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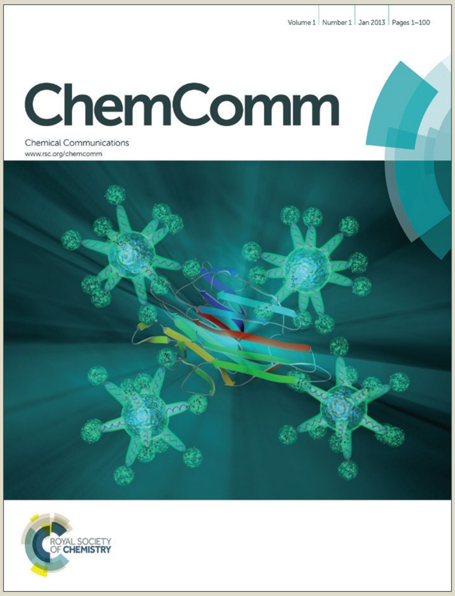

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A Sustainable Protocol for Facile Synthesis of Zinc-Glutamate MOF: Efficient Catalyst for Room Temperature CO_2 Fixation Reactions in Wet Conditions

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A water stable zinc-MOF (ZnGlu) catalyst was facilely prepared from the proteinogenic amino acid, L-glutamic acid at room temperature in aqueous medium. CO_2 fixations were promoted by the ZnGlu catalyst's inherently coordinated water and externally added water in yielding cyclic carbonate and cyclic urethane at room temperature. This eliminates the need for catalyst activation, making ZnGlu a ready-to-use catalyst. The enhanced CO_2 cycloaddition with added water hints at the application of ZnGlu in wet flue gas conversions. This is the first reported attempt of MOF in the cycloaddition of aziridine and CO_2.

Metal Organic Frameworks (MOFs) have been evolving as innovative materials, with its substantial contributions in gas capture and catalysis, by exploiting the versatility in porous functional architectures and metal containing nodes.[1] MOF-adsorbed gases have applications in energy (H_2, CH_4, etc.) and manufacture (CO_2 derived commodities).[2] CO_2 is a safe C1 feedstock abundantly available from combustions.[3] The 100% atom-economic transformations of CO_2, such as the synthesis of five-membered cyclic carbonates or cyclic urethanes represent ideal CO_2 utilization processes.[4] Cyclic carbonates are useful as solvents, electrolytes in batteries, raw materials for cosmetics and polymers etc.,[4b] while oxazolidinones (cyclic urethanes) are well-known chemical intermediates, precursors for organic/polymer synthesis, and pharmaceuticals.[4f,g] For effectuating CO_2 cycloadditions at ambient conditions (to avoid further CO_2 emission by fossil fuel burning), efficient catalysts[5] are required, which are heterogeneous.[6]

Current CO_2 capture scrubbers need desorption at high temperatures to recover the CO_2. MOFs being exceptionally efficient in CO_2 capture and catalysis, a single step capture-cum-transformation would save this energy. Transformation of CO_2 to cyclic carbonates using MOF catalysts started earlier this decade.[7] However, synthetic nature of ligands, toxic solvents, solvent remains in pores, and long synthesis durations at high temperatures hamper the eco-friendliness and energy rating for scaling up the MOF synthesis. Thus, facile and energy efficient synthesis of MOFs from natural ligands are highly desirable. The diminishing CO_2 uptake capacities or instability of MOFs under wet flue gases for CO_2 capture is also a haunting problem that necessitates pre-drying of flue gas.

The proteinogenic α-amino acids consists of COOH, NH_2, and functional group rich side chains. Such amino acids, or its modifications, were recently reported as homogeneous catalysts for CO_2 cycloadditions.[8] Very recently, we reported that water traces could promote cycloadditions of CO_2 with amino acid catalysts. Bio-MOFs made from amino acids could be the prospective class in connecting these two ends of CO_2 capture and transformation.[7a,9] Amino acid MOF (AA-MOFs) serve as frameworks that soften the reaction conditions, with the co-existence of Lewis acidic metals, base sites, and H-bonding groups. If water can promote the catalytic activity of AA-MOFs, a curse in CO_2 capture could be turned into an advantage, taking a double leap in the field of CO_2 chemistry by eliminating the need for flue gas drying and CO_2 desorption. In these efforts, L-glutamic acid was identified as the natural and economically viable spacer for AA-MOF (Scheme 1).

Scheme 1. Rapid synthesis of zinc-glutamate-MOF (ZnGlu); and cycloaddition of CO_2 with propylene oxide (PO) forming propylene carbonate (PC), and 2-methylaziridine (2-MeAz) forming 4-methyl-2-oxazolidinone (4-MeOx)

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Electronic Supplementary Information (ESI) available: Experimental details and methods, catalyst characterization using PXRD, FTIR, TGA, ORTEP diagram; catalyst recycle and characterization, and mechanism. See DOI: 10.1039/x0xx00000x

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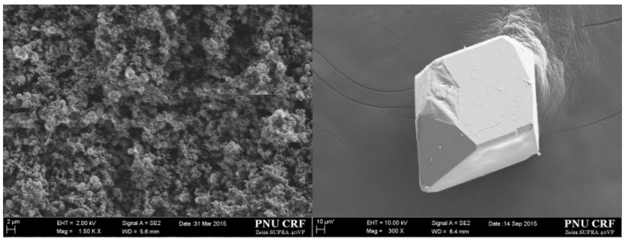


Fig. 1. FE-SEM image of rapidly prepared ZnGlu (left) in comparison with that of the single crystal (right).

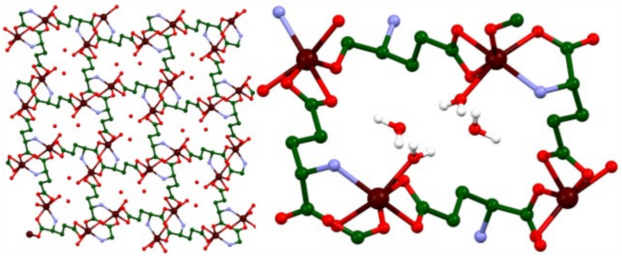


Fig. 2. Coordinated H_2O molecules and H-bonded ones (crystal lattices) in the framework of ZnGlu, viewed along c-axis. (a) packing diagram (b) pore. Legend: green C-atoms; red O-atoms; pink Zn; and blue N-atoms.

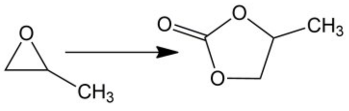
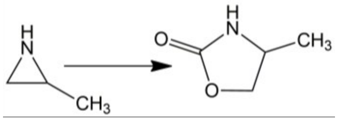
Zinc, for its Lewis acid character, is renowned active site in catalysis, and zinc-glutamate units are a part of active sites in biological systems (the enzyme carboxypeptidase that catalyze peptide degradation). Thus, a 3D-MOF zinc-glutamate-MOF (ZnGlu) with the structural formula $\{[Zn(H_2O)(C_5H_7NO_4)].H_2O\}_n$, was prepared instantly in aqueous medium by simple mixing at room temperature, avoiding synthetic ligands or solvents (Supplementary info, section S1.1 to S1.3 and Fig. S1). Further, its utility as a catalyst in CO_2 fixation for propylene carbonate (PC) and 4-methyl-oxazolidin-2-one (4-MeOx) synthesis from propylene oxide (PO) and 2-methylaziridine (2-MeAz) was tested at ambient conditions (Scheme 1). Also, to the best of our knowledge, this is the first ever report for 2-MeAz cycloadditions using MOF as catalyst.

The FE-SEM image of ZnGlu is shown in comparison with the single crystals, in Fig. 1. Even though clear crystalline edges are not visible in FE-SEM, a detailed analysis with PXRD technique revealed that the rapidly synthesized ZnGlu was crystalline in nature (Fig. S2).[10] FTIR spectra of the single crystal and the rapidly synthesized ZnGlu were also matching (Fig. S3). Further, the fairly high thermal stability of the material (up to 400 degrees) was evident from thermogravimetric analysis in the range 25 to 600 °C (TGA). ZnGlu showed thermal stability as high as the synthesized single crystals (Fig. S4). The chirality of the compound ZnGlu was characterized using solid state CD spectrum in KBr matrix (Fig. S5). The positive and negative cotton effects appeared at 535 and 495 nm, respectively.

The 3D structure of ZnGlu has Zn in distorted octahedral geometry by coordination with three glutamate moieties (deprotonated carboxylate ends) and one coordinated water.[10] ORTEP diagram depicting the coordination environment around zinc is shown in Fig. S6. In addition to this, water molecules are present in the crystal lattices (within the pores), each of them through multiple O-H…O hydrogen bonding interactions; one with the carboxylate oxygen and another with coordinated water molecule (Fig. 2). TG curve suggests the removal of lattice and coordinated water molecules at around 100 and 240 °C. The lattice water molecules (held weakly by H-bonding interactions) and the coordinated water molecules could thus be removed by vacuum drying (Fig. S4). The removal of lattice molecules facilitates substrate entrance. ZnGlu was also characterized for its CO_2 uptake at lower pressures below 1 atm (Fig. S7).

CO_2 cycloaddition with propylene oxide (PO) or 2-methylaziridine (2-MeAz) using various combinations are shown in Table 1. No product was detected in both reactions in the absence of any catalyst at room temperature (entries 1 and 6). The first set of experiments was performed with 42.6 mmol PO as the substrate (entries 1 to 5). With 1.6 mol% of ZnGlu catalyst in PO under room temperature at 1 MPa CO_2 pressure, propylene carbonate (PC) formation was very less at the end of 24 hours (entry 2). No MOFs till date have ever shown activities by itself at room temperatures. A tetrabutylammonium bromide (TBAB) cocatalyst (with high catalyst mol% and TBAB additives of upto 10 mol%) was necessary in promoting room temperature CO_2

Table 1. CO_2 cycloaddition reactions at room temperature using ZnGlu

Entry	Reaction	Catalyst[a]	mol%	Time (h)	PO/2-MeAz Conversion [PC/4-MeOx selectivity](%)
1		None	-	24	0
2		ZnGlu	1.6	24	Trace [-]
3		TBAB	1.6	24	4 [-]
4		ZnGlu/TBAB	1.6/1.6	24	65 [99]
5	PO→PC	ZnGlu/TBAB/H_2O	1.6/1.6/10	24	92 [99]
6		None	-	24	0
7		ZnGlu	0.8	24	Trace [-]
8		TBAB	0.8	24	48 [99]
9		ZnGlu/TBAB	0.8/0.8	24	90 [99]
10	2-MeAz→4-MeOx	ZnGlu/TBAB/H_2O	0.8/0.8/10	24	94 [99]

Reaction conditions: PO→PC conditions. PO = 42.6 mmol (3 mL), 1 MPa P_{CO2}, room temperature, 600 rpm; semi-batch.
2-MeAz→4-MeOx conditions. 2-MeAz = 28.3 mmol (2 mL), 1 MPa P_{CO2}, room temperature, 600 rpm; semi-batch.

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cycloadditions.[7a,b,l] Therefore, we also verified the possibility of TBAB cocatalyst, but with less amounts (1.6 mol%). TBAB alone in room temperature displayed only 4% PC yields (24h, entry 3). Interestingly, the combination of ZnGlu and TBAB (1.6 mol% each) in 24 h showed PC yields in 1+1>>2 manner (entry 4, 65% PO conversion and 99% PC selectivity). The binary system giving rise to higher yield is a clear-cut experimental evidence for synergistic catalysis. To our very surprise, the addition of water (10 mol%) highly enhanced the catalytic activities, yielding 92% PC under similar conditions, without compromising the selectivity to PC (entry 5). The CO_2 uptake in ZnGlu was 3.2 cm^3/g, even at a low pressure of 1 atm (Fig. S7). The BET surface area was derived as 3.02 m^2/g. Even though this is not quite a big value, high CO_2 adsorption was observed during the cycloaddition of PO using ZnGlu/TBAB catalyst with a drastic pressure fall recorded (CO_2 pressure dropped from 12 atm to 1 atm). Thus is because CO_2 chemisorption could have triggered as a result of the insertion of CO_2 to the ring opened epoxide bound to the catalyst in a synergistic manner.

The second set of CO_2 cycloaddition experiments (Table 1, entries 6 to 10) were performed with 2-MeAz as substrate. Even though our group and others have already studied this reaction, it is the first of its kind using MOF catalysts.[4f] As shown in entry 7, the catalyst alone (0.8 mol%) did not yield reasonable 4-MeOx. However, some conversion was shown with TBAB alone as catalyst (entry 8). The combination of ZnGlu and TBAB at room temperatures (entry 9) gave 90% conversion in 24 h (Fig. S8, S9). The addition of water had slight enhancing effects, taking conversions from 90 to 94% (entry 10). Thus, the overall trend was similar in both sets.

The catalyst was further tested for its recyclability (Section S 1.5 of the supporting information). In the case of PO-CO_2 cycloaddition, the first reuse was equally efficient, but a slight decrease in activity was observed in second and third reuse (Fig. S10). The recovered catalyst after the first reuse was dried and analyzed for PXRD and FTIR (Fig. S11 and S12). These results indicate that the recycled catalyst retained its structural identity. The ICP-OES analysis of the reaction mixture after catalyst recovery showed that only less than 6 ppm of zinc content was present in the product mixture. This means that, only 0.00065 mol% of metal content was leached (which amounts to 0.065% of leaching).

In catalysis, ZnGlu offers both Lewis acid sites and Lewis base sites. Water removal from the catalyst makes the pores accessible (for substrate entry and interactions), and further evacuation could create acidic open metal sites. A typical MOF with these active centers could have its mechanism via epoxide/aziridine binding to Zn center, ring opening by bromide anion at β-carbon center, CO_2 insertion between Zn and substrate, and the final ring closure (Fig. S13). However, in presence of adequate water, opportunistic catalysis[7n] is expected to take place similar to certain zeolitic imidazolate frameworks, where CO_2 insertion could occur in the labile Zn-OH_2 bonds. In the case of 2-MeAz, the significant conversions with TBAB alone (~40%) may be correlated to the increased electron density over NH group after the ring-opening of aziridine by TBAB. This NH group bind more easily with electrophilic C-atom of CO_2 (forming carbamate species). This was also evident when a sudden pressure fall was observed within the first few minutes of CO_2 addition to the reaction mixture. This additional interaction could be the reason for high conversions for 2-MeAz and PO even when the catalyst mol% was just the half of PO in 2-MeAz reaction (Table 1).

The ZnGlu catalyst represents a thermally and chemically stable, chiral MOF of natural origin that is instantly synthesized in aqueous media, that fits for CO_2 cycloaddition catalysis due to its inherent functional groups, coordinated water, or open metal sites. Thus, it paves way to the development of functional group rich amino acid MOFs. AA-MOFs from amino acids with N-heterocycle side chains (pyrrolidine, imidazole, indole or thiol) would exhibit better efficiencies in a task specific manner towards MOF as compact materials for CO_2 separation, storage and chemical transformation.

In summary, a three-dimensional amino acid-MOF, ZnGlu was instantly synthesized at room temperature by direct mixing, in aqueous media. Without any routine activation, it was employed as recyclable catalyst for CO_2 conversion to propylene carbonate, and first ever MOF catalyst reported for CO_2 conversion to oxazolidinones, that brings out its efficiency under wet conditions. Synergistic involvements evidenced from experimental results were explained using a plausible reaction mechanism. ZnGlu possesses good thermal and chemical stability, and it represents a MOF catalyst of high utility, made from economically viable constituents of natural origin, that is suitable for industrial scale up. The overall study (from catalyst preparation till catalysis) was performed out under minimal energy, with no external heating at any stage. The material has potentials in easy, fast, cheap, eco-friendly (aqueous) and energy efficient scale up of MOF production in industry, and the methodology has its potential in CO_2 capture and fixation from wet flue gas.

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