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A Microporous Metal–Organic Framework Catalyst for Solvent-free Strecker Reaction and CO₂ Fixation at Ambient Conditions

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ABSTRACT: The self-assembly of zinc(II) acetate tetrahydrate, a flexible tetrapyridyl ligand, tetrakis(3-pyridyloxymethylene)methane (3-tpom), a bent dicarboxylic acid, and 4,4'-(dimethylsilanediyl)bisbenzoic acid (H₂L) under solvothermal conditions has resulted in the formation of a microporous zinc(II)-organic framework, $\{[Zn_2(3-tpom)(L)_2]\cdot 2H_2O\}_n$ (1). The framework exhibits very good thermal stability as evident from the thermogravimetric analysis, which is further supported by variable temperature powder X-ray diffraction analysis. The microporous nature of the framework has been established by the gas adsorption analysis. The framework exhibits exceptionally selective carbon dioxide adsorption in contrast with other gases having comparatively larger kinetic diameters (3.64 Å for N₂ and 3.8 Å for CH₄) under ambient conditions (298 K and 1 bar



pressure). Further, the framework decorated with catalytically active unsaturated metal sites acts as a good catalyst toward the cycloaddition reaction of CO_2 with epoxides and the three-component Strecker reaction at ambient conditions and without the requirement of any solvent. The heterogeneous nature along with good catalytic activity at ambient and solvent-free conditions entitles 1 as an excellent catalyst for these organic transformations.

INTRODUCTION

Metal-organic frameworks (MOFs) have emerged as very provocative porous crystalline materials and have captured significant scientific interest due to their extraordinary structural tunability and functionality.^{1,2} The mixing of different building blocks (metal and organic ligands) into the MOF structures imparts interesting physical and chemical properties to the framework. The tailor-made synthesis and various synthetic routes enable the realization of MOF structures showing exceptional physicochemical stability and multifunctionality. The structural tenability of MOFs materials makes them potential candidates for a diverse range of applications,³ ⁻⁵ in particular, for heterogeneous catalysis.⁶ Catalytic activity into the MOF structures can be incorporated either by engineering coordinatively unsaturated metal sites^{10,11} or by introducing catalytically active functional groups into the linker backbone.¹⁰⁻¹

Among the various organic transformations, the chemical exploitation of carbon dioxide (CO₂) has been widely accepted as a greener and sustainable route to the syntheses of fine chemicals.^{13–16} However, the comparatively stable and inert nature of CO₂ limits the chemical fixation under mild conditions. In this context, metal-catalyzed cycloaddition of CO₂ with high energy substrates such as epoxides or azaridines, etc., to generate cyclic carbonates or carbamates is a one of the potential methodologies for CO₂ utilization^{17–19} as CO₂ presents an inexpensive, nontoxic, and renewable C1

feedstock and the product cyclic carbonates are important chemical intermediates for several fine chemicals and pharmaceuticals.^{18,20-27} Therefore, this approach not only provides a route to a valuable chemical commodity but also helps to reduce the greenhouse emissions.²⁸⁻³⁰ Taking into account the issues of catalyst reusability, rigorous separation, and purification of the product in homogeneous catalytic processes,^{17,22,31-36} many efforts have been made in order to develop efficient heterogeneous catalytic systems for the chemical fixation of CO_2 with epoxides,³⁷⁻⁴⁶ but most of them suffer from low catalytic activity and require harsh reaction conditions such as high temperatures and elevated pressures of CO_2 to activate the reaction. As discussed above, MOFs have been cited as potential contenders for heterogeneous catalysis. By virtue of their large surface area, high CO₂ selectivity, and pore surface decorated with Lewis/Brønsted acidic or basic sites along with the exceptional physicochemical stability, some of them have been tested as successful heterogeneous catalyst for the chemical fixation of CO₂ with

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epoxides;^{47–57} unfortunately, these represent just a small fraction of the entire MOF family. In view of these facts, we intended to design a highly stable and robust MOF with coordinatively unsaturated metal sites for efficient fixation of CO_2 to cyclic carbonates at ambient conditions. In addition, among various Lewis-acid-catalyzed organic transformations, the three-component Strecker reaction is an important C–N bond forming reaction where the product α -aminonitriles are adaptable starting materials for the synthesis of α -amino acid and their derivatives.⁵⁸

In the present work, we have synthesized a Zn(II)-based metal-organic framework $\{[Zn_2(3-tpom)(L)_2]\cdot 2H_2O\}_n$ (1) using a bent dicarboxylic acid 4,4'-(dimethylsilanediyl)bisbenzoic acid (H₂L) and an heteroatom-functionalized semirigid tetrapodal N-donor ligand, tetrakis(3-pyridyloxymethylene)methane (3-tpom) (Scheme 1) with a

Scheme 1. Chemical Structures of the Conformationally Flexible 3-tpom Ligand and Bent Dicarboxylate H₂L



motive to engineer a porous 3D framework with Lewis-acidic unsaturated metal sites and basic oxygen functionalities for selective CO₂ capture and its fixation to cyclic carbonates. The single-crystal X-ray diffraction (SCXRD) and thermogravimetric (TG) analysis reveal that 1 consists of a stable 3D structure. The powder X-ray diffraction (PXRD) analysis further corroborates thermal and chemical stability of 1 toward different organic solvents. Gas adsorption analysis exhibits the microporous nature of 1 and shows that 1 takes up a moderate amount of CO2 at 1 bar pressure and exhibits very good selectivity over other gases (N₂ and CH₄). Further, as a result of the coordinatively unsaturated metal centers in the framework, 1 shows excellent heterogeneous catalytic activity for the chemical fixation of CO₂ with epoxides at relatively milder conditions. In addition, 1 is also found to catalyze the three-component Strecker reaction involving carbonyl compounds, aromatic amine, and trimethylsilyl cyanide in a solvent-free condition and at ambient conditions to afford α aminonitriles in good yields.

EXPERIMENTAL SECTION

Materials and Physical Measurements. All reactions of *n*-BuLi were carried out in oven-dried glassware under an inert nitrogen atmosphere by using standard Schlenk techniques. Solvents were predried with KOH followed by distillation over benzophenone–Na, before their use in the reactions involving *n*-BuLi. The ligands H_2L and 3-tpom were synthesized using procedures in the literature.^{59,60} All other chemicals and reagents used for synthesis were purchased from commercial vendors and were used as received.

The ¹H and ¹³C NMR spectra of H₂L and 3-tpom were recorded at 25 °C on a Bruker ARX-400 spectrometer in DMSO- d_6 and CDCl₃ solutions, respectively. The chemical shifts are reported relative to the residual solvent signals. The elemental analysis (C, H, N) was carried out using Leco TruSpec Micro CHNS analyzer. Thermogravimetric

analysis was carried out under a flow of dinitrogen in the temperature range of 30-500 °C (at a heating rate of 10 °C/min) on a Shimadzu DTG-60H instrument. FTIR spectra of 1 and the ligands were recorded in the 4000–400 cm⁻¹ range on a PerkinElmer Spectrum I spectrometer with samples prepared as KBr pellets. The recording of powder X-ray diffraction data was accomplished by using parallel beam geometry (2.5° primary and secondary solar slits, 0.5° divergence slit with 10 mm height limit slit) on a Rigaku Ultima IV diffractometer equipped with 3 KW sealed-tube Cu K α X-ray radiation (generator power settings: 40 kV and 40 mA) and a DTex Ultra detector. Each sample was made into a fine powder using a mortar and a pestle and was placed on a glass sample holder for the room temperature measurement, while a copper sample holder was used for the variable temperature measurement. Data were collected over a 2-theta range of $5-50^{\circ}$ (5-40° for VT-PXRD) with a scanning speed of 2° per minute with 0.02° step. Gas sorption analysis was carried out on a BELSORP MAX (BEL, Japan) volumetric adsorption analyzer at different temperatures. Each gas of very high purity (99.995%) was used for the adsorption measurements. Powdered sample was activated at 393 K for 24 h and purged with ultrapure nitrogen gas on cooling. The measurement temperatures for sorption isotherms at different temperatures (263-298 K) were maintained with a circulating water bath connected to a chiller.

Synthesis of {[Zn_2(3-tpom)(L)_2]\cdot 2H_2O}_n (1). 30 mg (0.1 mmol) of H_2L and 22 mg (0.05 mmol) of 3-tpom were placed in a Teflon reactor along with 1 mL of DMF. A solution of 22 mg (0.1 mmol) of zinc acetate dihydrate in 4 mL of an ethanol/water (1:3) mixture was then added to this solution. The reactor was sealed in a stainless steel vessel and heated in a programmable oven at 120 °C for 48 h followed by slow cooling to room temperature at a rate of 3-4 °C/h. The colorless block-shaped crystals thus obtained were collected via filtration, washed with DMF and then with water, and air-dried. Yield: 42 mg (66%). Anal. calcd for $C_{59}H_{64}N_4O_{16}Si_2Zn_2$ (MW 1272.09): calcd %C, 55.70; %H, 5.10; %N, 4.41. Found: %C, 56.02; %H, 5.46; %N, 4.82. Selected FTIR peaks (KBr, cm⁻¹): 3430 (br), 1624 (s), 1601 (m), 1576 (s), 1548 (m), 1482 (m), 1435 (s), 1390 (s), 1369 (s), 1283 (s), 1244 (s), 1190 (w), 1101 (s), 1056 (m), 1018 (m), 829 (m), 814 (s), 772 (s), 760 (s), 722 (m), 697 (m), 642 (w).

Single Crystal X-ray Data Collection and Refinement. A suitable single crystal of 1 was chosen using an optical microscope and mounted in a nylon loop attached to a goniometer head. It was cooled to 100 K with a programmed flow of nitrogen gas. Based on the diffraction photographs and unit cell determination, its suitability was judged for collecting data on a Kappa APEX II diffractometer equipped with a sealed tube X-ray source with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) operating at 50 kV and 30 mA (with the crystal-to-detector distance fixed at 50 mm) through the program APEX2,⁶¹ as described earlier from our laboratory. Data were integrated by the program SAINT⁶¹ to obtain values of F^2 and $\sigma(F^2)$ for each reflection and to apply further correction for Lorentz and polarization effects and absorption (SADABS).⁶¹ The structure solution was accomplished by direct method using SHELXS program of SHELXTL package and refined by full-matrix least-squares methods with SHELXL-2014⁶² within the Olex2 crystallographic software suite.⁶³ The chosen space group based on systematic absences was confirmed by the successful refinement of the structure. For the completion of structure refinement with convergence, several full-matrix least-squares/difference Fourier cycles were performed. The treatment of disordered guest solvent molecules in 1 was handled by the solvent mask option in Olex2 software,63 and the potential solvent accessible area or void space was calculated using the PLATON software.⁶⁴ Final crystallographic parameters and basic information pertaining to data collection and structure refinement are summarized in Table 1. Selected bond lengths (Å) and bond angles (degree) are listed in Table S1. All figures were drawn using Mercury ver. 3.0⁶⁵ and Diamond ver. 3.2.⁶⁶

General Procedure for the Chemical Fixation of CO₂ with Epoxides Catalyzed by 1. In a typical reaction, 150 μ L (2 mmol) of epichlorohydrin was taken along with 0.5 mol % of the desolvated 1 and TBAB cocatalyst, and the mixture was allowed to react with CO₂

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Table 1. Crystallographic Data and Structure Refinement Parameters for 1

empirical formula	$C_{57}H_{52}N_4O_{12}Si_2Zn_2$			
formula weight	1171.94			
temperature/K	100.15			
crystal system	monoclinic			
space group	Cc			
a/Å	8.3003(5)			
b/Å	26.7153(18)			
c/Å	26.3110(17)			
$\alpha/^{\circ}$	90			
$\beta/^{\circ}$	90.138(2)			
$\gamma/^{\circ}$	90			
volume/Å ³	5834.3(6)			
Z	4			
$ ho_{\rm calc}~({\rm g/cm^3})$	1.334			
μ/mm^{-1}	0.925			
F(000)	2424.0			
crystal size/mm ³	$0.15 \times 0.15 \times 0.1$			
radiation	Mo $K\alpha$ ($\lambda = 0.71073$)			
2θ range for data collection/°	3.048 to 50.072			
index ranges	$-9 \le h \le 9, -31 \le k \le 31, -31 \le l \le 31$			
reflections collected	36720			
independent reflections	9764 $[R_{int} = 0.0461, R_{sigma} = 0.0621]$			
data/restraints/parameters	9764/2/694			
goodness-of-fit on F^2	1.076			
final R indexes $[I \ge 2\sigma(I)]$	$R_1^a = 0.0407, w R_2^b = 0.0973$			
final R indexes [all data]	$R_1 = 0.0502, wR_2 = 0.1158$			
largest diff. peak/hole/e Å ⁻³	0.56/-0.36			
Flack parameter	0.033(15)			
${}^{a}R_{1} = \Sigma F_{0} - F_{c} / \Sigma F_{0} . \ {}^{b}wR_{2} = [\Sigma w (F_{0}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{0}^{2})^{2}]^{1/2},$				
where $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, $P = (F_0^2 + 2F_c^2)/3$.				

that was provided with a balloon filled with CO_2 . The reaction was carried out at 40 °C in a solvent-free conditions. After the reaction completion, the product was extracted with chloroform and the solid catalyst was separated by filtration. The solvent was evaporated, and the product yield was determined by ¹H NMR spectroscopy.

General Procedure for the Three-Component Strecker Reaction Catalyzed by 1. In a typical reaction, a mixture of acetophenone (1 mmol), aniline (1 mmol), and TMSCN (1.25 mmol) was taken along with 1 mol % of the desolvated 1. The reaction mixture was allowed to stir at room temperature $(25-30 \ ^{\circ}C)$ under an inert atmosphere of nitrogen in solvent-free conditions. The product was extracted with chloroform and the solid catalyst was separated by filtration. The product was obtained by solvent evaporation, and the yield was determined by ¹H NMR spectroscopy.

Recyclability of 1. The recyclability experiment for both of the reactions was carried out under the similar reaction conditions. The catalyst was retrieved by filtration, washed with chloroform, and heated under vacuum for 5 h to regenerate the active catalyst, before it was used for the next catalytic cycle.

RESULTS AND DISCUSSION

The reaction of $Zn(OAc)_2 \cdot 2H_2O$ with H_2L and 3-tpom under solvothermal conditions afforded colorless block-shaped crystals of 1 in 66% yield (Scheme 2). Its molecular formula was established as $\{[Zn_2(3-tpom)(L)_2] \cdot 2H_2O\}_n$ by a combination of elemental analysis, TG, and SCXRD analyses.

Single-crystal X-ray diffraction analysis concedes that 1 crystallizes in a monoclinic crystal system, with the Cc space group (no. 9), with lattice parameters a = 8.3003(5) Å, b = 26.7153(18) Å, and c = 26.3110(17) Å (Table 1). There are two zinc atoms, two L²⁻, and one 3-tpom ligand in the

Scheme 2. Synthesis of 1

Zn(OAc) ₂ ·2H ₂ O + 3-tpom	+ H ₂ L <u>DMF/EtOH/H₂O</u> 120 °C, 48 h cool to 25°C in 24	{[Zn ₂ (3-tpom)(L) ₂]·2(H ₂ O)} _n (1)
	COOL to 25°C III 24	n

asymmetric unit. An ORTEP view of the asymmetric unit with an atom labeling scheme is shown in Figure S1. Each Zn(II) center adopts a N2O2-type tetrahedral coordination geometry with four coordination sites being occupied by two oxygen atoms from the carboxylate groups of two different L²⁻ and two nitrogen atoms from two different 3-tpom ligands. The asymmetric unit is further expanded by full span of L²⁻ and 3tpom to generate the overall 3D framework (Figure 1). Further simplification of the framework into the node and linker representation reveal that the framework exhibits a 4,4,4connected 3-nodal network topology (Figure S2), obtained by the TOPOS program.⁶⁷ The framework consists of open pores functionalized with four basic oxygen atoms of the 3-tpom ligand, and the coordinatively unsaturated Lewis-acidic metal sites imparts dual functionality to the framework. The total solvent accessible area or void space for 1 was estimated to be 13.1% (764/5834 Å³ per unit cell volume) by the PLATON software.⁶⁴ The presence of Lewis acidic metal sites and heteroatom functionality in 1 may act cooperatively for selective CO₂ capture and its chemical fixation.

The phase purity of 1 in bulk was checked by PXRD analysis. As shown in Figure S3, the PXRD pattern of the assynthesized, as well as the activated sample of 1, closely matches with that of the simulated PXRD pattern (obtained from the SCXRD data), indicating phase purity and retention of crystallinity upon thermal activation of the framework. TGA and in situ variable temperature PXRD measurements were carried out in order to check the thermal stability of 1. The TGA profile of 1 shows an initial weight loss of $\approx 3.5\%$ in the temperature range of 50-150 °C (Figure S4), which can be attributed to the loss of lattice solvent molecules (ca. 2.98%). The framework exhibits excellent stability up to 325 °C as no weight loss can be seen up to this temperature, after which a sudden weight loss indicates the framework decomposition. The TGA profile of the desolvated/activated sample of 1 does not show appreciable weight loss up to 325 °C, which further supports that the initial weight loss in the as-synthesized sample was due to the lattice solvent molecules. The in situ variable temperature PXRD experiment further shows that 1 is stable up to 300 °C (Figure 2a), and this data corroborates well with the TG experiments. In addition, the stability of 1 toward common organic solvents was also tested by PXRD diffraction analysis. The as-synthesized sample of 1 was immersed in different solvents for two days. After separation and drying of the sample, the PXRD data of 1 was recorded at room temperature. As shown in Figure 2b, 1 exhibits very good chemical stability toward these solvents in addition to its excellent thermal stability.

Gas adsorption studies were carried out in order to establish the permanent porosity in 1. The PXRD and TG analysis corroborates the retention of framework integrity and loss of lattice solvent molecules upon thermal activation process (Figures S3 and S4). The CO₂ adsorption isotherm at 195 K clearly demonstrate its microporous nature, and interestingly enough, 1 takes up a much smaller amount of N₂ (77 K) compared to CO₂ (195 K) (Figure S5).

The Brunauer–Emmett–Teller (BET) surface area and the Langmuir surface area were estimated to be 135 and 180 m²



Figure 1. Single-crystal structure of 1 with open channels (center) and enlarged views of the Lewis-basic and coordinatively unsaturated Lewisacidic metal sites in the framework.



Figure 2. (a) In situ variable-temperature powder XRD patterns of as-synthesized 1 and (b) powder XRD patterns of as-synthesized 1 after soaking in different solvents (for 2 days) at room temperature, indicating the thermal robustness and stability of 1 toward these solvents.



Figure 3. Binary mixture adsorption isotherms and selectivities for (a) CO_2/N_2 (15/85) and (b) CO_2/CH_4 (50/50) mixtures at 298 K and 1 bar pressure, obtained from IAST.

 g^{-1} , respectively (Figure S6), based on the CO₂ adsorption data at 195 K. The total pore volume was calculated to be 0.0608 cm³ g⁻¹. Single-component gas adsorption measurements were carried out for N₂, CH₄, and CO₂ at 298 K and 1 bar pressure. As shown in Figure S7, 1 takes up a relatively

higher amount of CO₂, which can be ascribed due to the unsaturated metal sites and plausible quadrupole–quadrupole interactions among CO₂ molecules coupled with exposed oxygen functionalities into the pores channels for enhanced Lewis base–Lewis acid interactions.^{68,69} In contrast, **1** exhibits

$CI + H + H + CO_2 1 atm. CI + H + H + H + H + H + H + H + H + H + $							
entry	1 (mol %)	TBAB (mol %)	T (°C)	<i>t</i> (h)	yield (%) ^b	TON ^d	TOF $(\min^{-1})^e$
1	0.5	0.5	40	5	34	68	0.22
2	0.5	0.5	40	10	65	130	0.21
3	0.5	0.5	40	15	85	170	0.18
4	0.5	0.5	40	20	91	182	0.15
5	0.5	0.5	40	24	>99	198	0.013
6	1	0.5	40	20	96	96	0.08
7	2	0.5	40	12	97	48.5	0.26
8	3	0.5	40	12	>99	33	0.07
9	0.5	0.5	60	10	97	194	0.32
10	0.5	0.5	80	5	>99	198	0.66
11	0.5	-	40	24	10	20	0.0013
12	-	0.5	40	24	15	-	-
13	$7n(OAc)^{c}$	0.5	40	24	18	_	_

Table 2. Optimization of the Reaction Conditions for the Cycloaddition of CO₂ with Epichlorohydrin Catalyzed by 1^a

^{*a*}Reaction conditions: epichlorohydrin (2 mmol) was reacted with CO_2 under one atmospheric pressure maintained with a balloon filled with CO_2 gas, in the presence of 1 and cocatalyst tetra(*tert*-butyl) ammonium bromide (TBAB) in a solvent-free condition. ^{*b*}Determined by ¹H NMR of the crude products. ^{*c*}1 mol % of zinc acetate dihydrate was used instead of 1. ^{*d*}Number of moles of product per mole of catalyst. ^{*e*}TON per minute.

much less uptake capacities for N2 and CH4 at the same temperature and under the same pressure. The quantitative binding strength of the CO₂ molecules with the framework was estimated by the Clausius-Clapeyron equation and a wellknown virial equation from the fits of their adsorption isotherms at different temperatures (Figures S8 and S9). The trend of isosteric adsorption enthalpy (Q_{st}) with respect to surface coverage is presented in Figure S10. The Q_{st} value at zero coverage (32.65 kJ mol⁻¹) is comparable with the values reported for some-well-known MOF materials (Table S2). Although 1 represents very low CO₂ uptake compared to wellknown MOF materials (Table S3), the selectivity of 1 for CO_2 is comparatively higher than that of most of the MOFs. The gas mixture adsorption selectivity was also evaluated using ideal adsorption solution theory (IAST) developed by Myers and Prausnitz for binary mixtures.⁷⁰ The CO₂-N₂ and CO₂-CH₄ selectivity at a general feed composition for flue-gas $(CO_2/N_2 = 15/85)$ and landfill gas $(CO_2/CH_4 = 50/50)$ up to 1 bar pressure and at 298 K are presented in Figure 3. The CO₂/N₂ and CO₂/CH₄ selectivity values of 87.6 and 15.7, respectively, indicate the very good selectivity and separation ability of 1 for CO₂. Further the values are higher than the selectivity values for well-known MOF and ZIF materials (Table S5).

The preferential adsorption and strong interaction of CO_2 with the framework was further established by grand canonical Monte Carlo (GCMC) simulation using a material studio program⁷¹ (see Supporting Information, Figure S11). The presence of high density Lewis-acidic unsaturatively coordinated metal sites and highly selective CO_2 affinity prompted us to study the potential of 1 as an active heterogeneous catalyst for the cycloaddition reaction of CO_2 with epoxides to form value-added cyclic carbonates at ambient conditions (30–40 °C and under 1 atm pressure of CO_2). For a standard reaction, epichlorohydrin was chosen with 1 as a catalyst (0.5 mol %) in conjunction with tetra(*tert*-butyl)ammoniumbromide (TBAB) as a cocatalyst (0.5 mol %). As shown in Table 2, 1 exhibits very good catalytic activity for the cycloaddition reaction of

epichlorohydrin with CO_2 at 40 °C with a yield of 99% over 24 h. The reaction condition was optimized for different reaction parameters, such as temperature, reaction time, and amount of the catalyst. With an increase in the amount of catalyst (3 mol %) and reaction temperature (80 °C), the reaction completes in only 12 and 5 h, respectively (entries 8 and 10, Table 2), whereas a very low product yield in the absence of either 1 or cocatalyst TBAB (entries 11 and 12, Table 2) indicates the synergistic role of 1 and TBAB during the catalytic process.

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In view of the good catalytic activity compared to other MOF materials (Table S6) and green chemistry principles, we further explored the catalytic activity of this system for the solvent-free chemical fixation of CO_2 with different epoxides at ambient conditions (40 °C and 1 atm pressure of CO_2) using 0.5 mol % of 1 and TBAB. The results are summarized in Table 3. A very good catalytic activity was observed for the cycloaddition reaction of propylene oxide, butylene oxide, as well as epoxyhexane with CO_2 , resulting in the corresponding cyclic carbonates in 99%, 94%, and 91% yield in each case (entries 1, 2, and 4, Table 3). Further, the epoxides substituted with long alkyl chains (allyl glycidyl ether and butyl glycidyl ether) and phenyl ring (styrene oxide) also gives the cyclic carbonates in good yields (entries 5–7, Table 3).

However, further increase in the size of the epoxide substrate has resulted in a decrease in the product yield. In case of largesized phenyl glycidyl ether only 55% product yield was obtained under the identical reaction conditions (entry 8, Table 3). This can be due to steric hindrance of the bulkier substrates to the active metal sites on the surface of 1.

In addition to the catalytic activity of 1 toward chemical fixation of CO_2 with epoxides, it was further tested for its activity toward Lewis-acid-catalyzed Strecker reaction. The three-component Strecker reaction between an aldehyde/ ketone, an amine, and cyano compounds is an important C–N bond forming reaction which is a direct and viable method for the synthesis of α -aminonitriles. However, there are reports where MOF materials have been used as a heterogeneous catalyst for this reaction, but these represent only a few

Table 3. Substrate Scope for the Cycloaddition Reaction of CO_2 with Different Epoxides Catalyzed by 1^a





^{*a*}Reaction conditions: 2 mmol of epoxide was reacted with CO_2 under one atmospheric pressure maintained with a balloon filled with CO_2 gas in the presence of 0.5 mol % of 1 and 0.5 mol % of cocatalyst tetra(*tert*-butyl) ammonium bromide (TBAB) in a solvent-free condition. ^{*b*}Average yield for a set of triplicate experiments determined by ¹H NMR of the crude products. ^{*c*}Number of moles of product per mole of catalyst. ^{*d*}TON per minute.

examples of MOFs derived from d^{10} metal ions. Also, the ketone derivatives being less reactive than aldehydes are known to exhibit very less yield for this reaction.^{72–75} Therefore, for a standard reaction, acetophenone was reacted with aniline and trimethylsilyl cyanide using 1 as the catalyst in a solvent-free condition. The progress of the reaction was monitored by TLC, and the final conversion was calculated by ¹H NMR spectroscopy. For a control experiment, a blank reaction carried out in the absence of 1 gave a much lower product yield, indicating the requirement of 1 for this reaction.

The catalytic activity was further studied for a various ketone derivative, ranging from substituted acetophenone, aliphatic, and cycloaliphatic ketones to heteroaromatic ketone derivatives. The results are summarized in Table 4. In all cases a good product yield was obtained in each case except for 4-methoxyacetophenone and 3-methyl acetophenone (entries 4 and 5, Table 4), which indicate the very good catalytic activity of 1. The lower product yields in the cases of 4-methoxyacetophenone and 3-methyl acetophenone are due to the electron-donating effect of the substituents, which decreases the nucleophilicity at the carbonyl carbon and therefore decreases the reactivity and the product yields. In order to confirm their identity and purity, the products in each

Table 4. Substrate Scope for the Three-Component Strecker Reaction of Different Ketone Derivatives Catalyzed by 1^a

سر سر سر	+	+	<mark>1</mark> , 1mol % _ 25-30 °C, 5h	- (HN SCOUL
Entry	Ketone	Product	Yield (%) ^b	TON ^c	TOF (min ⁻¹) ^d
1		NC	90	90	0.30
2	F C C	F	92	92	0.31
3) ₈₉	89	0.29
4	MeO	MeO	58	58	0.19
5	Ç [≜]	NC NC	65	65	0.22
6	Ĵ.		88	88	0.29
7	\checkmark		86	86	0.29
8	\bigcap°		89	89	0.29
9	\bigcirc°		88	88	0.29
10			82	82	0.27
11			72	72	0.24
12		NC NC N	76	76	0.25
13		NC N N	85	85	0.28
14		NC NC	17 ^e		

^{*a*}Reaction conditions: ketone (0.2 mmol), amine (0.2 mmol), TMSCN (0.25 mmol) and time (5 h). ^{*b*}Average percent yield for a set of triplicate runs, determined by ¹H NMR of the crude products. ^{*c*}TON per minute. ^{*d*}Number of moles of product per mole of catalyst. ^{*e*}Blank reaction.

of the cases were isolated and characterized by ¹H and ¹³C NMR spectroscopy (Figures S15–S56).

As an important prerequisite of reusability and stability for heterogeneous catalytic systems, the recycling experiments were carried out for both reactions. The cycloaddition reaction of epichlorohydrin and three-component reaction of acetophenone, aniline, and trimethylsilyl cyanide were conducted using 1 as a catalyst under the optimized reaction conditions. After completion of the reaction, the catalyst was separated by centrifugation, washed with DCM, dried under vacuum at 100 °C for 5 h to regenerate the active catalyst, and reused for the next catalytic experiment. The PXRD of the recovered catalyst in both cases exhibited no loss of crystallinity or phase purity of the catalyst even after three cycles of the reactions (Figure S57). Also, a product yield of 96% and 90% obtained in the third cycle for the cycloaddition reaction and Strecker reaction, respectively, indicate very little drop in the catalytic activity of 1 for both reactions (Figure S58). Further, to confirm the heterogeneous nature of 1, the catalytic reactions were stopped after a certain amount of time, and the catalyst was separated from the reaction mixture by centrifugation. The reaction was then continued under the same reaction conditions, during which no significant increase in the product yield was obtained (Figures S59–S60), indicating the heterogeneous nature of the catalyst and its active role as a catalyst in both of the reactions.

The very good catalytic activity of 1, for both reactions, can be attributed to the presence of the high density of Lewis acidic coordinatively unsaturated metal sites and pore walls functionalized with Lewis-basic oxygen atoms of the ligand. This Lewis acid—base pair is known to act synergistically not only to enhance the selectivity and uptake capacity of CO₂ but also to enhance the catalytic activity of the system.^{76,77}

On the basis of the present studies and the reported proposals,^{47–57,72–75} plausible mechanisms are presented in Figures S61 and S62 for both the reactions. The Lewis-acidic metal center interacts with the oxygen atom of epoxide or carbonyl group (electrophile), leading to the activation of the epoxy ring or the carbonyl group. In addition, the Lewis-basic O atoms help in driving the reaction by polarization of the CO₂ and its interaction to the epoxy ring or activating the corresponding nucleophile to generate the cyclic carbonates and α -aminonitriles in good yields.

CONCLUSIONS

In summary, we have synthesized a microporous 3D MOF, $\{[Zn_2(3-tpom)(L)] \cdot 2H_2O\}_n$ (1), based on a bent dicarboxylic acid and semirigid tetrapyridyl ligand under solvothermal conditions. The framework exhibits very good thermal and chemical stability. Due to the high density of Lewis acidic metal sites and pores functionalized with Lewis-basic oxygen atoms, 1 exhibits good CO₂ adsorption selectivity and catalytic activity toward chemical fixation of CO₂ with epoxides. Furthermore, it acts as an efficient catalyst for the solventfree three-component Strecker reaction under ambient conditions. With high thermal and chemical stability, the good catalytic activity and recyclability entitles 1 as an efficient heterogeneous catalyst for these organic transformations. However, the current work presents moderate CO₂ uptake, and additional efforts are being devoted to synthesize low density MOF structures with functionalized pores using functional rigid linkers for enhanced CO₂ uptake capacities.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03051.

Crystallographic data with selected bond lengths and angles, TGA results, and PXRD patterns (PDF)

Accession Codes

CCDC 1936340 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data request@ccdc.cam.ac.uk, or by contacting The Cam-

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Notes

The authors declare no competing financial interest.

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