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Chemical Fixation of CO₂ and Other Heterogeneous Catalytic Studies Employing a Layered Cu-Porphyrin Prepared Through Single-Crystal to Single-Crystal Exchange of a Zn-analogue

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Abstract: A solvothermal reaction of Zn(NO₃)₂.6H₂O, tetra-(4pyridyl)porphyrin (H₂TPyP) and 4,4'-Oxybis(benzoic acid) (H₂OBA) resulted in a new two-dimensional Zn-porphyrin MOF compound, $[Zn_2(C_{40}H_{24}N_8)_{0.5}(C_{14}H_8O_5)(DMA)](DMA)(H_2O)_6$, 1. The Zn(II) ions present in 1 could be ion-exchanged employing Cu(NO₃)₂.3H₂O solution at room temperature resulting in $[Cu_2(C_{40}H_{24}N_8)_{0.5}(C_{14}H_8O_5)(DMA)](DMA)(H_2O)_3, (Cu \in 1)$ compound. The extra-framework solvent molecules have been shown to be reversibly removed/exchanged without the collapse of the framework. The solvent-free Cue1 was explored as an active heterogeneous catalyst towards three different organic reactions: (i) chemical fixation of CO₂ into cyclic carbonate at room temperature under 1 atm; (ii) nitroaldol reaction under solvent free condition and (iii) three component coupling of aminopyridine, benzaldehyde and aryl alkynes followed by 5-exo-dig cyclization to produce an important pharmacophore imidazopyridine.

Introduction

Metal-Organic framework (MOF) compounds have been in the forefront of research for the last two decades.^[1] The continued interest is due to the many properties exhibited by this class of compounds in the areas of sorption, separation and catalysis.^[2] The MOFs also offer opportunities to control the structure to realize properties such as proton-conduction,^[3] magnetism^[4] etc. In recent times the structural emphasis of research on MOFs has migrated towards compounds with targeted properties.

The MOFs have been traditionally prepared by a cooperative and synergistic assembly between the metal ions and the organic ligand. The MOFs also encompass preassembled molecular entities such as cyclodextrin,^[5] porphyrin^[6] and metaloxo clusters^[7] as part of the structures. Such assemblage leads to structures that are not only interesting but also exhibit newer properties. We have been particularly intrigued by the porphyrin based assemblies that are incorporated as part of the MOF structures. Metalloporphyrins have been actively researched over the years for their use in many areas. The foremost being the Fe-porphyrin, which is an important co-factor in oxygen transport.^[8] Many metalloporphyrins have also been explored for catalysis.^[9] The versatility along with the rigidity of the metalloporphyrin is attractive in building new MOFs. The porphyrin MOFs can find applications in non-linear optics, ionphotosensitization exchange, selective catalysis, and photovoltoics.^[10] This area has attracted much attention over the

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years.^[11] We have been investigating the porphyrin based employing framework 5,10,15,20-tetrakis(4pyridyl)porphyrin(TPyP) along with aromatic dicarboxylates.^[12] In continuation of the theme, we have now prepared a new porphyrinic MOF [Zn₂(C₄₀H₂₄N₈)_{0.5}(C₁₄H₈O₅)(DMA)](DMA) (H₂O)₆, 1 employing TPyP, Zn²⁺ ion and 4,4'-oxybisbenzoic acid (H₂OBA) (Scheme 1). The compound crystallizes with a twodimensional layered structure. The Zn²⁺ ions were exchanged by Cu2+ ions by post-synthetic ion-exchange methods in a singlecrystal to single-crystal (SCSC) fashion forming the copper exchanged compound $[Cu_2(C_{40}H_{24}N_8)_{0.5}(C_{14}H_8O_5)(DMA)](DMA)(H_2O)_3$ (Cu∈1). The

copper compound, $Cu \in 1$, exhibits good catalytic activity for a number of organic reactions. In this paper, we present the synthesis, SCSC transformation studies, characterizations and catalytic behavior of the $Cu \in 1$ compound.



Reaction condition : (i) Zn(NO₃)₂.6H₂O/DMA/HBF₄/100°C/ 3days

Scheme 1: Scheme showing the sovothermal synthesis of 1.

Results and Discussion

Structure of $[Zn_2(C_{40}H_{24}N_8)_{0.5}(C_{14}H_8O_5)(DMA)]$ (DMA) (H₂O)₆,1: Compound 1 crystallizes in triclinic P-1 space group. The asymmetric unit contains 51 non hydrogen atoms (Figure S1 in the supporting information) of which two zinc atoms are distinct. Zn(1) exhibits a distorted square pyramidal geometry with four pyrrole nitrogen atoms [N(1), N(2), N(1)(#1) and N(2)(#2)] in the equatorial position and one oxygen atom [O(1)] from the solvent molecule in the axial position (Figure S2 in the supporting information). Zn(2) has a tetrahedral geometry with two carboxylate oxygen [O(2) and O(4)] from 4,4'-Oxybis(benzoic acid) and two nitrogen atoms [N(3) and N(4)] from TPyP ligand (Figure S2). The Zn(1) atom was observed to be moved away from the porphyrin plane towards the axially coordinated solvent molecule with a deviation of 0.610 Å. The Zn-O bond distances are in the range of 1.940(3)Å-2.069(8)Å and the Zn-N bond distances are in the range of 2.025(3)Å-2.139(4)Å. The structure consists of a connectivity between the Zn-porphyrin units and

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Zn-OBA units. Thus the Zn-porphyrin units are connected to Zn(2) atoms forming a one-dimensional chain (Figure 1a). The 1D chains are further connected by the 4,4'-Oxybis(benzoic acid) forming the 2D structure (Figure 1b). The 2D layers are stacked one over the other in an AAA... fashion (Figure 1c). The two-dimensional layers encompasses a large aperture of 26.3x21.6 Å (shortest atom-atom contact distance not including the van der Walls radii) within the sheet. Such is the disposition of the layers that pores of this diameter penetrate the entire structure in a direction perpendicular to the layers, thus yielding a solid with unidimensional pores. The channels are occupied by disordered solvent molecules. A PLATON calculation reveals a solvent accessible void volume of 62%.

The presence of channel-like features in 1 prompted us to explore the possibility of transmetallation of Zn²⁺ ions with Cu²⁺ ions. To this end the as-synthesized crystal were soaked in DMA solution of Cu(NO₃)₂ at room temperature. The copper nitrate solution was periodically replenished for better ion-exchange. It was observed that all Zn²⁺ ions can be fully exchanged by Cu²⁺ ions in 8 days. The replacement (>98%) was confirmed by EDAX and AAS (Figure S3 and S4 in the supporting information). We did not observe any change in the crystalline shape or size, suggesting that the metal-ion exchange is facile. In addition we observed that the Cu-exchanged sample (hereafter Cu∈1) exhibited identical PXRD pattern as that of the parent Zncompound (Figure S5 in the supporting information). Thus we have successfully carried out a single-crystal to single-crystal transmetallation in the present study. A single crystal structure study on the Cu-exchanged sample indicated an identical structure to that of the Zn-compound. It may be noted that the Cu∈1 sample would have a square-pyramidal copper within the porphyrin and a tetrahedral copper coordinated by two oxygens of OBA and two nitrogens from pyridine. We also explored the reversible transmetallation of Cu∈1 to the present Zn-compound by performing an similar experiment employing DMA solution of Zn(NO₃)₂.6H₂O. Even after 30 days of soaking, we did not observe the transmetallation to the parent Zn-compound.



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Figure 1. (a) Figure shows the connectivity between the Zn-porphyrinic units through the Zn-centers forming a one-dimensional unit; (b) The connectivity between the 1D units and the 4,4'-Oxybis(benzoic acid) forming two-dimensional arrangement; (c) The arrangement of layers. Arranged in a AAA...type stacking.

UV-vis and Photoluminescence Studies: The optical property of the compounds was examined at room temperature employing UV-vis and photoluminescence studies. Expectedly, the optical behavior strongly depends on the porphyrin unit in the structure. The solid state UV-vis spectra of compound 1 and **Cue1** exhibited Soret bands at 410 nm and 406 nm (S₀→S₂ absorption) and four Q bands in the range 450 nm-610 nm due to the π - π^* transitions of the H₂TPyP ligand (S₀→S₁) (Figure S6 in the supporting information). The red-shift of the absorption bands in 1 and **Cue1** compared to the H₂TPyP ligand and the reduction in the number of Q-bands indicate that the Zn²⁺ and the Cu²⁺ ions have been incorporated in the porphyrin core.

The emission spectra of both the Zn and Cu compounds were examined in the solid state at room temperature using an excitation wavelength of 410 nm (Figure S7 in the supporting information). The emission bands observed, in the range 532-663 nm in 1 and 531-669 nm in **Cue1**, are due to the intraligand emission from the H₂TPyP ligand. An emission band observed at ~532nm for 1 and **Cue1** may correspond to the $e_g \rightarrow a_{1u}$ transition. The bands observed in the range of 625 and 663 nm for 1; 631 and 669 nm for **Cue1** can be ascribed to $e_{gx} \rightarrow a_{2u}$ and $e_{gy} \rightarrow a_{2u}$ transitions respectively. The quantum yield for emission is 3.70 for 1 and 0.95 for **Cue1** (Figure S7 in the supporting information).

Thermal Stability:

(c)

Thermogravimetric analysis (TGA) was employed to investigate the thermal stability of the compounds. Thermogravimetric study on Zn-compound (1) (Figure S8 in the supporting information) exhibits a weight loss of 39.7% in the temperature range 30-205°C which would correspond to the loss of 2 DMA and 6H₂O molecules (calc. 39.6%). A flat region in the temperature range 205-335°C indicates that the compound may be stable upto 335°C. Above 335°C a steady weight loss was observed indicating collapse of the framework. We investigated the removal of solvent molecules from 1 and the stability of the framework. The as-synthesized 1 was kept in vacuum oven at 205°C. The evacuated sample exhibited a PXRD that is similar to the as prepared parent compound suggesting that the structural integrity is retained (Figure S9 in the supporting information). The evacuated sample readily absorbs solvent

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molecules, when immersed into the solvent. The resolvated sample exhibits a behavior that is comparable to the assynthesized sample under the TGA studies. The final calcined product was found to be crystalline and corresponds to ZnO (JCPDS: 36-1451) (Figure S10 in the supporting information). The removal of the water molecules from the compound was also investigated using *in-situ* temperature programmed IR measurements. The studies clearly indicated that the water molecules are completely removed ~180°C (Figure S11 in the supporting information). The evacuated sample (solvent removed) was also analyzed employing TGA studies. We observed no major weight loss upto 225°C, suggesting that the solvent molecules have been removed from the compound.

The Cu-compound (**Cu**∈1) also exhibited a similar behavior as that of 1 in the TGA study (Figure S8 in the supporting information). A weight loss of 32.1% in the range 30-207°C may correspond to the loss 2DMA and 3H₂O molecules (calc. 32.2%). The framework also appears to be stable upto 325°C and starts to collapse after that. The final calcined product was found to be CuO (JCPDS: 65-2309) (Figure S13 in the supporting information).

Catalytic studies on Cue1: To prepare the catalyst, we activated **Cue1** by immersing in MeOH for 5 days at room temperature. This methanol soaked sample was heated at 60° C in vacuum oven for 24 hrs which resulted in activated **Cue1** ready to be employed for catalytic investigations. A PXRD study of the activated sample indicated that the structural integrity was retained (Figure S14 in the supporting information). We have attempted three different catalytic reactions employing the activated **Cue1** catalyst.



Table 1: Table summarizing the Cue1 catalyzed cycloaddition of CO_2 and epoxides to form cyclic carbonates



Scheme 2. Possible mechanism for the formation of cyclic carbonate

(a) The cycloaddition reaction of epoxide and CO₂ under ambient conditions: Cyclic carbonates, formed by the coupling of epoxide and CO₂, have been of interest for their application as aprotic polar solvents, electrolyte for lithium battery, fuel additives, synthetic intermediates for polycarbonate etc.^[13] Many different catalysts such as metal oxides, zeolites, titanosilicate and ion-exchanged resins have been explored for the coupling



In a typical reaction, 20 mmol of the epoxide substrate, 0.065 g of tetra-n-tert-butylammonium bromide co-catalyst (TBAB, 10

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mol%) and 0.010 g (1 mol % based on Cu) **Cu** \in 1 were added into a Schlenk tube. The tube was purged with CO₂ at 1 atm under solvent free conditions onto a mechanical shaker for 30 h for completing the catalytic reaction. The mixture was then filtered and purified in a silica gel column to get the desired product. The catalyst recovered from the reaction, have been tested for recyclability. The studies confirmed that the catalyst can be effectively used upto four cycles without losing any activity (Figure S15 in the supporting information).



Scheme 3. A possible mechanistic pathway for the nitroaldol reaction

(b) The nitroaldol (Henry) reaction: The addition of nitroalkanes to carbonyl compounds known as Henry reaction (or nitroaldol) is considered as an effective, powerful and atomeconomic synthetic tool for the formation of carbon-carbon bond.^[16] There have been a number of different catalysts such as alkali metal hydroxides, alkoxides and many Zn and Cucomplexes have been explored for the nitroaldol reaction.^[17] It is still a challenge to develop new catalysts that can be effective in this nitroaldol reaction especially under mild conditions with recyclability.

Our compound contains tetrahedral copper center [Cu(2)] and we explored the nitroaldol reaction between aromatic aldehyde with nitromethane (Scheme 3) under solvent free conditions to generate the corresponding product (Table 2). To a mixture of 0.01 mmol (0.6 mL) nitromethane and 0.05 mmol aromatic aldehyde 10 mol% **Cu**e1 was added. The mixture was refluxed at 65°C over a period of 36 hrs. The progress and completion of the reaction was confirmed by TLC. The filtrate was evaporated in vacuum to obtain the product, which was further purified in a silica gel column using petroleum ether and ethyl acetate as the eluent. The catalyst was recovered by filtration, washed several times with methanol and kept in a vacuum oven at 60°C for 24 h. The recyclability studies indicate that the catalyst remains active for upto three cycles (Figure S16 in the supporting information).



Table 2: Summary of nitroaldol reaction of aromatic aldehyde and nitromethane catalyzed by Cu∈1

(c) Synthesis of imidazopyridine by three component coupling and 5-exo-dig cyclization: Imidazopyridine is an important pharmacophore. It has been found in many biologically active compounds.[18] Imidazo[1,2-a] is one of the key component present in several anxiolytic drugs like alpidem, necopidem, zolpidem etc. which are used for the treatment of insomenia.^[19] Various methodologies have been developed for the preparation of imidazopyridine and derivatives but mostly require multiple steps.^[20] A three component coupling reaction between aryl/heteroaryl/alkyl aldehydes, aminopyridine and terminal alkyne, catalyzed by copper compounds appears to be an effective method for this transformation. The reaction proceeds through the formation of the intermediate propargylamine which further undergoes a 5-exo-dig cyclization forming the imidazopyridine. We desired to explore the catalytic activity of Cue1 for this three component reactions.



Scheme 4: Possible mechanistic pathway for the three component synthesis of imidazopyridine

For this reaction, 5 mol% **Cu** \in 1 was added to the mixture containing 2-aminopyridine (1.1 mmol), benzaldehyde (1.2 mmol) and aryl alkynes (1mmol) in 1 ml toluene at 120°C under N₂ atmosphere (Scheme 4). The resulting mixture was stirred for 20 hrs for the reaction to complete and the desired imidazopyridine was obtained in good yields (87-91%) (Table 3). We have also attempted the same reaction in the presence of simple copper salt such as copper acetate, which resulted in poor conversion and yield (Table 3, entry 6). The progress of the reaction was much poorer in the absence of any catalyst (Table 3, entry 5. The recovered **Cu** \in 1 from the above reaction was found to be active for upto three cycles (Figure S17 in the supporting information) suggesting that the catalyst is stable and useful for multiple attempts.

Table 3: Summary of the three component coupling reaction catalyzed by $\ensuremath{\text{Cue1}}$

synthesized successfully employing TPyP and 4.4'-Oxybis(benzoic acid) . The accessibility of Zn2+ ions facilitates a post-synthetic metathesis with Cu2+ in a single crystal-single crystal fashion (Cu∈1). The Cu∈1 compound was found to be a good catalyst for a number of heterogeneous catalytic reactions. Thus the conversion of CO2 to cyclic carbonate under ambient condition, the nitroaldol reaction under solvent free conditions and the synthesis of imidazopyridine via three component coupling reaction have been explored and the Cue1 was found to be a good heterogeneous catalyst. In all the studies, we have observed catalytic activity only with Cu∈1 samples and not over the parent Zn-compound, suggesting that the catalytic activity is due to the presence of Cu(II) ions. The extra-framework solvent molecules can be reversibly removed/exchanged without the collapse of the framework. It appears that the porphyrin based MOFs with their considerable open structures provide opportunities to explore ion-exchange, sorption and heterogeneous catalysis. These studies are being pursued actively and the results would be reported elsewhere.

Experimental Section

Compound 1 was prepared employing a solvothermal method Information Scheme S1). A mixture of tetra-(4-(Supporting pyridyl)porphyrin (H₂TPyP) (0.02 mmol= 0.012 g); 4,4'-Oxybis(benzoic acid) (H₂OBA) (0.04 mmol=0.010g) and Zn(NO₃)₂.6H₂O (0.1 mmol= 0.029 g) was dissolved in 2 ml DMA. A small quantity of HBF₄ (12 µL) was added to the reaction mixture and the resulting solution was homogenized under continuous stirring for 30 min. The reaction mixture with a composition, 5 [Zn(NO₃)₂. 6H₂O] : 2 H₂OBA : 1 H₂TPyP : 1075 DMA : 5 HBF₄ was transferred into a PTFE lined stainless steel autoclave and heated at 100°C for 3 days. The product contained needle shaped purple colored crystals, which were filtered, washed with dry MeOH/DMA mixture and vacuum dried at room temperature (yield ~ 53% based on H₂TPyP). CHN analysis (%) for [Zn₂(C₄₀H₂₄N₈)_{0.5}(C₁₄H₈O₅)(DMA)](DMA)(H₂O)₆, **1** [Found (calcd) : C 54.21(54.13), H 5.85(5.83), N 6.88(6.66)].

 Table 4. Crystal Data and Structure Refinement Parameters for the prepared compounds

≡1					1	Cu∈1
			<u>A</u>	Empirical Formula	C ₃₄ H ₂₀ N ₄ O ₆ Zn ₂	C34H20Cu2N4O6
Entry	Catalyst	R	Yield	FormulaWeight	711.32	707.64
				Crystal System	Triclinic	Triclinic
1	Cu∈1	Ph	88%	Space Group	P-1	P-1
				a(Å)	14.125(3)	14.180(3)
2	Cu∈1	4-F-Ph	91%	b(Å)	14.216(3)	14.490(3)
-	ouer		0170	c(Å)	16.080(3)	16.141(3)
3	Cu∈1	4-Me-Ph	87%	a (deg)	81.516(8)	83.821(8)
5				β (deg)	75.377(8)	78.757(8)
4		Dh	00/	γ (deg)	89.547(9)	85.967(9)
4	1	Ph	<2%	Volume (Å ³)	3088.5(10)	3229.8(10)
-	No. o o to buot	Dh	Ne Des dust	Z	2	2
5	No catalyst	Ph	No Product	Temperature (K)	298(2)	298(2)
_				ρ _c (gcm ⁻³)	0.765	0.728
6	Cu(OAc) ₂ .H ₂ O	Ph	14%	$\mu(\text{mm}^{-1})$	0.803	0.683
				θ range (deg)	2.35-22.94	1.29-25.00
7	CuTPyP	Ph	11%	Wavelength (Å)	0.71073	0.71073
				<i>R1</i> , <i>wR</i> 2 [I>2σ(I)]	0.0933, 0.2549	0.0887, 0.2441
- 4		k		R1, wR2 (all data)	0.1204, 0.2747	0.1062, 0.2632
nclu	sions					
noru	310113			$a R_1 = \Sigma F_0 - F_c / \Sigma F_0 ; wR_2$	$= {\Sigma w(F_0^2 - F_c^2)] / \Sigma $	$[w(F_0^2)^2]^{1/2}$. $w = 1/[$
ne	ew Zn-ba	sed	2D porous M	OF (<i>aP</i>) ² + <i>bP</i>]. <i>P</i> = [max (F_0O) +	2(F _c) ²]/3, where a=	0.1623 and b= 0.00
<u>2</u> (C ₄₀ H ₂	24N8)0.5(C14H8O5)(DMA)](DI	MA)(H ₂ O) ₆ , 1 , w	/as a= 0.1597 and b= 0.0000 for	Cu∈1	

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Metal Exchange Studies:

Exchange of the Zn ions by Cu ions was attempted in a single crystal to single crystal (SCSC) fashion. To this end few single crystals of the Zn compound was immersed in a glass vial containing 0.1 M solution of Cu(NO₃)₂.3H₂O in DMA at 298K for 8 days. The Cu(NO₃)₂. 3H₂O (0.1M) was replaced periodically. The metal-exchanged crystals (**Cu**∈1) [Cu₂(C₄₀H₂₄N₈)_{0.5}(C₁₄H₈O₅)(DMA)](DMA)(H₂O)₃ were collected and soaked in DMA for 3 days to remove any excess free cations occluded in the pores. The Cu-exchanged samples as well as the Zn-sample were dark in color and in order to learn about the extent of metal exchange, we have performed EDAX (Figure S3) as well as AAS analysis (Figure S4). CHN analysis (%) for [Cu₂(C₄₀H₂₄N₈)_{0.5}(C₁₄H₈O₅)(DMA)](DMA)(H₂O)₃, **Cu**∈1 [Found (calcd) : C 54.86(54.80), H 4.20(4.24), N 8.45(8.41)]. This sample (**Cu**∈1) was used for all the studies reported in the manuscript.

Physical Measurements:

Elemental analysis was performed in a Thermo Finnigan EA Flash 1112 series instrument. Powder X-ray diffraction patterns were recorded in the 2θ range of 5–50° using Cu-Ka radiation (Philips X'pert Pro). The experimental PXRD patterns were found to be consistent with the simulated powder X-ray patterns generated from the single crystal structures (Mercury software version 1.4.1) (Figure S5 in the supporting information). IR spectra for the compounds were recorded (KBr pellet) using an FTIR spectrometer (Perking-Elmer Spectrum 1000) (Figure S18 in the supporting information). The room temperature IR spectrum of 1 and **Cue1** exhibit a broad band in the region of 3700-3000 cm⁻¹ due to the presence of lattice water molecules (O-H stretching). In addition the aromatic C-H stretching appears at ~ 2938 cm⁻¹. Other bands typical of the aromatic backbone of the porphyrin ligand were also observed. A sharp band at ~1615 cm⁻¹ would correspond to the coordinated COO group (Table S1 in the supporting information).

UV-vis spectra of the as synthesized compound (1) and metalexchanged compound (**Cue1**) were recorded at room temperature (PerkinElmer, Lambda 35). (Figure S6 in the supporting information). Solid-state photoluminescence studies of the compounds were carried out at room temperature using (PerkinElmer model-LS55) (Figure S7 in the supporting information). Thermogravimetric analysis (TGA) (Metler-Toledo) was carried out in the presence of nitrogen (flow rate = 20 mL/min) in the temperature range 30-1000°C (heating rate = 5°C/min) (Figure S8 in the supporting information). EDAX analysis was carried outemploying Quanta 200 FESEM (Figure S3 in the supporting information). Atomic absorption spectroscopy (AAS) was recorded using PerkinElmer Analyst 200 (Figure S4 in the supporting information). The products of the catalytic studies were analyzed using ¹H NMR spectroscopy employing tetramethylsilane as the internal reference (Figure S19-S27 in the supporting information).

Single Crystal Structure Determination:

The structure of the compounds (1 and Cue1) was determined using single crystal X-ray diffraction. The data sets were collected at 298K using Oxford Xcalibur (Mova) diffractometer equipped with an EOS CCD detector. The single crystal data were collected with the X-ray generator operating at 50kV and 0.8 mA (Mo K α , λ = 0.71073 Å). The cell refinements and data reductions were performed using the program Crysalis Red.^[21] Direct methods were employed for the structure solution and the structure was refined using the WINGX (version 1.63.04a)^[22] was used for refinement. The disordered solvent molecules in both the compounds were accounted for by using the SQUEEZE option present in the WinGX PLATON program. The hydrogen positions of the aromatic ligands were located initially from the difference Fourier maps, and for the final refinement, the hydrogen positions were fixed in a geometrically ideal position and refined using the riding mode. Final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers (1566676 for 1 and 1566677 for **Cue1**). The detail of structure determination is presented in Table4. Important bond length and bond distances are given in Table S2 and S3 in the supporting information.

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Layout 1:

FULL PAPER

Synthesis, structure and Cuexchange (SCSC fashion) of a porphyrin-based MOF has been described. Copper exchanged compound exhibits catalytic activity towards (i) chemical fixation of CO2 under ambient condition, (ii) nitroaldol reaction and (iii) three component coupling reaction.



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Chemical fixation of CO₂ and other Heterogeneous Catalytic Studies employing a Layered Cu-Porphyrin Prepared Through Single-Crystal to Single-Crystal Exchange of a Zn-analogue