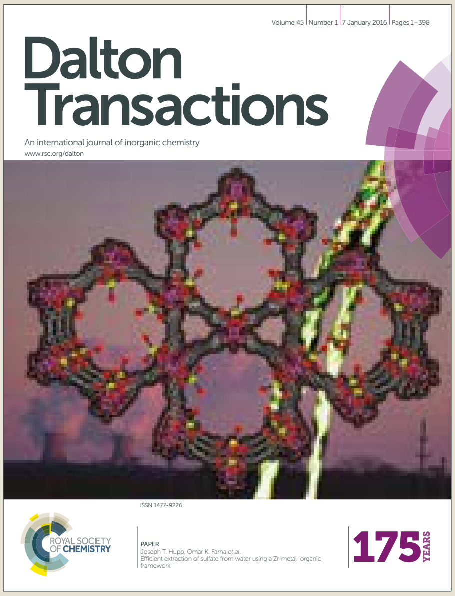
Dalton
Transactions

This article can be cited before page numbers have been issued, to do this please use: B. Yadav, M. Trivedi, A. K. Yadav, G. Singh, A. Kumar, G. Kumar, A. Husain and N. Rath, *Dalton Trans.*, 2019, DOI: 10.1039/C9DT01457H.



View Article Online
DOI: 10.1039/C9DT01457H

Journal Name

ARTICLE

Synthetic, Spectral, Structural and Catalytic activity of infinite 3-D and 2-D Copper(II) Coordination Polymers for Substrate Size-Dependent Catalysis for CO_2 Conversion

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Bhaskaran,[a] Manoj Trivedi,[a*] Anita K. Yadav,[b] Gurmeet Singh,[a*] Abhinav Kumar,[c] Girijesh Kumar,[d] Ahmad Husain,[e] Nigam P. Rath[f*]

Two copper(II) coordination polymers, *viz.* $[Cu_2(OAc)_4(\mu_4\text{-hmt})_{0.5}]_n$ (**1**), and $[Cu\{C_6H_4(COO^-)_2\}_2]_n.2C_9H_{14}N_3$ (**2**) have been synthesized solvothermally and characterized. The solid-state structure reveals that **1** is an infinite three-dimensional (3D) motif with fused hexagonal rings consisting of Cu(II) and hmt in μ_4-bridging mode, while **2** is infinite two dimensional (2D) motif containing Pht^{-2} in μ_1-bridging mode. CP **1** has a two-fold interpenetrated diamondoid network comprising of 4-connected **sqc6** topology with the point symbol of $\{6^6\}$, while **2** has Shubnikov tetragonal plane network possessing 4-connected node with **sql** topology with point symbol of {4^4.6^2}-VS [4.4.4.4.*.*]. Both CPs **1** and **2** serve as efficient catalyst for CO_2-based chemical fixation. Moreover, **1** demonstrate some of the highest reported catalytic activity value (%yield) among Cu-based MOFs for the chemical fixation of CO_2 with epoxides. **1** show high efficiency for CO_2 cycloaddition with small epoxides but its catalytic activity decreases sharply with increase in the size of epoxide substrates. The catalytic results suggested that the copper(II) motifs catalyzed CO_2 cycloaddition of small substrates had been carried out within the framework, while large subtrates could not enter into the framework for catalytic reactions. The high efficiency and size-dependent selectivity toward small epoxides on catalytic CO_2 cycloaddition make **1** a promising heterogeneous catalyst for carbon fixation and can be used as recoverable stable heterogeneous catalysts without losing performance. The solvent-free synthesis of the cyclic carbonate from CO_2 and an epoxide was monitored by *in situ* FT-IR spectroscopy and an exposed Lewis-acid metal sites catalysis mechanism was proposed.

Introduction

Carbon dioxide (CO_2) gas is the most important anthropogenic gas that has been cited as the leading culprit for average temperature increase globally and subsequent climate changes.[1] The emission of CO_2 from the power plants actually can be considered as an abundant carbon source. Besides the physical adsorption and permanent underground deposition of CO_2, an alternative and more efficient strategy for addressing anthropogenic CO_2 emission issues should be the one leading to catalytic chemical conversion of CO_2 into value-added chemicals and materials, so that the emitted CO_2 can be reused in the carbon recycling on the earth.[2,3] This approach not only reduces the anthropogenic greenhouse gas emission but also generates valuable chemical commodity to decrease our dependence on petrochemicals. Taking into account of the issues of the product purifications and catalyst recycling in homogeneous catalytic processes, some heterogeneous catalysts have been developed for the CO_2 chemical conversion.[3] Particularly, the coupling of CO_2 with epoxides into cyclic carbonates is a very efficient route for CO_2 utilization.[4] The cyclic carbonates are a kind of chemical intermediate in the production of plastics, organic solvents, and so on.[5] Homogeneous and heterogeneous catalysts have been developed for the cycloaddition of CO_2 and epoxides. To date, considerable homogeneous catalysts, including quaternary ammonium and phosphonium salts,[6] ionic liquids,[7] alkalimetal salts,[8] Schiff bases,[9] and metal-centered salen complex,[10] have been employed to promote transformation. Although they show effective conversion of the coupling of CO_2 with epoxides into cyclic carbonates, the inherent shortcomings of separation of the product and recycling of the catalyst limit the wide application of the homogeneous catalysts. Consequently, in order to overcome the defect of the homogeneous catalyst, heterogeneous catalysts, such as metal oxides,[11] functional polymers,[12] zeolites,[13] and porous organic polymers (POPs)[14] have been developed. However, most of them need high temperature (>100°C) to activate the reaction, which increases

---

[a] *Department of Chemistry, University of Delhi, Delhi-110007, INDIA. Email:* manojtri@gmail.com*; gurmeet123@gmail.com.*
[b] *Department of Chemistry, Rajdhani College, University of Delhi, Delhi-110015, INDIA*
[c] *Department of Chemistry, University of Lucknow, Lucknow-206007, INDIA*
[d] *Department of Chemistry and Center of Advanced Studies in Chemistry, Panjab University, Chandigarh-160014, INDIA*
[e] *Department of Chemistry, DAV University Jalandhar, Jalandhar-144012, INDIA*
[f] *Department of Chemistry & Biochemistry and Centre for Nanoscience, University of Missouri-St. Louis, One University Boulevard, St. Louis, MO 63121-4499, USA. Email:* rathn@umsl.edu

Electronic Supplementary Information (ESI) available: Experimental details, additional structural figures, crystallographic refinement details, PXRD, IR spectra. CCDC 1429033, 1879768 for (**1**), and (**2**). For ESI and crystallographic data in CIF

View Article Online
DOI: 10.1039/C9DT01457H

the cost of the reaction process. There are several requirements for an efficient heterogeneous catalyst for the cycloaddition of CO_2 and epoxide: first, high surface area and CO_2 adsorption capacity; second, enough Lewis/Brønsted acidic or basic sites to active the epoxide/CO_2; third, high stability and long durability upon exposure to the reaction conditions. Owing to their potential applications in various fields ranging from molecular magnetism, adsorption science and gas storage to photoluminescence and catalysis, the design and synthesis of coordination polymers (CPs) have acquired an extensive growth in recent years.[15] Amongst the variety of organic ligands, polycarboxylic acids and different *N*-donors derivatives have been broadly explored as building blocks and linkers for the construction of coordination networks.[15,16] Much research has also been focused on the development of new organic molecules with tunable properties for their subsequent use in crystal engineering.[4] Hexamethylenetetramine (hmt; $C_6H_{12}N_4$), also known as hexamine or urotropine, can be considered as one such simple heterocyclic compound with a cage like structure which because of its low cost, commercial availability and high solubility in water and polar organic solvents, has found a broad variety of applications, ranging from the production of phenolic resins and solid fuel tablets to be used in organic synthesis, medicinal and materials chemistry.[15u,17,18] As far as coordination chemistry is concerned, hmt is a versatile ligand capable of adopting different coordination modes that span from the terminal monodentate to bridging bi-, tri- and tetradentate modes.[14u,17,18] In addition, due to the good H-bond accepting properties, hmt is very often trapped by metal- organic compounds forming various molecular adducts and supramolecular structures.[15u,19,20] The use of hmt as a simple and convenient linker with a diamandoid-like geometry for the design of coordination polymers with other metals had been explored to a lesser extent.[15u] However, due to the extensive development of crystal engineering the interest in hmt had increased in recent years thereby resulting in the synthesis of a variety of one-(1D), two-(2D) and there-dimensional (3D) hmt-driven coordination polymers bearing different metals.[21-56] In addition, the aromatic carboxylic acid ligand, *o*-Phthalic acid has been widely explored as linker in synthesising coordination polymers.[57] The immense popularity of o-phthalic acid as linker in coordination polymers is because of its ability to provide different modes of coordination.[58,59] In all the previously reported coordination polymers, at least one other ligand is found to be present together with *o*-phthalic acid. o-phthalic acid in the absence of other ligands resulted in monomeric complexes when allowed to react directly with Cu(II) ion at room temperature.[60] There are very few report of coordination polymer based on *o*-phthalic acid alone without incorporating other ligands. Although these studies were primarily focused on exploring rich structural diversity and attractive molecular aesthetics of coordination polymers, the application of such compounds as functional materials still remain underdeveloped.[26,29,30,37,38b] Herein, we describe the synthesis, spectral and structural characterization of two copper coordination motif, namely $[Cu_2(OAc)_4(\mu_4\text{-hmt})_{0.5}]_n$ (**1**), $[Cu\{C_6H_4(COO\text{-})_2\}_2]_n.2C_9H_{14}N_3$ (**2**) and their catalysis for CO_2 cycloaddition with epoxides at 1 atm and room temperature.

Experimental section

Materials and Physical Measurements

All the synthetic manipulations were performed under nitrogen atmosphere. The solvents were dried and distilled before use following the standard procedures.[61] Copper cyanide, copper thiocyanate, copper acetate hydrate, ammonia solution, hexamethylenetetramine, glacial acetic acid, *o*-phthalic acid, 1-(2-Pyridyl)piperazine and epoxides were purchased from Sigma Aldrich Chemicals Pvt. Ltd. All the chemicals were used without further purification. Elemental analysis was performed using a Carlo Erba Model EA-1108 elemental analyzer and C, H and N are within ±0.4% of calculated values. IR (KBr) spectrum was recorded using a Perkin-Elmer and Bruker FT-IR spectrophotometer. Electronic and emission spectra of **1** and **2** were obtained on a Perkin Elmer Lambda-35 and a Horiba Jobin Yvon Fluorolog 3 spectrofluorometer, respectively. Thermogravimetric analysis was carried out in nitrogen using a TA DSC Q 200 instrument with a heating rate of 10°C min^{-1}. The powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Discover X-ray diffractometer (Cu-Kα 1.5405 Å). X-Ray photoelectron spectroscopy(XPS) (PHI 5000 Versa Prob II, FEI Inc.) with Auger electron spectroscopy module was used for obtaining XPS spectra. The ^1H and ^{13}C NMR spectra were recorded on a JEOL DELTA2 spectrometer at 400 MHz using TMS as an internal standard. The chemical shift values are recorded on the δ scale and the coupling constants (J) are in Hz. GC-MS studies were done with the Shimadzu-2010 instrument containing a DB-5/RtX-5MS-30Mt column of 0.25mm internal diameter with an oven temperature range of 90-180°C (5 min) at 4°C/min raised to 300°C at 4°C/min. Gas sorption isotherms were measured by using an ASAP 2020 adsorption equipment.

Synthesis of $[Cu_2(OAc)_4(\mu_4\text{-hmt})_{0.5}]$ (1). Copper cyanide (0.178 g, 2 mmol) was added slowly to a solution of CH_3OH (10 mL) and CH_2Cl_2 (10 mL) containing liquid NH_3 (0.5 mL, 30 mmol) and hexamethyleneamine (0.140 g, 1 mmol). The resulting solution was stirred at room temperature for 6 hours. Slowly, a blue color precipitates appeared which was dissolved by drop wise addition of glacial acetic acid. The resulting solution was filtered and left for slow crystallization in room temperature. Dark blue color block shaped crystals suitable for X-ray studies were obtained after four weeks. The same compound was also isolated by the reaction of different copper salts such as copper(I) thiocyanate, copper(II) acetate hydrate, and copper(II) nitrate hydrate under the similar condition mentioned above instead of copper cyanide. Yield: (0.980 g, 50%). Anal. calc. for $C_{11}H_{18}N_2O_8Cu_2$: C, 30.46; H, 4.15; N, 6.46. Found: C, 30.63; H, 4.45; N, 6.68. IR (cm^{-1}, KBr): ν = 3306, 3204, 3168, 1624, 1552, 1435, 1260, 1021, 933, 722, 700, 649, 598, 459. UV/Vis: λ_{max} ($\varepsilon[dm^3\ mol^{-1}\ cm^{-1}]$) = 273 (9090), 708 (20760).

View Article Online
DOI: 10.1039/C9DT01457H

Synthesis of $[Cu\{C_6H_4(COO^-)_2\}_2]_n.2C_9H_{14}N_3$ (2). Copper(II) acetate hydrate (0.182 g, 1 mmol) was added slowly to a solution of CH_3OH (10 mL) and CH_2Cl_2 (10 mL) containing liquid NH_3 (0.5 mL, 30 mmol), 1-(2-Pyridyl)piperazine (0.163 g, 1 mmol). The resulting solution was stirred at room temperature for 4 hours. Slowly, a blue color precipitates appeared which was dissolved by drop wise addition of *o*-phthalic acid (0.166 g, 1 mmol) in 10 ml water. The resulting solution was filtered and left for slow crystallization in room temperature. Dark blue color block shaped crystals suitable for X-ray studies were obtained after one week. The same compound was also isolated by the reaction of different copper salts such as copper(I) thiocyanate, copper(I) cyanide, and copper(II) nitrate hydrate under the similar condition mentioned above instead of copper acetate hydrate. Yield: (0.576 g, 80%). Anal. calc. for $C_{34}H_{36}N_6O_8Cu$: C, 56.66; H, 5.00; N, 11.66. Found: C, 56.83; H, 4.88; N, 11.76. IR (cm^{-1}, KBr): ν = 2823, 2738, 2659, 2495, 1608, 1577, 1544, 1504, 1444, 1400, 1359, 1307, 1273, 1219, 1172, 1082, 1031, 977, 941, 860, 835, 788, 744, 702, 648, 594, 538, 505, 447, 410. UV/Vis: λ_{max} (ε[dm^3 mol^{-1} cm^{-1}]) = 284 (8079), 690 (16081).

X-ray structure determination

A crystal of appropriate size was mounted on a glass fiber and the intensity data for **1** were collected on an Oxford Xcalibur S CCD area detector diffractometers using graphite monochromatized Mo-Kα radiation at 293(2) K. CrysAlisPro, an Agilent Technologies software package[62], was used for data collection and data integration for **1**. Intensity data sets for **2** was collected on a Bruker APEX II CCD area detector diffractometer using graphite monochromatized Mo-Kα radiation at 100(2) K. SAINT software packages were used for data collection and data integration for **2**. Structure solution and refinement were carried out using the SHELXTL-PLUS software package.[63] The non-hydrogen atoms were refined with anisotropy thermal parameters. All the hydrogen atoms were treated using appropriate riding models. The computer programme PLATON was used for analyzing the interaction and stacking distances.[63]

General Experimental Procedure for 1/2-catalysed cycloaddition of CO_2 to cyclic carbonates

1 mol% of **1**/**2** (4.33 mg/4.89 mg/2.47 mg) and tetra-n-tertbutylammonium bromide (TBAB, 0.3 mmol) were added into the Schlenk reaction tube (10 mL). CO_2 (balloon) and 20 mmol of epoxides were introduced into the reaction mixture under stirring at 1 atm under solvent free environment at room temperature for 18 h. The yields were calculated based on ^1H NMR analysis. The recovered catalyst was collected by centrifuge, washed by fresh CH_3Cl and dried in vacuum.

Results and discussion

Synthesis

Copper(II) coordination polymers, *viz.* $[Cu_2(OAc)_4(\mu_4\text{-hmt})_{0.5}]_n$ (**1**), and $[Cu\{C_6H_4(COO\text{-})_2\}_2]_n.2C_9H_{14}N_3$ (**2**) were obtained in good yield by the reaction of MX (M=Cu: X= CN^-, SCN^-)/MX_2 (M=Cu: X= CH_3COO-, NO_3^-) with liquid NH_3 in a stoichiometric ratio in a mixture of dichloromethane and methanol (1:1 V/V) containing hmt/1-(2-Pyridyl)piperazine under solvothermal condition. All motifs are air stable solid, insoluble in water and other common organic solvents but soluble in dimethyl sulfoxide and do not show any signs of decomposition in solution upon exposure to air. The hmt ligand adopts the less common tetradentate mode in **1**. Compound **1** show bands at 929-1021 cm^{-1} and 1228-1260 cm^{-1} corresponding to CN stretching of hmt moiety (See Fig. S1, ESI†). The carboxyl group of the acetate ligand bridges the copper centers with both of their oxygen atoms. The ν_{as} CO_2 in **1** at 1552-1558 cm^{-1} and ν_s at 1418-1435 cm^{-1}, is typical of the bridging carboxylate of the copper(II) carboxylate dimer.[53b] Compound **2** showed characteristic peaks due to the ligation of carboxylate. The peaks appearing in the region 1577-1608 cm^{-1} can be attributed to $\nu_{asym}(COO^-)$ vibrations while the peaks in the range 1359-1400 cm^{-1} can be attributed to $\nu_{sym}(COO^-)$ vibrations (See Fig. S2, ESI†). The acid-base properties of the copper(II) coordination polymers **1** and **2** have been studied. In basic media, no structural change is observed in **1** and **2** when the solid is dispersed for 24 h in 1 M NaOH solution by the PXRD. However, in acidic conditions, PXRD reveals a structural change in **1** and **2** when the solid is dispersed for 24 h in 1 M HCl solution. The single crystal X-ray refinement detail for **1-2** are summarized in Table 1 (ESI†), and selected bond lengths and angles and hydrogen bond parameters are presented in Table 2 and Table 3 (ESI†), respectively. Fig. 1 presents the overhead and perspective views of the crystal structures of **1** and **2**. Compound **1** shows six-membered rings (See Fig. S3, ESI†). This is a consequence of the hmt nodes adopting an undistorted tetrahedral geometry and coordinating to four spacers. Its ethyl analogue was published by Zaworotko *et al.* in 2001[53a] and the phenyl analogue was reported by Ghosh *et al.* in 2013.[53b] Compound **1** crystallizes in the tetragonal space group P4(2)/nnm. The dinuclear copper carboxylate paddle wheel spacers which exhibit square-pyramidal coordination to four basal oxygens [Cu(1)-O(1)= 1.945(5) Å, Cu(1)-O(2)$^{\#2}$ = 1.965(5) Å, Cu(1)-O(2)$^{\#3}$ = 1.965(5) Å] and one apical nitrogen [Cu(1)-N(1) = 2.343(6) Å] having Cu···Cu separation of 2.6317(19) Å [Cu(1)-Cu(1)$^{\#2}$]. These distances are comparable to other copper complexes having hmt as ligand.[53] As expected, the sheets of **1** are linear, and the packing of adjacent sheets appears to be the consequence of their shape. The methyl groups efficiently fill the hexagonal cavities, which have sides of 1.17 nm and diagonals of 1.87 nm, and mitigate against the inclusion of solvent molecules. The framework of **1** contains hexagonal channels with dimension of 18.7 × 16.4 Å^2 and made up of six tetrahedrally coordinated hmt molecules (Fig. 2). The 3D framework of **1** can be simplified topologically by considering the nodes corresponding to the centroid of organic ligand as secondary building unit as a uninodal 4-connected net and the linear bifunctional paddle wheel inorganic linkers (See Fig. S4 to Fig. S6, ESI†).[64] Topological analysis suggest that compound **1** is a 3-D, two-fold diamondoid network comprising of 4-connected **sqc6** topology with the point symbol of $\{6^6\}$ (Fig. 3 & 4). The τ parameter (five-coordinated species)[65] for the coordination in **1** is 0 which indicated that the geometry is

View Article Online
DOI: 10.1039/C9DT01457H

perfectly square pyramidal. Compound **2** shows that phthalate ion acts as a bridging ligand in the formation of infinite 2-D coordination polymer. Each Cu(II) ion is coordinated with four phthalate ligands completing an octahedral structure with six O atoms and two 1-(2-Pyridyl)piperazium ions in the lattice. Out of the four phthalate two coordinates to the Cu(II) through both O atoms of one carboxylate as chelate. These two chelating carboxylates are found to be in trans position to each other. Each of the other carboxylates (of these two phthalates) binds to another Cu(II) through only one O atom while the other O dangles as keto group.

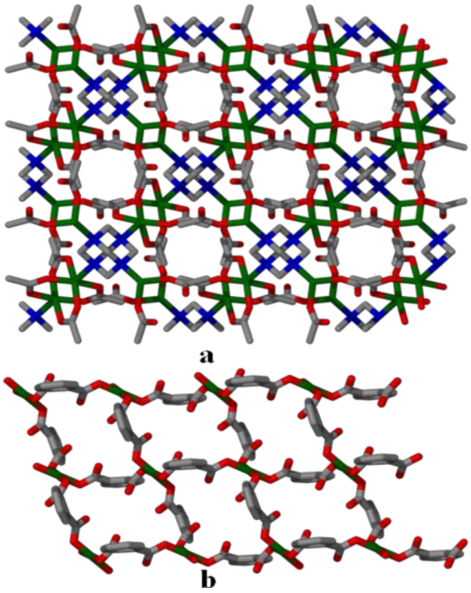


Fig. 1. Overhead and perspective views of 3D and 2D network (H and 1-(2-Pyridyl)piperazium atoms omitted for clarity) seen in the crystal structure of $[Cu_2(OAc)_4(\mu_4\text{-hmt})_{0.5}]$ (**1**; **a**), and $[Cu\{C_6H_4(COO^-)_2\}_2]_n.2C_9H_{14}N_3$ (**2**; **b**).

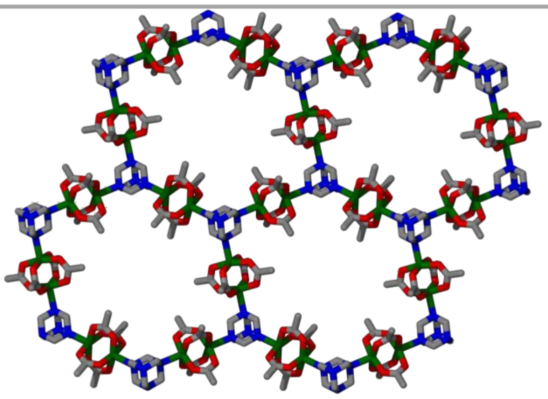


Fig. 2. Hexagonal channels in **1** made of six tetrahedrally coordinated hmt molecule.

The other two trans coordination sites of the Cu(II) are fulfilled by carboxylate O atoms of phthalate of which the remaining carboxylates chelate to two Cu(II). In this way, a two dimensional network is generated where each phthalate acts as a bridge between two Cu(II), and coordinating to one Cu(II) by the monodentate carboxylate oxygen and to another Cu(II) by chelating carboxylate. In compound **2**, the two trans O-Cu(II)-O angles created each by the two O atoms of a chelating carboxylate and the Cu(II) ion were found to be equal which is 52.89◦. The other two O-Cu(II)-O angles were of value 127.2(2)◦. Interestingly the axial Cu(II)-O bonds were not perfectly perpendicular to the plane of four equatorial O atoms from two chelating carboxylates. Each of the axial Cu(II)-O bonds were found to be tilted slightly towards one of the two equatorial chelating carboxylate pairs. The O-Cu(II)-O angles involving one axial O atom and the O atoms from one pair of chelating carboxylate are 93.02◦ and 96.22◦ while these angles with the other pair of carboxylate are 83.78◦ and 86.98◦. The distance between the two Cu(II) bound O atoms belonging to the same carboxylate is 2.364 Å while the distance between the two O atoms (on the same side of the coordination core) belonging to two different carboxylates is 4.251 Å. Topological analysis suggests that compound **2** is a Shubnikov tetragonal plane network comprising of a 4-connected sql topology with point symbol of $\{4^4.6^2\}$-VS [4.4.4.4.*.*] (Fig. 5).[64a]

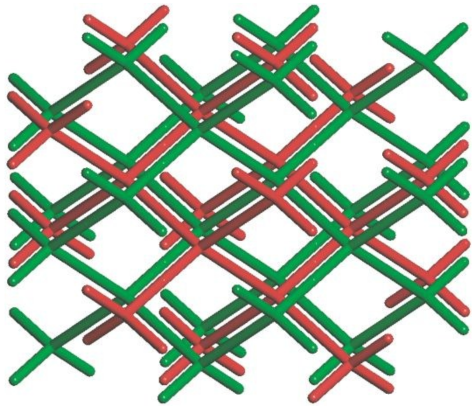


Fig. 3. Two-fold interpenetrated diamondoid network comprising of 4-connected ***sqc6*** topology in **1**.

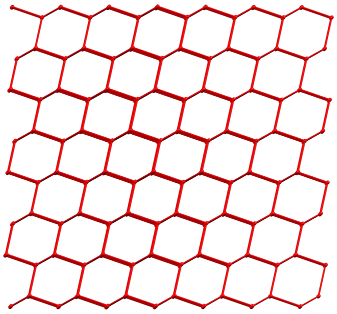


Fig. 4. Diamondoid 4-connected uninodal network in **1**.

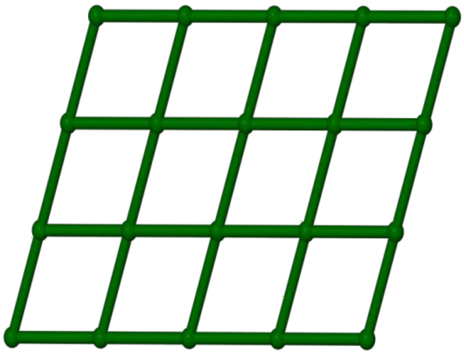


Fig. 5. Topology of **2** showing shubnikov tetragonal plane network comprising of 4-connected node with **sql** topology.

XPS behaviour.

The valence of copper in **1** and **2** have been proved with the aid of X-ray photoelectron spectroscopy (See Fig. S7 to Fig. S8, ESI†). As shown in Fig. S10 to Fig. S11, the wide scan spectra of **1** and **2** indicates that it consists of the elements Cu, N, O, and C. The wide scan spectra of Cu2p having two absorption band at 933.12 to 933.70 eV and 953.20 to 953.35 eV which corresponds to the bonding energy of Cu2p3/2 and Cu2p1/2, respectively. Along with this, there are two more absorption bands corresponding to the strong satellites of Cu2p3/2 and Cu2p1/2 indicate the presence of copper in +2 oxidation state.

Electronic and Emission Spectroscopy.

The UV-vis absorption spectra of **1** and **2** were measured in the DMSO solution (Fig. 6). The absorption maxima from 273 to 284 nm of **1** and **2** in the ultraviolet region are assigned to intraligand transitions. CPs **1** and **2** also exhibit broad bands in the visible region with absorption maxima at 690 nm to 708 nm which are attributed to d-d transitions of copper(II) systems (Fig. 6).[64] Compounds **1** and **2** were non-emissive on excitation at 690 nm to 708 nm. However, on excitation at 273 nm to 284 nm, **1** exhibited two broad emission peaks centered at 364 nm and 755 nm. However, **2** showed one broad band at 368 nm (Fig. 7). Luminescence response for these compounds is due to ligand-to-metal charge transfer.[57,58,66,67]

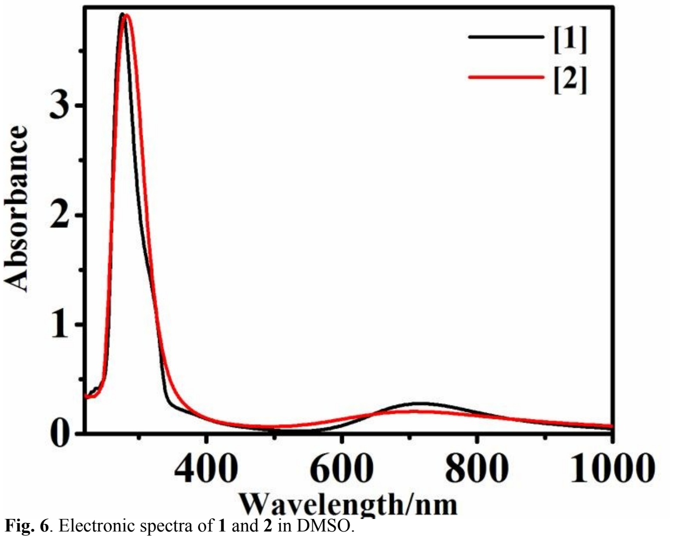


Fig. 6. Electronic spectra of **1** and **2** in DMSO.

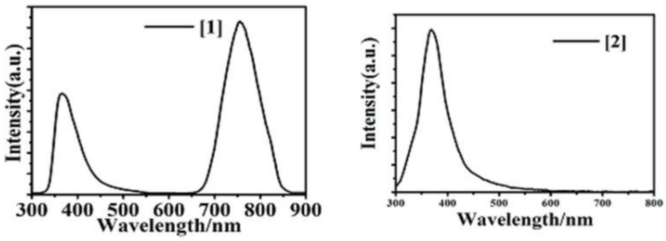


Fig. 7. Emission spectra of **1-2** in DMSO on excitation at 273 nm, and 284 nm, respectively.

Thermogravimetric analysis.

Thermogravimetric analyses (TGA) of **1-2** were performed under nitrogen with heating rate 10˚C min^{-1} to gain information about the decomposition and/or volatility of the compound. The TGA results (Fig. S9, ESI†) indicate that the framework of **1**, and **2** are stable up to *ca.* 150°C, 170°C and then starts to disrupt and decompose abruptly. The first major weight loss (63.42%) occurred in the range of 150-280°C in **1** and then the second minor weight loss (5.22%) is in between 281-404°C leading to 31.36%, thermally stable final product which corresponds to the calculated value 33.02% for Cu_2O. On the other hand, the weight loss was observed from 171°C to 505°C. The first weight loss is a well-defined step with initiation temperature 180°C due to loss of water molecules while the second and the third weight losses are combined ones with initiation temperatures ca. 258°C and 390°C, respectively leading to 32.26% product which corresponds to the calculated value 32.11% for CuO.

N_2 Absorption.

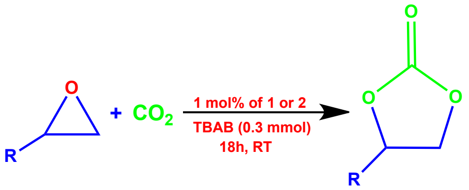
The N_2 adsorption/desorption isotherms of **1-2** were measured at 77 K to investigate the apparent surface areas and pore volumes of the materials. Compound **1** gave rise to reversible typical type-I adsorption isotherm with a BET surface area up to 176 m^2 g^{-1}, Langmuir surface area 234 m^2 g^{-1}, and a total micropore volume of 0.0810 cm^{-3} g as evaluated by Dubinin-Astakhov (DA) method which indicated microporosity (Fig. S10, ESI†). The compound **2** was nonporous in nature.

Kinetic study by TGA for CO_2 adsorption.

The CO_2 mitigation studies were performed by using a TGA (Fig. S11, ESI†). The compound **1** (5-10 mg) was placed in to an alumina pan and adjusted operating temperature. **1** was heated to 200°C to activate or remove moisture and kept isothermally condition in N_2 atmosphere for 30 min. It was then brought to 50°C and kept again isothermally in CO_2 atmosphere for 1h. Compound **1** indicates 1.52% CO_2 capturing in terms of weight gain. It has been seen from BET that **1** showed high surface area (>100 m^2/gm).

Catalytic performances for the conversion of epoxides into cyclic carbonates with CO_2.

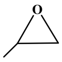
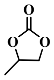
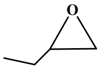
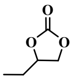
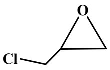
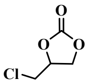
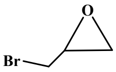
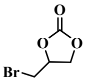
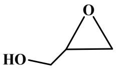
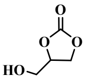
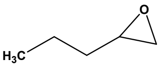
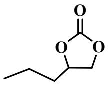
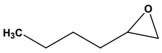
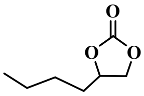
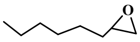
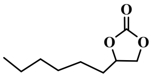
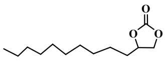
The Cu(II) coordination polymers (**1-2**) with the incorporation of copper metal sites and nitrogen-rich hexamethylene tetraamine/1-(2-Pyridyl)piperazium units within the framework inspired us to investigate its heterogeneous catalytic activity for the cycloaddition reaction of CO_2 with epoxides. Among CO_2 chemical conversion reactions, catalyzed CO_2 cycloaddition with epoxides has been intensively investigated recently due to their wide range of applications in the production of carbonates, as an important synthetic intermediates in pharmaceutical and electrochemical industries.[68]



Scheme 1. Catalytic cycloaddition of CO_2 with epoxides to produce cyclic carbonates.

View Article Online
DOI: 10.1039/C9DT01457H

Table 1. **1/2** catalysed cycloaddition of epoxides with CO_2.[a]

Entry	Substrate	Products	Yields (%)[b]/TON[c]	
			1	**2**
1.			95/1900	75/1500
2.			85/1700	60/1200
3.			87/1740	68/1360
4.			90/1800	65/1300
5.			96/1920	80/1600
6.			6/120	NR[d]
7.			6/120	NR[d]
8.			6/120	NR[d]
9.			5/100	NR[d]

[a]Reaction conditions: epoxide (20 mmol), catalyst (1 mol%), and TBAB (0.3 mmol) under carbon dioxide (1 atm) at RT for 18 h. [b]The yields were determined by ^1H NMR analysis.; [c]TON = (moles of product)/(moles of the catalyst).; [d]NR= No reaction.

Therefore, catalytic performance of compounds **1**-**2** in the cycloaddition of CO_2 with epoxides to produce various carbonates was explored (scheme 1). HKUST-1 was taken as a catalyst in these heterogenous reactions as control experiments. The reactions were carried out using the epoxide (20 mmol) and carbon dioxide in the presence of a co-catalyst, tetrabutyl ammonium bromide (TBAB, 0.3 mmol) and catalyst loading [**1**-**2**, 1 mol%] at room temperature and 1 atm pressure for 18 h. Yields of the obtained cyclic carbonates produced from CO_2 with different epoxides catalyzed by **1**-**2** and HKUST-1 has been determined under the identical conditions. As shown in Table 1 and Fig.7, it has been observed that **1** showed high efficiency in the CO_2 cycloaddition as compared to compound **2** especially with small-sized epoxides (Table 1; Entry 1 to 5) which is due to presence of higher number of available undercoordinated metal ions in the paddlewheel units in **1**.[69] The reaction yields of cyclic carbonates are 75-95% for 2-methyloxirane, corresponding to TON of 1500-1900; 60-85% for 2-ethyloxirane, corresponding to TON of 1200-1700; 68-87% for 2-(chloromethyl)oxirane, corresponding to TON of 1360-1740; 65-90% for 2-(bromomethyl)oxirane, corresponding to TON of 1300-1800; 80-96% for 2-(hydroxymethyl)oxirane corresponding to TON of 1600-1920 per compound **1**-**2**. A small decrease in yield was observed when the hydroxyl was substituted with chloride or bromide substituent. In the absence of co-catalyst TBAB, the reaction catalysed by compound **1** or **2** yielded 10-15% after 18h. However, in the absence of **1** or **2**, the same reaction catalysed by the co-catalyst TBAB alone gave only 8% yield so the combination of **1** or **2** and TBAB gave the best result. The comparison of the yields clearly indicates that the **1** shows greater performance than HKUST-1 but almost similar to MOFs[68e,68f,70] for catalytic CO_2 cycloaddition with epoxides at the same conditions. The high catalytic activity of **1** can be ascribed to the increase in CO_2 affinity *via* the introduction of the nitrogen-rich hexamethylenetetramine groups into the framework. To probe the size-selectivity in the cycloaddition reaction of CO_2 with epoxides, larger epoxide substrates such as 1,2-epoxypentane, 1,2-epoxyhexane, 1,2-epoxyoctane, and 1,2-epoxydodecane were employed. The product yields for **1** showed sharp decreases and afforded only 5-6% (entries 6-9 in Table 1) catalytic product and the corresponding TON values were 100-120. However, **2** showed no reaction. This suggests that large substrates are unable to access the catalytic sites decorated inside the framework of **1** or **2**. These observations also indicate that the former reactions with small substrates

View Article Online
DOI: 10.1039/C9DT01457H

(entries 1-5 in Table 1) were indeed occurred within the framework of **1**/**2**, and therefore verifying the size selectivity. The remarkably high efficiency and the size selectivity to small epoxides for catalytic CO_2 cycloaddition confirm that **1** is a suitable heterogeneous catalyst for carbon fixation. A comparison of catalytic efficiency of the **1** and **2** with other Cu-MOFs catalysts, already described in literature for the preparation of carbonates, revealed advantage of **1** in term of better yield with shorter reaction time at room temperature (Table 2). In the backdrop of these findings, **1** is found to be a very excellent catalyst for efficient synthesis of small carbonates. To examine the recyclability, taking the CO_2 cycloaddition with glycidol as an example, the catalyst **1**/**2** were successively reused in 5 runs without losing performance in the catalytic efficiency (Fig. S12, ESI†). The stability of **1**/**2** was also proven by the PXRD measurements, showing that the PXRD patterns of the recycled **1**/**2** are in good agreement with calculated pattern from its crystal data. The PXRD results indicate that the framework retained its structural integrity very well after the catalytic reactions (Fig. S13-Fig. S14, ESI†). To shed light on the mechanism of the heterogeneous catalytic CO_2 fixation, *in situ* FT-IR measurements were performed to monitor the reaction process of **1** at room temperature and 1 atm CO_2 pressure (Fig. 8). The absorption intensities of the carbonyl group characteristic peaks (ν(C=O)), centered at 1740 cm^{-1}, rapidly increased with the reaction time, indicating the formation of 2-(hydroxymethyl)oxirane. The typical asymmetric vibrations (2340 cm^{-1}) of CO_2 was observed after the addition of glycidol during the reaction and disappeared at the end of the reaction. Based on the structural features and catalytic performances as well as the *in situ* FT-IR results, a tentative mechanism for the **1**/**2**-catalyzed cycloaddition of epoxide and CO_2 into cyclic carbonates is proposed,[70] and is shown in Fig. 9. The coupling reaction is initiated by the ring-opening of the epoxide with the help of Bu_4NBr to afford a Cu-bound alkoxide in an S_N2-type reaction. The subsequent addition of CO_2 to the ring-opened epoxide was preferred by the presence of Bu_4NBr, which stabilized the polarized intermediate resulting in a metal carbonate capable of cyclization to form a cyclic carbonate with the regeneration of the catalyst.

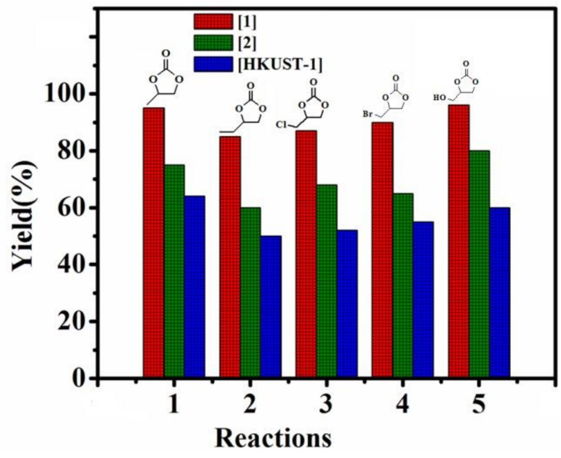


Fig.7. Yields of various cyclic carbonates prepared from the cycloaddition reaction of CO_2 with epoxides catalyzed by compounds **1**(Red), **2**(Green) and HKUST-1.

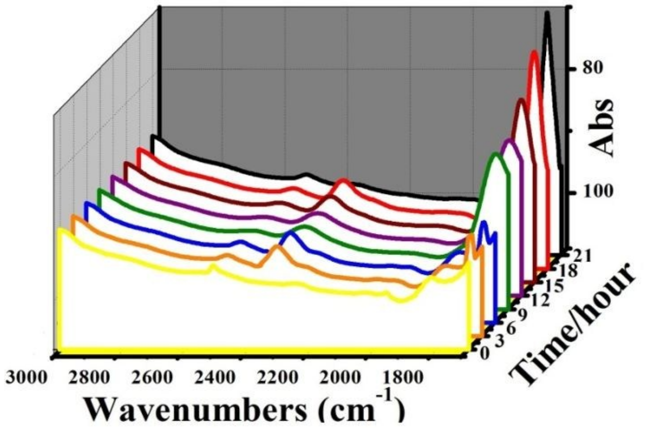


Fig. 8. *In* situ FT-IR spectra of the synthesis of 2-(hydroxymethyl)oxirane catalyzed by **1** at room temperature under 1 atm CO_2 pressure.

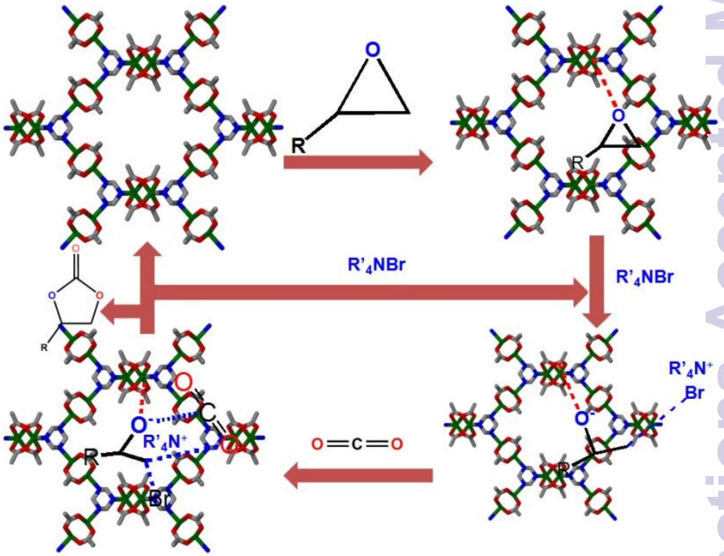


Fig. 9. The proposed mechanism for the cycloaddition reaction of epoxide and CO_2 to form cyclic carbonates catalyzed by **1** in the presence of TBAB.

Conclusions

In summary, we have synthesized two copper (II) coordination polymers, *viz.* $[Cu_2(OAc)_4(\mu_4\text{-hmt})_{0.5}]_n$ (**1**), and $[Cu\{C_6H_4(COO^-)_2\}_2]_n.2C_9H_{14}N_3$ (**2**) and subsequently their utilization as a heterogeneous catalyst for the cycloaddition of carbon dioxide to epoxides. Significantly, the catalyst **1** possesses excellent recyclability, and it doesn't showed decline in activity during the first four cycles of reaction. The constructed material incorporating both exposed metal sites and nitrogen-rich hmt/1-(2-Pyridyl)piperazium groups make it promising heterogeneous catalyst for CO_2 chemical conversion with small substrates, which have been confirmed by remarkably high efficiency and size selectivity for catalytic CO_2 cycloaddition with epoxides. Research along this line is going on in our laboratory.

View Article Online
DOI: 10.1039/C9DT01457H

Table 2. Comparative catalytic performance of the **1** and **2** with others previously reported Cu-MOFs catalysts for cycloaddition of epoxides with CO_2.

Entry	Cu-MOFs	Co-catalyst	Reaction conditions T[K]/P[atm]/Time[h]	% yield	Ref.
1.	$[Cu_3(BTC)_2]$ or HKUST-1	n-Bu_4NBr	273/1 atm./48h	49	68g
2.	$[Cu_2(BPTC)(H_2O)_2]$or MOF-505	n-Bu_4NBr	273/1 atm./48h	48	68g
3.	[CuL1] or BIT-C	n-Bu_4NBr	333/1 atm./6h	95-99	70j
4.	$[Cu(HIP)_2(BPY)]$	-	393/12 atm./6h	10-73	70g
5.	$Cu_2(Cu\text{-}TACTMB)(H_2O)_3(NO_3)_2$ or MMCF-2	n-Bu_4NBr	273/1 atm/48h	42-95	68g
6.	$Cu_6(Cu\text{-}TDPBPP)(HCO_2)_4(H_2O)_6$ or MMPF-9	n-Bu_4NBr	273/1 atm/48h	30-87	70p
7.	Cu_4MTTP	n-Bu_4NBr	273/1 atm/48h	83-96	70e
8.	$[Cu_7(H_1L)_2(TPT)_3(H_2O)_6]$	n-Bu_4NBr	373/9.86 atm/3-12h	>99	70m
9.	$[Cu_2(C_{20}H_{12}N_2O_2)(COO)_4]_n$	n-Bu_4NBr	273/1 atm/48h	88-96	70n
10.	[Cu-ABF@ASMNPs]	DBU	353/1atm/12h	89-92	
11.	$[Cu_{24}(BDPO)_{12}(H_2O)_{12}]\cdot 30DMF\cdot 14H_2O$ or (JUC1000)	TBABr	298/1 atm/48	29-96	70k
12.	$[Cu_2L(H_2O)_2]4H_2O2DMF$	n-Bu_4NBr	373/9.86 atm./2-6h	64->99	70l
13.	$[Cu_2 (BDC)_2 (DABCO)]$	-	373/8 atm./12h	13	70f
14.	FJI-H14	n-Bu_4NBr	353/0.15 atm/24h	27-95	70r
15.	$\{[Cu_6(L)_3(H_2O)_6].(14DMF)(9H_2O)\}_n$	n-Bu_4NBr	298/1 bar/8-24h	30-95	70s
16.	$[Cu_5(TPTC)_3(BPDC\text{-}NH_2)_{0.5}(H_2O)_5]$ (1-NH_2)	n-Bu_4NBr	298/1 atm/36h	50	70t
17.	$[Cu_5(TPTC)_3(BPDC\text{-}Urea)_{0.5}(H_2O)_5]$ (1-Urea)	n-Bu_4NBr	298/1 atm/36h	19-98	70t
18.	$[Cu_2(OAc)_4(\mu_4\text{-}hmt)_{0.5}]_n$	n-Bu_4NBr	273/1 atm./18h	87-96	Present work
19.	$[Cu\{C_6H_4(COO\text{-})_2\}_2]_n.2C_9H_{14}N_3$	n-Bu_4NBr	273/1 atm./18h	60-80	Present work

Acknowledgements

This project was financially supported by the Department of Science and Technology, New Delhi, India (Grant No. EMR/2016/006624). Special thanks are due to Professor P.J. Sadler, University of Warwick, UK and Professor Josef Michl, University of Colorado, USA for their kind encouragement. We acknowledge funding from the National Science Foundation (CHE0420497) for the purchase of the APEX II diffractometer.

Notes and references

1 (*a*) J.-R. Li, Y. Ma, M.C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P.B. Balbuen, H.-C. Zhou, *Coord. Chem. Rev.* 2011, **255**, 1791; (*b*) Y.-S. Bae, R.Q. Snurr, *Angew. Chem., Int. Ed.* 2011, **50**, 11586; (*c*) K. Sumida, D.L. Rogow, J.A. Mason, T.M. McDonald, E.D. Bloch, Z.R. Herm, T.-H. Bae, J.R. Long, *Chem. Rev.* 2012, **112**, 724; (*d*) J. Liu, P.K. Thallapally, B.P. McGrail, D.R. Brown, J. Liu, *Chem. Soc. Rev.* 2012, **41,** 2308.

2 (*a*) C.D.N. Gomes, O. Jacquet, C. Villiers, P. Thuery, M. Ephritikhine, T. Cantat, *Angew. Chem., Int. Ed.* 2012, **51**, 187; (*b*) X.-B. Lu, D.J. Darensbourg, *Chem. Soc. Rev.* 2012, **41**, 1462.

3 (*a*) K. Iizuka, T. Wato, Y. Miseki, K. Saito, A. Kudo, *J. Am. Chem. Soc.* 2011, **133**, 20863; (*b*) Y. Xie, T.-T. Wang, X.-H. Liu, K. Zou, W.-Q. Deng, *Nat. Commun.* 2013, **4**, 1960; (*c*) W. Tu, Y. Zhou, Z. Zou, *Adv. Mater.* 2014, **26**, 4607; (*d*) S. Lin, C.S. Diercks, Y.-B. Zhang, N. Kornienko, E.M. Nichols, Y. Zhao, A.R. Paris, D. Kim, P. Yang, O.M. Yaghi, C.J. Chang, *Science* 2015, **349**, 1208.

4 (*a*) M. Yoshida, M. Ihara, *Chem.-Eur. J.* 2004, **10**, 2886; (*b*) J. Bayardon, J. Holz, B. Schäffner, V. Andrushko, S. Verevkin, A. Preetz, A. Börner, *Angew. Chem., Int. Ed.* 2007, **46**, 5971.

5 (*a*) B. Schäffner, F. Schäffner, S.P. Verevkin, A. Börner, *Chem. Rev.* 2010, **110**, 4554; (*b*) H.S. Kim, J.J. Kim, B.G. Lee, O.S. Jung, H.G. Jang, S.O. Kang, *Angew. Chem., Int. Ed.* 2000, **39**, 4096.

6 (*a*) V. Caló, A. Nacci, A. Monopoli, A. Fanizzi, *Org. Lett.* 2002, **4**, 2561; (*b*) J. Wang, J.G.W. Yang, G. Yi, Y. Zhang, *Chem. Commun.* 2015, **51**, 15708.

7 (*a*) H. Kawanami, A. Sasaki, K. Matsui, Y. Ikushima, *Chem. Commun.* 2003, 896; (*b*) B.-H. Xu, J.-Q. Wang, J. Sun, Y. Huang, J.-P. Zhang, X.-P. Zhang, S.-J. Zhang, *Green Chem.* 2015, **17**, 108; (*c*) Y.J. Kim, R.S. Varma, *J. Org. Chem.* 2005, **70**, 7882.

8 S.R. Jagtap, M.J. Bhanushali, A.G. Panda, B.M. Bhanage, *Catal. Lett.* 2006, **112**, 51.

9 (*a*) S. Iksi, A. Aghmiz, R. Rivas, M.D. González, L. Cuesta-Aluja, J. Castilla, A. Orejón, F.E.E. Guemmout, A.M.J. Masdeu-Bultó, *Mol. Catal. A: Chem.* 2014, **383-384**, 143; (*b*)

10 M. Ulusoy, O. Şahin, A. Kilic, O. Büyükgüngör, *Catal. Lett.* 2011, **141**, 717.

11 (*a*) A. Decortes, M.M. Belmonte, J. Benet-Buchholz, A.W.

View Article Online
DOI: 10.1039/C9DT01457H

Kleij, *Chem. Commun.* 2010, **46**, 4580; (*b*) D. Tian, B. Liu, Q. Gan, H. Li, D.J. Darensbourg, *ACS Catal.* 2012, **2**, 2029.

12 K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, *J. Am. Chem. Soc.* 1999, **121**, 4526.

13 (*a*) Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu, K. Ding, *Angew. Chem., Int. Ed.* 2007, **46**, 7255; (*b*) X.-L. Meng, Y. Nie, J. Sun, W.-G. Cheng, J.-Q. Wang, H.-Y. He, S.-J. Zhang, *Green Chem.* 2014, **16**, 2771.

14 (*a*) K. Huang, J.-Y. Zhang, F. Liu, S. Dai, *ACS Catal.* 2018, **8**, 9079; (*b*) K. Huang, F. Liu, S. Dai, *J. Mater. Chem.* A, 2016, **4**, 13063; (*c*) F. Liu, K. Huang, S. Ding, S. Dai, J. Mater. Chem. A, 2016, **4**, 14567; (*d*) F. Liu, K. Huang, Q. Wu, Sheng Dai, *Adv. Mater.* 2017, **29**, 1700445; (*e*) F. Liu, K. Huang, C.-J. Yoo, C. Okonkwo, D.-J. Tao, C.W. Jones, S. Dai, *Chem Eng J*, 2017, **314**, 466.

15 (*a*) R. Srivastava, D. Srinivas, P. Ratnasamy, *Appl. Catal., A* 2005, **289**, 128; (*b*) A.K. Kinage, S.P. Gupte, R.K. Chaturvedi, R.V. Chaudhari, *Catal. Commun.* 2008, **9**, 1649.

16 (*a*) N.L. Rosi, J. Eckert, M. Eddaoudi, D.T.J. Kim, M. O'Keefe, O.M. Yaghi, *Science* 2003, **300**, 1127; (*b*) K. Biradha, A. Ramanan, J.J. Vittal, *Cryst. Growth Des.* 2009, **9**, 2969; (*c*) A. Santra, I. Senkovska, S. Kaskel, P.K. Bharadwaj, *Inorg. Chem.* 2013, **52**, 7358; (*d*) C. He, K. Lu, D. Liu, W. Lin, *J. Am. Chem. Soc.* 2014, **136**, 5181; (*e*) A. Aijaz, T. Akita, N. Tsumori, Q. Xu, *J. Am. Chem. Soc.* 2013, **135**, 16356; (f) D. De, T.K. Pal, S. Neogi, S. Senthilkumar, D. Das, S.S. Gupta, P.K. Bharadwaj, *Chem. Eur. J.* 2016, **22**, 3387; (g) S.S. Nagarkar, S.M. Unni, A. Sharma, S. Kurungot, S.K. Ghosh, *Angew. Chem., Int. Ed.* 2014, **53**, 2638; (*h*) S.R. Batten, D.R. Turner, S.M. Neville, *Coordination Polymers: Design, Analysis and Application, Royal Society of Chemistry*, London, 2009; (*i*) A.S. Abd-El-Aziz, C.E. Carraher Jr., C.U. Pittman Jr., M. Zeldin (Eds.), *Macromolecules Containing Metal and Metal-Like Elements*. Vol. **5** *Metal-Coordination Polymers*, Wiley, 2005; (*j*) J.L. Atwood, J.W. Steed (Eds.), *Encyclopedia of Supramolecular Chemistry*, *Taylor & Francis*, London, 2004; (*k*) C.B. Aakeroy, N.R. Champness, C. Janiak, *CrystEngComm* 2010, **12**, 22; (*l*) K.M. Fromm, J.L. Sague, L. Mirolo, *Macromol. Symp.* 2010, **291-292**, 75; (*m*) J.J. Perry IV, J.A. Perman, M.J. Zaworotko, *Chem. Soc. Rev.* 2009, **38**, 1400; (*n*) S. Qiu, G. Zhu, *Coord. Chem. Rev.* 2009, **253**, 2891; (*o*) M.J. Zaworotko, *Cryst. Growth Des.* 2007, **7**, 4; (*p*) S. Kitagawa, K. Uemura, Chem. Soc. Rev. 2005, 34, 109; (*q*) C.N.R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem. Int. Ed.* 2004, **43**, 1466; (*r*) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* 2004, **43**, 2334; (*s*) C. Janiak, *Dalton Trans.* 2003, 2781; (*t*) S.L. James, *Chem. Soc. Rev.* 2003, **32**, 276; (*u*) B. Moulton, M.J. Zaworotko, *Chem. Rev.* 2001, **101**, 1629; (*v*) A.M. Kirillov, *Coordination Chemistry Reviews* 2011, **255**, 1603.

17 (*a*) R.L. LaDuca, *Coord. Chem. Rev.* 2009, **253**, 1759; (*b*) S. Noro, S. Kitagawa, T. Akutagawa, T. Nakamura, *Progr. Polym. Sci.* 2009, **34**, 240; (*b*) A.Y. Robin, K.M. Fromm, *Coord. Chem. Rev.* 2006, **250**, 2127; (*c*) K. Biradha, M. Sarkar, L. Rajput, *Chem. Commun.* 2006, 4169; (*d*) B.-H. Ye, M.-L. Tong, X.-M. Chen, *Coord. Chem. Rev.* 2005, **249**, 545.

18 (*a*) M.T. Harvey, *Further Studies on Phenolic Hexamethylenetetramine Compounds*, BiblioBazaar, LLC, 2009; (*b*) E. Luck, M. Jager, S.F. Laichena, *Antimicrobial Food Additives: Characteristics, Uses Effects*, Vol. **2**, Springer, 1997; (*c*) A.C. Potter, *Reactions of Hexamethylenetetramine with Model Phenols: Model Studies Related to Novolac resins*, University of Melbourne, School of Chemistry, 1997; (*d*) G.R. Maxwell, *Synthetic Nitrogen Products: a Practical Guide to the Products and Processes*, *Kluwer Academic/Plenum Publishers*, 2004; (*e*) K. Eller, E. Henkes, R. Rossbacher, H. Hoke, *Amines, "Aliphatic" in Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag, Weinheim, 2005; (f) N. Blazevic, D. Kolbah, B. Belin, V. Sunjic, F. Kajfez, *Synthesis-Stuttgart* 1979, **3**, 161; (g) J.M. Dreyfors, S.B. Jones, Y. Sayed, *Am. Ind. Hyg. Assoc. J.* 1989, **50**, 579.

19 S.-L. Zheng, M.-L. Tong, X.-M. Chen, *Coord. Chem. Rev.* 2003, **246**, 185.

20 See the Cambridge Structural Database (CSD, version 5.31, Aug 2010): F.H. Allen, *Acta Crystallogr.* 2002, **B58**, 380.

21 (*a*) Q. Shi, Z.-M. Zhang, Y.-G. Li, Q. Wu, S. Yao, E.-B. Wang, *Inorg. Chem. Commun.* 2009, **12**, 293; (*b*) A. Trzesowska, R. Kruszynski, *Trans. Met. Chem.* 2007, 32, 625; (*c*) G. Singh, B.P. Baranwal, I.P.S. Kapoor, D. Kumar, R. Frohlich, *J. Phys. Chem. A* 2007, **111**, 12972; (*d*) S.C. Manna, A.K. Ghosh, J. Ribas, M.G.B. Drew, C.-N. Lin, E. Zangrando, N.R. Chaudhuri, *Inorg. Chim. Acta* 2006, **359**, 1395; (*e*) D. Chopra, P. Dagur, A.S. Prakash, T.N.G. Row, M.S. Hegde, *J. Cryst. Growth* 2005, **275**, e2049; (f) D.-L. Long, P. Kogerler, L.J. Farrugia, L. Cronin, Dalton Trans. 2005, 1372; (*g*) D.-L. Long, P. Kogerler, L.J. Farrugia, L. Cronin, *Angew. Chem. Int. Ed.* 2003, **42**, 4180; (*h*) D. Sun, R. Cao, Y. Sun, X. Li, W. Bi, M. Hong, Y. Zhao, *Eur. J. Inorg. Chem.* 2003, 94; (*i*) J. Jiang, M.J. Sarsfield, J.C. Renshaw, F.R. Livens, D. Collison, J.M. Charnock, M. Helliwell, H. Eccles, *Inorg. Chem.* 2002, **41**, 2799; (*j*) W. Yan, J. Yu, R. Xu, G. Zhu, F. Xiao, Y. Han, K. Sugiyama, O. Terasaki, *Chem. Mater.* 2000, **12**, 2517.

22 S. Hazra, B. Sarkar, S. Naiya, M.G.B. Drew, A. Frontera, D. Escudero, A. Ghosh, *Cryst. Growth Des.* 2010, **10**, 1677.

23 J.-J. Wang, Z. Chang, A.-S. Zhang, T.-L. Hu, X.-H. Bu, *Inorg. Chim. Acta* 2010, **363**, 1377.

24 A. Banerjee, P. Maiti, T. Chattopadhyay, K.S. Banu, M. Ghosh, E. Suresh, E. Zangrando, D. Das, *Polyhedron* 2010, **29**, 951.

25 Z.-P. Deng, L.-H. Huo, Y.-M. Xu, S. Gao, H. Zhao, *Z. Anorg, Allg. Chem.* 2010, **636**, 2492.

26 (*a*) F.A. Mautner, L. Ohrstrom, B. Sodin, R. Vicente, *Inorg. Chem.* 2009, **48**, 6280; (*b*) R.-Y. Li, Z.-M. Wang, S. Gao, *CrystEngComm* 2009, **11**, 2096.

27 P.T. Ndifon, M.O. Agwara, A.G. Paboudam, D.M. Yufanyi, J. Ngoune, A. Galindo, E. Alvarez, A. Mohamadou, *Trans. Met. Chem.* 2009, **34**, 745.

28 Y. Bai, W.-L. Shang, D.-B. Dang, J.-D. Sun, H. Gao, *Spectrochim. Acta A* 2009, **72**, 407.

29 M. Xue, G. Zhu, H. Ding, L. Wu, X. Zhao, Z. Jin, S. Qiu, *Cryst. Growth Des.* 2009, **9**, 1481.

30 M.J. Lim, C.A. Murray, T.A. Tronic, K.E. de Krafft, A.N. Ley, J.C. de Butts, R.D. Pike, H. Lu, H.H. Patterson, *Inorg. Chem.* 2008, **47**, 6931.

31 (a) A. Ray, J. Chakraborty, B. Samanta, S. Thakurta, C. Marschner, M.S. El Fallah, S. Mitra, *Inorg. Chim. Acta* 2008, **361**, 1850; (*b*) M.A.S. Goher, M.R. Saber, R.G. Mohamed, A.K. Hafez, F.A. Mautner, *J. Coord. Chem.* 2009, **62**, 234.

32 A. Trzesowska, R. Kruszynski, *J. Coord. Chem.* 2008, **61**, 2167.

33 S.G. Baca, I.L. Malaestean, T.D. Keene, H. Adams, M.D. Ward, J. Hauser, A. Neels, S. Decurtins, *Inorg. Chem.* 2008, **47**, 11108.

34 Y. Chen, Y.-L. Wang, S.-M. Ying, S.-L. Cai, *Acta Crystallogr.* 2007, **E63**, m2751.

35 A.K. Ghosh, D. Ghoshal, M.G.B. Drew, G. Mostafa, N.R. Chaudhuri, *Struct. Chem.* 2006, **17**, 85.

36 J.K. Clegg, K. Gloe, M.J. Hayter, O. Kataeva, L.F. Lindoy, B. Moubaraki, J.C. McMurtrie, K.S. Murray, D. Schilter, *Dalton Trans.* 2006, 3977.

37 R. Wang, D. Yuan, F. Jiang, L. Han, Y. Gong, M. Hong, *Cryst. Growth Des.* 2006, **6**, 1351.

38 (*a*) J.K. Clegg, L.F. Lindoy, J.C. McMurtrie, D. Schilter, *Dalton Trans.* 2006, 3114; (*b*) J.K. Clegg, S.S. Iremonger, M.J. Hayter, P.D. Southon, R.B. Macquart, M.B. Duriska, P. Jensen, P. Turner, K.A. Jolliffe, C.J. Kepert, G.V. Meehan, L.F. Lindoy, *Angew. Chem. Int. Ed.* 2010, **49**, 1075.

39 J. Chakraborty, B. Samanta, A.S. Batsanov, J. Ribas, M.S.E. Fallah, S. Mitra, *Struct. Chem.* 2006, **17**, 401.

40 J. Chakraborty, B. Samanta, G. Rosair, V. Gramlich, M.S.E Fallah, J. Ribas, T. Matsushita, S. Mitra, *Polyhedron* 2006, **25**, 3006.

41 Q. Fang, G. Zhu, M. Xue, J. Sun, Y. Wei, S. Qiu, R. Xu, *Angew. Chem. Int. Ed.* 2005, **44**, 3845.

42 Q. Liu, Y.-Z. Li, H. Liu, F. Wang, Z. Xu, *J. Mol. Struct.* 2005, **733**, 25.

43 W.-G. Lu, H.-W. Liu, C.-H. Peng, X.-L. Feng, J. Chin., *Inorg. Chem.* 2005, **21**, 409.

44 Q. Fang, G. Zhu, M. Xue, J. Sun, G. Tian, G. Wu, S. Qiu, *Dalton Trans.* 2004, 2202.

45 Q. Liu, Y.-Z. Li, Y. Song, H. Liu, Z. Xu, *J. Solid State Chem.* 2004, **177**, 4701.

46 S. Konar, P.S. Mukherjee, M.G.B. Drew, J. Ribas, N.R. Chaudhuri, *Inorg. Chem.* 2003, **42**, 2545.

47 (a) Q. Liu, B. Li, Z. Xu, X. Sun, K.-B. Yu, Y.-Z. Li, *J. Coord. Chem.* 2003, **56**, 771; (b) S. Konar, S.C. Manna, E. Zangrando, T. Mallah, J. Ribas, N.R. Chaudhuri, *Eur. J. Inorg. Chem.* 2004, 4202.

48 S. Banerjee, M.G.B. Drew, A. Ghosh, *Polyhedron* 2003, **22**, 2933.

49 S.R. Batten, A.R. Harris, K.S. Murray, J.P. Smith, *Cryst. Growth Des.* 2002, **2**, 87.

50 S. Wang, M.-L. Hu, S.W. Ng, *Acta Crystallogr.* 2002, **E58** m242.

51 R. Cao, Q. Shi, D. Sun, M. Hong, W. Bi, Y. Zhao, *Inorg. Chem.* 2002, **41**, 6161.

52 Q. Liu, B. Li, Z. Xu, X. Sun, K. Yu, *Trans. Met. Chem.* 2002, **27**, 786.

53 (a) B. Moulton, J. Lu, M.J. Zaworotko, *J. Am. Chem. Soc.* 2001, **123**, 9224; (*b*) S. Hazra, S. Naiya, B. Sarkar, M.G.B. Drew, A. Ghosh, Polyhedron 2013, **65**,193.

54 L. Pan, N. Zheng, Y. Wu,W. Zhang, X. Wu, *Inorg. Chim. Acta* 2000, **303**, 121.

55 Y. Zhang, J. Li, M. Nishiura, T. Imamoto, *J. Mol. Struct.* 2000, **520**, 259.

56 S.R. Batten, B.F. Hoskins, R. Robson, *Chem. Eur. J.* 2000, **6**, 156.

57 M.-L. Tong, S.-L. Zheng, X.-M. Chen, *Acta Crystallogr.* 2000, **C56**, 960.

58 (*a*) S.G. Baca, M.T. Reetz, R. Goddard, I.G. Filippova, Y.A. Simonov, M. Gdaniec, N. Gerbeleu *Polyhedron* 2006, **25**, 1215; (*b*) S.G. Baca, I.G. Filippova, C. Ambrus, M. Gdaniec, Y.A. Simonov, N. Gerbeleu, O.A. Gherco, S. Decurtins, *Eur. J. Inorg. Chem.* 2005, 3118; (*c*) G. Smith, A.N. Reddy, K.A. Byriel, C.H.L Kennard, J. Chem. Soc., *Dalton Trans.* 1995, 3565;. (*d*) A. Escuer, R. Vicente, F.A. Mautner, M.A.S Goher, *Inorg. Chem.* 1997, **36**, 1233; (*e*) P. Lightfoot, A. Snedden, *J. Chem. Soc. Dalton Trans.* 1999, 3549; (*f*) H.-X. Zhang, B.-S. Kang, A.-W. Xu, Z.-N. Chen, Z.-Y. Zhou, A.S.C Chan, K.-B. Yu, C. Ren, *J. Chem. Soc. Dalton Trans.* 2001, 2559; (*g*) S. Wang, Y. Hou, E. Wang, Y. Li, L. Xu, J. Peng, S. Liu, C. Hu, *New J. Chem.* 2003, **27**, 1144; (*h*) A. Thirumurugan, S. Natarajan, *J. Chem. Soc., Dalton Trans.* 2004, 2923.

59 S.G. Baca, I.G. Filippova, O.A. Gherco, M. Gdaniec, Y.A. Simonov, N.V. Gerbeleu, P. Franz, R. Basler, S. Decurtins, *Inorg. Chim. Acta* 2004, **357**, 3419.

60 I. Shimizu, R. Tsuchiya, E. Kyuno, *Bull. Chem. Soc. Jpn.* 1967, **40**, 1162.

61 B.S. Furniss, A.J. Hannaford, V. Rogers, P.W.G. Smith, A.R. Tatchell, Vogel's Textbook of Practical Organic Chemistry, Longman, London, 4th edn, 1978.

62 G.M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.,* 2007, **64**, 112.

63 (*a*) G.M. Sheldrick, SHELX-97 Programme for Refinement of Crystal Structures, University of Gottingen, Gottingen, Germany, 1997; (*b*) A.L. Spek, PLATON, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46A**, C34.

64 (*a*) V.A. Blatov, *IUCr CompComm Newsl.* 2006, **7**, 4-38; (*b*) S.L. Cai, S.R. Zheng, J. Fan, R.H. Zeng, W.G. Zhang, *CrystEngComm*, 2016, **18**, 1174.

65 A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., *Dalton Trans.* 1984, 1349-1356.

66 J.K. Nath, A. Mondal, A.K. Powell, J.B. Baruah, *Crystal Growth & Design*, 2014, **14 (9)**, 4735.

67 (*a*) A. Banerjee, P. Maiti, T. Chattopadhyay, K.S. Banu, M. Ghosh, E. Suresh, E. Zangrando, D. Das, *Polyhedron* 2010, **29**, 951; (*b*) Y. Bai, W.-L. Shang, D.-B. Dang, J.-D. Sun, H. Gao, *Spectrochimica Acta Part A* 2009, **72**, 407.

68 (*a*) J. Song, Z. Zhang, S. Hu, T. Wu, T. Jiang, B. Han, *Green Chem.* 2009, **11**, 1031; (*b*) C.M. Miralda, E.E. Macias, M. Zhu, P. Ratnasamy, M.A. Carreon, *ACS Catal.* 2012, **2**, 180; (*c*) X. Zhou, Y. Zhang, X. Yang, L. Zhao, G.J. Wang, *Mol. Catal. A: Chem.* 2012, **361-362**, 12; (*d*) H.-Y. Cho, D.-A. Yang, J. Kim, S.-Y. Jeong, W.-S. Ahn, *Catal. Today* 2012, **185**, 35; (e) O.V. Zalomaeva, A.M. Chibiryaev, K.A. Kovalenko, O.A. Kholdeeva, B.S. Balzhinimaev, V.P. Fedin, *J. Catal.* 2013, **298**, 179; (*f*) 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.* 2013, **135**, 17105; (*g*) W.-Y. Gao, Y. Chen, Y. Niu, K. Williams, L. Cash, P.J. Perez, L. Wojtas, J. Cai, Y.-S. Chen, S. Ma, *Angew. Chem., Int. Ed.* 2014, **53**, 2615; (*h*) M.H. Beyzavi, R.C. Klet, S. Tussupbayev, J. Borycz, N.A. Vermeulen, C.J. Cramer, J.F. Stoddart, J.T. Hupp, O.K. Farha, *J. Am. Chem. Soc.* 2014, **136**, 15861; (*i*) J. Zheng, M. Wu, F. Jiang, W. Su, M. Hong, *Chem. Sci.* 2015, **6**, 3466; (j) X. Han, X.-J. Wang, P.-Z. Li, R. Zou, M. Li, Y. Zhao, *CrystEngComm* 2015, **17**, 8596; (*k*) M. North, R. Pasquale, C. Young, *Green Chem.* 2010, **12**, 1514; (*l*) M. Ding, H.-L. Jiang, *ACS Catal.* 2018, 8, 3194; (*m*) A. Monfared, R. Mohammadi, A. Hosseinian, S. Sarhandia, P. D.K. Nezhad, *RSC Adv.* 2019,**9**, 3884; (*n*) H. He J.A. Perman G. Zhu, S Ma, *small*, 2016, **46**, 6309; (*o*) H.-H. Wang, L. Hou, Y.-Z. Li, C.-Y. Jiang, Y.-Y. Wang, Z. Zhu, *ACS Appl. Mater. Interfaces* 2017, **9 (21)**, 17969; (*p*) J. Lan, M. Liu, X. Lu, X. Zhang, J. Sun, *ACS Sustainable Chemistry & Engineering* 2018, **6 (7)**, 8727; (*q*) J. Liang, Y.-B. Huang, R. Cao, *Coordination Chemistry Reviews*, 2019, **378**, 32.

69 S.M.J. Rogge, A. Bavykina, J. Hajek, H. Garcia, A.I. Olivos-Suarez, A. Sepúlveda-Escribano, A. Vimont, G. Clet, P. Bazin, F. Kapteijn, M. Daturi, E. V. Ramos-Fernandez, F.X. Llabrés i Xamena, V. Van Speybroeck, J. Gascon, *Chem. Soc. Rev.*, 2017, **46**, 3134

70 (*a*) X.-S. Wang, S.Q. Ma, P.M. Forster, D.Q. Yuan, J. Eckert, J.J. López, B. J. Murphy, J. B. Parise, H.C. Zhou, *Angew. Chem.,* 2008, **38**, 7373; (*b*) X.-S. Wang, S.Q. Ma, P.M. Forster, D.Q. Yuan, J. Eckert, J.J. López, B. J. Murphy, J. B. Parise, H.C. Zhou, *Angew. Chem., Int. Ed.*, 2008, **47**, 7263; (*c*) Y.G. Lee, H.R. Moon, Y.E. Cheon, M.P. Suh, *Angew. Chem., Int. Ed.,* 2008, **47**, 7741; (*d*) S.-S. Yu, X.-H. Liu, J.-G. Ma, Z. Niu, P. Cheng, *Journal of CO_2 Utilization* 2016, **14**, 122;(*e*) P.-Z. Li, X.-J. Wang, J. Liu, J.S. Lim, R. Zou, Y. Zhao, *J. Am. Chem. Soc.* 2016, **138**, 2142; (*f*) C.-Y. Gao, H.-R. Tian, J. Ai, L.-J. Li, S. Dang, Y.-Q. Land, Z.-M. Sun, *Chem. Commun.* 2016, **52**, 11147; (*g*) S.S.-Y. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams, *Science* 1999, **283**, 1148; (*h*) B. Ugale, S.S. Dhankhar, C.M.

View Article Online
DOI: 10.1039/C9DT01457H

Nagaraja, *Inorg. Chem.* 2016, **55**, 9757; (*i*) E.E. Macias, P. Ratnasamy, M.A. Carreon, *catalysis today* 2012, **198**, 215; (*j*) B. Zou, L. Hao, L.F. Zhi, M. G. Shi, L.C. Hui, L. Chang, W. Hu, *Journal of Catalysis* 2015, **329**, 119; (*k*) H. He, Q. Sun, W. Gao, J.A. Perman, F. Sun, G. Zhu, B. Aguila, K. Forrest, B. Space, S. Ma, *Angew. Chem. Int. Ed.* 2018, **57**, 4657; (*l*) R.K. Sharma, R. Gaur, M. Yadav, A. Goswami, R. Zbořil, M.B. Gawande, *Sci Rep.* 2018, **8**, 1901; (*m*) J. Ai, X. Min, C.-Y. Gao, H.-R. Tian, S. Dang, Z.-M. Sun, *Dalton Trans.,* 2017, **46**, 6756; (*n*) P.-Z. Li, X.-J. Wang, J. Liu, H. S. Phang, Y. Li, Y. Zhao, *Chem. Mater.* 2017, **29 (21)**, 9256; (*o*) B. Mousavi, S. Chaemchuen, B. Moosavi, K. Zhou, M. Yusubov, F. Verpoort, *ChemistryOpen* 2017, **6**, 674; (*p*) W.Y. Gao, L. Wojtas, S. Ma, *Chem. Commun.* 2014, **50**, 5316; (*q*) X. Huang, Y. Chen, Z. Lin, X. Ren, Y. Song, Z. Xu, X. Dong, X. Li, C. Hu, B. Wang, *Chem. Commun.*, 2014, **50**, 2624; (*r*) L. Liang, C. Liu, F. Jiang, Q. Chen, L. Zhang, H. Xue, H.-L. Jiang, J. Qian, D. Yuan, M. Hong, *Nature Communications* 2017, **8**, 1233; (*s*) V. Sharma, D. De, R. Saha, R. Das, P.K. Chattaraj, P.K. Bharadwaj, *Chem. Commun.*, 2017, **53**, 13371; (*t*) L.-Q. Wei, B.-H. Ye, *Inorg. Chem.* 2019, **58**, 4385.

View Article Online
DOI: 10.1039/C9DT01457H

Graphical Abstract: Synopsis and Pictogram

Copper(II) coordination polymers $[Cu_2(OAc)_4(\mu_4\text{-hmt})_{0.5}]_n$ (**1**), and $[Cu\{C_6H_4(COO^-)_2\}_2]_n.2C_9H_{14}N_3$ (**2**) have been synthesized and characterized. **1** showed high efficiency for CO_2 cycloaddition with small epoxides but its catalytic activity decreases sharply with increase in the size of epoxide substrates.