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Flexible Zn-MOF Exhibiting Selective CO_2 Adsorption and Efficient Lewis Acidic Catalytic Activity

Rashmi A. Agarwal,[a]* Anoop K. Gupta,[b] Dinesh De[b]

[a]Department of Civil Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

[b]Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India

ABSTRACT: A two dimensional, tetragonal porous metal organic framework **{[Zn_2(TBIB)$_2$(HTCPB)$_2$]·9DMF·19H_2O}$_n$ (1)** has been synthesized under hydrothermal conditions by employing 1,3,5-tri(1H-benzo[d]imidazol-1-yl)benzene (TBIB) and 1,3,5-Tris(4′-carboxyphenyl-)benzene (H_3TCPB). But non-covalent supramolecular interactions between the layers make this framework three dimensional, generating porosity in one dimension. Flexibility arises due to the presence of two types of large linkers wherein some functional groups of the ligands are not coordinated with the metal ion. Desolvated polymer shows moderate CO_2 uptake (65 cm^3 g^{-1} at 195 K and 1 bar) at low temperature and pressure. Compound **1** acts as a highly efficient heterogeneous catalyst towards the formation of cyclic carbonate through cycloaddition of CO_2 as well as towards the synthesis of quinoline derivatives by the Friedländer reaction. Presence of the free -COOH, -C=O groups and uncoordinated -N atoms on the wall of the pores make this framework an excellent candidate for the catalytic reactions without activation of the compound.

INTRODUCTION

The field of porous coordination polymers (PCPs) or metal organic frameworks have attracted a tremendous attention due to their large surface area, tuneable pore sizes and versatile architectures, lead to a variety of applications such as gas adsorption, separation and heterogeneous catalysis.[1-10] PCPs are often much more dynamic and flexible (3rd generation

compounds) which is due to the supramolecular non-bonding interactions present within the framework. Utilization of two large linkers causes flexibility in the framework due to adjustment of the linkers according to the coordination modes of the metal ion. In the presence or absence of guest molecules adjustments take place within the framework according to the availability of the space due to the presence of different types of non-bonding interactions shown by shrinking or elongation of the framework.[11] These structures can be transformed depending upon the external stimuli and thus having unique properties. Specifically ligand molecules undergo rotation due to the presence of large space.[12]

Exertion of abundantly available CO_2 towards the synthesis of fine chemicals is a recently very sustainable approach.[13,14] Global warming due to the high release of CO_2 from anthropogenic activities have attracted huge global drive towards the carbon dioxide capture and sequestration.[15]

Most of the previous studies have shown that formation of cyclic carbonate and other catalytic reactions occur due to presence of open metal sites.[16] MOF functionalized with nitrogen bases and other polar functional groups ($-NH_2$, $-OH$, $-NO_2$, $-COOH$, $-SO_3H$, etc.) enhances the selectivity towards CO_2.[17]

In the MOFs, vacant metal sites are generated by removing the metal bound solvent molecules. This process needs too much time, because first solvent exchange experiment is performed to replace the lattice as well as metal bound solvent molecules by low boiling solvent then finally, solvent exchanged sample is applied towards heating under high vacuum. During these processes, different MOFs can lose their crystallinity as well as, the chances for collapsing the frameworks are increases.[18] But recent studies have shown that host guest interactions are very important for high gas uptake as well for excellent catalytic activity.[19]

Herein the synthesized MOF have a number of free functional groups (-COOH, C=O and -N) which efficiently catalyse the reaction without activating the compound. Effective means for addressing environmental issues, the development of sustainable chemical sciences involves new technologies and efficient processes. Weaker non-covalent interactions such as hydrogen bonds, van der Waals forces and π-π contacts may also strongly influence the formation of coordination polymers.[20]

EXPERIMENTAL SECTION

Materials and Physical Measurements. All the chemicals were reagent grade from Aldrich and used without further purification. Solvents were purchased from S. D. Fine Chemicals, India. Characteristic spectroscopic techniques and X-ray structural studies have been provided in the Supporting Information.

Synthesis of 1,3,5-tri(1H-benzo[d]imidazol-1-yl)benzene (TBIB). TBIB was synthesized according to the previous study.[21]

Synthesis of 1,3,5-Tris(4′-carboxyphenyl-)benzene (H_3BTB). H_3BTB was prepared according to the published procedure.[22]

Synthesis of $\{[Zn_2(TBIB)_2(HBTB)_2]\cdot 9DMF\cdot 19H_2O\}_n$. A mixture of $Zn(NO_3)_2.6H_2O$ (60 mg, 0.188 mmol), TBIB (20 mg, 0.047 mmol), H_3BTB (20.6 mg, 0.047 mmol) and DMF:H_2O (3 ml, 3:1 v/v) was placed in a Teflon-lined stainless steel autoclave. The autoclave was heated up to 80 °C under autogenous pressure for 48 h and then allowed to cool to room temperature at a rate of 10 °C/h. Colourless crystals of the complex were obtained by filtration and washed with DMF followed by acetone. Yield = 80%. Anal. Calcd. for $C_{135}H_{170}N_{21}O_{40}Zn_2$ = C, 56.71; H, 5.95; N, 10.29%. Found: C, 56.45; H, 5.7; N, 10.40%. FT-IR (KBr pellets, cm-1): 3362 (broad), 1711 (m), 1672 (s), 1607 (s), 1551 (s), 1501(s), 1382 (s), 1231 (s), 773 (s) (Figure S1).

General Procedure for the Cycloaddition of CO_2 to Epoxides. As-synthesized compound (heterogeneous catalyst) was used directly without activation. Reactions were carried out in a Schlenk tube with stirring at room temperature depending on the substrate, and CO_2 (99.999%) bubbling. Epoxide (20 mmol), catalyst **1** (10 wt%), and co-catalyst TBAB (1 mmol) were added. Upon completion the reaction, the reaction mixture and catalyst were separated by filtration to obtain a crude compound. This crude mixture was given for ^{1}H NMR (in $CDCl_3$) to calculate the yield.

General Procedure for the Friedlander reaction

The reaction mixture containing 2-aminoaryl ketones (0.5 mmol), ethyl acetoacetate (1 mmol), and catalyst **1** (5 wt%) was placed in a RB at 85 ºC for 24 h with continuous stirring. As confirmed by the TLC, after completion of the reaction the reaction mixture is filtered to get the crude product. This crude product was purified by column chromatography by utilizing ethyl acetate/hexane (1/10 : v/v) as eluent to get the pure product.

RESULTS AND DISCUSSION

A flexible, layered PCP has been synthesized by the hydrothermal reaction of $Zn(NO_3)_2.6H_2O$ with TBIB and H_3TCPB in DMF and water at 80 °C for 48 h. 3D structure was generated via non-covalent supramolecular interactions between the layers creating porous structure showing 1D channels. Single crystal X-ray study reveals that **1** crystallizes in the monoclinic space group $P2_1/c$ and asymmetric unit consisting of two Zn(II) ions, two TBIB, two $HTPCB^{2-}$ ligands along with 9 DMF and 19 H_2O solvent molecules in the lattice. Zn1 has tetrahedral geometry MN_2O_2 with coordination from two N atoms of benzimidazole of two different TBIB and two O atoms of two carboxylates of two $HTCPB^{2-}$ ligands (Figure 1a). Metal ions in a 1D chain are connected by TBIB ligand and layered structure is created by metal ion coordination with $HTPCB^{2-}$ (Figure 1b). One benzimidazole -N atom of each TBIB ligand and two C=O group along with one -COOH of each $HTPCB^{2-}$ are free. Layers

are stacked in ABAB... fashion (Figure 1c) and are connected via non-covalent hydrogen and pi-pi bonding interactions as shown in Figure 1d leading to a three dimensional porous structure with 1D channels (including Vander Wal radii 13.5 × 8.3 $Å^2$) along the crystallographic *a* axis. Solvent accessible void volume was calculated to be 38% after squeezing solvent molecules. Topological analysis was carried out by using TOPOS software showing that Zn(II) metal ion has 4 connected node with point symbol $\{4^4.6^2\}$ and topological type sql/Shubnikov tetragonal plane net (topos&RCSR.ttd) (Figure S2).

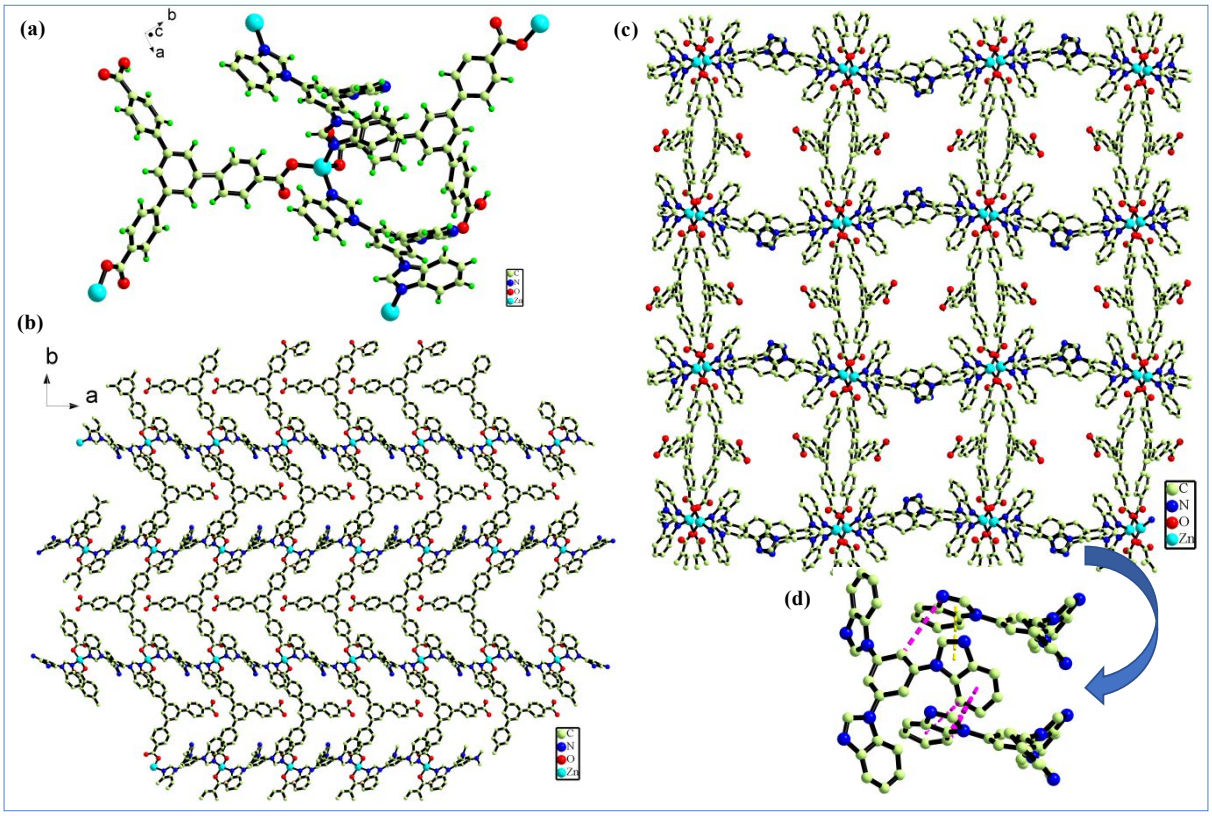


Figure 1. (a) Coordination environment around Zn(II) metal center, (b) layered structure of the polymer, (c) 3D structure and 1D pore formation through supramolecular interactions between layers, (d) interactions between TBIB of two different layers.

Thermal stability of the compound **1** has been checked by thermogravimetric analysis. TGA curve (Figure S3) shows weight loss of ~36.3% (calculated ~35%) corresponding to loss of all solvent molecules (water and DMF) from the cavities of the polymer between the

temperatures 80–290 °C. Compound is stable up to 350 °C after that decomposition takes place.

VTPXRD measurements (Figure S4) show that compound breathe at room temperature because in the PXRD of as-synthesized compound, diffraction peaks are slightly shifted towards higher 2θ value when compared with the simulated pattern. It shows that framework is slightly shrinked as temperature is increased.

Gas adsorption studies

Before gas adsorption measurements as-synthesized compound was first activated by immersing it in the DCM solvent to replace all the solvent molecules with the low boiling solvent molecules. After that it was heated up to 70 °C at high vacuum to make it free from all DCM molecules to generate **1a** (de-solvated).

To check the porosity of de-solvated compound **1a** gas adsorption studies have been done at low pressure (1 bar) and low temperature for H_2 and N_2 (77 K) and for CO_2 (195 K). Compound exhibits selectivity towards CO_2 gas showing type 1 adsorption isotherm revealing its microporous nature with saturation adsorption up to 65 cm^3g^{-1} with slight hysteresis at low temperature and pressure as shown in Figure 2. The Brunauer-Emmett-Teller (BET) surface area, calculated from CO_2 sorption at 195 K is 138 m^2 g^{-1}. As PXRD measurements (Figure S4) reveal that **1** is a highly flexible coordination polymer because even at room temperature, its peaks get shifted slightly towards higher 2θ angle but at increasing temperatures peaks shifting is more towards higher 2θ angle. It leads to the higher shrinkage in the polymer with respect to the increase in temperature. That is why at room temperature CO_2 adsorption is only 11.4 cm^3g^{-1} due to contraction in the framework (Figure S6). Pore size distribution analysis shows (Figure S5) that pores have an average diameter of 1.8 nm with pore volume approximately ~0.10 cm^3g^{-1} due to shrinkage. H_2 gas is not

adsorbed due to its non-polar nature while framework has polarity due to the presence of free functional groups in both the linkers. N_2 sorption does not takes place at the surface of the flexible polymer due to the presence of 1D pores and large kinetic diameter of N_2. While CO_2 is a polar molecule and it needs polar environment to get inside the structure due to having higher quadrupole moment. Presence of free -COOH, C=O groups and uncoordinated benzimidazole N atoms provide polarity to the wall of the pore, facilitating CO_2 gas adsorption. But in this MOF there are free carboxylic acid groups which are present at the pore surface and CO_2 groups are also acidic in nature so gas adsorption is decreased due to repulsive nature of the same charges.

Previous literature studies show that mesoporous silica materials have larger sorption properties for CO_2 over a wide range of pressures at different temperatures reported by Sayari et al.[23] But modified mesoporous silica structures with triamine and polyethylenimine (PEI) functionalization with different pore lengths show fast CO_2 adsorption properties.[24,25] CO_2 adsorption in Na-A zeolite at 273–333 K temperature and desorption at higher temperature (573–673 K) has been reported by Zukal et. al. where small portion of CO_2 retain in the form of surface carbonates.[26] Zeolitic structures cannot be functionalized/tuned according to the requirement. High CO_2 uptake (5.28 mmol/g) have been observed in Mg-MOF-74 (CPO-27-Mg) at 40 °C and at low pressure under dry conditions due to the strong interaction of open metal sites (OMSs) with CO_2 molecules. But presence of moisture affects the gas uptake because then water molecules are coordinated with the OMSs.[27-29] Cu-BTC also have unsaturated Cu metal sites which helps in CO_2 adsorption accurately calculated by employing a combined DFT-ab initio computational scheme.[30] Synthesis of functionalized MOFs by introducing a high density of free amine groups in Mg-MOF-74 showed exceptionally high uptake of CO_2 due to strong affinity towards CO_2 even in the presence of high humidity.[31]

Monodentate hydroxide also have strong reversible interaction with CO_2 via the formation and decomposition of bicarbonate.[32] But in present case due to flexible nature of the framework even at room temperature, CO_2 adsorption decreases at higher temperature because of contraction in the framework. Recently selective uptake of CO_2 has been done by a number of different groups wherein MOF featuring free N and carboxylate O atoms.[33-35]

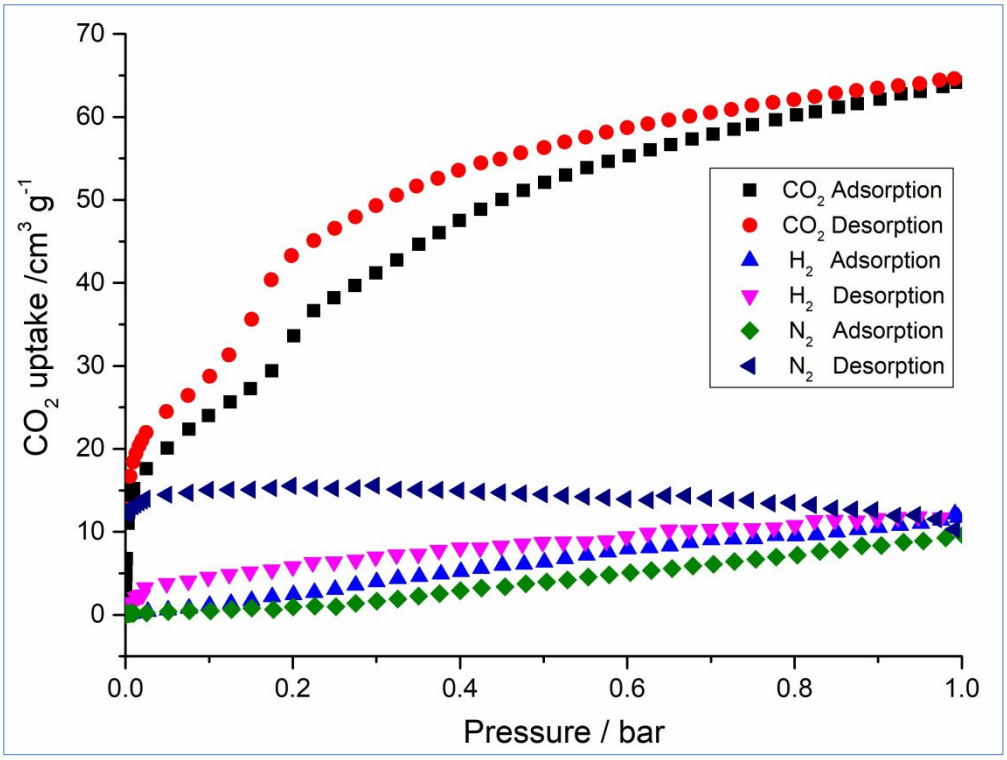


Figure 2. Gas adsorption isotherm of **1**: CO_2 at 195 K temperature, H_2 and N_2 at 77 K temperature and 1 atm pressure.

This polymer shows different catalytic reactions without activating the framework due to the presence of free acidic groups (-COOH) inside the cavities which initiate the catalysis. On the other hand free C=O and N atoms of the benzimidazole groups are also present in the structure leading to the enhancement of the rate of the reaction. A great effect of the flexibility or breathing effect of the **1** even at room temperature which arises due to the presence of two large linkers having a number of free groups (non-coordinated) which can be adjusted according to the coordination mode of the metal ion. There are a number of metal

organic frameworks which undergo these type of reactions having Lewis acidic sites along with the basic sites in the framework performing synergistic catalysis.[36-53] Unsaturated metal sites can be generated after removal of coordinated solvent molecules during activation at high temperature. It takes a long time to prepare catalysts for the reaction. Recent MOFs containing open metal sites along with MNPs (metal nanoparticles) embedded in the cavities of the polymer have been synthesized for catalytic reactions.[54-61] In this case first MOF will be synthesized after that NPs encapsulation occurs. It is not only a costly process but also a time consuming process because activation is required after each cycle of the catalysis. In the case of zeolites, size of the product molecule is limited by the size of the pore apertures as well as these zeolitic structures are deactivated by the small amount of coke which can block the access of the reactants towards the active sites.[62, 63]

While molecular sieves are not only very expensive but also should not be exposed to water due to giving off heat. Its dust can also irritate sensitive tissues as well as after following a shutdown, temperatures in a molecular sieve bed can stay hot for weeks so bed should be cooled properly to switch it for adsorption.

Cycloaddition of CO_2 to Epoxides

The structural observation of **1**, shows several important features like the presence of free protonated carboxylic acid groups, carbonyl groups and the presence of Lewis basic sites originating from the rich N-containing TBIB ligand. Because of the permanent porosity of the framework with open channels it captures CO_2 selectively which enable substrate diffusion. Due to these prominent features in **1**, heterogeneous catalytic activity has been evaluated through the cycloaddition of CO_2 to various epoxides to yield value added product, cyclic organic carbonates. Cyclic carbonates have gained much attention due to their broad spectrum of applications such as polar aprotic solvents, electrolytes for lithium-ion batteries, pharmaceutical/fine chemical intermediates, and in many biomedical applications.[21,22] Cyclic

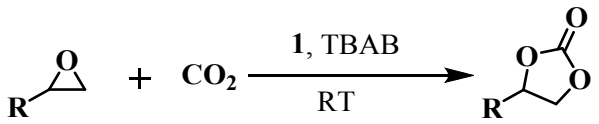
carbonates are also used as constituents of oils and paints and as monomers for the synthesis of polycarbonates[23] and polyurethanes[22] since they can undergo ring-opening polymerization. The cycloaddition of styrene oxide with CO_2 into phenyl ethylene carbonate was selected as a model reaction to explore the catalytic behaviour of the MOF. The cycloaddition reaction has been carried out at room temperature, 1 atm pressure of CO_2 under solvent-free conditions using catalyst (**1**, 30 mg) with tetra-*n*-tertbutylammonium bromide (TBAB, 60 mg) as co-catalyst for 24 h. The results are summarized in Table 1. The cycloaddition reaction could not occur remarkably in the absence of either of the MOF catalyst or co-catalyst (entry 5 and 6). If H_3TCPB is taken as a homogeneous catalyst along with TBAB as a co-catalyst then 20% yield of the cyclic carbonate is obtained. It was found that the styrene oxide could be converted into the corresponding cyclic carbonate with excellent yield (>99 %) when both catalyst and TBAB were used combinedly (entry 1).

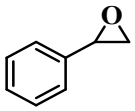
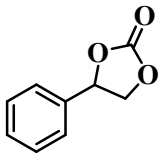
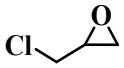
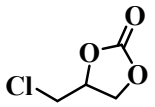
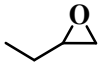
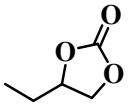
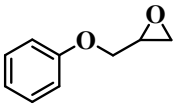
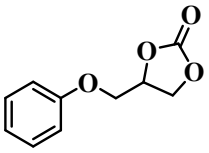
The activity of the catalyst was then evaluated in more depth. Such, high catalytic activity was also observed for the cycloaddition of CO_2 with various epoxide substrates to produce corresponding cyclic organic carbonates under the same reaction conditions (Table 1). Specifically, epichlorohydrin and 1,2-butylene oxide reacts efficiently with the yields of >99% (Table 1, entry 2) and >99% (Table 1, entry 3), respectively. Phenyl glycidyl ether was little bit less reactive due to the steric effect of the substrates, while a yield of 82% was still achieved (Table 1, entry 4).

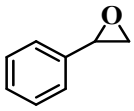
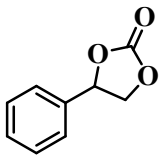
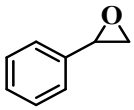
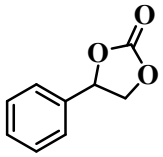
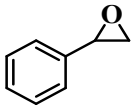
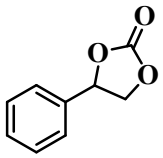
To judge the heterogeneous nature of the MOF catalyst, filtration test have been performed with the model reaction using optimized reaction conditions to ensure that the catalytic activities do not originate from leaching of any metal ions from the MOF structure. After 24 h, the MOF catalyst was removed by filtration and the reaction was allowed to continue. As expected, there was no significant increase in the formation of styrene carbonate detected after the MOF catalyst was removed. Indeed, this result primarily provides strong support for

the fact that the catalytic reaction was heterogeneous in nature. Recycling studies were then undertaken using the optimized conditions where the reaction mixture was filtered to collect the catalyst and washed several times with chloroform and then by acetone. After drying at room temperature the catalyst was regenerated and further used it for subsequent runs and checked its recyclability. In the model reaction, MOF catalyst was reused up to five successive times with the yield of styrene carbonate slightly decreasing in the first run to 82% after that yield is constant till fifth run (Figure S7). PXRD analysis was performed on the recycled MOF catalyst, in which structural preservation was proven (Figures S8).

Table 1. Coupling of various epoxides with CO_2 at room temperature and at atmospheric pressure using 1[a]



Entry	Epoxide	Catalyst	Co-catalyst	Time (h)	Cyclic Carbonate	Yield (%)[b]
1		**1**	TBAB	24		>99
2		**1**	TBAB	24		>99
3		**1**	TBAB	24		>99
4		**1**	TBAB	24		82

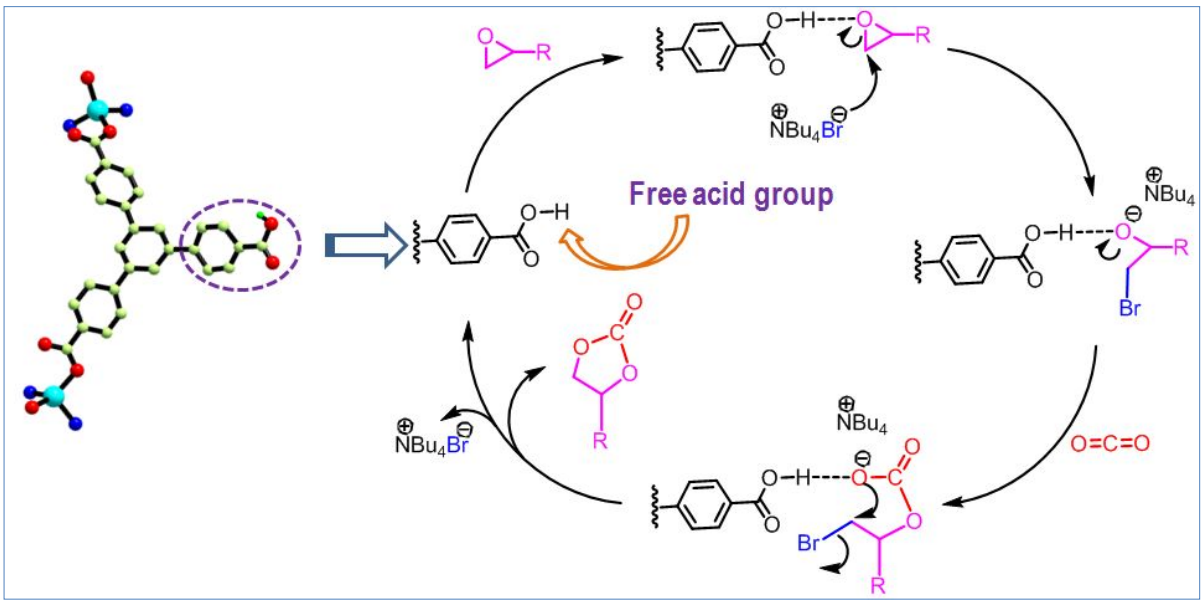
5		**1**	None	24		7
6		None	TBAB	24		12
7		H_3TCPB	TBAB	24		20

[a]Reactions were carried out in a 10 mL two-necked round bottom flask at room temperature and CO_2 bubbling. Epoxide (20 mmol, 1 equiv), **1** (0.0025 equiv), TBAB (0.05 equiv). No solvent was added. [b]Yields were calculated using 1H NMR analysis by integration of epoxide versus cyclic carbonate peaks (see the Supporting Information Figures S9-S12).

As heterogeneous catalyst **1** has free COOH, C=O groups (one COOH group and two C=O groups free for one H_3TCPB linker) along with non-coordinated benzimidazole N atoms which are decorated at the surface of the pores so there is no need to activate this catalyst due to the presence of protonated carboxylic acid groups. Recently cyclic carbonate formation in MOF was demonstrated by Li et al and Wang et al due to the presence of Lewis acidic metal sites and uncoordinated carboxylate O atoms.[34, 35] Previous literature propose the mechanism that free carboxylic acid groups help in catalyzing the reaction efficiently.[64,65] But framework was activated at higher temperature to remove lattice solvent molecules as well as coordinated solvent molecules. But in this case as-synthesized compound was used directly. COOH group of the catalyst initiates formation of non-covalent interaction with the epoxide substrate followed by ring opening through simultaneous nucleophilic attack of bromide ion from co-catalyst TBAB. After that CO_2 reacts with the O atom of the epoxide in a

electrophilic manner forming a carbonate intermediate. Finally cyclic carbonate is formed through intramolecular ring closure.

Scheme 1. Proposed mechanism for the synthesis of cyclic carbonate by the catalyst 1



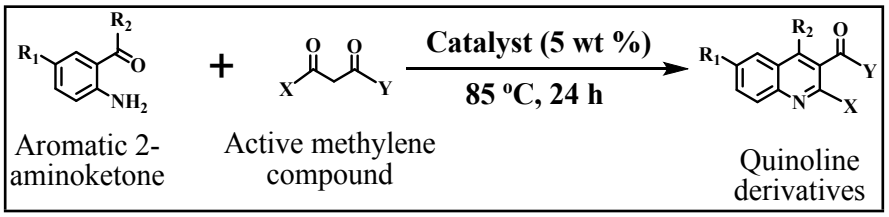
Friedländer reaction : synthesis of quinoline derivatives. As mentioned earlier that high thermal stability, large pore volume as well as free carboxylic acid (-COOH) groups along with the free C=O and -N, groups in the frameworks makes it a good Lewis acid heterogeneous catalyst. To check its Lewis acid nature, Lewis acid catalysed reaction has been performed. Here, synthesis of quinoline derivatives via the Friedländer reaction, has been demonstrated by employing catalyst **1** (Scheme 2). Quinoline is an important and ubiquitous backbone in innumerable biological and pharmaceutical molecules.[66] Quinoline derivatives exhibit antibacterial, antimalarial, anti inflammatory, anti-asthmatic, anti-hypertensive and tyrosine kinase PDGF-RTK inhibiting properties.[67, 68] Moreover, quinolines act as synthons for the synthesis of nanostructures and polymeric materials that convoy the optoelectronic or NLO properties with excellent mechanical strengths.[69, 70] Since, quinolines are important in industry, pharmacology and synthetic points of view, numerous versatile synthetic procedures have been reported for their synthesis.[71-74] Among those, the Friedländer

hetero-annulation is one of the most simple and a direct route for the quinoline synthesis. In Friedländer hetero-annulation reaction, different poly substituted quinoline derivatives have been synthesized through reaction between an aromatic 2-aminoaldehyde or ketone and an active methylene containing carbonyl compounds.[75, 76] However, there has been tremendous development towards the synthesis of quinoline derivatives using acid catalyst, by avoiding the use of the traditionally basic conditions.[77-79] Apart from conventional protic acids, many other catalysts have also been used for the Friedländer synthesis.[80, 81] MOFs having open metal sites which act as Lewis-acids, have already shown catalytic activity for the Friedländer reaction.[82] Perez-Mayoral et al. investigated CuBTC catalyzed Friedländer condensation by a combination of different experimental techniques as well as by DFT based modelling and found that CuBTC showed improved catalytic activity when compared with other MOFs e.g. in BEA and (Al)SBA-15 containing high concentraion of Lewis acid sites.[83, 84]

As already mentioned that the activation process to generate active sites or vacant metal sites is a prolonged process and the chances for the degradation of frameworks are increases.

In the present study, a carboxylate based Zn-MOF (**1**) has been designed that have free carboxylic acid groups at the pore surface of the framework. Catalytic behaviour of **1** showed its huge potential as a promising acidic heterogeneous catalyst for the synthesis of quinoline derivatives (Scheme 3).

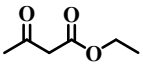
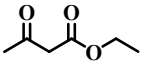
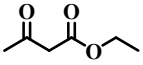
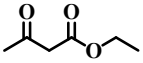
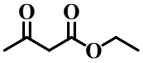
Scheme 2. Synthesis of quinoline derivatives via the Friedländer reaction between aromatic 2-aminoketone and active methylene compounds

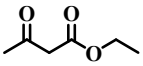
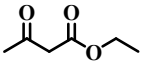


At first, the model reaction between 2-aminobenzophenone (0.5 mmol) and ethyl acetoacetate (1 mmol) have been done in the presence of **1** (5 wt%) at 85 ºC for 24 h which gave the

desired compound in 97% isolated yield (Table 1, Entry 1). A possible mechanism for the synthesis of quinolines using this catalyst is shown in Scheme 3, where the free carboxylic acid group catalyses the reaction in the same way as shown by the vacant metal sites in CuBTC MOF due to the hard Lewis acid character.[83] It is shown in the Table 1 that the various aromatic 2-aminoketone (0.5 mmol) have been used with ethyl acetoacetate (1 mmol) in presence of catalyst **1** (5 wt%) under solvent-free conditions at 85 ºC for 24 h, to give the respective quinoline derivatives in moderate to excellent yields. The 98% and 94% yields was observed with 4-chloro and 4-nitro substituted 2-aminobenzophenone respectively (Table 1, entries 2 and 3). Also, the catalytic activity of **1** was tested with 2-aminoacetophenone and ethyl acetoacetate (1 mmol) that afforded product with 95% Yield (Table 1, entry 4). The heterogeneous catalytic activity of **1** showed superiority over both the homogeneous zinc salt i.e. zinc acetate as well as the H_3TCPB which gave the desired product in low yields that is 26% and 21%, respectively (Table 1, entry 5 and 6). Also, the non-catalyst experiment was performed, in which 2-aminobenzophenone and ethyl acetoacetate was reacted in absence of any catalyst that showed very low yield (9%) (Table 2, entry 7), confirming the catalytic activity of **1**.

Table 2. Friedländer reaction between different aromatic 2-aminoketone and different active methylene compounds[A]

Entry	Catalyst	Aromatic 2-aminoketone		Active methylene compound	Yield (%)[B]
		R_1	R_2		
1	**1**	H	Ph		97
2	**1**	Cl	Ph		98
3	**1**	NO_2	Ph		94
4	**1**	H	Me		95
5	**$Zn(OAc)_2 \cdot (H_2O)_2$**	H	Ph		26

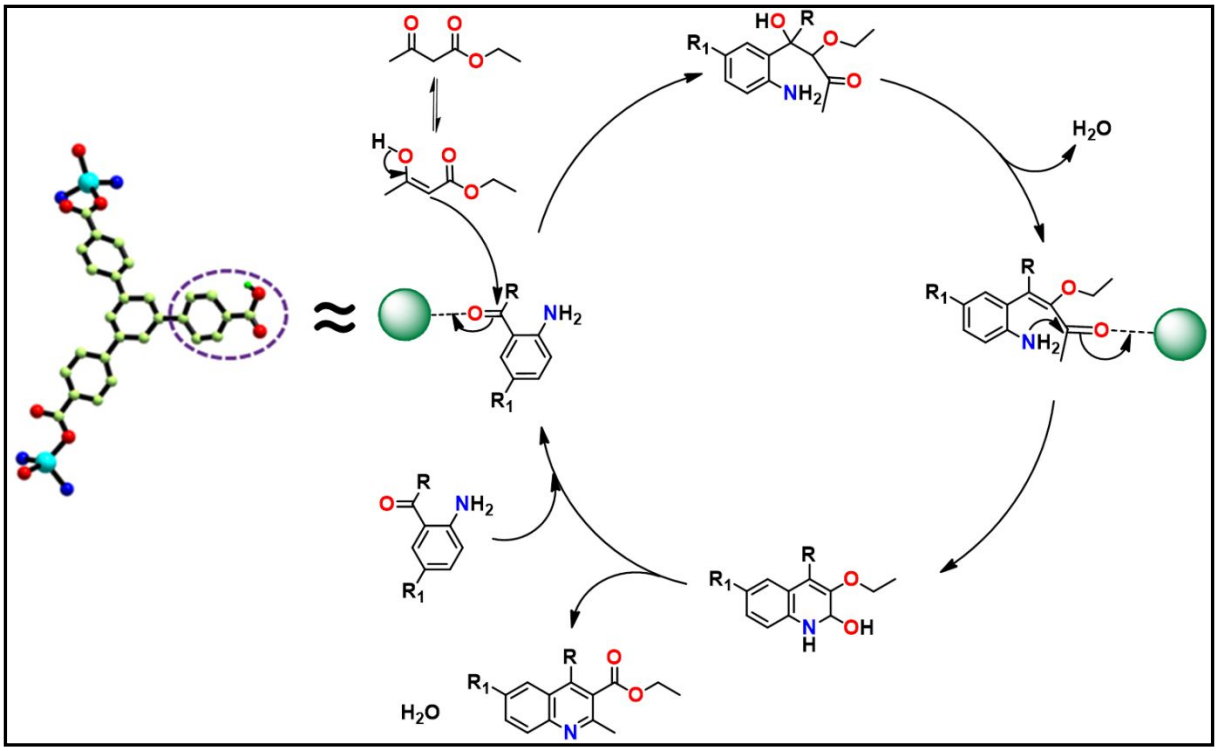
6	**H_3TCPB**	H	Ph		21
7	**No Catalyst**	H	Ph		9

[A] 2-aminoaryl ketones (0.5 mmol), ethyl acetoacetate (1 mmol), and catalyst **1** (5 wt %), sealed tube 85 ºC for 24 h. [B] Yield of the isolated product after flash chromatography.

As described above, the heterogeneous nature of **1** was confirmed by the hot filtration experiment, as well as the framework is reusable and the framework integrity was maintained during the recyclability experiments.

These data show that **1** is a proficient Lewis-acid catalyst in Friedländer reactions with varied substrates. In each case, the characterization of desired product was achieved by the ^{1}H, ^{13}C NMR spectroscopy (Figures S13–S20).

Scheme 3. Proposed Mechanism for the synthesis of quinoline derivatives through Friedländer reaction



CONCLUSIONS

Hydrothermally synthesized flexible Zn-based 2D porous coordination polymer shows selective CO_2 gas adsorption. It breathes at room temperature due to the presence of two large

size linkers, but at higher temperature flexibility is increased. It acts as an excellent heterogeneous catalyst towards the chemical fixation of CO_2 to cyclic carbonates as well as towards the synthesis of quinoline derivatives through Friedländer reaction. Catalytic activity is due to the presence of free protonated COOH groups in the polymer which are decorated at the surface of the pores. There are free C=O groups along with non-coordinated benzimidazole N atoms which assist the reactivity of the catalyst.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI ;

with Physical measurements, X-ray structural studies, IR, TGA, PXRD and NMR spectra.

X-ray crystallographic data of **1** (CCDC number -1819056).

AUTHOR INFORMATION

Corresponding Author

E-mail: rashmi.a.agarwal@gmail.com

Notes

The authors declare no competing financial interest.

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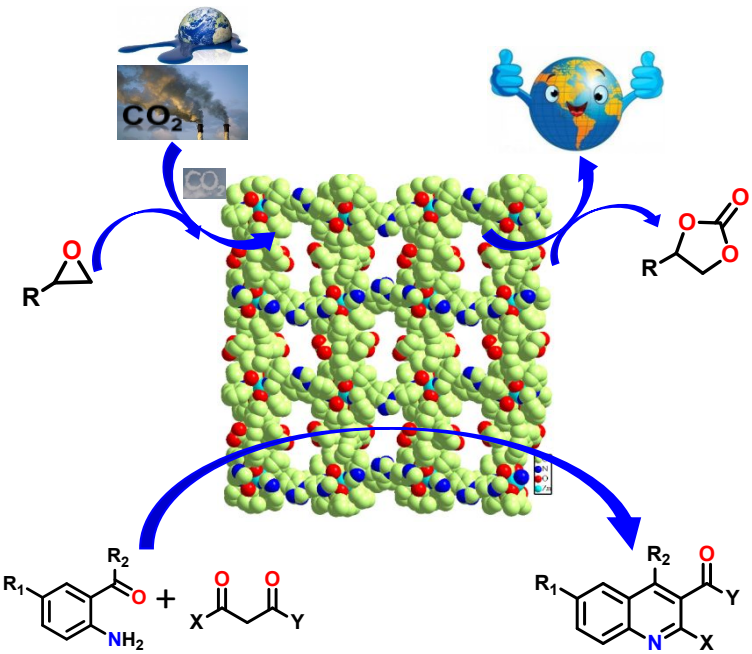
Flexible Zn-MOF Exhibiting Selective CO_2 Adsorption and Efficient Lewis Acidic Catalytic Activity

Rashmi A. Agarwal,[a]* Anoop K. Gupta,[b] Dinesh De[b]



Zn(II) based flexible porous coordination polymer shows excellent heterogeneous catalytic activity due to the presence of Lewis acidic groups in the large linkers. Transformation of CO_2 in to cyclic carbonates as well as synthesis of quinoline derivatives through Friedländer reaction could be done successfully by using this polymer.