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From Zn(II) to Cu(II) Framework via Single-Crystal to Single-Crystal Metathesis with Superior Gas Uptake and Heterogeneous Catalytic Properties

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ABSTRACT: In this work, a Zn(II) framework, $\{[Zn_2(L)_4(H_2O)_4] \cdot (7DMF)(7H_2O)\}n$ ($\mathbf{1}_{Zn}$), has been synthesized using a bent tetracarboxylic acid ligand ($\mathbf{H}_4\mathbf{L}$). The structure of $\mathbf{1}_{Zn}$ contains $[Zn_2(COO)_4]$ paddle-wheel secondary building units with axial sites occupied by water molecules. Interestingly, the isostructural Cu(II) framework $\{[Cu_2(L)_4(H_2O)_4] \cdot (7DMF)(7H_2O)\}_n$ ($\mathbf{1}_{Cu}$) has been obtained via single-crystal to single-crystal metathesis reaction. The activated $\mathbf{1}_{Cu}$ (denoted as $\mathbf{a1}_{Cu}$; a stands for activated) has open coordination sites. This species showed enhanced CO₂ adsorption and heterogeneous catalytic properties for the Hantzsch coupling reaction involving condensation of an aldehyde with ethyl acetoacetate and ammonium acetate to produce 1,4-dihydropyridines, and three-component coupling of amines, aldehydes and alkynes to generate propargylic amines with high efficiency.

Keywords: Transmetalation; single crystal to single crystal; Gas Sorption; Catalysis.

INTRODUCTION

The design and synthesis of porous metal-organic frameworks (MOFs) has attracted remarkable attention because of their potential application in gas adsorption, catalysis, and so on.¹ For potential applications, particularly in gas adsorption and catalysis, MOFs should have high stability² that is still a challenging problem. It is well known that MOFs built with multi-metal clusters as nodes, known as the secondary building units (SBUs), impart rigidity to a framework besides stabilizing the MOF.³ Recently, the metal ions exchange (also known as metathesis)⁴ or

the organic linkers exchange⁵ have been reported. The metal ion exchange in single crystal to single crystal (SC-SC) fashion is a powerful technique for obtaining new materials endowed with enhanced stability and property. This process offers an alternative and effective route for accessing materials when the conventional direct synthesis fails.⁶ As an example, MOFs with $[Zn_2(COO)_4]$ paddle-wheel SBUs often collapse when the axially coordinated solvent molecules are removed exhibiting inferior applications.⁷ However, transmetalation of $[Zn_2(COO)_4]$ SBU of the pristine MOF with a metal ion such as Cu^{2+} (higher in the Irving-Williams series) without losing crystallinity is a fascinating technique that afford more stable frameworks with superior applications.⁵ Although the exchange of metal ions are simple, convenient and well reported, but most of the reports deals with incomplete transmetalation.⁸ Recently, several groups including our group have reported complete exchange of Zn^{2+} ions by the Cu^{2+} ions in a $[Zn_2(COO)_4]$ SBU containing MOF.⁷



Scheme 1. Synthesis of MOF 1_{Zn}.

Herein, we report the solvothermal synthesis of a Zn(II)-MOF, $\{[Zn_2(L)_4(H_2O)_4] \cdot (7DMF)(7H_2O)\}_n$ ($\mathbf{1}_{Zn}$) (Scheme 1), with paddle-wheel SBUs which was found to be of low thermal stability. This compound readily underwent complete SC-SC transmetalation at room temperature (RT) to afford the isostructural $\mathbf{1}_{Cu}$, that was thermally

robust and could be activated to produce guest free framework $\mathbf{a1}_{Cu}$. This activated compound exhibited significant capacity of adsorbing CO₂ gas besides showing heterogeneous catalytic activity.

EXPERIMENTAL SECTION

Materials and measurements. Reagent grade chemicals *p*-Anisidine (99%), 1-bromo-3,5dimethylbenzene (97%), trimethyl borate (99%), $Zn(NO_3)_2 \cdot 6H_2O$ (98%) and $Cu(NO_3)_2 \cdot 3H_2O$ (99%) were obtained from Sigma-Aldrich and used as received. All the solvents and Bromine were procured from S. D. Fine Chemicals (India) that were freshly purified prior to use.

Physical Measurements

The following Spectroscopic data were collected. IR spectra (KBr disk, 400–4000 cm⁻¹) were recorded on a Perkin-Elmer model 1320 spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded with a Bruker D8 Advance diffractometer equipped with nickel-filtered Cu K_a (1.5418 Å) radiation. The tube voltage and current were 40 kV and 40 mA, respectively. Microanalyses of all the compounds were carried out by using a Perkin-Elmer Series II, elemental analyzer model 2400. Electron paramagnetic resonance (EPR) spectra were obtained on a Bruker EMX EPR spectrometer. ICPMS measurements were carried out using Thermo-iCAP Q. Thermogravimetric analyses (TGA) (heating rate of 5 °C/min under nitrogen atmosphere) were performed with a Mettler Toledo Star System. ¹H NMR and ¹³C NMR spectra were recorded either on a JEOL ECX 500 FT (500, 125 MHz respectively) or on a JEOL ECS 400 FT (400, 100 MHz respectively) instrument in CDCl₃ or in DMSO-*d*₆ with Me₄Si as the

internal standard. The ESI-Mass data were obtained in a WATERS-Q-Tof Premier Mass Spectrometer.

X-Ray Structural Studies

The crystal data for $\mathbf{1}_{\mathbf{Zn}}$ has been collected on a Bruker SMART CCD diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å). The program SMART⁹ was used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT⁶ for integration of the intensity of reflections and scaling, SADABS¹⁰ for absorption correction, and SHELXTL¹¹ for space group and structure determination and least-squares refinements on F². The crystal structure were solved and refined by full-matrix least-squares methods against F² by using the program SHELXL-2014¹² using Olex-2 software.¹³ All the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen positions were fixed at calculated positions and refined isotropically. The solvent molecules in $\mathbf{1}_{\mathbf{Zn}}$ and $\mathbf{1}_{\mathbf{Cu}}$ are highly disordered. Therefore, the PLATON-SQUEEZE¹⁴ program was used to remove those peaks. The solvent molecules were calculated on the basis of combined study of TGA, elemental analysis, and removed electron counts which are included in the molecular formula. The crystal and refinement data are collected in Table S1, while selected bond distances and angles are given in Table S2 and S3.

Synthesis of ligand H₄L. Synthesis of the ligand, 2'-amino-5'-methoxy-[1,1':3',1''-terphenyl]-3,3",5,5"-tetracarboxylic acid (H₄L) was achieved in a multi-step procedure as illustrated in Scheme 2.



Scheme 2. Synthetic procedure for the ligand, H₄L

Synthesis of 2,6-dibromo-4-methoxybenzenamine (B). Compound 2,6-dibromo-4methoxylaniline was synthesized according to slightly modified procedure reported in literature.¹⁵ A solution of *p*-anisidine (5 g, 40.63 mmol) in methanol:DCM (50:40 mL) was vigorously stirred during the addition of bromine (4.9 mL, 95.48 mmol) drop wise over a period of 30 min in an ice-bath and then left for overnight stirring. Then the mixture was transferred to a 500 mL beaker and left for evaporation in the hood. When the volume was reduced to ~ 40 mL, white needle-shaped crystals appeared that was filtered off and washed with small amount of cold methanol and dried in air. The reaction afforded 22.5 g (~75% yield) of the title compound.

Synthesis of tetraethyl 2'-amino-5'-methoxy-[1,1':3',1''-terphenyl]-3,3'',5,5''tetracarboxylate (D). A solution of 3,5-bis(ethoxycarbonyl)phenylboronic acid (8.4 g, 39.84

mmol), and 2,6-dibromo-4-methoxybenzenamine (4.0 g, 18.12 mmol) in 1,4-dioxane (190 mL) was mixed with a solution of sodium carbonate (5.76 g, 54.33 mmol) and palladium triphenylphosphine (656 mg) in water (10 mL). The mixture was allowed to stir at 90°C overnight under nitrogen atmosphere. The mixture was allowed to cool to RT and then evaporated to dryness. The desired compound was extracted with ethyl acetate in water. The organic layer after drying over anhydrous sodium sulfate was evaporated under reduced pressure. This compound was recrystallized from DCM:MeCN (1:9) as a pale yellow block shaped crystals in ~85% yield, (8.2 g). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 8,46 (s, 2H), 8.24 (s, 4H), 6.77 (s, 2H), 4.38 (q, 8H), 3.73 (s, 3H), 1.35 (t, 12H) ppm; ¹³C (125 MHz, DMSO-*d*₆): δ = 164.87, 151.35, 140.48, 135.52, 134.13, 131.01, 128.09, 126.46, 116.00, 61.27, 55.57, 14.11 ppm. ESI-MS: (m/z): 564.22 (100%) [M+H]⁺ (Figs. S1–S3).

Synthesis of 3'-amino-1,1':4',1"-terphenyl-3,3",5,5"-tetracarboxylic acid (H₄L). To a solution of the ester **D** (2.00 g, 3.65 mmol) in methanol (100 mL) and water (50 mL), KOH (1.46 g, 26.07 mmol) was added in hot condition. The mixture was refluxed overnight. After removal of most of the solvent, water was added to fully dissolve the precipitate and acidified with concentrated HCl up to pH ~3 in an ice-bath. The yellow precipitate formed was collected by filtration, washed with ice cold water and dried *in vacuo* to obtain the ligand, H₄L with an yield of 1.46 g (90%). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 8.41 (s, 2H), 8.10 (s, 4H), 6.88 (s, 2H), 3.70 (s, 3H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 166.38, 140.12, 133.74, 132.17, 131.63, 131.25, 130.64, 128.42, 125.81, 19.63; ESI-MS: (m/z): 450.08 (100%) [M-H]⁺. FTIR (KBr pellets) (cm⁻¹): 3441.79 (br), 2926.23 (m), 1707.80 (s), 1631.86 (w), 1598.69 (m), 1472.27 (m), 1427.76 (m), 1267.22 (w), 1211.03 (s), 1107.61 (w), 1044.89 (m), 920.85 (w), 862.87 (w),

766.14 (m), 674.04 (m), 656.91 (m). Anal. calcd. for C₂₃H₁₇NO₉: C, 61.20; H, 3.80; N, 3.10%. Found: C, 61.25; H, 3.78; N, 3.15% (Figs. S4–S7).

Synthesis of {[$Zn_2(L)_4(H_2O)_4$]·(7DMF)(7H₂O)}_n (1_{Zn}). Zn(NO₃)₂·6H₂O (60 mg, 0.20 mmol), and H₄L (20 mg, 0.044 mmol) were dissolved in 2 mL DMF and 1 mL H₂O. The mixture was placed in a Teflon-lined stainless steel autoclave and heated under autogenous pressure to 90 °C for 3 d and then allowed to cool to room temperature slowly. Block-shaped colorless crystals of 1_{Zn} were collected by filtration and washed with DMF and methanol. Finally the crystal was dried in the air. Yield ~55%. FTIR (KBr pellets) (cm⁻¹): 3395.97 (broad), 1702.98 (m), 1618.21 (s), 1567.39(m), 1468.24(w), 1426.65 (m), 1363.42 (s), 1224.84 (w), 1208 (m), 1147.69 (w), 1042.29 (m), 920.37 (m), 856.77 (w), 778.43 (s), 717.06 (s). Anal. Calcd. For C₅₁H₈₀N₁₀O₂₆Zn₂: C, 44.39; H, 5.84; N, 10.15%. Found: C, 44.41; H, 5.82; N, 10.12% (Fig. S8).

Synthesis of {[$Cu_2(L)_4(H_2O)_4$]·(7DMF)(7H₂O)}*n* (1_{Cu}). The as-synthesized single crystals of 1_{Zn} were soaked in DMF for 2 days to remove any remaining reactants and unwanted products that may be adhered. During the soaking process, the solvent was refreshed twice. After that, the crystals were immersed in DMF solution of $Cu(NO_3)_2$ ·3H₂O (0.05 M) at room temperature for about 7 d. During this period, the solution was replaced with a fresh solution of $Cu(NO_3)_2$ ·3H₂O in DMF after each day. The Cu-exchanged crystals (1_{Cu}) were washed thoroughly with DMF and kept in DMF for 2 d to remove any excess metal salt from the pores of the framework. FTIR (KBr pellets) (cm⁻¹): 3388.99 (broad), 1620.14 (m), 1561.50 (s), 1468.17(w), 1426.47(m), 1363.63 (s), 1208.70 (m), 1147.87 (w), 1111.26 (w), 1042.99 (m), 920.37 (w), 856.59 (w), 777.33 (s), 718.67 (s). Anal. Calcd. For $C_{51}H_{82}N_{10}O_{26}Cu_2$ (1_{Cu}): C, 44.44; H, 6.0; N, 10.16 %. Found: C, 44.48; H, 6.12; N, 10.19% (Fig. S8).

Heterogeneous catalysis

Catalyst $\mathbf{1}_{Cu}$ was activated by heating at 120 °C under high vacuum for a period of 8 h in order to remove all traces of lattice and coordinated solvent. Before activation crystals were soaked in methanol for four days, which was changed two times per day with fresh methanol. The sample thus produced ($\mathbf{a1}_{Cu}$) was used for Hantzsch condensation and three-component coupling reaction involving amines, aldehydes and alkynes. Hantzsch condensation of aldehyde, ethyl acetoacetate with NH₄OAc without any salts or additives to afford 1,4-dihydropyridines, with excellent to good yields. Dihydropyridines have emerged as one of the most important classes of drugs for cardiovascular diseases and have more biological and medicinal interest.¹⁶ Furthermore, $\mathbf{a1}_{Cu}$ shows three-component coupling of amines, aldehydes and alkynes to afford propargylamines which are versatile intermediates in organic synthesis, also being important structural elements of natural products and therapeutic drug molecules.¹⁷

General procedure for the synthesis of Hanstzsch esters (1,4-Dihydropyridines). Reactions were carried out in a Schlenk tube with stirring at room temperature using 1ml dry DCM as a solvent. Aldehyde (2 mmol), Ethylacetoacetate (4.1 mmol), NH₄OAc (2 mmol) and catalyst $a1_{Cu}$ (5 mol %) were added. Upon completion, the reaction mixture and catalyst were separated by filtration to obtain crude compound. This crude mixture was extracted with DCM and further purified with small column of silica gel using hexane/ethyl acetate as the eluent.

General procedure for the synthesis of propargylamines by one-pot A³-coupling reactions. Synthesis and work-up procedure is same as above used in Hantzsch synthesis. Here the reactions were carried out at 70 °C using aldehyde (1 mmol), alkyne (1 mmol) and amine (1 mmol).

RESULTS AND DISCUSSION

A solvothermal reaction of the organic linker, H_4L , and $Zn(NO_3)_2$ in a mixed solvent of N,N'dimethyl formamide (DMF) and H₂O at 90 °C for 3 days afforded colorless block shaped crystals of 1_{Zn} . The structure was determined using single-crystal X-ray diffraction studies. On the basis of single-crystal X-ray diffraction analysis, thermogravimetric analysis (TGA, Fig. S9), and elemental analysis, $\mathbf{1}_{\mathbf{Zn}}$ could be formulated as $\{[\mathbf{Zn}_2(\mathbf{L})_4(\mathbf{H}_2\mathbf{O})_4] \cdot (7\mathbf{DMF})(7\mathbf{H}_2\mathbf{O})\}_n$. The phase purity of the bulk material was further confirmed using powder X-ray diffraction (PXRD, Fig. S10). Single-crystal X-ray diffraction analysis revealed that 1_{Zn} crystallized in the $P6_3/mmc$ space group with assymteric unit comprised of a quarter of the ligand, L^{4-} , a Zn(II) ion and a coordinated water molecule each with half occupancy. As expected, the framework nodes in 1_{Zn} were composed of paddlewheel dinuclear $[Zn_2(COO)_4]$ secondary building units (SBUs; Fig. 1a) (The Zn···Zn bond distance was 2.982(3) Å) which were bridged by the carboxylate groups of L^4 . The Zn···O bond distances fall in the range, 1.962(3) to 2.014(4) Å) to form a three dimensional framework. As depicted in Fig. 1b two types of spherical cage were found in the framework 1_{Zn} : one larger cage (green color) of about 10 Å in diameter and the other smaller cage (yellow color) of about 8 Å in diameter. These cages were further connected to each other via small triangular windows of dimensions ~5 Å. The bigger cage was in close proximity with the methoxy group while the smaller cages were decorated with the -NH₂ groups.



Fig. 1. (a) Coordination environment around Zn^{2+} ions in 1_{Zn} , (b) spherical cages in 1_{Zn} .

The empty space in the framework was filled with disordered solvent molecules whose composition was established from thermogravimetric weight-loss, IR spectra and elemental analysis. The values were in good agreement with PLATON¹¹ calculated solvent-accessible void volume which was found to be 60.4% (4357.2/7208.9 Å³) of the total cell volume.

 1_{Zn} was found to be stable up to 60 °C as confirmed by thermogravimetric analysis (Fig. S9) and VTPXRD (Fig. S10). As Zn(II), a d¹⁰ ion without any ligand field stablization energy, upon removal of axially bound water molecule, its coordination number changed from 5 to 4 and the coordination geometry changed from square pyramidal to tetrahedral and collapsing of the system. In case of Cu(II) SBUs, the departure of the axially bound water changed the coordination geometry to a stable square planar. This encouraged us to explore post-synthetic transmetalation in 1_{Zn} . Upon dipping single crystals of 1_{Zn} in a Cu(NO₃)₂·3H₂O (0.05 M)

solution of DMF at room temperature, crystals gradually changed from colourless to greenish blue within 7 d. Optical microscopic observation revealed that the pristine crystals retain their original morphology during the exchange process (Fig. S11). Primarily EPR spectrum was taken to confirm the exchange of Zn^{2+} with a Cu^{2+} ion (Fig. S12) of the greenish blue crystals. Also, the PXRD pattern before and after the metal exchange remained unaltered (Fig. S13). The exchange of Zn^{2+} with a Cu^{2+} ion and the kinetics (Fig. 2) were also monitored by energy dispersive X-ray (EDX) (Fig. S14). It showed 70% replacement of Zn²⁺ by Cu²⁺ within 2 d, while 95% exchange took place in 6 d. A complete exchange was achieved in 7 d. Inductively coupled plasma mass spectrometry (ICP-MS) measurements showed 99.66% Cu(II) ions and 0.34 % Zn(II) ions present (see SI). The replacement of the Zn(II) ions in $\mathbf{1}_{Zn}$ could be achieved only partially with metal ions like Co^{2+} and Ni^{2+} . However, the Cu^{2+} ions in $\mathbf{1}_{Cu}$ could not be replaced by other metal ions like Zn^{2+} , Co^{2+} and Ni^{2+} . Hence, the metal exchange process is irreversible here. Fortunately, the single crystallinity of $\mathbf{1}_{Cu}$ was maintained after an exchange period of 7 d, allowing single-crystal X-ray data collection. The X-ray structural study indicated (Table S1) that $\mathbf{1}_{Zn}$ and the transmetalated product $(\mathbf{1}_{Cu})$ are iso-structural. It should be mentioned here that all attempts for direct synthesis of 1_{Cu} remained unsuccessful.



Fig. 2. Kinetic profile of the Zn(II) to Cu(II) exchange process.

The compound $\mathbf{1}_{Cu}$ was found to be stable beyond 180 °C, as confirmed by its thermogravimetric analysis (Fig. S9) and VTPXRD (Fig. S15) measurements. As mentioned earlier, the framework started break down in case of $\mathbf{1}_{Zn}$ at 60 °C while $\mathbf{1}_{Cu}$ maintained its integrity beyond 180 °C. Also, in case of $\mathbf{1}_{Cu}$ the crystallinity was preserved after the removal of coordinating water molecule (Fig. S16). The reasonably high thermal stability, 3D porous structure and presence of axially vacated paddle-wheel SBU prompted us to test the gas adsorption measurements.

Gas adsorption studies.

Before gas sorption analysis, the as-synthesized compounds were solvent-exchanged with dry methanol and then heated at 120°C under high vacuum for 12 h to yield fully activated frameworks $\mathbf{a1}_{\mathbf{Zn}}$ and $\mathbf{a1}_{\mathbf{Cu}}$. The permanent porosity of $\mathbf{a1}_{\mathbf{Zn}}$ and $\mathbf{a1}_{\mathbf{Cu}}$ were unambiguously established by nitrogen adsorption experiments at 77 K. As shown in Fig. 3a, $\mathbf{a1}_{\mathbf{Zn}}$ showed merely an uptake of 62.1 cc/g while $\mathbf{a1}_{\mathbf{Cu}}$ exhibited a reversible type I sorption behavior revealing its microporous nature with a maximum N₂ uptake of 494 cc g⁻¹ corresponding to the BET surface area of 1512 m²g⁻¹.

Presence of the free amine groups prompted us to carry out CO₂ adsorption measurements at 273 and 298 K, and the results are illustrated in Fig. 3b. At 273 K and 1 bar pressure, an adsorbed amount of 174 cc g⁻¹ (34.2 wt %) while at 298 K an uptake of 116 cc g⁻¹ (22.8 wt %) were recorded reached for **a1**_{Cu}. On the other hand, for **a1**_{Zn}, the maximum uptake at 273 was 23.3 cc g⁻¹ (4.6 wt %) whereas at 298 K it dropped to merely 13.6 cc g⁻¹ (2.7 wt %).

These results clearly implied that after transmetalation, the framework showed much more improved adsorption capacity.^{7, 18}



Fig. 3. Physisorption isotherms: (a) N_2 at 77 K, and (b) CO_2 at 273 and 298 K.

Catalytic study

(i) Hantzsch coupling. The efficacy of $a1_{Cu}$ as a catalyst in Hantzsch coupling reaction was studied for the synthesis of 1,4-dihydropyridines. For this, benzaldehyde, ammonium acetate and ethyl acetylacetonate were chosen as the substrates in the model reaction under different catalyst loading at room temperature. The reaction was carried out in the presence of 2, 3, 4 and 5 wt % of the catalyst under the same conditions, that showed improved yield with increasing the catalyst loading. Further, increasing the catalyst loading (10 wt %) did not improve the yield significantly. It should be pointed out that in the absence of catalyst, the reaction was very sluggish and even after a prolonged reaction time (24 h), substantial amounts of starting

materials remained unreacted (Table 1, entry 12) with only ~13 % yield. It should be emphasized that in this waste-free catalytic system, no byproduct was observed in the reaction.

The basic nature of the amine-decorated MOF played an important role in the synthesis of 1,4-dihydropyridines with excellent yields (90%; Table 1, entry 1) in comparison to a similar non-amine isostructural MOF (PCN-306) (83%) (Table 1, entry 2). The catalytic activity of $\mathbf{a1}_{Cu}$ is better than or comparable to other reported MOF, such as Er-MOF (92 % yield) reported by Hajiashraf *et al.*¹⁹, TMU-33 (91.2 % yield) reported by Morsali *et al.*²⁰, IRMOF-3 (89% yield) reported by Morsali *et al.*²¹ When the model reaction was run using $\mathbf{a1}_{Zn}$, the product was obtained in 24% yield in 12 h (Table 1, entry 13). In order to examine the scope of this process, and to demonstrate the diversity of $\mathbf{a1}_{Cu}$, the optimized conditions were applied to a series of substrates as collected in Table 1.







^{*a*}Reaction conditions: Aldehyde (1 mmol), NH₄OAc (1 mmol) and ethyl acetoacetate (4.1 equiv) and cat. (5 wt %), r.t. for 4h. ^{*b*}Isolated yields based on aldehyde.

The possibility of recycling and reusing the catalyst was examined. After completion of the reaction, the mixture was treated in CH₂Cl₂ and the catalyst was removed by filtration. The catalyst was washed with CH₂Cl₂, dried and heated at 120 °C under vacuum for 5 h to reuse in the next run. The catalyst could be recycled at least four times without measurable loss of its activity (Fig. S18). Formation of the desired product, 1,4-dihydropyridines, was confirmed by the ¹H NMR and ¹³C NMR data (Figs. S19–S38). Further investigation of the heterogeneous nature of the catalyst as well as stability of the framework was carried out using a filtration test. After 1 h of the reaction, the reaction mixture was filtered and the catalyst was removed. Then, the supernatant was left stirring at the same reaction conditions. Within 3 h of further reaction time, no distinguishable changes were recognized in the reaction conversion (Fig. S39). Also, the PXRD pattern of 1_{Cu} before and after the reaction indicates that the framework remained intact after the catalytic reaction (Fig. S16). A tentative mechanism for the Hantzsch coupling reactions²⁰ was proposed and is given in the SI (Scheme S1).

(ii) A³-coupling reactions. The development of heterogeneous catalysts for preparing propargylamines by the A³ coupling reaction remains an active research area.²² As is known, propargylamines are versatile intermediates in organic synthesis, also being important structural elements of natural products and therapeutic drug molecules.²³ In this work, the A³-coupling reaction was chosen to evaluate the activity of the $\mathbf{a1}_{Cu}$. The reaction afforded 100% selectivity to the product of propargylamine. In an effort, the coupling reaction of benzaldehyde (1 mmol), phenylacetylene (1.1 mmol), and pyrrolidine (1.1 mmol) was carried out using 5 mol % of $\mathbf{a1}_{Cu}$

at 70 °C for 12 h. The reaction produced 93% isolated yield (Table 2, entry 1). Subsequently, various aldehydes, alkynes, and amines were similarly coupled as summarized in Table 2. However, the reaction was found to be highly affected by the nature of the aldehyde. Aryl aldehyde having electron donating group decreased the reactivity of the reaction and gave lower yields (Table 2, entry 2). Aryl aldehydes having electron withdrawing group on the other hand, displayed higher reactivity (Table 2, entry 3). In case of piperidine, we got slightly higher yield (96%) (Table 2, entry 9) than that of pyrrolidine (93%). A variety of aromatic alkynes were coupled with benzaldehyde and pyrrolidine in the presence of the **al**_{Cu} catalyst. In each case the reaction afforded the corresponding propargylamines in excellent yields (Table 2). Formation of the desired product, propargylamines, was confirmed by the ¹H NMR and ¹³C NMR data (Figs. S40–S57). The catalytic activity of **al**_{Cu} is better than or comparable to other reported MOF, such as Cu(II)-MOF (89 % yield) reported by Kostakis *et al.*²⁴, Cu(I)-MOF (89 % yield) reported by Kostakis *et al.*²⁴, Cu(I)-MOF (89 % yield) reported by Wang *et al.*²⁶, Cu(I)-modified zeolites, Cu¹-USY (95% yield) reported by Sommer *et al.*²⁷

After 3 h of reaction, the catalyst was separated by hot filtration and the filtrate was allowed to react under identical reaction conditions for another 9 h. As a result, no further conversion was detected after the catalyst removal (Fig. S58). As shown in Fig. S59 in the SI, 1_{Cu} could be recycled for at least four runs without a significant loss of performance. PXRD data of the recycled catalyst showed that its crystalline structure was retained (Fig. S17). A tentative mechanism for the A³-coupling reactions was proposed based on previous report²⁸ and is given in the SI (Scheme S2)

Table 2. Synthesis of propargylamines by A³-coupling reactions^a



^{*a*}Reaction conditions: Aldehyde (1 mmol), acetylene (1.1 mmol), pyrrolidine (1.1 mmol), and cat. (5 mol %), 70 °C for 12 h. ^{*b*}Isolated yields based on aldehyde.

Conclusions

We have successfully synthesized a thermally robust and porous Cu-framework $\mathbf{1}_{Cu}$ from the isostructural less stable Zn-framework $\mathbf{1}_{Zn}$ using a post-synthetic metathesis approach. Unlike the activated $\mathbf{a1}_{Zn}$, $\mathbf{a1}_{Cu}$ exhibited significant N₂ and CO₂ adsorption properties. Compound $\mathbf{a1}_{Cu}$, having both high populations of Lewis acid and basic sites, showed excellent catalytic performance in the Hantzsch coupling reaction as well as three-component coupling of amines, aldehydes and alkynes to generate propargylic amines with high efficiency.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the at DOI: X-ray crystallographic data of 1_{Zn} (CCDC 1838277) and 1_{Cu} (CCDC 1838278) (CIF) Materials and methods, X-ray structural studies, ESI-MS spectra, IR spectra, TGA, PXRD, NMR spectra, and additional Fig.s (pdf).

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Notes

The authors declare no competing financial interest.

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