

Supporting Information

Stabilization of Cu₂O nanoparticles on a 2D metal-organic framework for catalytic Huisgen 1, 3-dipolar cycloaddition reaction

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Experimental Section

Materials

All reagents were obtained from commercial sources and used without further purification. High purity Zn(NO₃)₂·6H₂O, 4,5-imdazoledicarboxylic acid (H₃imdc) and ,4'-bipyridyl (bipy) were purchased from Aldrich Chemical Co. and used as received.

Synthesis of {[Zn(Himdc)(bipy)_{0.5}](DMF)}_n (**1**)

Zn(NO₃)₂·4H₂O (0.25 mmol, 0.074 g) was dissolved in 12.5 mL acetonitrile with constant stirring. 4,5-imdazoledicarboxylic acid (H₃imdc) (0.25 mmol, 0.039 g) and 4,4'-bipyridyl (bipy) (0.125 mmol, 0.0195 g) was dissolved in 12.5 mL N,N-dimethylformamide (DMF) solution and stirred well for 30 min to obtain a homogeneous solution. Acetonitrile solution (2 mL) of Zn(NO₃)₂ is slowly and carefully layered on top of the ligand solution of DMF (2 mL) using the 2 mL buffer solution of acetonitrile and DMF (1:1). Colorless block single crystals grew at the junction of the two different solvents after two weeks. The crystals were separated and washed with acetonitrile, which was subjected to X-ray diffraction. Yield: 80%. Anal. Calcd. for C₁₃H₁₃N₄O₅Zn: C, 42.19; H, 4.7; N, 16.9. Found: C, 41.88; H, 4.63; N, 16.64%. IR (KBr cm⁻¹); 1669-1685 ν(COO); 2265 ν_s(CN); and 1557 ν_s(Ar C=C).

Preparation of Cu₂O@**1a**

The compound **1** was desolvated at 433 K under vacuum (10⁻⁵ Torr) for 1h, which resulted in removal of DMF molecules. **1a** (0.02 g, 0.01 mmol) was immersed in water (2 mL) by sonication for 2 minutes. Copper sulphate (1.5 mL; 2 mmol) was added followed by the addition of Hydrazine hydrate (10 μL, 0.02 M). The obtained mixture was washed thoroughly with distilled water and finally dried in an oven at 333 K. The resulting solid has been characterized by IR, PXRD and TEM.

Procedure for catalytic reactions

In a typical reaction, 48 mg (0.2 mmol) of 1, 3, 5-methylazido benzene and 71.4 mg (0.7 mmol) of phenyl acetylene is taken in a schlenk tube and dissolved in mixture of *t*-

BuOH/H₂O (3ml, 2:1). Then catalytic amounts of **Cu₂O@1a** (0.5 mol%) followed by Et₃N (0.5 ml) is added to the reaction mixture and stirred at 50 °C for 7 hrs. Precipitates were collected by filtration, washed with water and dissolved in chloroform. Catalyst is separated from Crude mixture by centrifugation and the crude is analysed for GC-MS analysis. Products were qualitatively analysed by ¹H NMR analysis.

Characterization Techniques

Physical Measurements

Elemental analysis of **1** was carried out using a Thermo Scientific Flash 2000 CHN analyzer. Powder X-ray diffraction (PXRD) patterns of **1**, **1a**, and **Cu₂O@1a** were recorded on a Bruker D8 Discover instrument using Cu-K α radiation. For TEM measurements were measured on a JEOL JEM 3010 instrument operating at an accelerating voltage of 300 kV, the samples were prepared by dispersing the powder products in water by sonication before drop casting on a carbon-coated copper grid. Inductively coupled plasma-optical emission spectral (ICP-OES) analyses of **Cu₂O@1a** were carried out using a Perkin Elmer OPTIMA 7000 spectrometer.

Adsorption Measurements

CO₂ adsorption studies of **Cu₂O@1a** hybrid were carried out using QUANTACHROME AUTOSORB-1C analyzer. The adsorbent sample of about 100-150 mg was heated at 493 K under a high vacuum (10⁻¹ Pa) for 18 h prior to measurements. The adsorbate was charged into the sample tube and then the change of the pressure was monitored and the degree of adsorption was determined by the decrease of the pressure at the equilibrium state. All operations were computer-controlled and automatic.

¹H-NMR Analysis

¹H-NMR spectra were recorded in CDCl₃ with TMS as an internal standard at ambient temperature on a Bruker AVANCE 400 (400 MHz) Fourier transform NMR spectrometer (S4-S6)

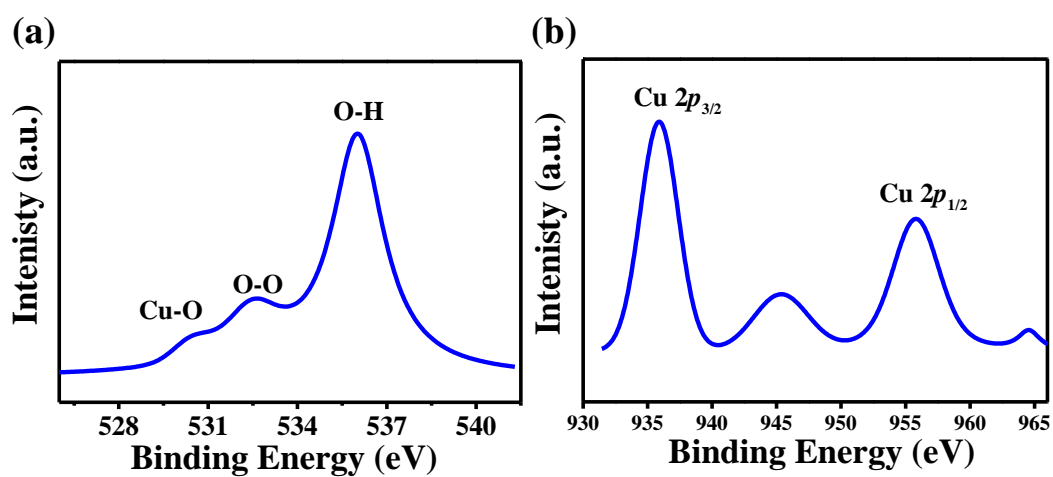


Fig. S1 XPS of (a) O1s and (b) Cu2p_{3/2} and Cu2p_{1/2} core level spectra of **Cu₂O@1a**.

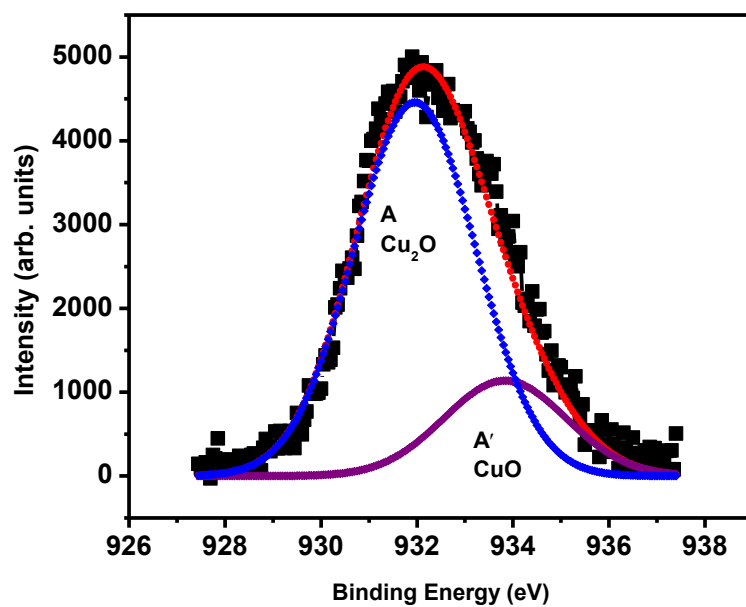


Fig. S2 XPS Cu2p_{3/2} core level spectra of **Cu₂O@1a**. The decolvoluted peaks A and A' correspond to Cu₂O and CuO respectively.

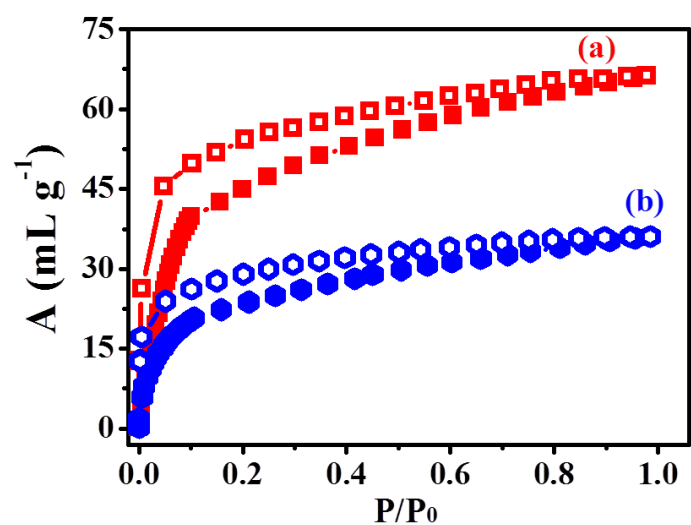


Fig. S3 CO₂ adsorption isotherms at 195 K of (a) **1a** (b) **Cu₂O@1a**.

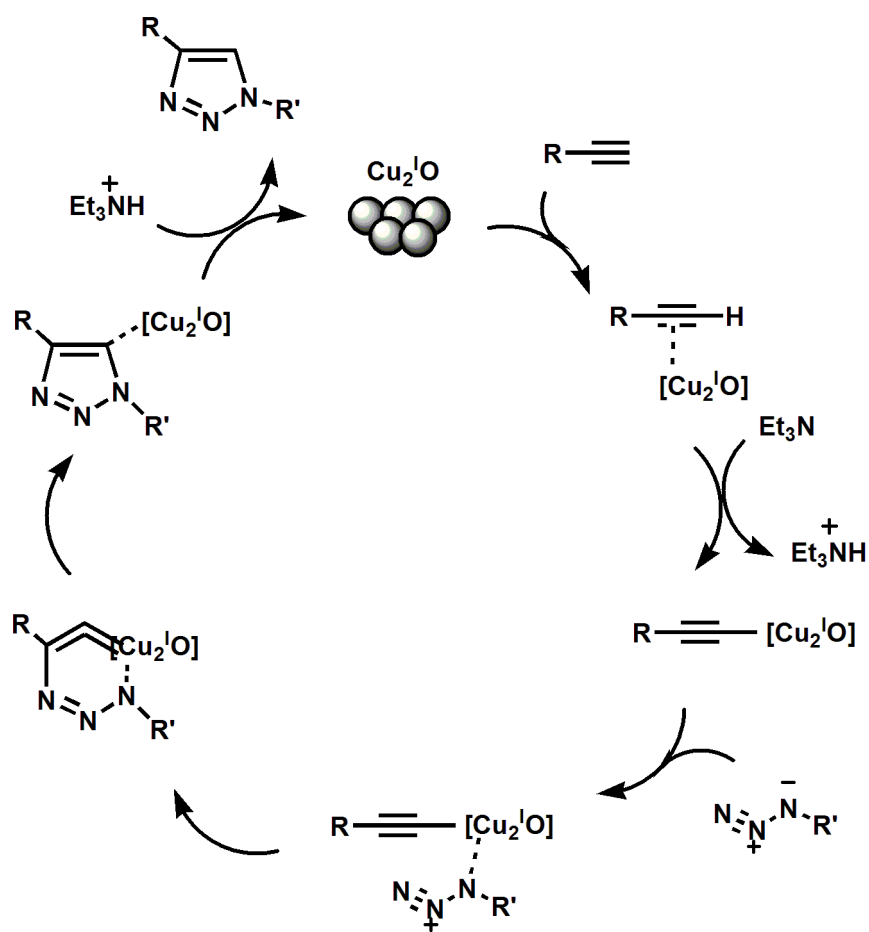


Fig. S4 Proposed mechanism of **Cu₂O@1a** catalytic cycle for the formation of 1,2,3-triazole.

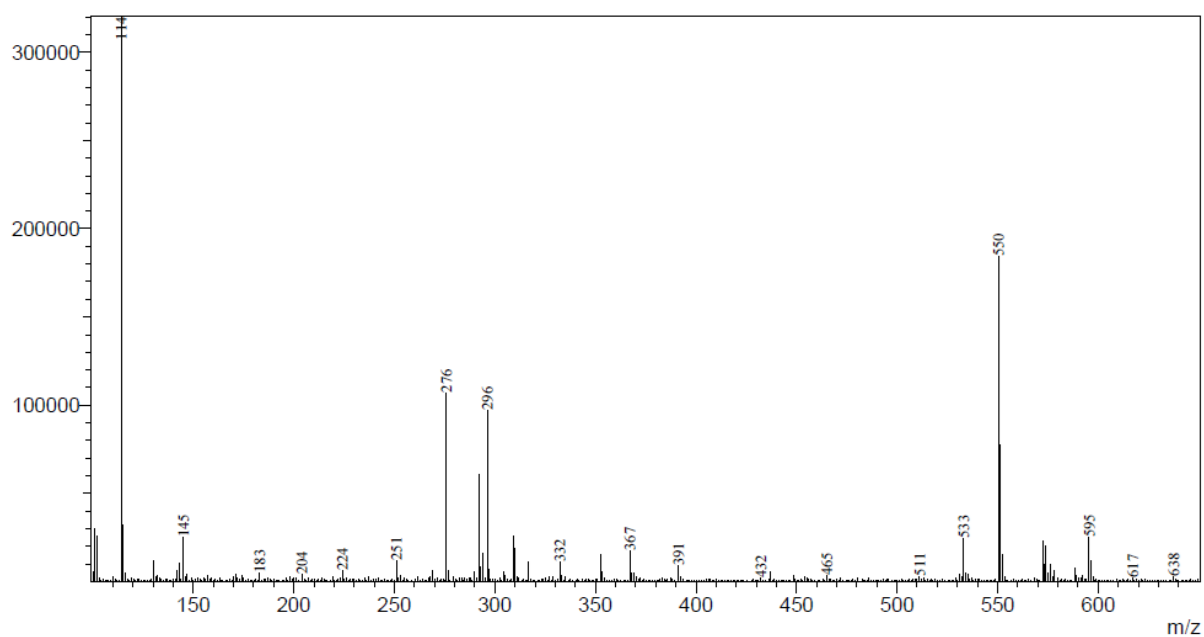


Fig. S5 Mass spectrum of cyclised product of 1, 3, 5- methylazidobenzene and phenyl acetylene

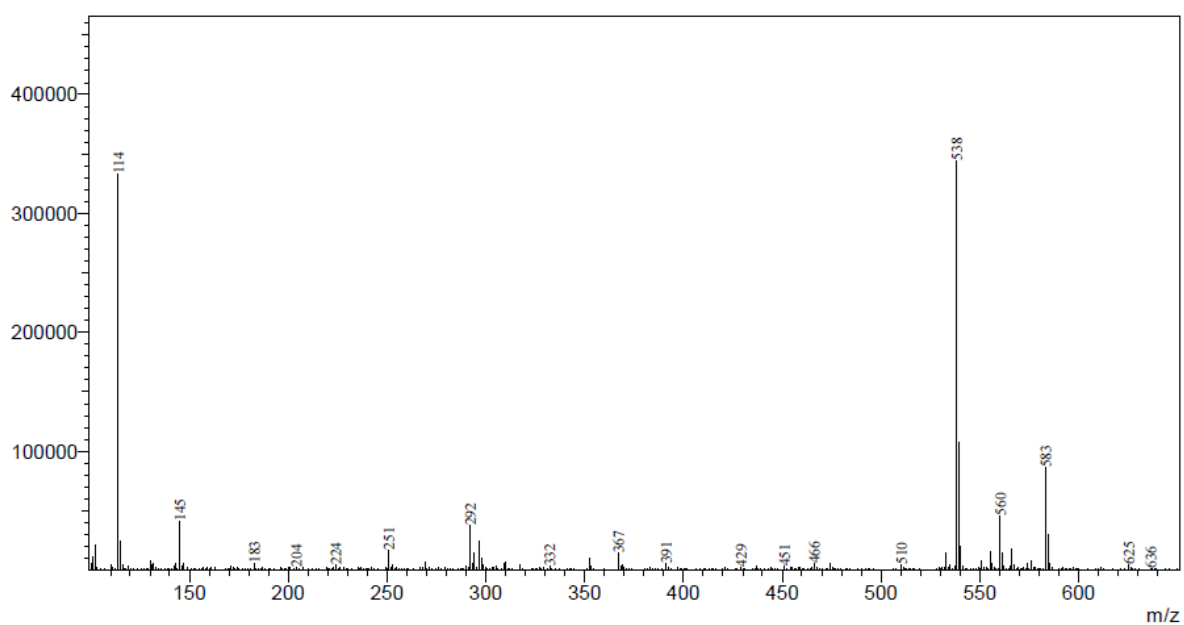


Fig. S6 Mass spectrum of cyclised product of 1, 3, 5- methylazidobenzene and ethyl propiolate

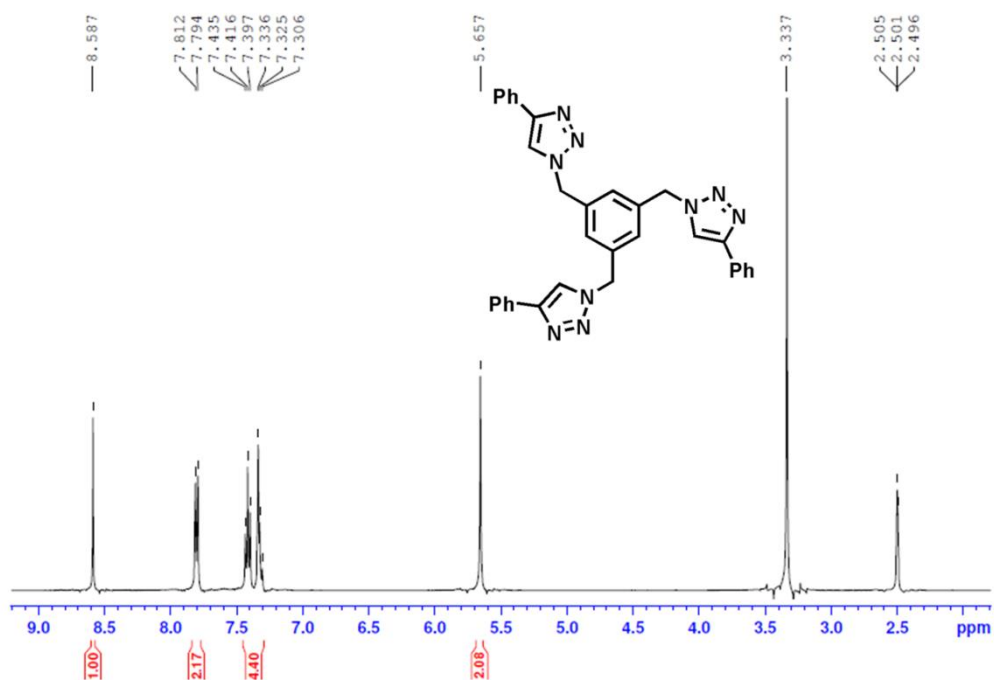


Fig. S7 $^1\text{H-NMR}$ spectra of cyclised product of 1, 3, 5- methylazidobenzene and phenyl acetylene in CDCl_3 .

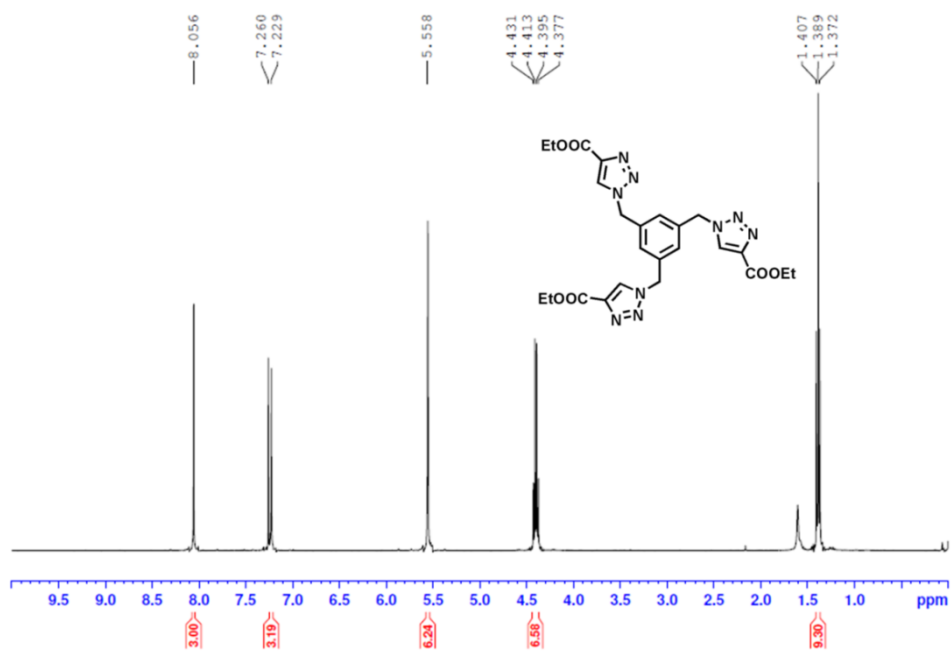


Fig. S8 $^1\text{H-NMR}$ spectra of cyclised product of 1, 3, 5- methylazidobenzene and ethyl propiolate in CDCl_3 .

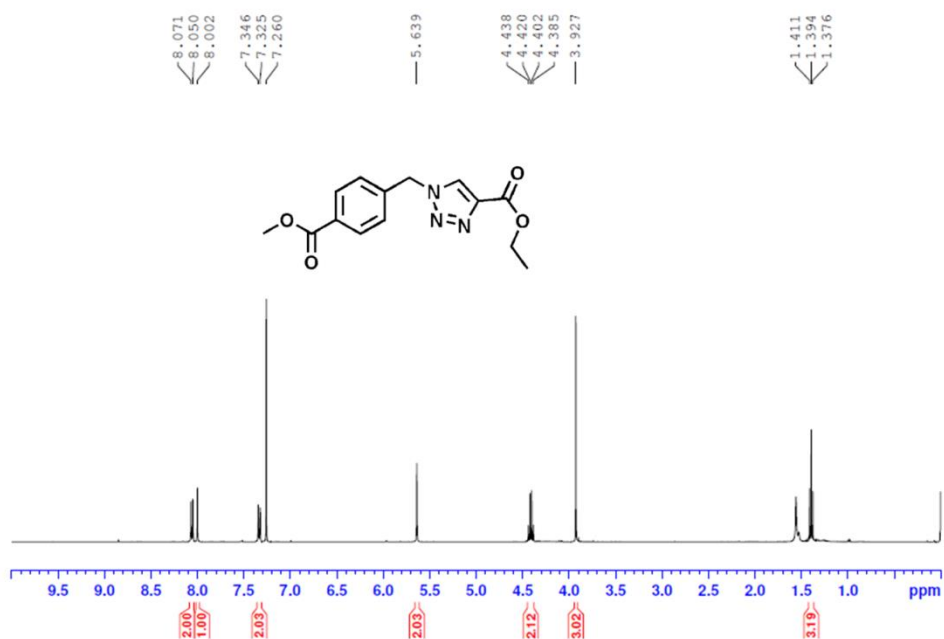


Fig. S9 ¹H-NMR spectra of cyclised product of methyl (4-methylazido)benzoate and ethyl propiolate in CDCl₃.

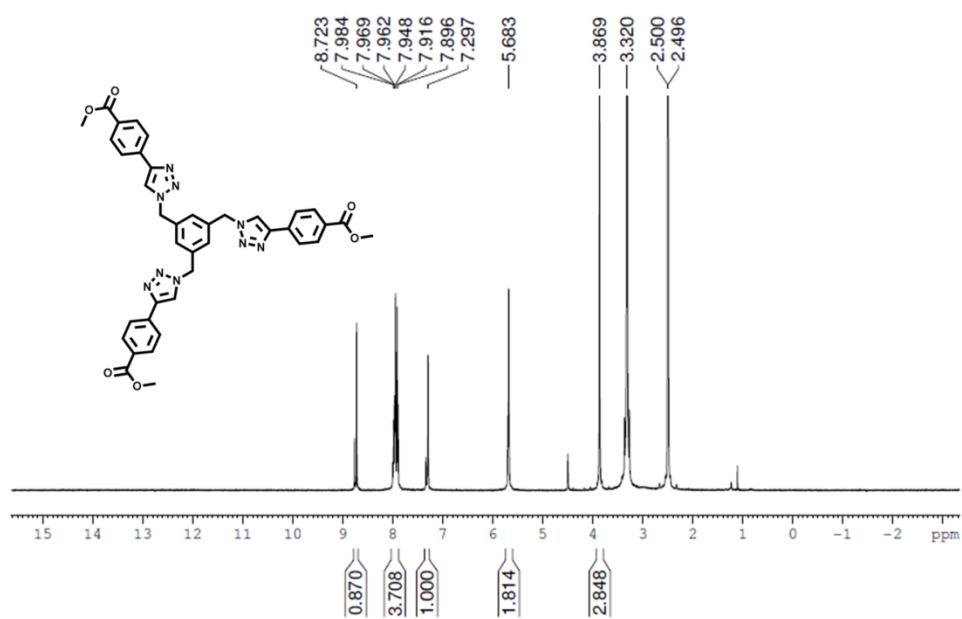


Fig. S10 ¹H-NMR spectra of cyclised product of 4-ethynyl-ethylbenzoate and 1, 3, 5-methylazidobenzene in dms-*d*₆.

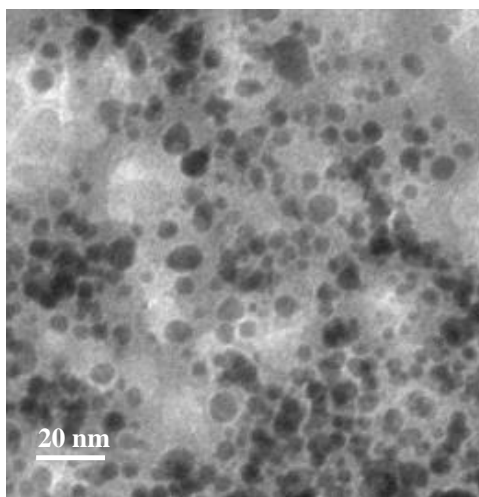


Fig. S11 TEM image of $\text{Cu}_2\text{O}@1\text{a}$ after three catalytic cycles.

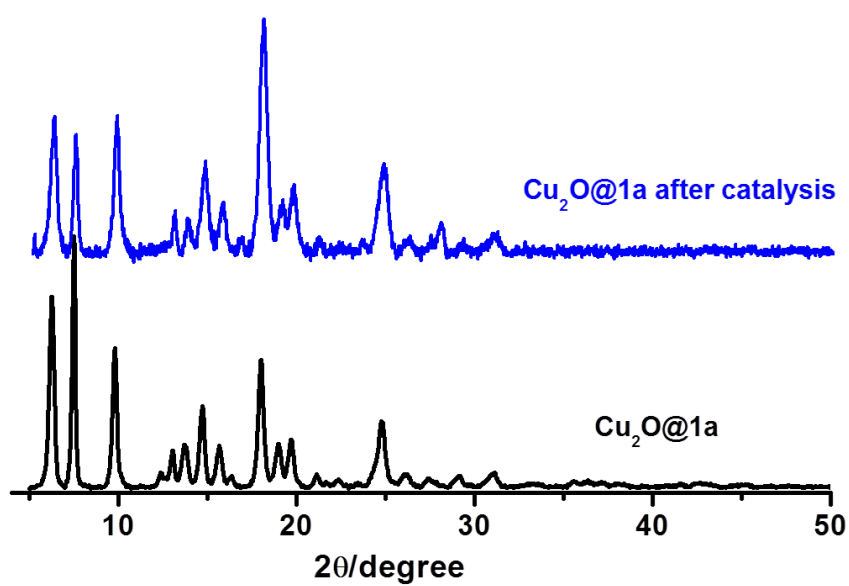


Fig. S12 PXRD pattern of $\text{Cu}_2\text{O}@1\text{a}$ before (black) and after (blue) three catalytic cycles.

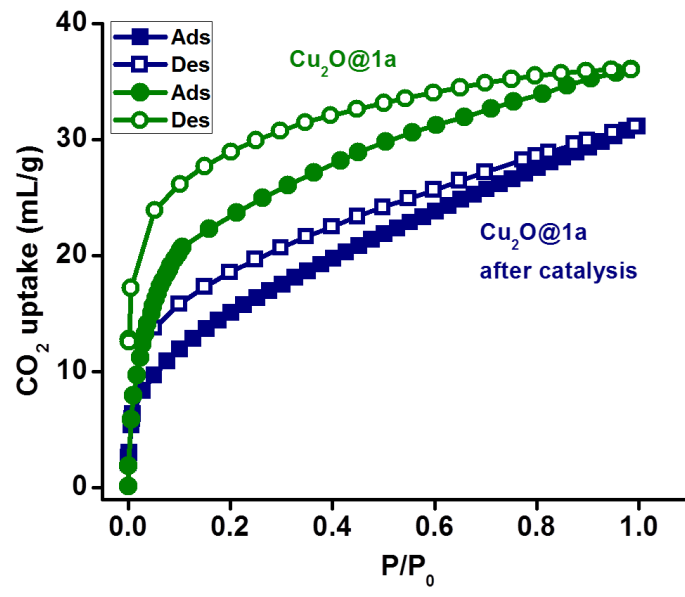


Fig. S13 CO₂ adsorption isotherm of Cu₂O@1a before (navy) and after (green) three catalytic cycles at 195 K upto 1 atm.