

Crystal Engineering of an *nbo* Topology Metal–Organic Framework for Chemical Fixation of CO₂ under Ambient Conditions**

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Abstract: Crystal engineering of the *nbo* metal–organic framework (MOF) platform MOF-505 with a custom-designed azamacrocyclic ligand (1,4,7,10-tetraazacyclododecane-*N,N,N',N''*-tetra-*p*-methylbenzoic acid) leads to a high density of well-oriented Lewis active sites within the cuboctahedral cage in MMCF-2, [Cu₂(Cu-tactmb)(H₂O)₃(NO₃)₂]. This MOF demonstrates high catalytic activity for the chemical fixation of CO₂ into cyclic carbonates at room temperature under 1 atm pressure.

Carbon dioxide (CO₂), as the major greenhouse gas, accumulates in the atmosphere at an alarming pace and is suspected to cause global warming over the past several decades. It is thus imperative to develop viable carbon dioxide capture and sequestration (CCS) technologies to reduce the greenhouse emissions.^[1] The drawbacks of energy-cost, corrosion, and inefficiency for amine-based wet-scrubbing systems which are currently used in industry,^[2] have prompted the exploration of alternative approaches for CCS. Extensive efforts have been dedicated to the development of functional nanoporous materials, such as activated carbons,^[3] zeolites,^[4] metal–organic frameworks (MOFs),^[5] and porous organic polymers,^[6] to capture CO₂; captured CO₂ is proposed to be sequestered by deposition in underground reservoirs.^[7]

A different yet attractive means of effective sequestration can turn to chemical conversion of captured CO₂ into value-added chemicals, such as dimethyl carbonate,^[8] cyclic carbonate,^[9] *N,N'*-disubstituted ureas,^[10] formic acid,^[11] and others.^[12] Given their wide applications in pharmaceutical and fine chemical industries,^[13] cyclic carbonates formed by the coupling of epoxide with CO₂ have been of intense interest. Although some homogeneous catalysts have been widely

used for the formation of cyclic carbonate in industry,^[14] the processes require high temperatures and pressures as well as rigorous separation and purification of the products.^[15] This necessitates the development of highly efficient heterogeneous catalysts for synthesizing cyclic carbonates particularly under mild conditions. Several types of heterogeneous catalysts, such as metal oxides, zeolites, titanosilicate, and ion-exchanged resin, have been explored to catalyze the coupling reactions of epoxides with CO₂, but only under the conditions of high temperatures (>100 °C) and high CO₂ pressures (>3 MPa),^[16] thus increasing the cost of reaction processes in terms of both capital and energy input. Therefore, there is still a need to search for new types of heterogeneous catalysts that are capable of efficiently converting CO₂ into cyclic carbonates under the very mild reaction conditions (that is, ambient conditions).

Metal–organic frameworks,^[17] which feature structural versatility,^[18] modularity^[19] and amenability to be designed with specific functionality,^[20] have been explored as a new type of functional materials for heterogeneous catalysts over the past decade.^[21] Although several existing MOFs have recently been evaluated as heterogeneous Lewis acid catalysts for chemical conversion of CO₂, high pressure and high temperature reaction conditions are required to achieve high efficiency,^[22] which could be presumably due to the low density of active sites in those MOFs. To achieve a high density of catalytically active sites in MOFs, one appealing approach is to decorate vertexes, and/or edges, and/or faces of polyhedral cages in MOFs with catalytically active centers, thereby affording MOF-based nanoreactors.^[23] This kind of nanoreactor can not only exhibit a high density of active sites within the confined nanospace, but can also allow the active sites to orient well toward the center of the cage, thus facilitating the interactions between the active sites and substrates,^[24] with the expectation of efficiently catalyzing the coupling reactions of epoxides with CO₂ under very mild conditions. Herein, we show how to achieve such a MOF-based nanoreactor that can convert CO₂ into cyclic carbonates with high efficiency at room temperature under 1 atm pressure by crystal engineering of the *nbo* MOF platform with a custom-designed azamacrocyclic ligand.

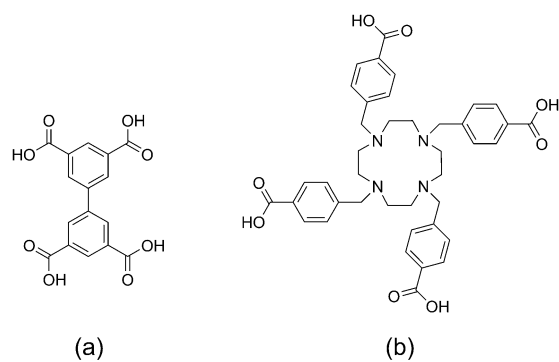
The prototypal *nbo* MOF platform^[25] is exemplified by MOF-505,^[25a] which is based upon 3,3',5,5'-biphenyltetracarboxylate ligand (bptc; Scheme 1a) and copper paddlewheel secondary building units (SBUs). MOF-505 consists of a cuboctahedral cage with 12 copper paddlewheels residing on the vertexes (Figure 1a). As the 12 copper centers on the vertexes are not well-oriented toward the center of the cuboctahedral cage, their full accessibility for the substrates

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[**] We acknowledge the University of South Florida for financial support of this work. The crystal diffraction of MMCF-2 was carried out at the Advanced Photo Source on beamline 15ID-B of ChemMatCARS Sector 12 (NSF/CHE-0822838, DE-AC02-06CH11357).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201309778>.



Scheme 1. The ligands that serve as linkers in MOF-505 and MMCF-2: a) 3,3',5,5'-biphenyltetracarboxylic acid (H_4bptc); b) 1,4,7,10-tetrazacyclododecane- N,N',N'',N''' -tetra- p -methylbenzoic acid ($H_4tactmb$).

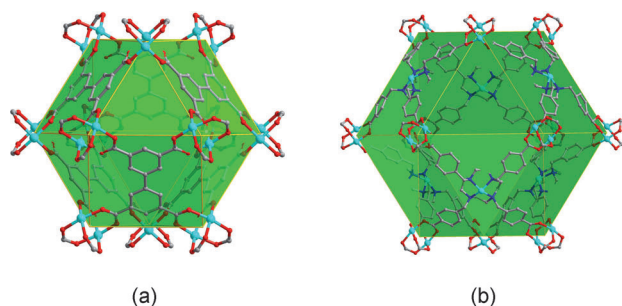


Figure 1. The cuboctahedral cage of a) MOF-505 and b) MMCF-2.

entering the cage could be restricted, thus leading to possible limited performances as Lewis acid catalysts. One way to introduce additional active copper sites that can be aligned toward the cage center, thus promoting the interactions between active sites and substrates, is by decorating the six square faces of the cuboctahedral cage with copper centers. This has been achieved by a crystal engineering approach in the **nbo** topology MOF, MMCF-2 (MMCF denotes metal-macrocylic framework) as reported herein, in which each of the six square faces of the cuboctahedral cage is occupied by the Cu^{II} metalated azamacrocycle (Figure 1b). As expected, the cuboctahedral cage of MMCF-2 can function as highly efficient Lewis acid-based nanoreactor for the cycloaddition of CO_2 and epoxide under ambient conditions, with twice the efficiency of the parent MOF-505.

MMCF-2 was prepared as dark-blue block-shaped crystals (empirical formula: $[Cu_2(Cu-tactmb)(H_2O)_3(NO_3)_2]$) by the self-assembly of the azamacrocylic tetracarboxylate ligand, 1,4,7,10-tetrazacyclododecane- N,N',N'',N''' -tetra- p -methylbenzoic acid ($H_4tactmb$; Scheme 1b)^[26] with $Cu(NO_3)_2$ under solvothermal conditions. Single-crystal X-ray diffraction analysis conducted at the Advanced Photo Source, Argonne National Laboratory revealed that MMCF-2 crystallizes in the $Pm\bar{3}m$ space group, with $a = 21.753(2)$ Å. It consists of $Cu_2(COO)_4$ SBUs that serve as one type of 4-connected square planar nodes as well as the tetracarboxylate *tactmb* ligands that can be deemed as another type of 4-connected square planar nodes, thereby affording the expected **nbo** topology. Every six *tactmb* ligands connect 12 paddle wheel

SBUs to form a nanoscopic cuboctahedral cage with six Cu^{II} metalated azamacrocylic occupying the six square faces (Figure 1b), meaning an addition of six center-oriented copper sites as compared to the cuboctahedral cage in MOF-505.^[25a] MMCF-2 is porous and exhibits a solvent accessible volume of about 69 % as calculated by PLATON.^[27]

The phase purity of MMCF-2 was verified by powder X-ray diffraction (PXRD) studies, which indicate that the diffraction patterns of the fresh sample are consistent with the calculated ones (Supporting Information, Figure S2). Thermogravimetric analysis (TGA) studies on freshly prepared MMCF-2 (Supporting Information, Figure S3) show a continuous weight loss of guest molecules from room temperature to about 290 °C followed by the decomposition of the framework, as similar to other **nbo** topology MOFs.^[25] The permanent porosity of MMCF-2 was assessed by N_2 adsorption studies at 77 K (Supporting Information, Figure S4), revealing a Brunauer–Emmett–Teller (BET) surface area of about $450\text{ m}^2\text{ g}^{-1}$ (corresponding to a Langmuir surface area of ca. $540\text{ m}^2\text{ g}^{-1}$).

Given the high density of copper sites in the cuboctahedral cage of MMCF-2 (Supporting Information, Figure S5) and its capability to adsorb substantial amount of CO_2 at ambient temperature (Supporting Information, Figure S8), we decided to evaluate its performances as Lewis acid based nanoreactor in the context of cycloaddition of CO_2 and epoxides to form cyclic carbonates at room temperature and under 1 atm pressure. Control experiments were conducted for homogeneous Cu^{II} metalated azamacrocycle of *Cu-tactmb* and MOF-505. As shown in Figure 2 and Table 1,

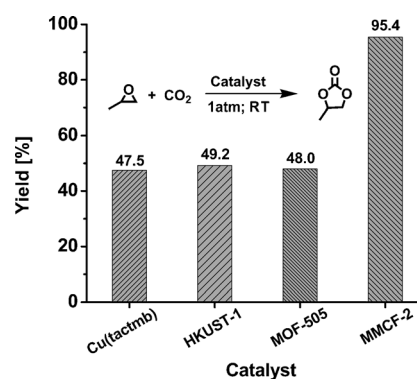












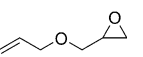
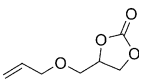
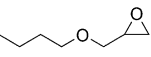
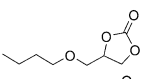




Figure 2. The yield of propylene carbonate from cycloaddition of propylene oxide and CO_2 catalyzed by *Cu(tactmb)*, HKUST-1, MOF-505, and MMCF-2 after 48 h at room temperature under 1 atm CO_2 pressure.

MMCF-2 demonstrates highly efficient catalytic activity for cycloaddition of propylene oxide with CO_2 into propylene carbonate at room temperature under 1 atm CO_2 pressure with a yield of 95.4 % over 48 h (Table 1, entry 1). This compares favorably to the corresponding value for homogeneous *Cu(tactmb)* (47.5 % yield, Table 1, entry 2) and MOF-505 (48.0 % yield, Table 1, entry 3). MMCF-2 also outperforms the benchmark polyhedral cage-containing copper MOF, HKUST-1, which exhibits a moderate activity with

Table 1: Various carbonates from different epoxides catalyzed by various catalysts.^[a]

Entry	Catalyst	Epoxides	Products	Yield [%]
1	MMCF-2			95.4
2	Cu(tactmb) ^[b]			47.5
3	MOF-505			48.0
4	HKUST-1			49.2
5	MMPF-9			87.4
6	MMCF-2			88.5
7	MMCF-2			43.3
8	MMCF-2			42.1
9	MMCF-2			37.6

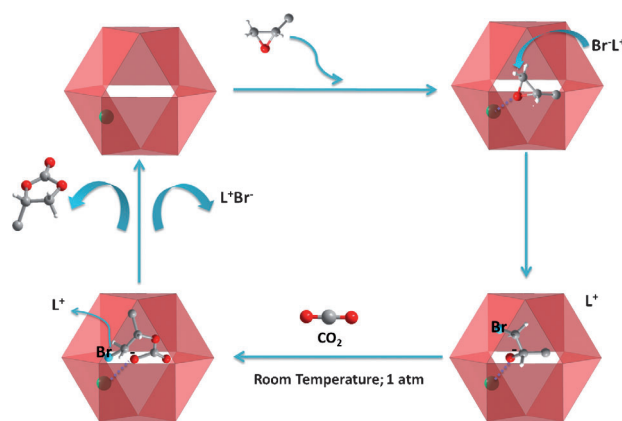
[a] Reaction conditions: epoxide (25.0 mmol) with catalyst (0.125 mol% per paddlewheel units), *n*Bu₄NBr (0.58 g), under 1 atm CO₂ at room temperature for 48 h. [b] Cu(tactmb) loaded as the same amount of azamacrocycle within MMCF-2.

propylene carbonate yield of 49.2% over 48 h under similar reaction conditions (Table 1, entry 4). We reasoned that the high catalytic activity of MMCF-2 for chemical fixation of CO₂ under ambient conditions should be mainly attributed to the high density of active sites with some of them well-oriented in the cuboctahedral cage, which could promote the interactions between substrates and active sites. This is supported by the fact that MMCF-2 can catalyze the cycloaddition of propylene oxide with CO₂ into propylene carbonate as about twice efficiency as MOF-505, although number of active copper sites in the cuboctahedral cage of MMCF-2 is 50% more than that in the cuboctahedral cage of MOF-505 (18 for MMCF-2 vs. 12 for MOF-505). The importance of the well-oriented active copper sites in the cuboctahedral cage is also evidenced by the higher catalytic activity of MMCF-2 compared to the high-density active sites containing MOF, MMPF-9^[28] (95.4% for MMCF-2 vs. 87.4% for MMPF-9) (Table 1, entry 5). These results thus highlight the Cu^{II}-azamacrocycle decorated cuboctahedral cage in MMCF-2 as a highly efficient Lewis acid-based nanoreactor for chemical conversion of CO₂ into cyclic carbonate under ambient conditions. Indeed, the ability of MMCF-2 to chemically convert CO₂ into cyclic carbonate with high efficiency under such mild conditions of room temperature and 1 atm pressure is advantageous to some existing MOFs^[22] and

metal–salen-based porous organic networks,^[16e,29] which require high-pressure and high-temperature reaction conditions to achieve high efficiency. The evaluation of MMCF-2 on converting CO₂ into value-added chemicals such as cyclic carbonates also represents a step beyond the numerous studies on CO₂ physisorption in MOFs^[5,30] and recent investigations on chemical fixation of CO₂ into carbonic acid/carbonate in MOFs.^[31]

We examined the performances of MMCF-2 in chemical fixation of CO₂ with epoxides substituted with different functional groups under ambient conditions. A high catalytic activity was also observed for cycloaddition of butylene oxide with CO₂ into butylene carbonate at room temperature and 1 atm pressure with a yield of 88.5% over 48 h (Table 1, entry 6). Interestingly, with the increase of molecular sizes of epoxide substrates, a dramatic yet steady decrease in the yield of cyclic carbonates was observed, as indicated by the 43.3% formation of 3-allyloxy-1,2-propylene carbonate (Table 1, entry 7), 42.1% formation of 3-butoxy-1,2-propylene carbonate (Table 1, entry 8), and 37.6% formation of 3-phenoxy-1,2-propylene carbonate from allyl glycidyl ether (Table 1, entry 9), butyl glycidyl ether, and benzyl phenyl glycidyl ether, respectively. This could be possibly ascribed to the limited diffusion of large-sized epoxide substrate molecules into the cuboctahedral cage of MMCF-2 thus exerting size-selective catalysis.^[21,32]

On the basis of some previous reports,^[22] a tentative mechanism is proposed for the cycloaddition of epoxide and CO₂ into cyclic carbonate catalyzed by the strong Lewis acid based catalyst of MMCF-2, as illustrated in Scheme 2: The



Scheme 2. A representation of the tentatively proposed catalytic mechanism for the cycloaddition of epoxide and CO₂ into cyclic carbonate catalyzed by MMCF-2 (green sphere: open metal site; L⁺ = tetra-*n*-tertbutylammonium).

coupling reaction is initiated by binding the epoxide with the Lewis acidic copper site in the cuboctahedral cage of MMCF-2 through the oxygen atom of epoxide to thus activate the epoxy ring. Subsequently, the Br[−] generated from *n*Bu₄NBr attacks the less-hindered carbon atom of the coordinated epoxide to open the epoxy ring. This is followed by the interaction of CO₂ with the oxygen anion of the opened epoxy ring form an alkylcarbonate anion, which is then converted

into the corresponding cyclic carbonate through the ring closing step. We deduce that a high density of copper Lewis acid sites well-oriented toward the cage center could boost the synergistic effect with $n\text{Bu}_4\text{NBr}$ through the confined nanospace, thus promoting the cycloaddition reaction, which thereby leads to high catalytic activity of MMCF-2 for chemical conversion of CO_2 into cyclic carbonates under ambient conditions. Indeed, detailed mechanistic studies to probe the intermediates during the cycloaddition reaction could be necessary, and research along this line will be conducted in the near future.

In summary, a polyhedral cage-based nanoreactor featuring a high density of catalytically active yet well-oriented copper sites has been achieved in MMCF-2 by decoration of the **nbo** topology platform of MOF-505, with a custom-designed azamacrocyclic ligand which is metalated in situ with Cu^{II} . MMCF-2 demonstrates excellent performance in the context of chemical fixation of CO_2 into cyclic carbonates at room temperature under 1 atm pressure that is superior to the parent MOF-505 and the other copper-based MOF of HKUST-1. The crystal engineering approach for the generation and alignment of a high density of catalytically active centers within the confined nanospace by the custom design of functional ligands is expected to be a broadly applicable way for the development of new classes of highly efficient heterogeneous catalytic systems for chemical fixation of CO_2 and related reactions.

Received: November 10, 2013

Revised: January 5, 2014

Published online: February 4, 2014

Keywords: carbon dioxide · chemical fixation · crystal engineering · metal–organic frameworks · nbo topology

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