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An excellent 3D Cu-MOF with exposed Lewis acidic Cu sites for CO_2 adsorption and catalytic fixation *via* Cyclic Carbonate synthesis

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[#]*A.K.G. dedicates this work to Prof. P. K. Bharadwaj on the occasion of his 74th Birthday.*

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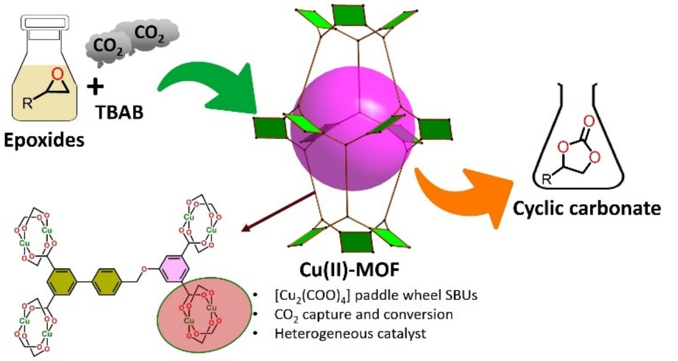
Article



ABSTRACT

A novel 3D porous **Cu(II)**-metal-organic framework (**MOF**) with exposed Lewis acidic Cu sites has been synthesized under solvothermal conditions utilizing the new tetratopic linker, 4′-((3,5-dicarboxyphenoxy)methyl)-[1,1′-biphenyl]-3,5-dicarboxylic acid. The synthesized **Cu(II)-MOF** is thoroughly characterized by various physicochemical methods: powder XRD, TGA, FTIR, and gas adsorption studies. The microporous **Cu(II)-MOF** material featuring open channels which after activation affords unsaturated Lewis acidic Cu(II) metal sites, proved to be a good capturing agent for CO_2. The gas adsorption isotherms indicate that activated **Cu(II)-MOF′** is efficient in CO_2 uptake and in the presence of epoxides and TBAB as co-catalysts it leads the CO_2 chemical fixation into five-membered cyclic carbonates under mild and solvent free reaction conditions. The implication of unsaturated Cu(II) metal sites and their synergism with TBAB for the chemical fixation of CO_2 were probed using various epoxides by observing the appreciable conversion. Moreover, the catalyst **Cu(II)-MOF′** upholds its adequate stability as well as recyclability for five consecutive cycles without apparent loss in its catalytic activity. Under nearly similar reaction conditions, the results signify a comparable CO_2 conversion with various reported MOF-based catalysts. Finally, a plausible mechanism for CO_2 fixation with epoxide under the catalytic influence of **Cu(II)-MOF′** has been proposed.

Keywords: Copper-metal-organic frameworks (MOFs), CO_2 capture, chemical conversion, heterogeneous catalysis, cyclic carbonates

INTRODUCTION

The ascending industrialization and global population are intensifying the planetary energy demand which is mostly met by fossil fuel burning that causes decimation in the global climate.[1,2] According to the NASA global climate change reports, Mauna Loa Observatory, Hawaii measures the global average concentration of atmospheric CO_2 was about 378 ppm in 2005 and rising recklessly to 418 ppm (current), shift towards the hazardous zone with progressing time. Various governments affianced in the Kyoto Protocol of the United Nations Framework Convention on Climate Change to reduce CO_2 emission.[3] Contrary to its antagonistic environmental implications, the chemical exploitation of CO_2, an abundant renewable C1 resource,[4] has been extensively employed for fine chemical synthesis via an alternative sustainable approach,[5] which spurring the research in sustainable and green carbon science.[6] Such ventures not only mitigate the greenhouse effect but also afford value-added intermediated and/or products that are extensively used as electrolytes in lithium-ion batteries, intermediates as well as precursors in pesticides, pharmaceuticals, and cosmetics.[7-10] Acid-catalyzed synthesis of cyclic organic carbonates *via* cycloaddition of CO_2 and epoxides is a highly atom-economical process. The industrial production of cyclic carbonates requires drastic reaction temperatures and pressures and has self-explanatory shortcomings of separation, purification, and recycling of homogeneous catalysts.[11] Also, it experiences the use of noxious reactants like phosgene gas, haloformates, or carbon monoxide.[12-14] This has directed attention to developing promising CO_2 capture and sequestration (CCS) technologies for the dilemma between rising energy demand and the pressing deterioration of the global climate.[15] Considerably, these anxieties have been overcome by exploring versatile heterogeneous catalysts such as zeolites, coordination

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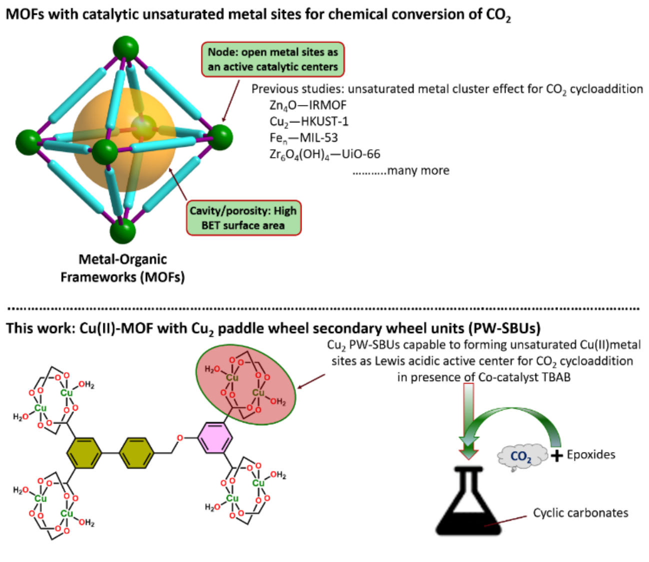
complexes, metal oxides, graphite oxide, and functional polymers, which usually suffer from leaching or poor activity in vast situations.[16-20] Recently, various research groups have focused on practical applications by utilizing an innovative and efficient class of porous heterogeneous systems, *i.e.*, metal-organic frameworks (MOFs) for the chemical conversion or fixation of CO_2 and epoxides.[21,22] However, new approaches for the capture of CO_2 and its conversion into fine chemicals through effortless separation and recyclability that feature non-leaching characteristics are still highly desirable.

MOFs are ordered hybrid structures having high porosity, tunable composition, and pore surface, and have drawn considerable research attention in the field of selective gas adsorption and separation, effective heterogeneous catalysis, water splitting, drug delivery, ferroelectricity, fluorescence sensing, etc.[23-28] Due to the tailorable nature of MOFs, they become promising porous materials and could be selectively adsorbed as well as chemically convert the CO_2 molecule. Consequently, the released CO_2 could be recycled from the carbon cycling on the earth.[29] Among many strategies, the creation of open metal sites (OMSs) in a MOF material not only provides the adsorption sites for CO_2[30] but can also be employed as heterogeneous Lewis acid catalysts for the efficient chemical conversion of CO_2 into cyclic carbonate (Scheme 1).[31] The combined benefits of MOFs in the context of adsorbent and heterogeneous catalysts make them an excellent material of choice that satisfies the dual requirements for capture and conversion of CO_2,[32] and may fulfill several crucial features such as chemical and thermal stability, considerable selective adsorption capacity for CO_2, and high density of accessible OMSs as Lewis acidic and/or other Brønsted acidic sites.[33] Liang *et al.* have utilized a 4,4-connected ***NbO***-type Cu-MOF[34] synthesized from a semirigid tetracarboxylate ligand 5-(3,5-dicarboxybenzyloxy)-isophthalic acid (identical to the linker of present work), having the binuclear paddlewheel-type $[Cu_2(COO)_4]$ cluster.[35]



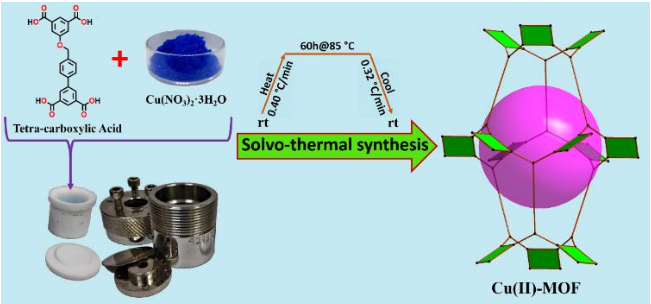
Scheme 1. Exposed Lewis acidic open metal sites for CO_2 fixation via cyclic carbonate synthesis.

Upon heating, a porous MOF embellished with unsaturated metal centers was formed that possessed high BET surface area (1773 m^2 g^{-1}) and high CO_2 uptakes of 170 cm^3 g^{-1} (7.59 mmol g^{-1}) and 122 cm^3 g^{-1} (5.45 mmol g^{-1}) under 0.95 bar at 273 and 298 K, respectively, and exhibited CO_2/N_2 adsorption selectivity is 21.13 times at 273 K.[35] Therefore, the blueprint for the construction of new MOFs with the above-mentioned features is an appealing project for the capture and conversion of CO_2.

Taking aforesaid discussion into account, in the present report, we have designed and synthesized a new linker *i.e.* 4′-((3,5-dicarboxyphenoxy)methyl)-[1,1′-biphenyl]-3,5-dicarboxylic acid, (**H_4L**) containing ether bridging among the isophthalic acid coordination sites on both ends (Scheme1). The thermally stable **Cu(II)-MOF** with a $[Cu_2(COO)_4]$- type paddlewheel cluster has been constructed using linker (**H_4L**), and having uniformly distributed channels with large pore volume and exposed unsaturated metal centers (UMCs) is a potential microporous material for chemical fixation of CO_2 to cyclic carbonates. The excellent CO_2 loading capacity and accessible Lewis acidic catalytic Cu sites with TBAB co-catalyst, efficiently fixate CO_2 with epoxides to afford cyclic carbonates under mild and solvent-free conditions with excellent recyclability and no substantial loss in catalytic activity has been observed. Also, the possible synergistic mechanism of **Cu(II)-MOF**/TBAB catalysts for the chemical conversion of CO_2 has been proposed.

RESULTS AND DISCUSSION

The tetratopic linker 4′-((3,5-dicarboxyphenoxy)methyl)-[1,1′-biphenyl]-3,5-dicarboxylic acid (**H_4L**) has been synthesized through substitution followed by hydrolysis of corresponding tetraester (Scheme S1). The assembly of the **H_4L** ligand with $Cu(NO_3)_2 \cdot 3H_2O$ under solvothermal conditions produced a fine block-shaped, blue-colored **Cu(II)-MOF** (Scheme 2).



Scheme 2. Synthetic scheme for the construction of **Cu(II)-MOF**.

Several attempts have been made to prepare the crystals suitable for single-crystal diffraction characterizations, however, unsuccessful. However, the structure of the synthesized sample for **Cu(II)-MOF** was deduced from the PXRD. The PXRD pattern of the synthesized **Cu(II)-MOF** matches well with simulated PXRD patterns of ZJNU-50 which was constructed by using an identical and nearly equal length of the linkers (Figure 1).[36] Therefore, it can be concluded that **Cu(II)-MOF** has an identical network architecture with ZJNU-50, except for the ether bond (-O-) instead of a slim C≡C triple bond bridging two isophthalate groups in the ligand of **Cu(II)-MOF**.

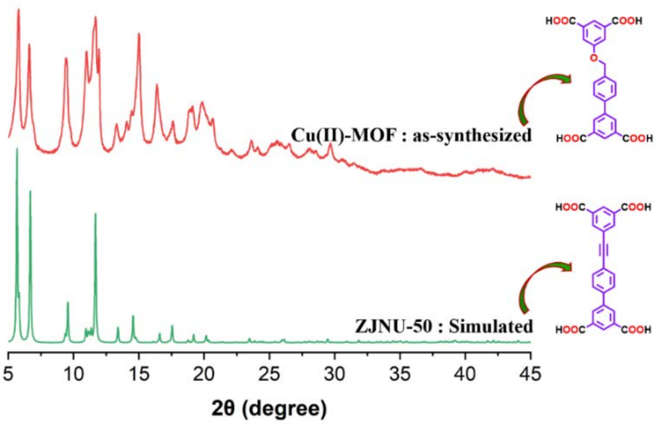


Figure 1. Comparison of PXRD patterns of the synthesized **Cu(II)-MOF** and simulated ZJNU-50[36]. The molecular structures of the used linkers are shown on the right side.

Owing to the isomorphic structure of **Cu(II)-MOF** with ZJNU-50, the framework of **Cu(II)-MOF** can therefore be deduced from the crystallographic data of ZJNU-50, and the $[Cu_2(COO)_4]$ secondary building units (SBUs) can be determined for **Cu(II)-MOF** (Figure 2a). The assembly of $[Cu_2(COO)_4]$ SBU with the isophthalate groups forms the typical type-I windows[36,37] viewing along the c-axis (Figure 2c), and creates two types of cages by the assembly of the **H_4L** ligand with the $[Cu_2(COO)_4]$ SBUs (Figure 2b). The assembly of the 4-connected **H_4L** ligand and the 4-connected paddle-wheel SBUs gives rise to an *NbO* network, with the point symbol of $6^4 8^2$.[38,39] The overall architect incorporated with solvent molecules in their pores, and could be removed by subjecting the as-synthesized **Cu(II)-MOF** towards a solvent exchange process with acetone followed by their activation at 90 °C under high vacuum. The activated sample (**Cu(II)-MOF′**) are structurally identical with the as-synthesized one that is verified by matching their PXRD patterns (Figure S8) and infrared spectroscopy (Figure S10). Furthermore, the TGA measurements show that **Cu(II)-MOF** can remain stable up to ~280 °C (Figure S11).

Gas Adsorption Studies

The nitrogen adsorption-desorption measurements were carried out at 77K. The N_2 sorption isotherm showed the type IV isotherms with an H1 hysteresis loop (Figure 3a).[40] The steep uptake of N_2 gas at P/P_0 <0.01 is the characteristic of microporous materials.[41] The Brunauer-Emmett-Teller (BET) surface area and pore size distributions were estimated from the N_2 sorption isotherm (Figure S12a and 3b). The BET-specific surface area of **Cu(II)-MOF** was found to be 864 $m^2\ g^{-1}$ with pore volumes of 0.901 $cm^3\ g^{-1}$. The uniform pore size distribution, peak centered at 1.26 nm (12.6 Å), was obtained based on the QSDFT method (Figure 3b). The external surface area estimated from the t-plot method was found to be 204 $m^2\ g^{-1}$, accounting for the large micropore area of 660 $m^2\ g^{-1}$ (Figure. S12b).

The CO_2 uptake capacities were measured at two different temperatures, 273K and 298K (Figure 3c and S13a). The CO_2 uptake capacity was found to be 3.95 mmol g^{-1} (88.4 $cm^3\ g^{-1}$ or 17.4 wt%) at 273 K and 1 bar. At the same time, the CO_2 uptake was obtained at 2.33 mmol g^{-1} (52.2 $cm^3\ g^{-1}$ or 10.2 wt%) at 298 K and 1 bar.

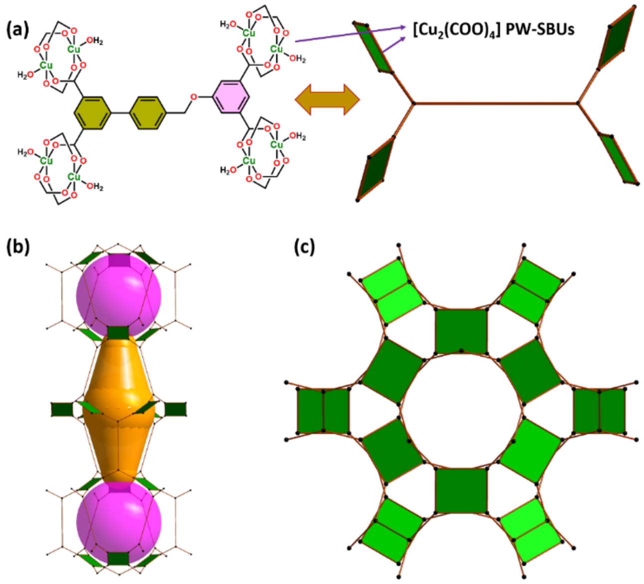


Figure 2. (a) Schematic diagram showing the ligation of **H_4L** linker with Cu^{2+} ions to form **Cu(II)-MOF** containing $[Cu_2(COO)_4]$ SBUs; (b) two different types of cages; and (c) view of the 1D channels in the framework along the c-axis. The crystal model of **Cu(II)-MOF** was built by replacing the C≡C triple bond of ZJNU-50 with an ether bond (-O-).

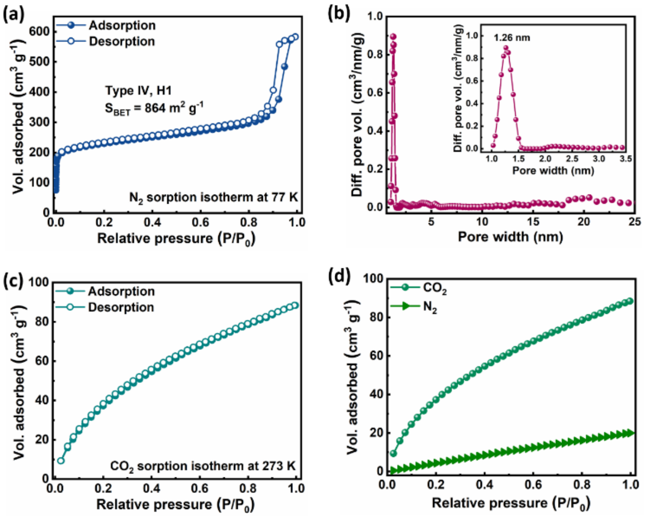
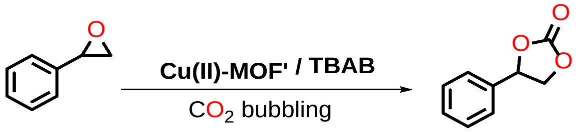


Figure 3 (a) Nitrogen sorption isotherm at 77K, (b) Pore size distribution profile obtained from N_2 adsorption isotherm using non-local density functional theory (c) CO_2 sorption isotherms of **Cu(II)-MOF** measured at 273 K, and (d) Selectivity of CO_2 uptake over N_2 measured at 273 K and 1 bar.

We calculated the isosteric heat of adsorption (Q_{st}) for **Cu(II)-MOF** using the CO_2 adsorption isotherms collected at two different temperatures (273 and 298 K), applying the Clausius-Clapeyron equation (Figure S13b). The Q_{st} value was found to be 28.3 kJ/mol. The high Q_{st} value suggests the affinity of CO_2 towards **Cu(II)-MOF**, indicating the favorable physisorption of gas molecules within the porous frameworks of the materials.[42] We further calculated the selectivity for CO_2 adsorption over N_2 in binary mixtures using experimental single-component isotherms applying an ideal adsorbed solution theory (IAST). An equilibrium partial pressure of 0.85 bar for N_2 and 0.15 bar for CO_2 in the bulk phase was considered as the flue gas contains approximately 15% of CO_2. The CO_2/N_2 selectivity for **Cu(II)-MOF** was found to be 10 at 273 K (Figure 3d).

Catalytic conversion of CO_2 to Cyclic Carbonates

The structural observation of **Cu(II)-MOF** shows that the larger channel of the activated **Cu(II)-MOF′** framework comprised with the high-density of the easily accessible unsaturated metal sites which has been established as a convenient CO_2 adsorbent, encouraged us to further investigate its heterogeneous catalytic activity towards chemical fixation of CO_2 via cyclic carbonate synthesis. The present study was concerned with the chemical fixation of CO_2 with epoxides (20 mmol) by using a mixed catalytic system *i.e.* activated **Cu(II)-MOF′** as a catalyst along with tetrabutyl ammonium bromide (TBAB) as a co-catalyst at 90 °C for 12 h (Scheme 3).



Scheme 3. Cycloaddition reaction of CO_2 with epoxides catalyzed by **Cu(II)-MOF′**.

The optimization of the reaction conditions *i.e.* time, **Cu(II)-MOF′** / TBAB loading, and TBAX (X = Br, I, and Cl) selection, were ascertained by choosing the styrene oxide as a model reactant. Initially, the catalytic conversion of CO_2 was carried out with styrene oxide (20 mmol) by using activated **Cu(II)-MOF′** (15 mg) along with TBAB (0.4 mmol) at 90 °C for 12 h (Figure 4) approaching complete conversion, 97% (Table1; entry1, Figure S14 and S15). Concurrently, to achieve competent reaction conditions, several catalytic reactions were executed with varying the temperature, and loading of **Cu(II)-MOF′** and TBAB (Table 1; entries 1–4).

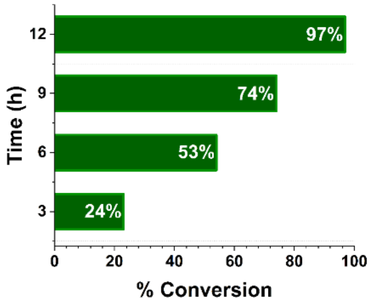


Figure 4. Influence of the reaction time on catalytic performance of **Cu(II)-MOF′** / TBAB.

With the same reaction parameters, the MOF−co-catalyst [(tetrabutylammonium iodide (TBAI) and tetrabutylammonium chloride (TBAC)] combinations give only 35% and 28% conversions, respectively (Table 1, entries 1, 5 and 6), indicating TBAB is a better choice. Due to the bulkiness of TBAI compared to TBAB causes slow diffusion in the MOF channel or toward the active sites attributed to less conversion, while in the case of TBAC, less conversion compared to TBAB can be attributed to poor nucleophilic and leaving the property of Cl^- than Br^-.

Table 1. Optimization of the reaction condition for the cycloaddition of CO_2 with styrene oxide (as model substrate) catalyzed by **Cu(II)-MOF′** under various conditions. [a]

Entry	Cu(II)-MOF′ / Co-catalyst	Temp. (°C)	Time (h)	SO conversion (%)#
1.	15 mg / TBAB (0.4 mmol)	90	12	97
2.	10 mg / TBAB (0.3 mmol)	80	12	56
3.	15 mg / TBAB (0.4 mmol)	80	12	78
4.	10 mg / TBAB (0.3 mmol)	90	12	61
5.	15 mg / TBAI (0.4 mmol)	90	12	35
6.	15 mg / TBAC (0.4 mmol)	90	12	28
7.	-- / --	90	12	No conversion
8.	15 mg / --	90	12	No conversion
9.	-- / TBAB (0.4 mmol)	90	12	31

[a] Reaction Conditions: Styrene oxide (2.3 mL, 20 mmol), solvent-free, **Cu(II)-MOF′** (10 & 15 mg), CO_2 (bubbling), TBAX (0.3 & 0.4 mmol), 80-90 °C, 12 h. #Catalytic conversion was determined by ^1H NMR spectroscopy.

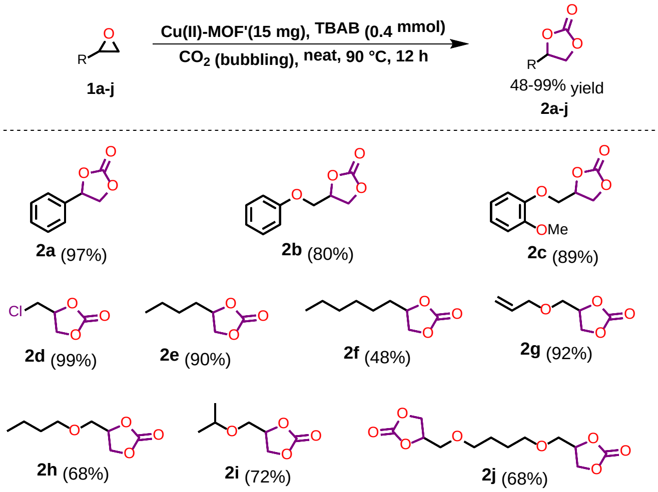
The best catalytic performance for the model substrate was achieved with 15 mg and 0.4 mmol of **Cu(II)-MOF′** and TBAB (Figure S16), respectively, as well as with TBAB, among other ammonium halide salts (Figure S17). We also studied the catalyst and co-catalyst free reaction conditions which failed to provide any cyclic carbonate formation (Table 1; entry 7). Meanwhile, the synergy between **Cu(II)-MOF′** and TBAB towards their catalytic potential was proved by performing the catalytic CO_2 conversion under the influence of the independent **Cu(II)-MOF′** and TBAB with the model substrate (styrene oxide), where it showed no and 31 % conversion (Table 1; entries 8 and 9), respectively (Figure S18). These independent catalytic performances corroborate that both catalyst and co-catalyst is an essential requirement, where bromide ion (offered by TBAB) is acting as a nucleophile and enables the opening of the epoxide rings and, thereby, endorses the cyclic carbonate formation.[31]

Table 2. Recycling catalytic test [a]

entry	Cycle	Conversion (%)[b]
1	fresh	97
2	first	91
3	second	90
4	third	88
5	fourth	86

[a] Reaction Conditions: Styrene oxide (20 mmol), **Cu(II)-MOF′** (15 mg), TBAB (0.4 mmol), CO_2 (bubbling), 90 °C, 12 h. Based on the ^1H NMR of styrene epoxide and cyclic carbonate

The robustness and sustainability of a catalytic system is a prime requirement to perform their activity in multiple cycles, here, the present catalytic system is executed by their reusability experiment till five cycles (Table 2). After completion of each catalytic cycle, the **Cu(II)-MOF′** was separated through filtration followed by their washing with chloroform/acetone and drying to use it in the consecutive cycles. The reusability studies reveal that, till five cycles the catalytic activity is similar for each run and no appreciable loss in the conversion of CO_2 was observed (Table 2 and S19). The framework integrity of **Cu(II)-MOF′** of each cycle was quite consistent with the original one, confirmed by recording their PXRD after each cycle, which rule out the probability of metal leaching (Figure 5a). Furthermore, the heterogeneity of **Cu(II)-MOF′** was supported by performing the hot filtration experiment using the model substrate, where the reaction mixture was filtered after 3 h in hot condition, without washing it, and immediately the filtrate was further allowed for the reaction at the optimized reaction conditions. We have not observed any considerable progress with time in terms of conversion of epoxide (Figure 5b, and S20).



Scheme 4. Substrate screening to yield of various cyclic carbonates from the cycloaddition of CO_2 with corresponding epoxides using catalyst **Cu(II)-MOF′** with TBAB. [a]Reaction conditions: epoxide (20 mmol), **Cu(II)-MOF′** (15 mg), TBAB (0.4 mmol), 90 °C, CO_2 (bubbling), 12 h. The conversion was evaluated from the ^{1}H NMR spectra by integration of epoxide versus cyclic carbonate peaks (Supporting Information, page S24, and S32-S40).

To ascertain the broader scope and generality of the present catalytic system towards the CO_2 chemical fixation was explored with a range of epoxides bearing different substituent groups and molecular sizes [styrene oxide (**1a**); phenyl glycidyl ether (**1b**); glacidyl-2-methoxy phenyl ether (**1c**); epichlorohydrin (**1d**); 1,2-epoxy hexane (**1e**); 1,2-epoxy octane (**1f**); allyl glycidyl ether (**1g**); butyl glycidyl ether (**1h**); glycidyl isopropyl ether (**1i**); 1,4-butane diol diglycidyl (**1j**)] and the result being summarized in Scheme 4. Under the optimized reaction conditions, cycloaddition of CO_2 with phenyl glycidyl ether and glacidyl-2-methoxy phenyl ether shows 80% and 89% conversion, respectively (Figure S21 and S22). The catalytic yield of an epoxide with a $-CH_2OPh$ group is significantly lower than those of other epoxides with shorter substituents.[43] Compared to aromatic epoxides, the aliphatic epoxides with smaller size *i.e.* epichlorohydrin shows an excellent conversion (Figure S23). Among the aliphatic epoxides, as the substituent sizes increase, the conversion into cyclic carbonates significantly decreases from 93% for allyl glycidyl ether (Figure S24) to 90% for 1,2-epoxy hexane (Figure S25), 68% for butyl glycidyl ether (Figure S26), 63% for glycidyl isopropyl ether (Figure S27), and only 48% for 1,2-epoxy octane (Figure S28).

The reduced catalytic capability of Cu(II)-MOF′ for the above-mentioned epoxides can be predominantly attributed to the fact that the impediment in the diffusion rate of large-sized epoxides through porous voids greatly decreases the contact of substrates with the catalytic sites, resulting in a steady decrease in the cyclic carbonate conversion.[44,45] With the bifunctional 1,4-butane diol diglycidyl, we observed the formation of only one product (68% conversion) bearing two carbonate groups (Figure S29).

Finally, the catalytic potential of **Cu(II)-MOF′** has been introduced to compare with paddle wheel SBUs containing various Cu(II) metal ion-based MOF as heterogeneous catalysts for the catalytic fixation of CO_2 and epoxides to cyclic carbonates (see Table 3). The catalytic potential of a MOF, for the conversion of CO_2 to cyclic carbonates, depends mainly on the porosity of MOF, the type of acidic catalytic center (Lewis acid or Brønsted acid), coordination sphere and linkers with various functional groups. Therefore, for the sake of comparison, all the chosen MOFs in Table 3 have copper ion-based paddlewheel SBUs as active catalytic sites, formed by polycarboxylate linkers. Here, we are comparing the catalytic conversion of the styrene oxide (1a), epichlorohydrin (1d), and Allyl glycidyl ether (1g) as well as the reaction conditions and times have also been taken under consideration. Compared to various reported MOF catalysts, the excellent catalytic activity of **Cu(II)-MOF′** toward CO_2 cycloaddition with epoxides, illuminates its believability as a new valuable family member for MOFs to heterogeneous epoxide CO_2 cycloaddition catalysts.

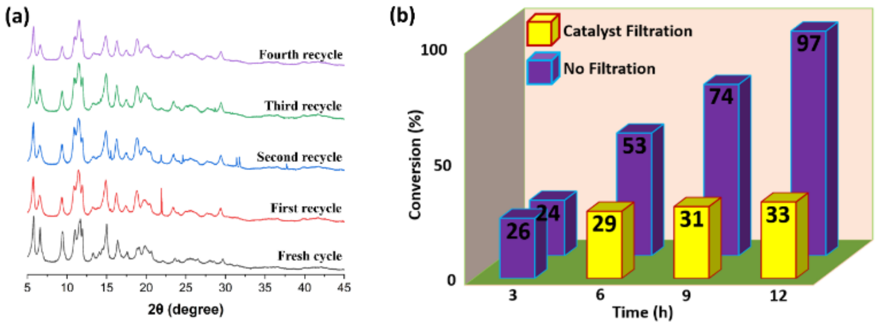


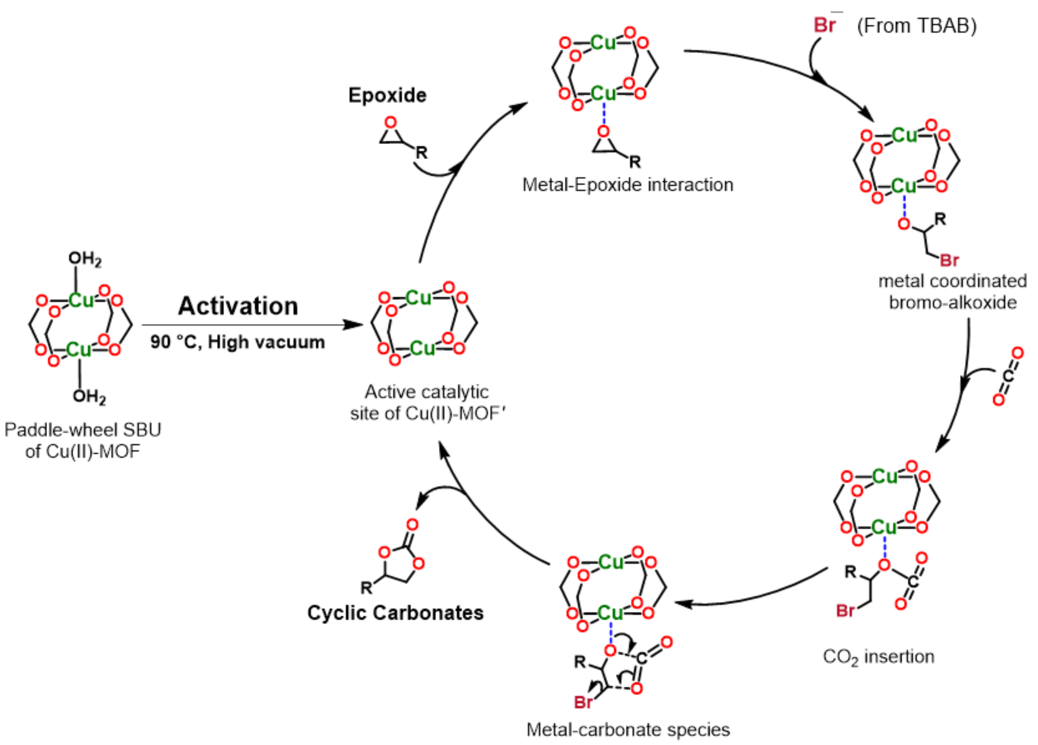
Figure 5. (a) PXRD pattern of the catalyst **Cu(II)-MOF** after each catalytic reaction cycle showing the framework integrity, (b) Reaction time examination for hot-filtration experiment showing the heterogeneous nature of catalyst **Cu(II)-MOF**

Table 3. Comparison of catalytic performance of **Cu(II)-MOF′** with reported MOFs of Cu(II) ion-based SBUs towards chemical fixation of CO_2 with epoxides.

S. No.	MOF	Catalyst	Cocatalyst	Epoxide	Temperature / Pressure	Time (h)	Conv (%)/Yield(%)	Ref
1.	1	0.4 mol%	0.2 mol%	**1a** (17 mmol)	70 °C / 1 bar	16	90/--	[31]
2.	MMCF-2	0.125 mol%	0.58 g	**1g** (25 mmol)	rt / 1 bar	48	--/37.6	[44]
3.	LCu′	5 wt %	1 mmol	**1a** (-- mmol)	120 °C / 20 bar	12	50/--	[46]
4.	[Cu-MOF]	5 wt %	1.0 mol%	**1a** (20 mmol)	70 °C / 1 atm	10	92/--	[47]
5.	[Cu-MOF]	0.01 mmol	2 mol%	**1a** (25 mmol)	100 °C / 1 bar	4	69/--	[48]
6.	1′	0.2 mol%	1 mmol	**1a** (20 mmol)	rt / 1 bar	8	--/ 89	[49]
7.	Cu(II)-MOF	0.02 mmol	--	**1d** (20 mmol)	80 °C / 8 bar	24	93/--	[50]
8.	1	0.2 mol%	0.5 g	**1d** (20 mmol)	rt / 1 atm	48	88/--	[51]
9.	HKUST-1	20mg		**1a** (20 mmol)	100 °C / 2 Mpa	4	–/48	[52]
10.	MMPF-9	0.31 mmol	0.58 g	**1g** (25 mmol)	rt / 1 bar	48	--/29.7	[53]
11.	HNUST-9	9 mg	1 mmol	**1a** (20 mmol)	80 °C / balloon pressure	48	44.3/--	[54]
12.	1	0.4 mol%	0.5 mol%	**1a** (2.0 mmol)	60 °C / 0.1 MPa	12	99/--	[55]
13.	1a	0.01 mmol	0.3 mmol	**1a** (20 mmol)	100 °C / 1MPa	6	64.1/--	[56]
14.	CZJ-10	0.001 mmol	0.2 mmol	**1a** (2 mmol)	rt / 1 atm	50	--/>99	[57]
15.	[TMOF-1]	1 mol%	10 mol%	**1d** (20 mmol)	rt / 1 bar	48	--/92	[58]
16.	**Cu(II)-MOF**	15 mg	0.4 mmol	**1a, 1d, 1g** (20 mmol)	90 °C / CO_2 (bubbling)	12	97, 99, 93/--	**This Work**

Plausible mechanism for the Cu(II)-MOF′ catalyzed chemical fixation of CO_2 into cyclic carbonates

Based on the structural features and previous reports,[59] we propose the plausible catalytic cycle for the CO_2–epoxides cycloaddition reaction using the **Cu(II)-MOF′** and TBAB (Scheme 5). In the present work, the coordinatively unsaturated Lewis acidic Cu(II) metal centers and bromide ions from TBAB, together act as a binary catalyst system. The catalytic reaction is initiated by the coordination of the epoxide oxygen atom to the unsaturated Lewis acidic Cu(II) center and activating the epoxy ring.[60] Subsequently, the bromide ion generated from the TBAB opens the epoxide ring from the less sterically hindered carbon atom and leads to the formation of the metal-coordinated bromo-alkoxide intermediate, considered a rate-limiting step.[53,61] In the next step, the CO_2 interacts with the oxygen of the bromo-alkoxide intermediate leading to the CO_2 insertion. Finally, intramolecular ring-closing yields the corresponding cyclic carbonate with concomitant elimination of the corresponding cyclic carbonate along with the regeneration of the active catalytic sites.



Scheme 5. The plausible mechanism for **Cu(II)-MOF** catalyzed chemical fixation of CO_2.

EXPERIMENTAL SECTION

Reagents and Chemicals

The starting chemicals, as well as $Cu(NO_3)_2 \cdot 3H_2O$ (98%) were obtained from commercial suppliers; Sigma Aldrich, and Alfa Aesar, and used as received. Various used cyclic epoxides were purchased from TCI Chemicals (India). Deionized (DI) water obtained from the Milli-Q system with a resistivity of 18.2 MΩ.cm was used throughout the experiment. Other reagents were purchased from commercial suppliers and used without further purification. All solvents were procured from S. D. Fine Chemicals, India, and used after the drying/purifying by following standard methods.

General methods

Powder X-ray diffraction (PXRD) experiments were conducted on a PANalytical Empyrean XRD instrument equipped with monochromatic Cu Kα(1.54 Å) radiation. Data were acquired for 2θ values of 5° to 50°. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA-6000 instrument. The samples were heated under a nitrogen atmosphere from 30 ℃ to 800 ℃at a rate of 10 ℃min^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance III 400/500 NMR spectrometer at 400/500 MHz and 100/125 MHz, respectively, in $CDCl_3$ and DMSO-*d*$_6$ with Me_4Si as the internal standard. High-resolution mass spectroscopic (HRMS) analysis is performed on quadrupole-time-of-flight Bruker MicroTOFQ II mass spectrometer equipped with an ESI source. The IR spectrum was recorded directly on a PerkinElmer FT-IR spectrometer, Spectrum two.

The Quantachrome Autosorb-iQ XR equipment was used for the gas sorption measurements. Prior to the measurement, the sample was soaked in dry acetone for 8 days with changing the acetone twice in a day to exchange DMF and water solvent molecules. N2 gas adsorption-desorption measurements were carried out at 77 K to determine the surface area and the porosity. ASIQwin software was used to analyze all the isotherms. Degassing of the samples was carried out under a high vacuum using the same instrument for 16 h at 90 ℃ before the analysis. The pore size distribution was obtained by analyzing the N_2 adsorption isotherms using the quenched solid density functional theory (QSDFT) method.

Ligand Synthesis

The ligand 4′-((3,5-dicarboxyphenoxy)methyl)-[1,1′-biphenyl]-3,5-dicarboxylic acid has been synthesized via a substitution reaction by using diethyl 5-hydroxyisophthalate and dimethyl 4'-(bromomethyl)-[1,1'-biphenyl]-3,5-dicarboxylate, followed by the hydrolysis of the corresponding ester in alkali solutions, and details are provided in supporting information (Scheme S1 and Figure S1-S7).

MOF Synthesis and its activation

In a typical synthesis, 20 mg of the synthesized tetracarboxylic linker (4′-((3,5-dicarboxyphenoxy)methyl)-[1,1′-biphenyl]-3,5-dicarboxylic acid), 45 mg of $Cu(NO_3)_2.3H_2O$, 1mL of deionized water, 2 mL of DMF, and 2 drops of HCl (12N) were added in a teflon-lined stainless autoclave. Afterward, the autoclave was kept in a microprocessor oven at 85 ºC for 60 h with heating and cooling rates of 0.4 °C/minute and 0.32 °C/minute, respectively. Blue-colored block-shaped crystals of **Cu(II)-MOF** were collected by filtration: yielding 23 mg.

In the activation process, firstly the as-prepared **Cu(II)-MOF** was immersed in dry acetone for 8 days while changing the acetone twice a day. The framework integrity of the acetone exchanged framework remains sustainable which is proved by the matching PXRD pattern of the acetone exchanged framework (**Cu(II)-MOF$_{AE}$**) with the **Cu(II)-MOF** (Figure S8). Secondly, **Cu(II)-MOF$_{AE}$** was heated at 90 °C under a high vacuum to accomplish a completely solvent-free framework (**Cu(II)-MOF′**), having coordinatively unsaturated Lewis acidic Cu(II) ions, that could be easily recognized by its change in color from cyan-green to dark violate (Figure S9). The PXRD spectrum of **Cu(II)-MOF′** is in good accordance with the **Cu(II)-MOF** and **Cu(II)-MOF$_{AE}$**, suggesting that frameworks remain intact in their structural integrity after the process of activation (Figure S8).

Catalytic study for the chemical conversion of CO_2

The catalytic chemical conversion of CO_2 was performed as reported in the literature,[31] where a mixture of epoxide (20 mmol), catalyst **Cu(II)-MOF′** (15 mg), and co-catalyst Bu_4NBr (tetra butyl ammonium bromide, TBAB) (0.4 mmol) in a 10 mL Schlenk tube was stirred at 90 °C under continuous bubbling of CO2 (99.999%). After achieving the maximum conversion at a substantial reaction time, the reaction mixture was filtered and the catalyst was washed with $CHCl_3$ and acetone. The product conversion of the reaction was evaluated from the filtrate using ^{1}H NMR spectroscopy through the integration of epoxide hydrogen (IH_{CE}) versus cyclic carbonate hydrogen (IH_{CC}) peaks in the ^{1}H NMR spectra.

CONCLUSION

In summary, by using a novel tetratopic linker, 4′-((3,5-dicarboxyphenoxy)methyl)-[1,1′-biphenyl]-3,5-dicarboxylic acid, we have successfully generated a paddle-wheel SBUs containing microporous *NbO*-type **Cu(II)-MOF** having identical network architecture with ZJNU-50. The evacuated framework featuring exposed unsaturated Cu(II) metal sites decorated channels, shows both the excellent BET surface area of 864 m^2 g^{-1} and CO_2 uptake capacity (3.95 and 2.33 mmol·g^{-1} at 1 bar for 273 and 298 K, respectively) with a CO_2/N_2 selectivity of 10 at 273 K. Furthermore, **Cu(II)-MOF′** exhibits excellent catalytic activity for chemical fixation of CO_2 with various epoxides *via* synthesis of five-membered cyclic carbonates under solvent-free and ambient reaction condition. Also, the synergy between exposed unsaturated Cu(II) metal sites and TBAB signifies the comparable catalytic CO_2 conversion to various reported Cu(II) paddle wheel MOFs. The wider substrate scope and excellent recyclability, signify its prospective for practical utilization of CO_2 to valuable chemicals.

SUPPORTING INFORMATION

Synthetic methodology, details of gas adsorption analysis, % conversion calculation, ^{1}H & ^{13}C NMR, HRMS-ESI, PXRD, FT-IR, TGA, and ^{1}H NMR spectra of the cyclic carbonates **2a-2j** are available in the Supporting Information as PDF (available from article page online).

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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