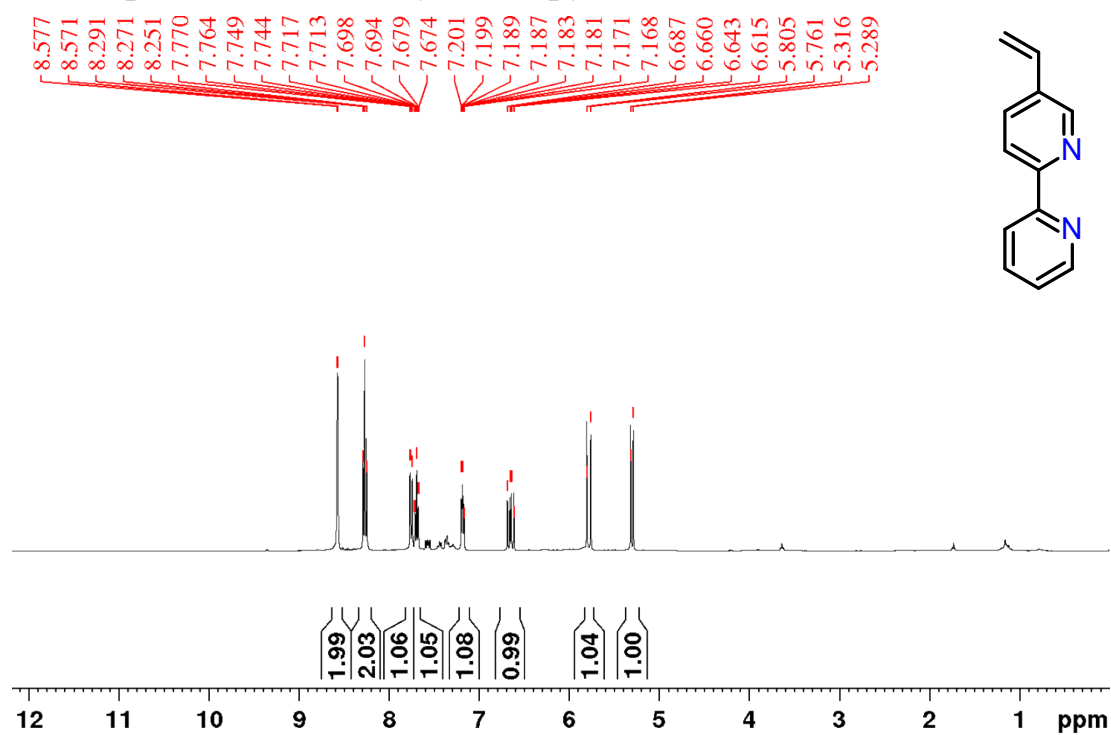


Fig S1. $^1\text{H-NMR}$ spectra of 5-vinyl-2,2'-bipyridine in CDCl_3

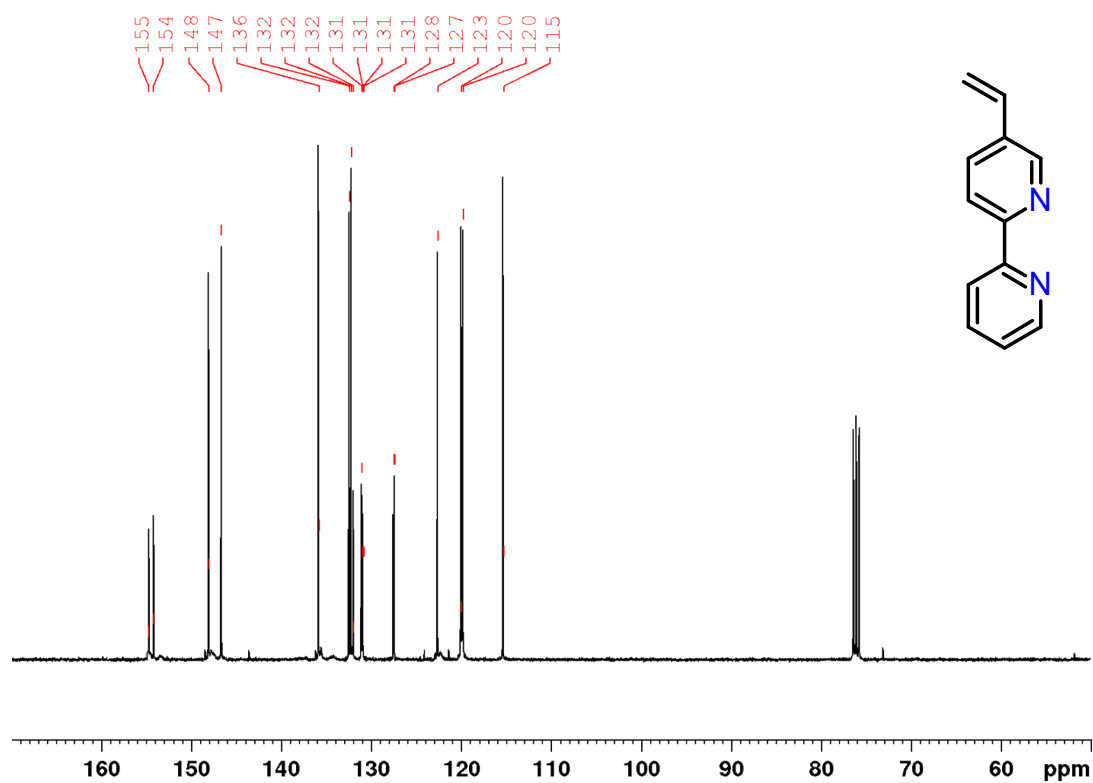


Fig S2. $^{13}\text{C-NMR}$ spectra of 5-vinyl-2,2'-bipyridine in CDCl_3

Chemical composition and textural properties of the materials

Table S2. Summary of elemental analyses and the textural properties of the N-POP-1 polymers and the Cu@N-POP-1 catalysts.

Materials	%wt C	%wt H	%wt N	%wt Cu	V _{micro} (cm ³ /g)	S _{bet} (m ² /g)
05N-POP-1	87	7.6	1.3	-	0.21	650
20N-POP-1	84.7	6.9	2.4	-	0.26	840
50N-POP-1	81	5.9	7.6	-	0.31	950
75N-POP-1	69.5	5.3	9.1	-	0.35	1030
N-POP-2	70.3	5	11.3	-	0.48	1300
50N-POP-3	81	6	8.5	-	0.22	670
Cu@05N-POP-1	85.6	7.1	1.4	1.02	0.18	590
Cu@20N-POP-1	80.5	6.9	2.2	3.5	0.18	575
Cu@50N-POP-1	74.3	5.9	7.3	3.1	0.31	900
Cu@75N-POP-1	67.1	4.9	8.6	3.5	0.29	860
Cu@N-POP-2	67.1	4.8	11.1	3.2	0.42	1240
Cu@50N-POP-3	74.03	5.7	7.6	3.2	0.19	600

N₂ adsorption isotherm of the materials

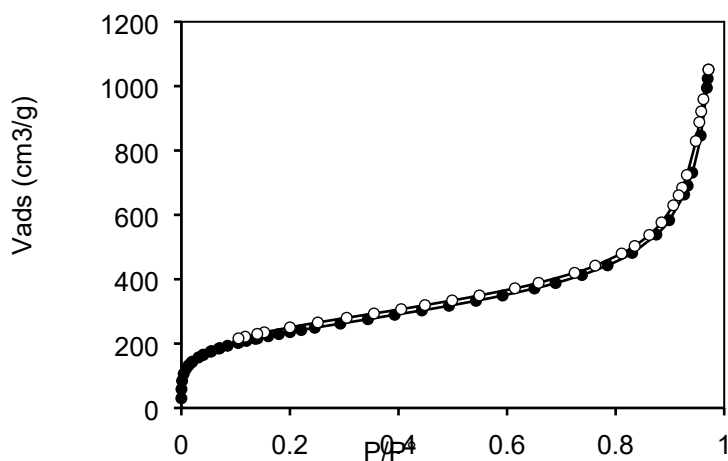


Fig S3. N₂ adsorption isotherm (77 K) of PDVB

Table S3. Henry's adsorption constant and total porous volume of POP and Cu@POP from acetonitrile adsorption isotherm (298K)

Sample	Henry's adsorption constant. (mol/g/kPa) ¹	Total porous volume (cm ³ /g)
05N-POP-1	1.23E-03	1.03
20N-POP-1	2.00E-03	1.07
50N-POP-1	5.04E-03	1.24
75N-POP-1	7.97E-03	1.11
N-POP-2	1.64E-02	1.57
50N-POP-3	3.80E-03	1.17
Cu@05-N-POP-1	1.83E-03	0.94
Cu@20-N-POP-1	3.14E-03	0.85
Cu@50N-POP-1	7.05E-03	1.28
Cu@75N-POP-1	5.90E-03	0.96
Cu@N-POP-2	1.20E-02	1.32
Cu@50N-POP-3	5.09E-03	1.40

¹ measured in the linear domain of acetonitrile adsorption isotherm (between 0 and 0.1 kPa)

¹³C NMR spectra of the porous polymers

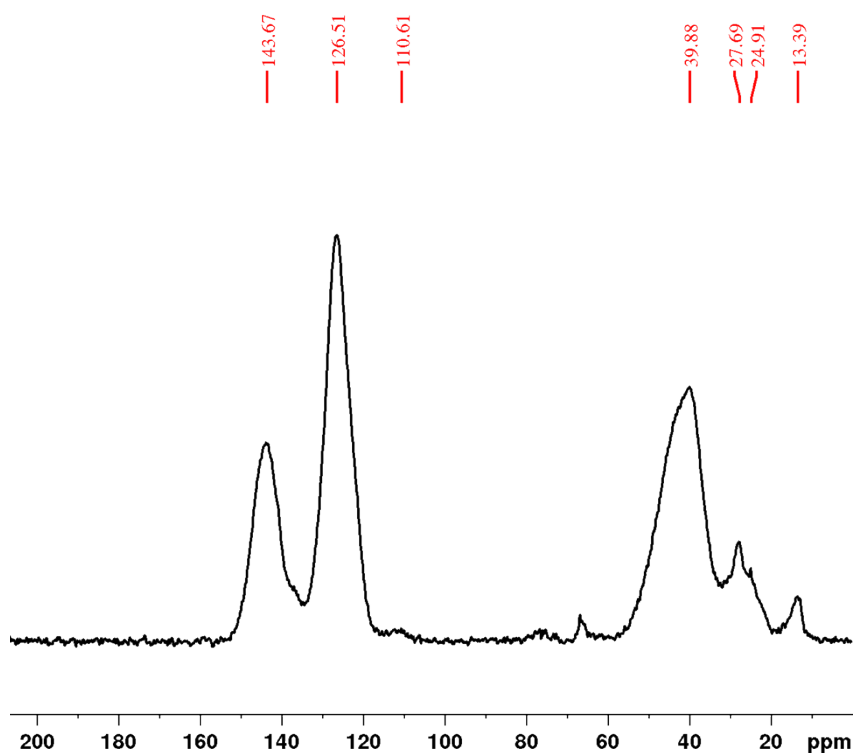


Fig S4. Solid state ¹³C-NMR of Porous Poly (Divinylbenzene)

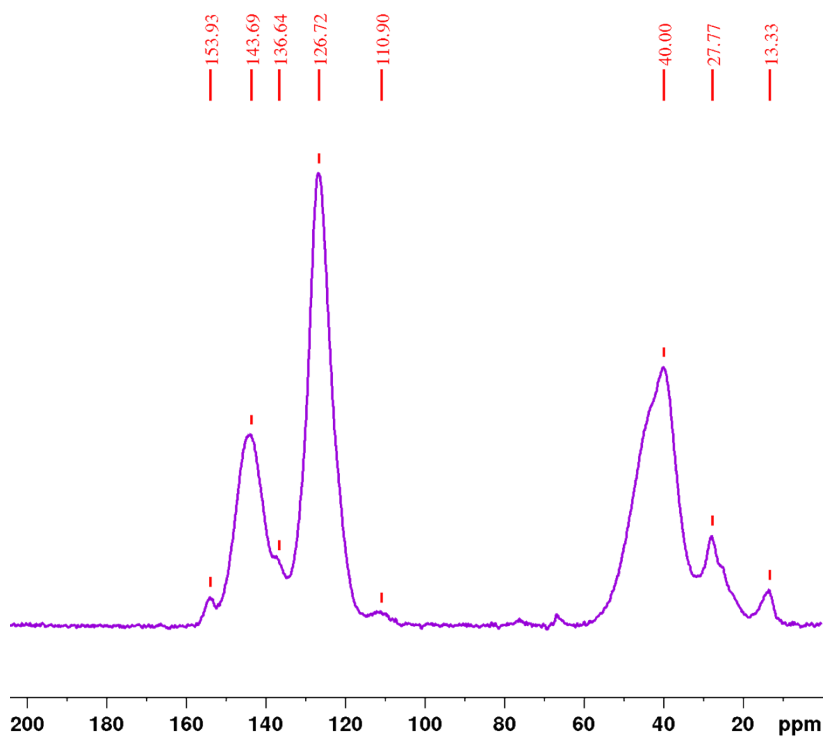


Fig S5. Solid state ^{13}C -NMR of 05N-POP-1

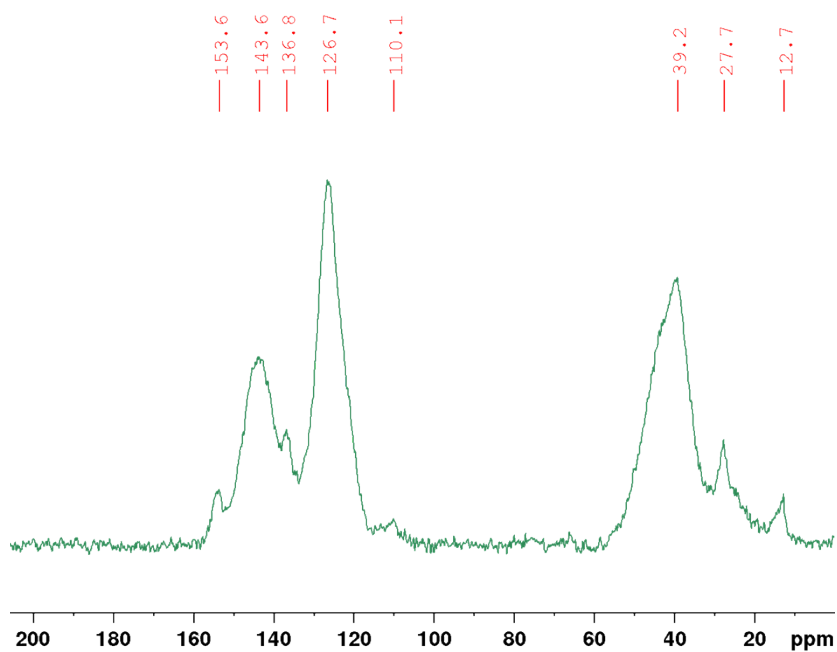


Fig S6. Solid state ^{13}C -NMR of 20N-POP-1

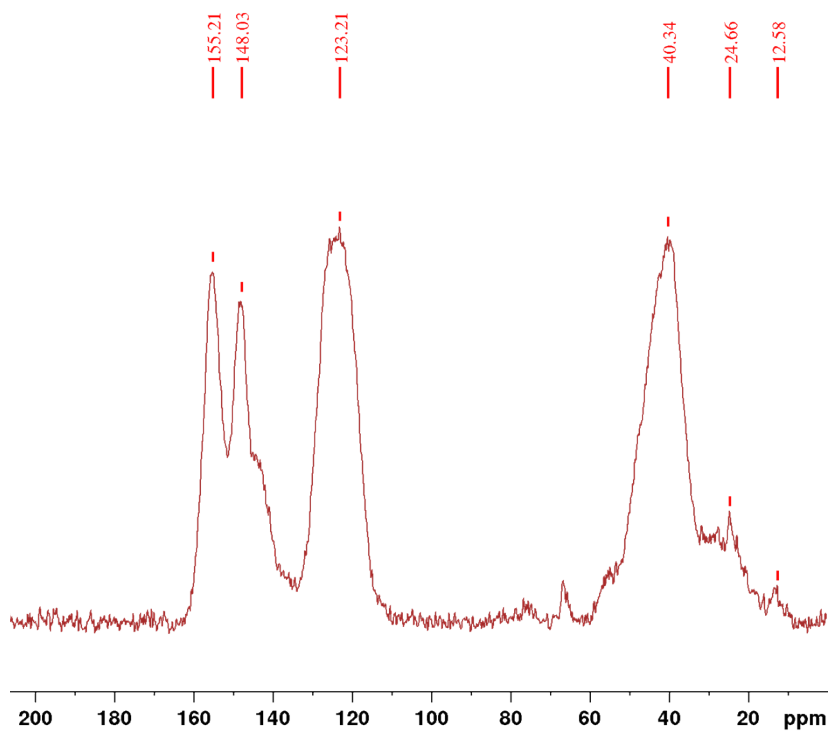


Fig S7. Solid state ^{13}C -NMR of 50N-POP-1

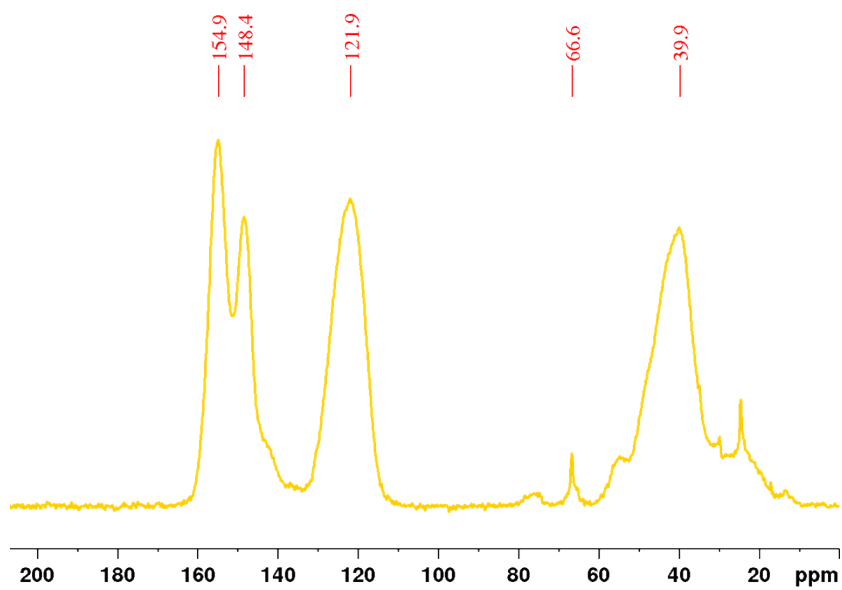


Fig S8. Solid state ^{13}C -NMR of 75N-POP-1

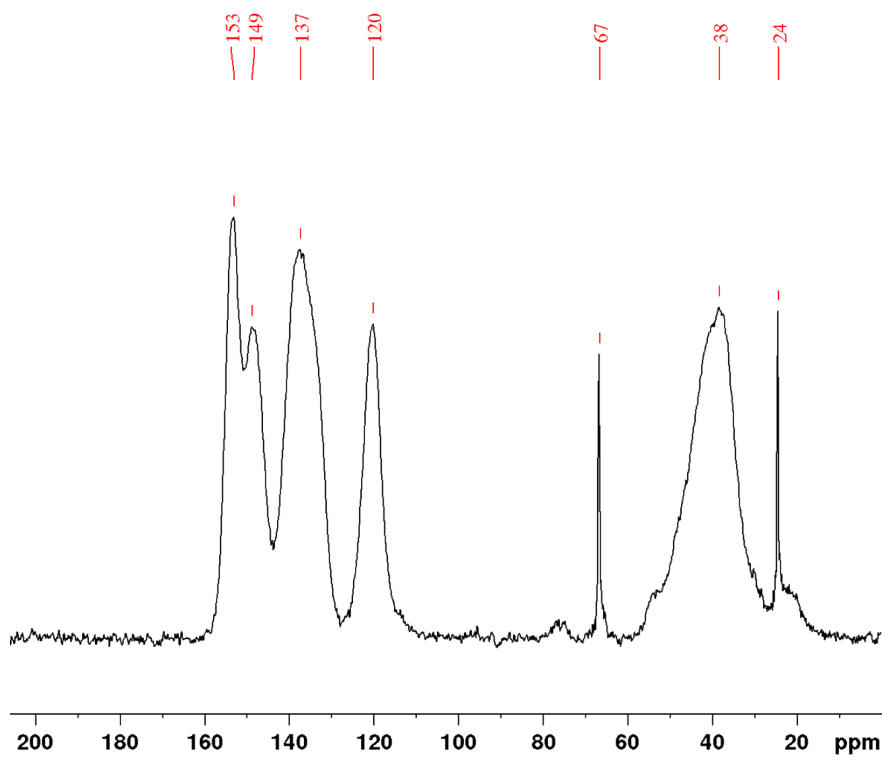


Fig S9. Solid state ^{13}C -NMR of N-POP-2

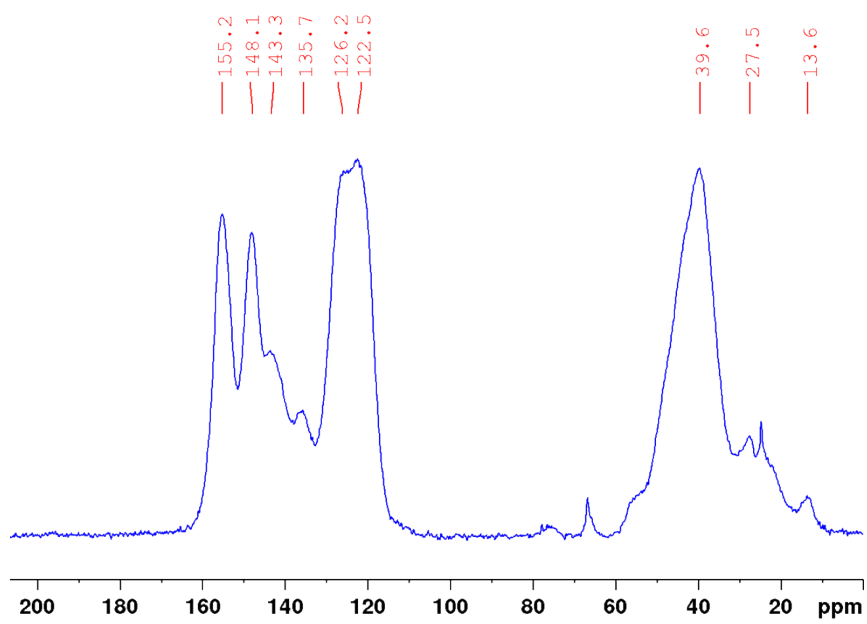


Fig S10. Solid state ^{13}C -NMR of 50N-POP-3

^{13}C NMR spectra of the copper materials

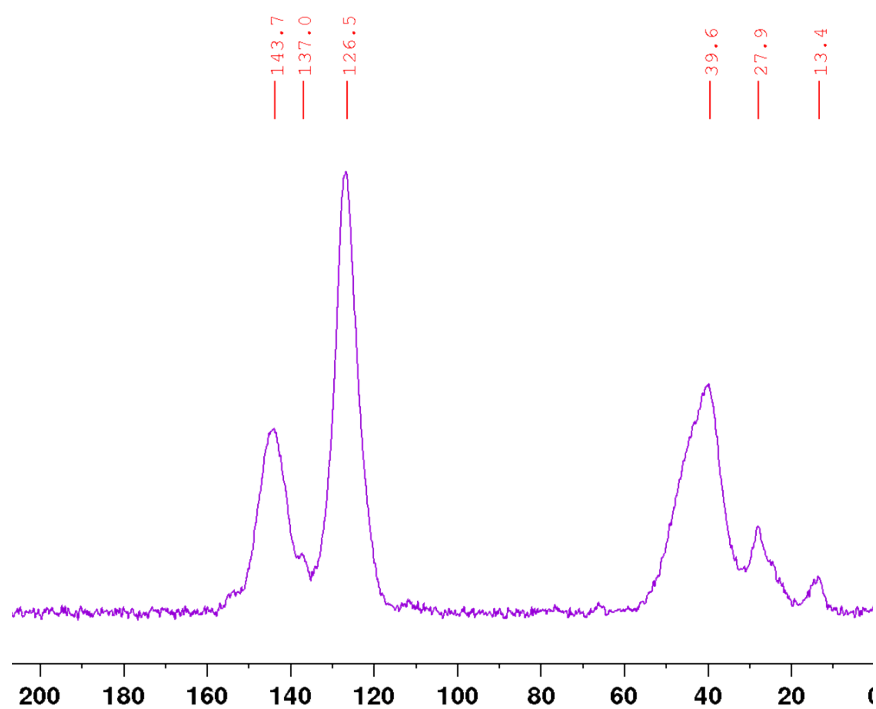


Fig S11. Solid state ^{13}C -NMR of Cu@05N-POP-1

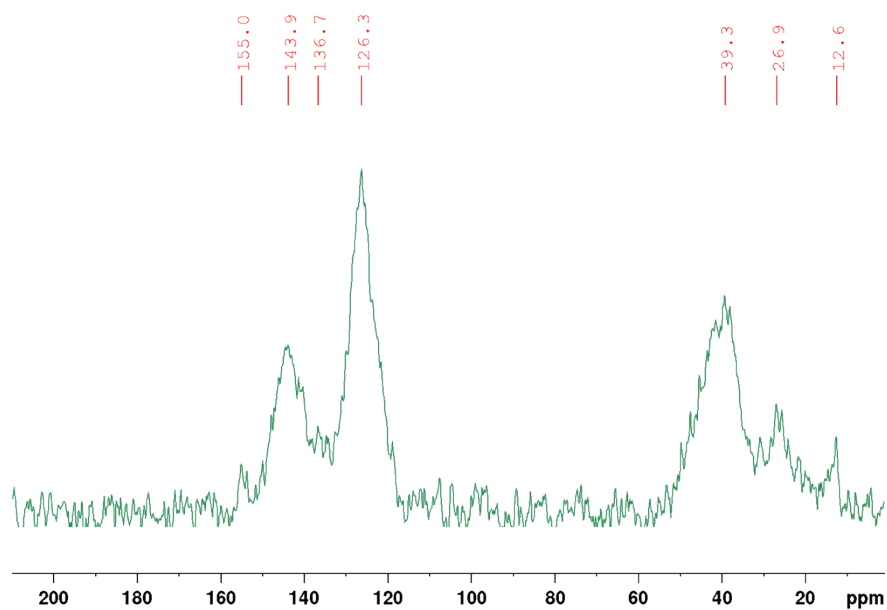


Fig S12. Solid state ^{13}C -NMR of Cu@20N-POP-1

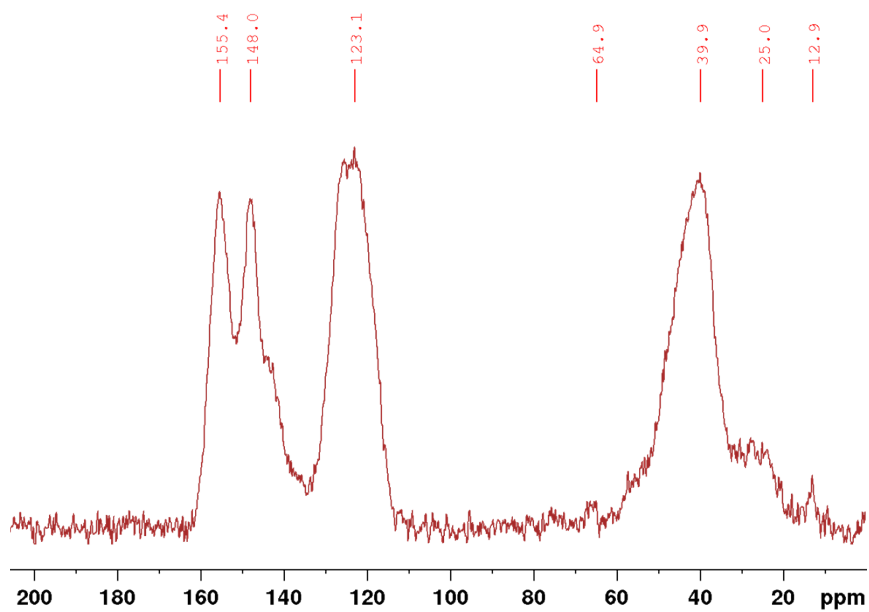


Fig S13. Solid state ^{13}C -NMR of Cu@50N-POP-1

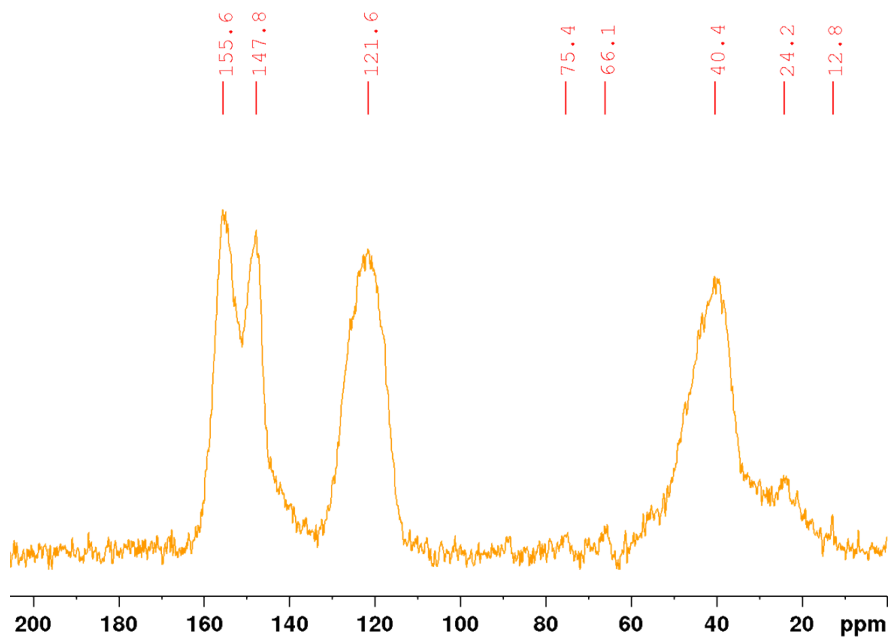


Fig S14. Solid state ^{13}C -NMR of Cu@75N-POP-1

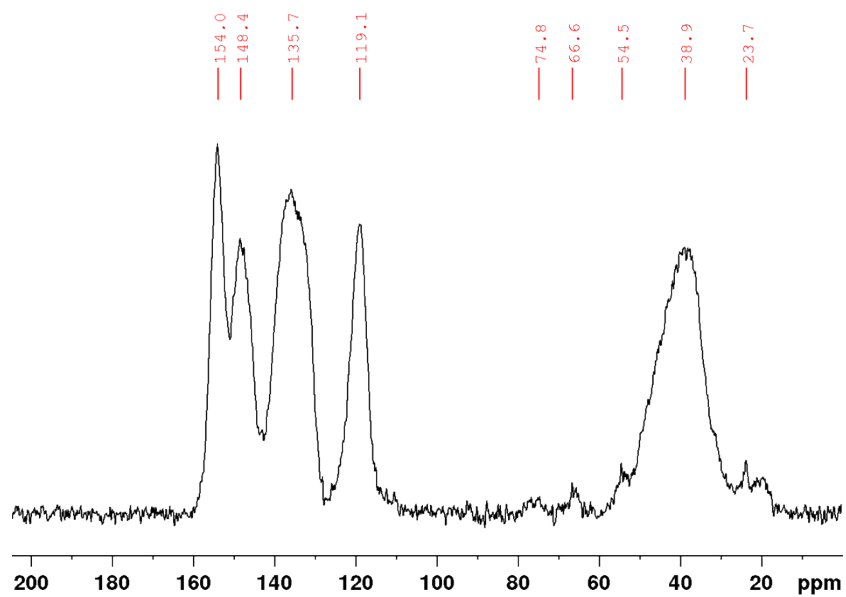


Fig S15. Solid state ^{13}C -NMR of Cu@N-POP-2

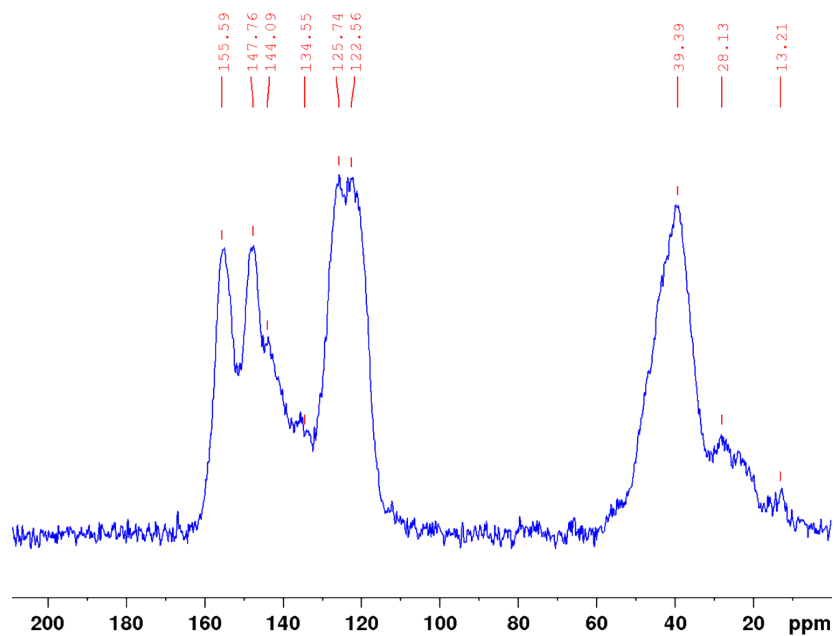


Fig S16. Solid state ^{13}C -NMR of Cu@50N-POP-3

FT-IR spectra of the materials

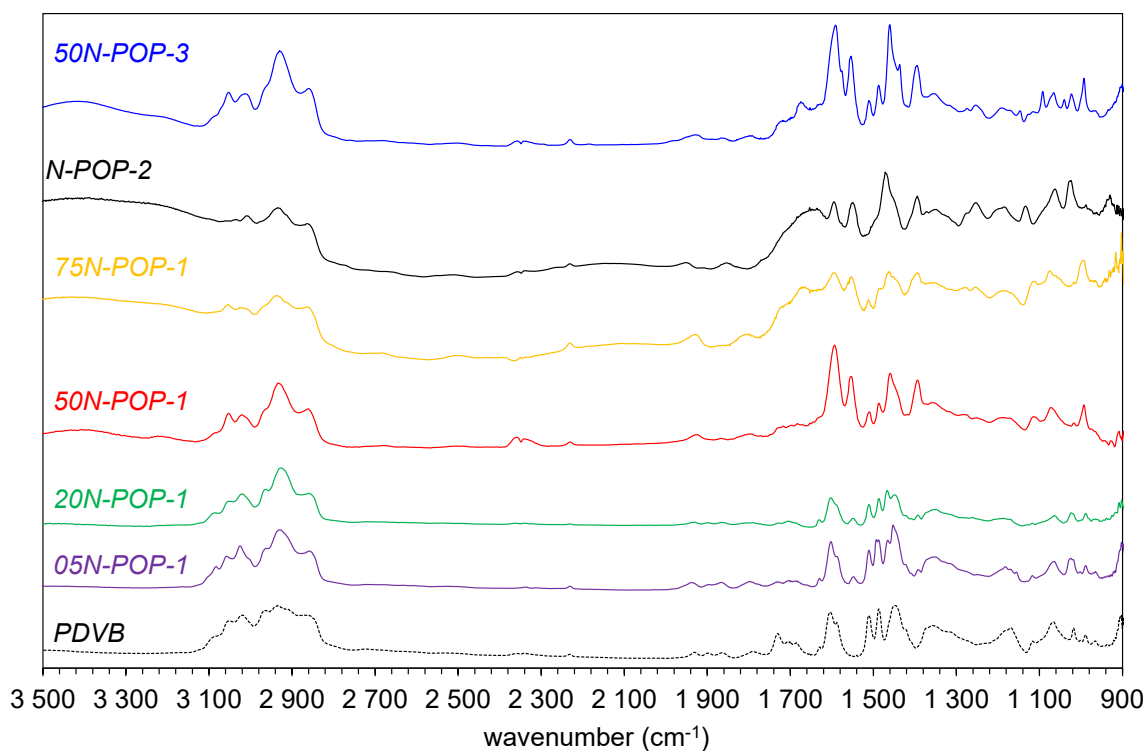


Fig S17. FT-IR spectra of porous polydivinylbenzene (dashed line) 05N-POP-1 (purple), 20N-POP-1 (green), 50N-POP-1 (red), 75N-POP-1 (yellow), N-POP-2 (black) and 50N-POP-3 (blue).

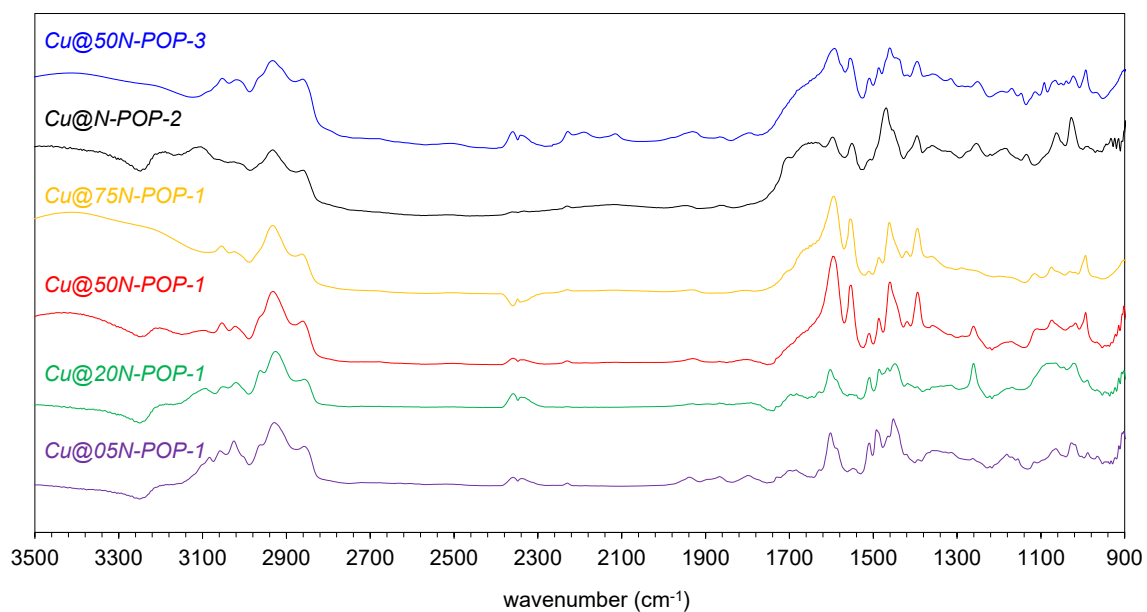


Fig S18. FT-IR spectra of Cu@05N-POP-1 (purple), Cu@20N-POP-1 (green), Cu@50N-POP-1 (red), Cu@75N-POP-1 (yellow), Cu@N-POP-2 (black) and Cu@50N-POP-3 (blue).

X-ray photoelectron spectroscopy spectra of the copper materials

It has to be noted that XPS spectra recorded for Cu@05N-POP-1 and Cu@20N-POP-1 did not present clear and attributable Cu 2p signals, with a detrimentally high signal to noise ratio, despite the presence of Cu in similar amount (see Table S2).

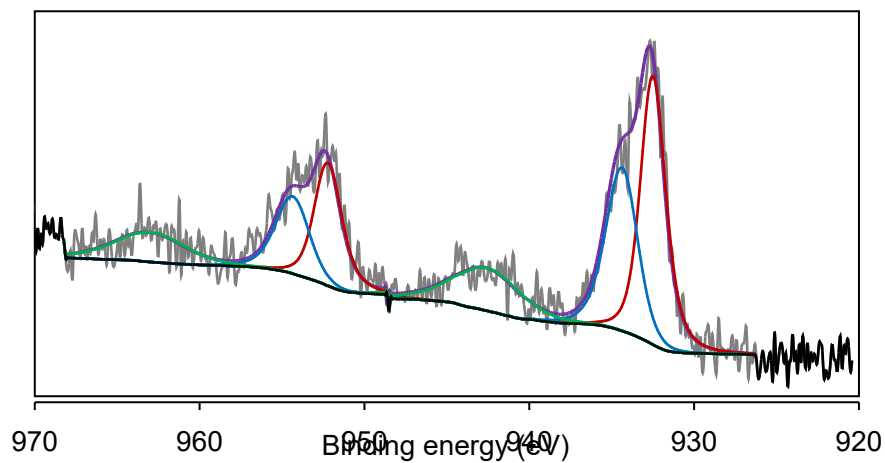


Fig S19. Cu 2p XPS spectrum of Cu@50N-POP-1

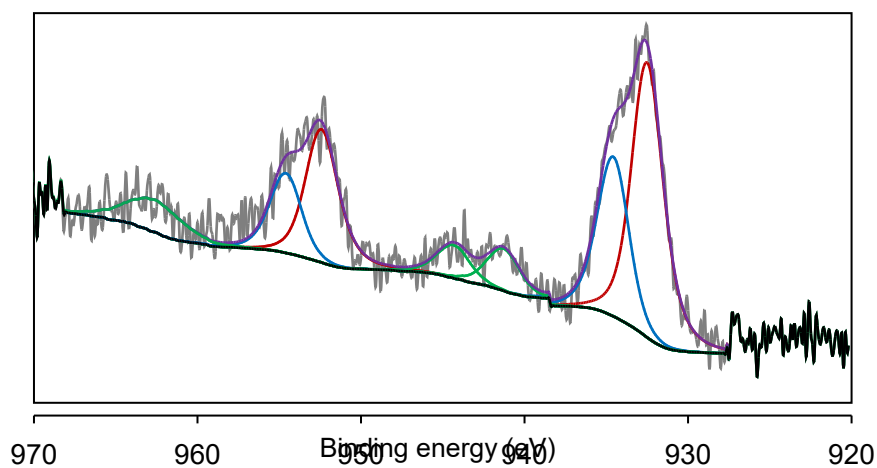


Fig S20. Cu 2p XPS spectrum of Cu@75N-POP-1

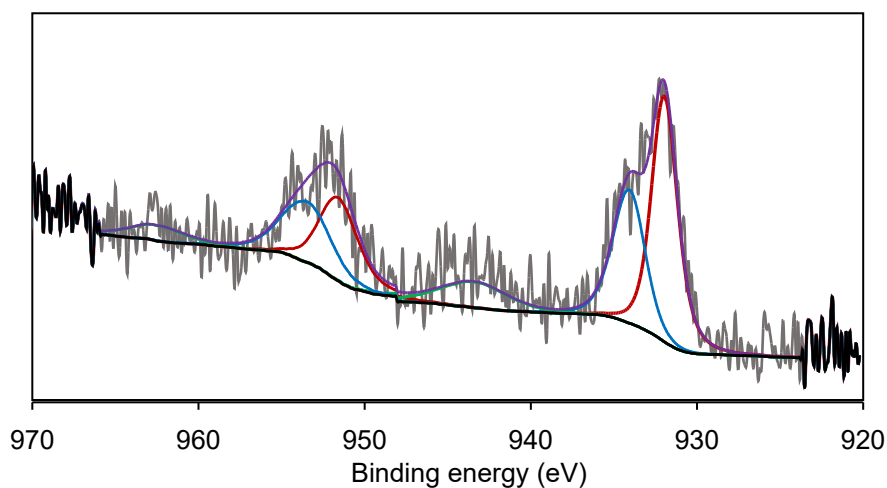


Fig S21. Cu 2p XPS spectrum of Cu@POP-2

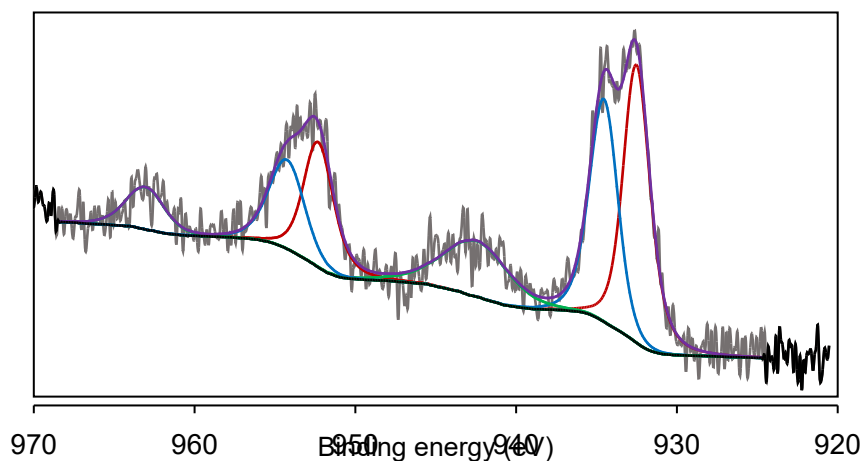


Fig S22. Cu 2p XPS spectrum of Cu@50N-POP-3

Table S4. Surface elemental composition measured by XPS

Sample	Surface % At					
	Cu ⁺	Cu ²⁺	Br	C	N	O
Cu@50N-POP-1	0.3	0.3	0.5	90.3	6.4	2.2
Cu@75N-POP-1	0.5	0.4	0.8	87.5	8.2	2.6
Cu@N-POP-2	0.3	0.3	0.6	85.4	10.3	3.1
Cu@N-POP-3	0.3	0.4	0.9	89.6	7.0	1.8

Heterogeneous catalysis protocol

50 mg of di-*p*-tolylamine (0.25 mmol) and approximately 25 mg of **Cu@N-POP-1/2/3** ($\approx 13 \mu\text{mol}$ of Cu) catalyst were added to a 10 mL Schlenk tube equipped with a magnetic stirring bar. Then the flask was sealed with a silicon septum and the atmosphere in the schlenk was replaced by pure O₂. 4 mL of acetonitrile was injected to the Schlenk tube through the septum and then mixed well. The reaction mixture was allowed to heat at 60 °C with stirring at 800 rpm for 6 hours. After 6 hours, the mixture was cooled down and 0.35 mmol of tetrachloroethane were added. The tetrachloroethane was used as an internal standard for ¹H NMR analysis after the reaction. The solid catalyst was separated from the reaction mixture by centrifugation. The solid was washed thoroughly with acetonitrile (3 x 5mL) and all the sets of liquid were collected and combined. 0.2 mL of the acetonitrile solution after reaction was diluted in CDCl₃ and analyzed by ¹H NMR to calculate the conversion and the yield by comparing the amount of product formed with amount of internal standard in the reaction.

Homogeneous catalysis protocol

A solution of copper in acetonitrile (0.5 mL; 12 μmol Cu) is added to a 10 mL schlenk under pure O₂. A solution of 2,2'-bipyridine in acetonitrile (0.5 mL; 12 μmol) and a solution of di-*p*-tolylamine (3 mL; 0.25 mmol) were also added to the schlenk. The reaction mixture was allowed to heat at 60 °C with stirring at 800 rpm for 6 hours. After 6 hours, the mixture was cooled down and 0.35 mmol of tetrachloroethane were added. The mixture is filtrated on silica bed then the acetonitrile solution after reaction was diluted in CDCl₃ and analyzed by ¹H NMR to calculate the conversion and the yield by comparing the amount of product formed with amount of internal standard in the reaction.

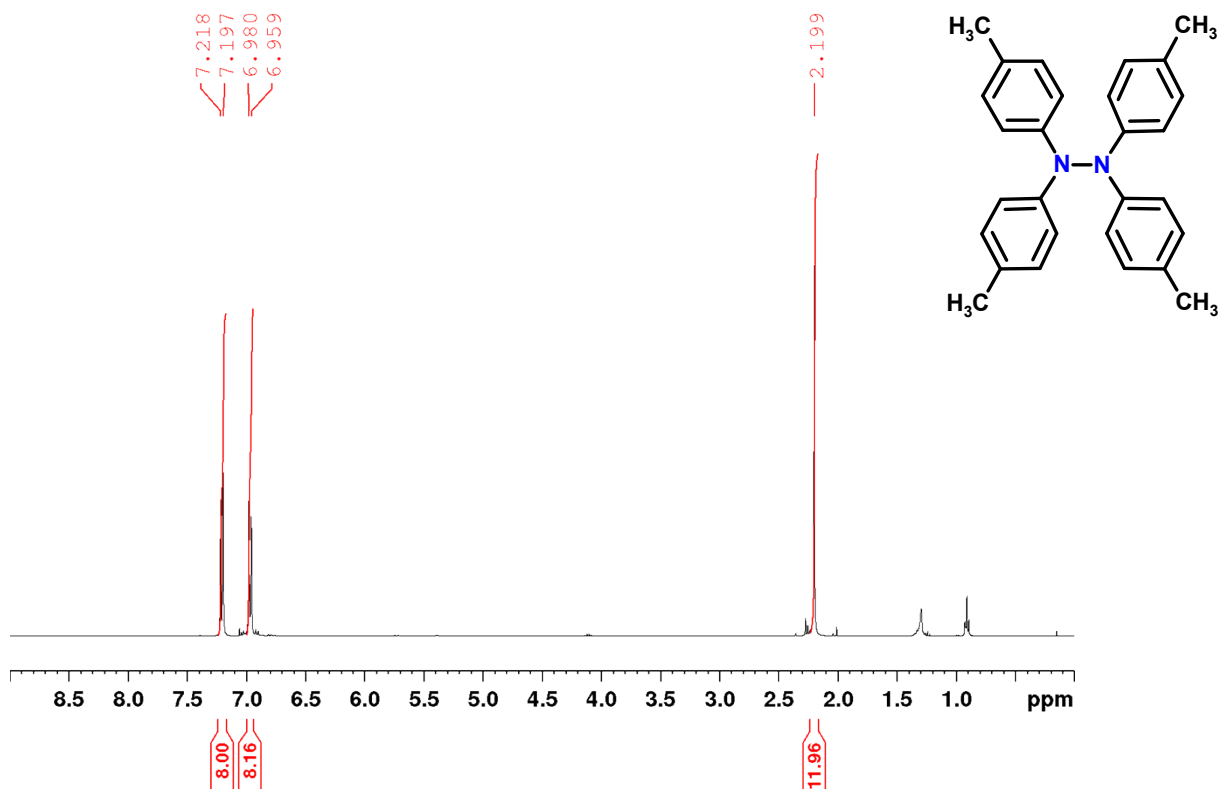


Fig S23. $^1\text{H-NMR}$ spectra of tetra-tolyl-hydrazine in CDCl_3

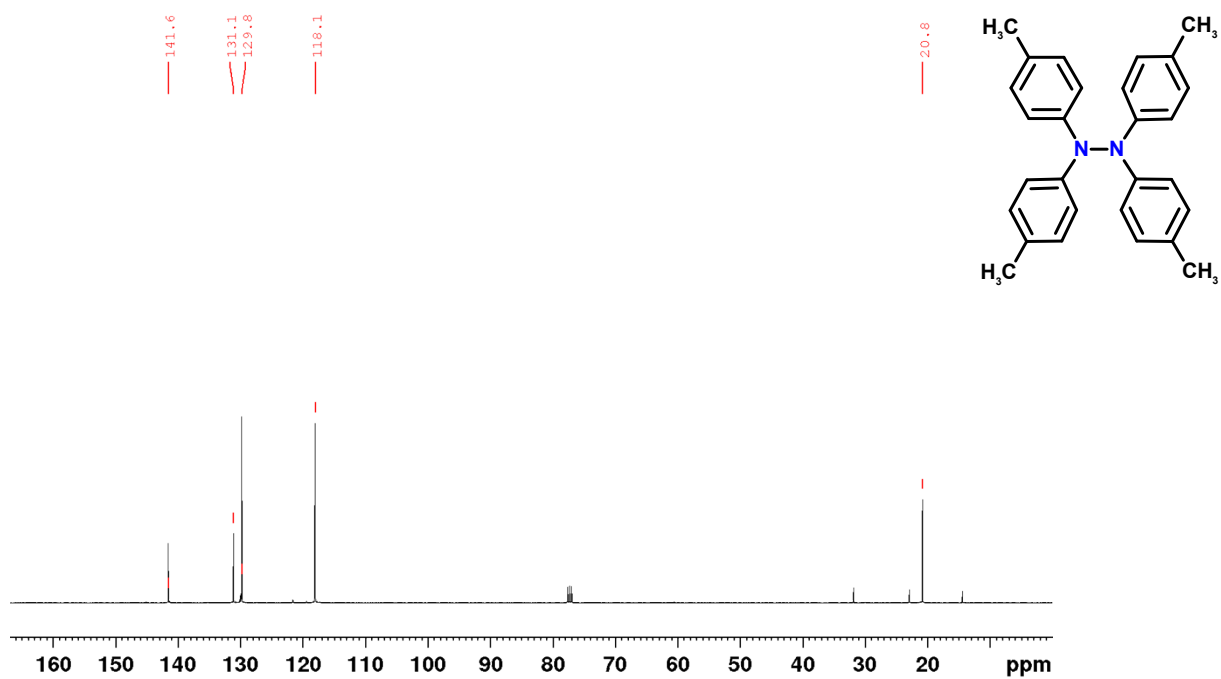


Fig S24. $^{13}\text{C-NMR}$ spectra of tetra-tolyl-hydrazine in CDCl_3

Catalytical performances of homogeneous and heterogeneous systems

Table S5. Catalytic activity of Cu@Bpy materials in standard conditions (60 °C, 6h in MeCN)

Catalyst	nCu (μmol)	ratio Bpy/Cu	Ratio Cu / Substrat	Conversion (%)	Yield (%)	TON*
CuBr + PDVB	12	0	5%	0%	0	0
75N-POP-1	0	0	0%	0%	0	0
N-POP-2	0	0	0%	0%	0	0
50N-POP-3	0	0	0%	0%	0	0
Cu@05N-POP-1	5	3	2%	5	3	0.6
Cu@20N-POP-1	13	2	5%	31	25	2.4
Cu@50N-POP-1	13	5	5%	50	45	4.5
Cu@75N-POP-1	14	6	5%	83	80	7.8
Cu@N-POP-2	13	8	5%	43	40	4.0
Cu@50N-POP-3	14	5	5%	94	85	8.5
Cu@75N-POP-1	7.7	6	2.5%	68.9	65.6	11.1
Cu@50N-POP-3	5.7	5	2.5%	68.2	66.9	15.5

*calculated from the molar amount of product by molar amount of Cu

Table S6. Catalytic activity of homogeneous systems in standard conditions (60 °C, 6h in MeCN)

Catalytic system	nCu (μmol)	ratio Bpy/Cu	Ratio Cu / Substrat	Conversion (%)	Yield (%)	TON*	Carbon balance (%)
CuI / 2,2'-Bpy	12	1	5%	91.1	80.6	7.94	89.4
CuBr / 2,2'-Bpy	12	1	5%	96.1	76.3	7.88	80.2
Cu(Ac) ₂ / 2,2'-Bpy	12	1	5%	62.3	60.5	7.13	98.1
CuBr ₂ / 2,2'-Bpy	12	1	5%	22.1	21.7	2.28	99.6
CuCl ₂ / 2,2'-Bpy	12	1	5%	3.8	0.0	0.00	96.2
CuBr	12	1	5%	0.8	0.8	0.08	100.0

*calculated from the molar amount of product by molar amount of Cu

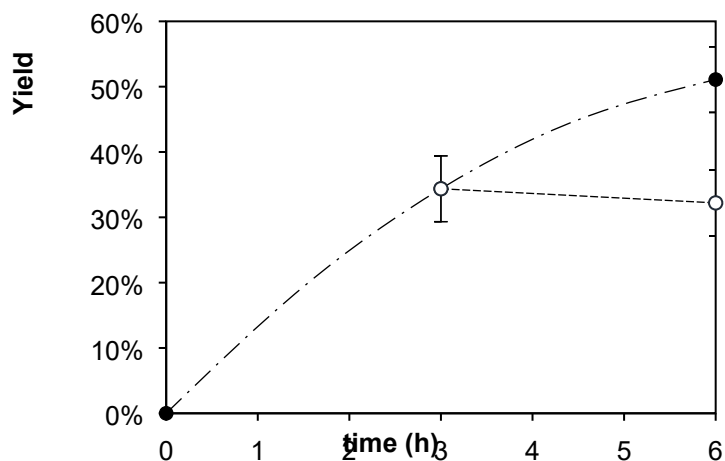


Fig S25. Comparison of the Kinetics (solid circles) and hot filtration (after 3 hours, empty circles) test of *N-N* coupling catalyzed by Cu@50N-POP-1 ($n_{Cu} = 13 \mu\text{mol}$, $n_{substrate} = 0.25 \text{ mmol}$) at 60°C in acetonitrile.

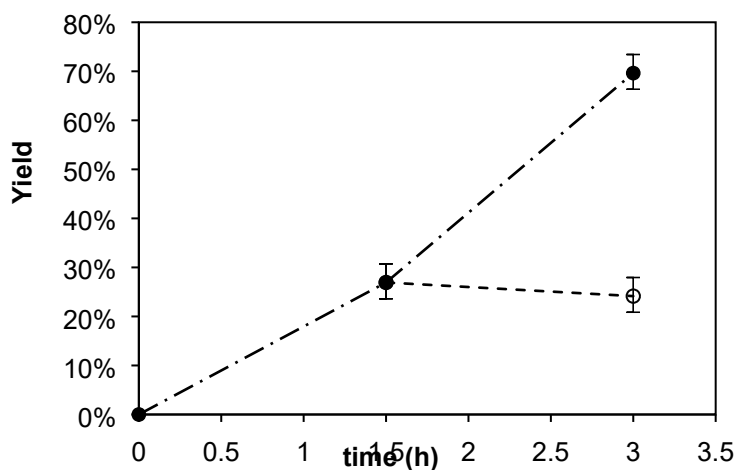


Fig S26. Comparison of the Kinetics (solid circles) and hot filtration (after 1.5 hours, empty circles) test of *N-N* coupling catalyzed by Cu@50N-POP-3 ($n_{Cu} = 6 \mu\text{mol}$, $n_{substrate} = 0.25 \text{ mmol}$) at 60°C in acetonitrile.

Post-reaction catalyst analyses

Table S7. Copper content in the catalysts before & after reaction measured by X-ray fluorescence

Sample	%wt Cu before catalysis	%wt Cu after catalysis
Cu@75N-POP-1	3.53	3.48
Cu@50N-POP-3	3.10	3.13

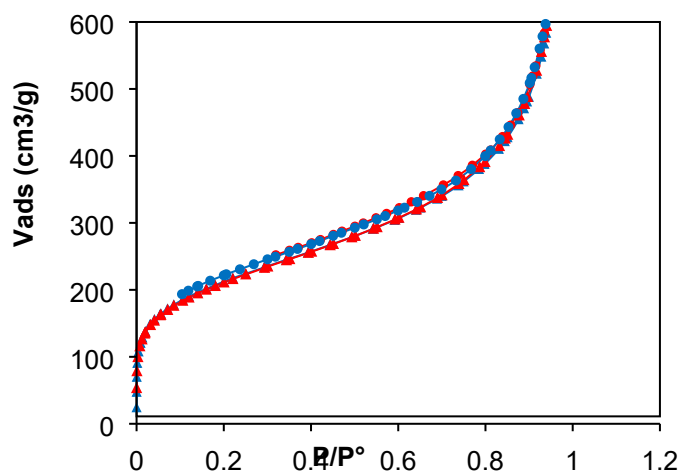


Fig S27. N_2 sorption isotherms (77 K) of Cu@75N-POP-1 before catalysis (blue) and after catalysis (red)

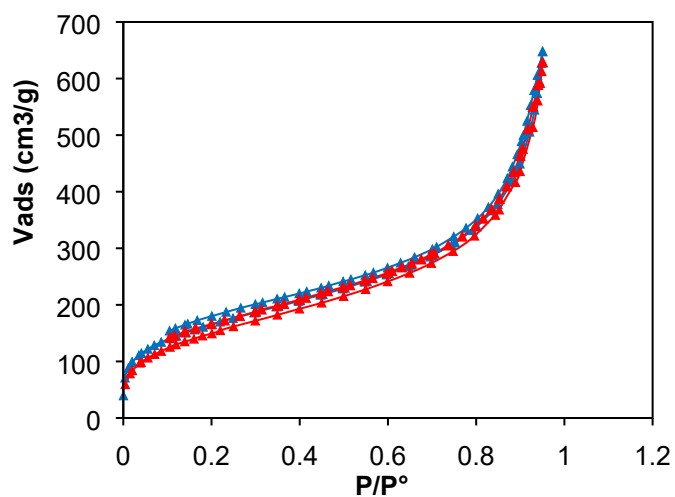


Fig S28. N_2 sorption isotherms (77 K) of Cu@50N-POP-3 before catalysis (blue) and after catalysis (red)

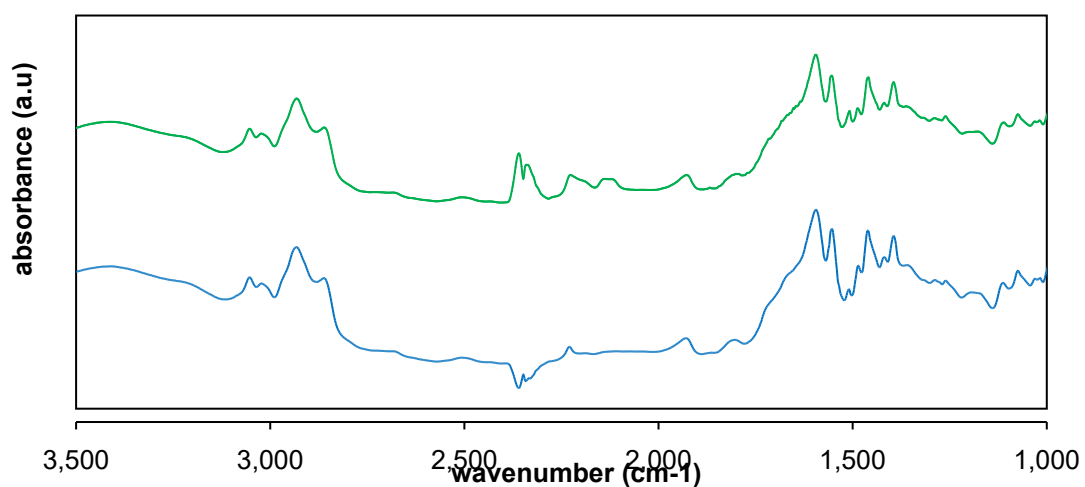


Fig S29. FT-IR spectra of Cu@75N-POP-1 before catalysis (blue) and after catalysis (green)

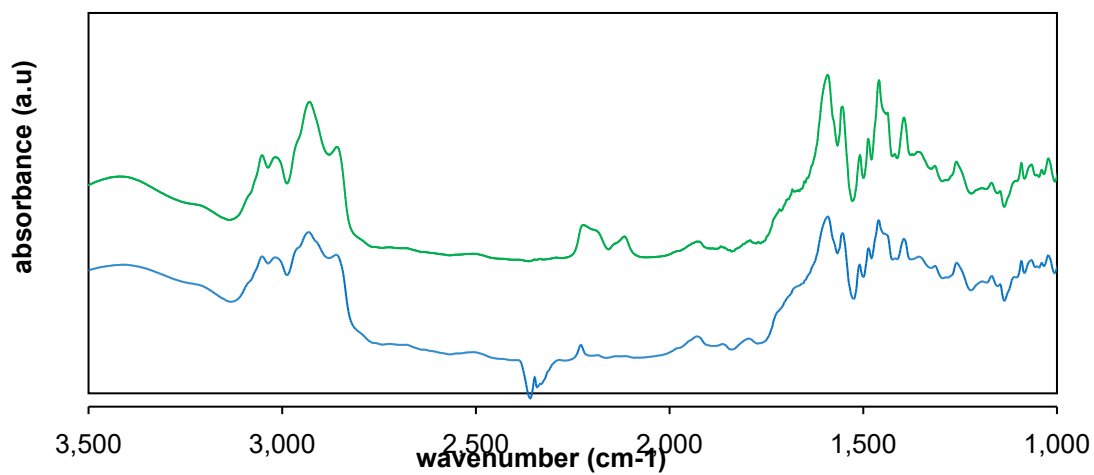


Fig S30. FT-IR spectra of Cu@50N-POP-3 before catalysis (blue) and after catalysis (green)

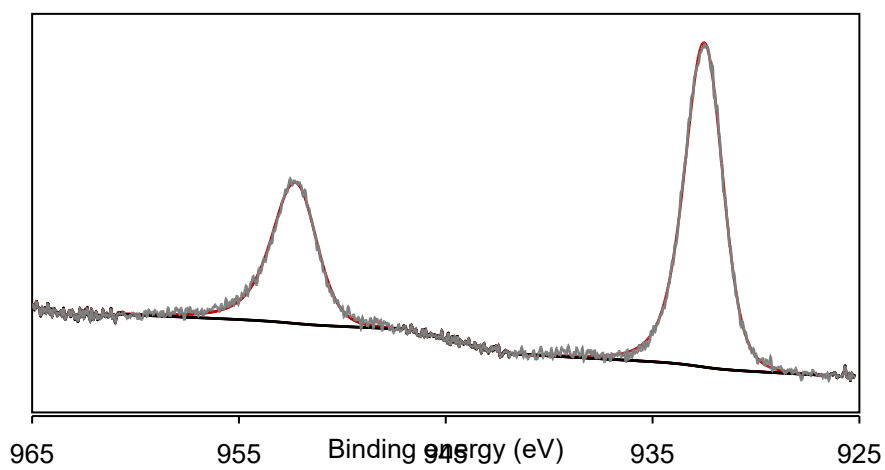


Fig S31. Cu 2p XPS spectrum of Cu@75N-POP-1 after catalysis

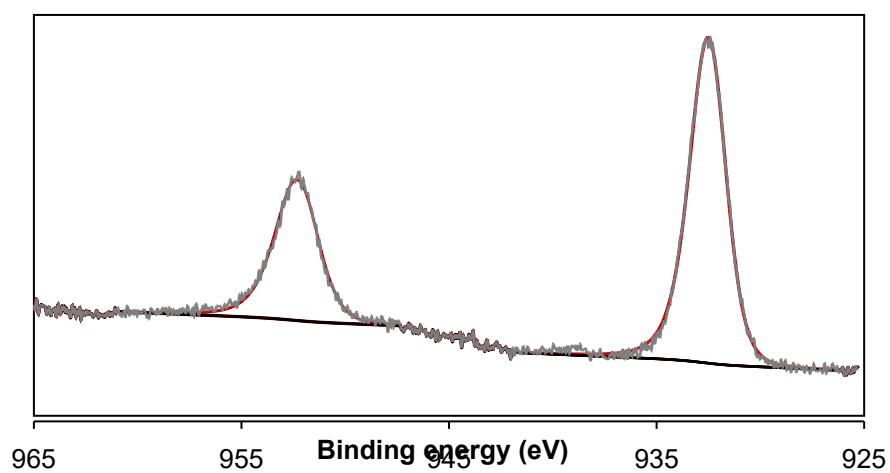


Fig S32. Cu 2p XPS spectrum of Cu@50N-POP-3 after catalysis

Table S8. Surface elemental composition measured by XPS

Sample	Surface % At					
	Cu ⁺	Cu ²⁺	Br	C	N	O
Cu@75N-POP-1 before catalysis	0.5	0.4	0.8	87.5	8.2	2.6
Cu@N-POP-3 before catalysis	0.3	0.4	0.9	89.6	7.0	1.8
Cu@75N-POP-1 after catalysis	0.9	-	0.4	87.9	8.0	2.8
Cu@N-POP-3 after catalysis	0.8	-	0.3	89.9	7.0	2.0

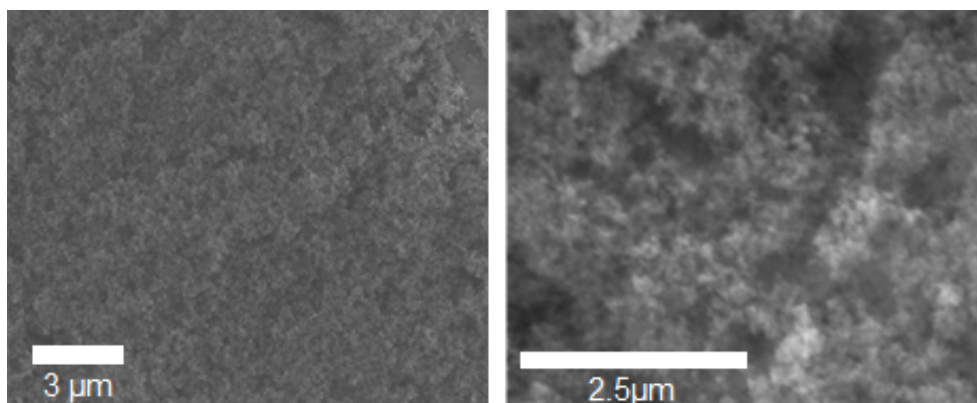


Figure S33. SEM micrographs of Cu@75N-POP-1.

References

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