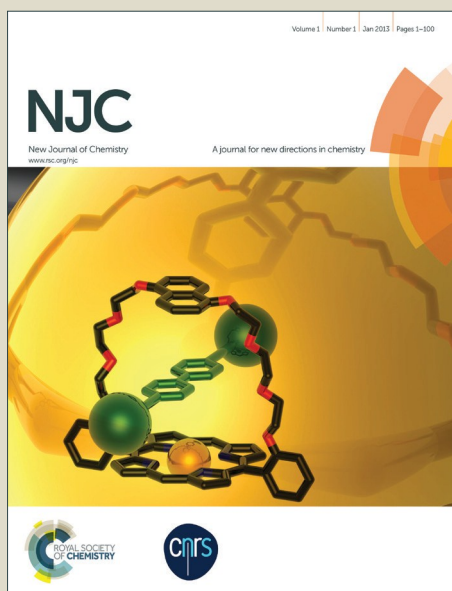


# NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

## Isomorphous MOFs functionalized by free-standing acylamide and organic groups serving as self-supported catalysts for CO<sub>2</sub> cycloaddition reaction

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Lili Song, Chao Chen,\* Xiangbin Chen, Ning Zhang\*

**Abstract** In this work, we demonstrate the catalysis capability of a series of isomorphous MOFs functionalized on the pore wall by both acylamide and -H, -OH, NH<sub>2</sub>, -NO<sub>2</sub>, -COOH groups in the aspects of CO<sub>2</sub> cycloaddition reaction. Without any co-catalyst all these MOF materials exhibited excellent catalysis capability but different catalytic activities dependent on the organic groups decorated on the pore wall, revealing the best catalysis capability for MOF functionalized by -NH<sub>2</sub> groups on the pore wall and synergetic catalytic effect from both acylamide and organic groups. Furthermore, we also estimated the recycle of -NH<sub>2</sub> functionalized MOF material, and found that the catalyst could be used for at least four times without significant decrease in its catalytic activity.

### 1. Introduction

Conversion of CO<sub>2</sub> to five-membered cyclic carbonate is one of the most important processes<sup>[1]</sup>, which is a 100% atom economic reaction and incorporates other “green” principles<sup>[2]</sup>. The product five-membered cyclic carbonate are valuable industrial raw materials, which are widely employed as aprotic solvents, electrolytes in lithium-ion batteries, intermediates for the pharmaceutical, monomer units of polycarbonates, chemical ingredients for preparing medicines or agricultural chemicals, alkylating agents, and so on<sup>[3]</sup>. Due to such uses, numerous homogenous and heterogeneous catalysts for this reaction have been described over the last 30 years. For example, ionic liquids<sup>[4]</sup>, quaternary ammonium and phosphonium salt<sup>[5]</sup>, alkali metal halides<sup>[6]</sup>, inorganic oxides<sup>[7-8]</sup>, organometallic complexes<sup>[9-10]</sup>, modified molecular sieves<sup>[11-12]</sup>, metal oxide<sup>[13]</sup>, ion-exchange resins<sup>[14]</sup>, metal-organic frameworks<sup>[15-17]</sup>, nanoparticles<sup>[18]</sup> and so on.

Homogeneous catalysts usually exhibited the advantages of high activity and selectivity. At the same time, separating the catalyst from the product was a complicated process, such as distillation after the reaction, may result in the decomposition of the catalyst or formation of by-products.<sup>[19]</sup> Therefore, much of the current research has been focused on the employment of heterogeneous catalysts. However, most of the reported heterogeneous catalytic systems suffer from at least one of the following disadvantages: instability of catalyst, need for co-catalysts, longer duration for the completion of reaction etc.<sup>[20]</sup> The development of efficient recoverable and reusable heterogeneous catalysts need no co-catalyst has received much attention.

From the researches, many organic functional groups decorated in the catalysts played crucial roles for the CO<sub>2</sub> cycloaddition reaction. For example, nitrogen basic moieties NH group<sup>[21-23]</sup>, hydroxyl group<sup>[24-26]</sup>, carboxylic group<sup>[24-25,27]</sup> activated the epoxide ring via hydrogen bonds. As reported, hydrogen bonding had a positive effect on the ring-opening of epoxide<sup>[27-28]</sup>, which made the reaction to proceed smoothly. In addition, CO<sub>2</sub> could be activated by amine groups, which might be beneficial for the insertion of CO<sub>2</sub> into the C–O bond of epoxides, as previously reported for solid basic catalysts<sup>[29-30]</sup>. Nevertheless, very little was experimentally and theoretically known about whether a synergistic effect exists leading by these functional groups for the CO<sub>2</sub> cycloaddition reaction.

Previously we successfully utilized Metal-organic frameworks (MOFs) as catalyst for CO<sub>2</sub> cycloaddition reaction<sup>[31]</sup>. MOFs are formed by metal atoms linked together with multi-functional organic ligands. Studies have shown that large differences in catalytic efficacy result from the organic frameworks surrounding the metals, which claim the advantages of this unique material acting as catalyst. Thus the concept of self-supported catalysis maybe applied via synthesis of a particular structural MOF immobilizing proper functional groups onto the pore surface to enhance their interactions. Herein, we employed MOFs containing functional groups both could activate CO<sub>2</sub> or epoxide encountered in the wall as self-supported catalyst for the reaction.

### 2. Experimental

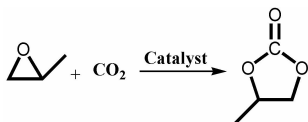
#### 2.1. Materials

The materials were prepared according to the literature.<sup>[32]</sup> The approach is based on analogous organic struts: H<sub>2</sub>aip(5-aminoisophthalic acid), H<sub>2</sub>ip (isophthalic acid), H<sub>2</sub>hip (5-hydroxyisophthalic acid), H<sub>2</sub>nip(5-nitroisophthalic acid), and H<sub>3</sub>BTC (1,3,5-benzenetricarboxylic acid). Zn(L)(ip)·(DMF)(H<sub>2</sub>O)<sub>1.5</sub> (**1-H**), Zn(L)(hip)·(DMF)(H<sub>2</sub>O) (**1-OH**),

Institute of Applied Chemistry, College of Chemistry, Nanchang University, Nanchang, Jiangxi 330031, P. R. China.  
Fax: +86 79183969514; Tel: +86 791 83779427;  
E-mail: chaochen@ncu.edu.cn (C. Chen). nzhang.ncu@163.com (N. Zhang)

Zn(L)(aip)·(H<sub>2</sub>O) (**1-NH<sub>2</sub>**), Zn(L)(nip)·(DMF)<sub>0.5</sub> (H<sub>2</sub>O)<sub>0.5</sub> (**1-NO<sub>2</sub>**), Zn(L)(HBTC)·(H<sub>2</sub>O)<sub>2</sub> (**1-COOH**) were synthesized by solvo(hydro)-thermal syntheses strategy with Zn(NO<sub>3</sub>)<sub>2</sub>, L(N<sup>4</sup>,N<sup>4'</sup>-di(pyridin-4-yl)biphenyl-4,4'-dicarboxamide) and multi-carboxylate ligands. Before being used as catalysts, the MOFs were activated by drying at 130 °C under vacuum for 6 hours to remove the guest molecule.

## 2.2. Cycloaddition reaction



The cycloaddition of CO<sub>2</sub> to epoxides was performed using propylene oxide (PO) as substrate. All the catalytic reaction experiments were conducted in a stainless steel pressure reactor with a stirrer. The reactor was charged with PO (3.5ml), catalyst (0.07 mmol). After the reactor was fed with CO<sub>2</sub> to a desired pressure, the autoclave with its contents was heated to a desired temperature and stirred for a designated period of time. Then the reactor was cooled to 5-10 °C in an ice-water bath, and excess gases were vented out slowly. The catalyst was separated by filtration and the reaction mixtures were analyzed by GC-MS.

## 2.3. General information

All solvents were obtained commercially and used without further purification. Powder X-ray diffraction (PXRD) was performed on a Siemens D5005 diffractometer with filtered Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 40 kV and 30 mA. Diffraction patterns were collected from 5° to 40° with a step size of 2° min<sup>-1</sup>. Thermogravimetric measurements were carried out with a TA SDTQ600 instrument. Samples were heated to 800 °C at a heating rate of 10 °C min<sup>-1</sup> under an air atmosphere (50 mL min<sup>-1</sup>). CO<sub>2</sub> adsorption isotherms were measured with a Micromeritics ASAP 2020 system.

## 3. Results and discussion

### 3.1. Characterization

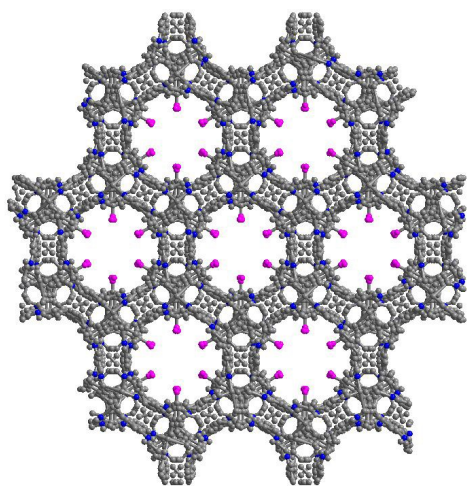


Figure 1 The structure of these MOFs. The highlighted in blue is acylamide groups, and the red one is R (R = -H, -OH, -NH<sub>2</sub>, -NO<sub>2</sub>, -COOH).

These prepared MOFs show isomorphous frameworks, consisting of a 1-D regular hexagonal channel structure (Figure

1). In the channel, acylamide group with different organic groups of -H, -OH, -NO<sub>2</sub> and -COOH were decorated to understand the synergistic catalytic behavior of these functional groups. Their pore diameters are in the range of 7.0-9.4 Å. Phase purity of these bulk samples was confirmed by powder X-ray diffraction (PXRD). (Fig. 2).

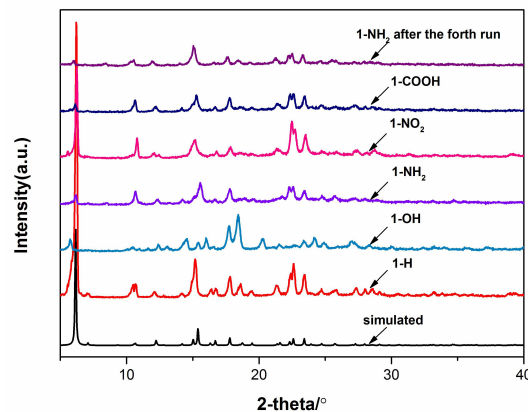


Figure 2. PXRD patterns of these MOFs.

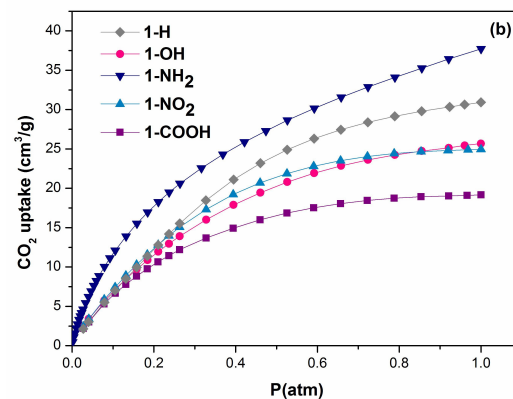
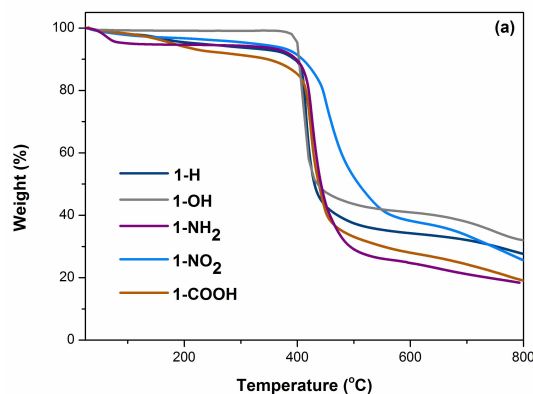


Figure 3. (a) Results of the thermogravimetric analyses (b) Comparison of the absolute loading of CO<sub>2</sub> at 0 °C.

The thermogravimetric curves of these materials were shown in Fig. 3a. Weight loss process attributing to the decomposition of samples is observed at around 380 °C. It should be noted that the reaction temperature for the cycloaddition reaction was 100 °C, far below the destruction temperature of the catalysts. It worth mentioning that CO<sub>2</sub> can significantly absorbed into these MOF materials, which makes the activity of CO<sub>2</sub> in it possible and suitable. -NH<sub>2</sub> group in the **1-NH<sub>2</sub>** framework promoted the adsorption of

carbon dioxide on the solid surface, but other organic groups such as -OH, -COOH, and -NO<sub>2</sub> had little effect on the CO<sub>2</sub> adsorption (Fig. 3b). This gas selective behavior can be explained by the stronger affinity of -NH<sub>2</sub> group to CO<sub>2</sub> via the formation of carbamate species, which is essentially create high substrate concentrations at the catalytic sites and favors the CO<sub>2</sub> cycloaddition reaction.

### 3.2. Catalytic activity

With the high CO<sub>2</sub> adsorption ability, **1-NH<sub>2</sub>** was chosen as the typical catalyst for the following investigation. Entries 1 and 2 in Tab.1 shows the dependence of propylene carbonate (PC) yield and selectivity on initial CO<sub>2</sub> pressure. It could be seen that the PC yield was strongly affected by initial CO<sub>2</sub> pressure. In the low pressure (2 MPa), there was a poor PC yield (18%) and selectivity (82%). Further rise of pressure to 3 MPa resulted in acute increase of PC yield (92%) and selectivity (>99%). Such an effect of CO<sub>2</sub> pressure on catalytic activity has also been observed in other catalytic systems<sup>[33-34]</sup>. An increase of CO<sub>2</sub> pressure is a positive factor for PO conversion, which increases the surface concentration of CO<sub>2</sub>. Hence, rather than promoting the interaction between PO and catalyst, a higher CO<sub>2</sub> pressure enhances the catalytic activity. The effect of temperature on the reaction was also studied in the range of 80-110 °C (Table 1 Entries 2-5). Conversion increased with the increasing temperature below 100 °C, and reached maximum at 100 °C. No further conversion was observed of 110 °C. The yield of PC reached 92% with increasing reaction time up to 6 h (Figure 4). Extended reaction times of 9 h (Table 1 Entry 6) did not appear to have further effects on the yield. Hence, a reaction time of 6 h was chosen to be optimum in this study.

The catalytic activity of **1-NH<sub>2</sub>** for the cycloaddition of CO<sub>2</sub> to PO was compared with those of other catalysts. The results were summarized in Table 1. In the absence of a catalyst, there was no reaction whatsoever. It could be seen that all catalysts were effective for the conversion of PO to PC. **1-NH<sub>2</sub>** functioned with acylamide and -NH<sub>2</sub> groups displayed maximum activity (yield of 92%) and selectivity (>99%) (Entry 2). In order to understand the role of -NH<sub>2</sub> group, the MOF was modified by -H to remove -NH<sub>2</sub>. The resultant was catalyst **1-H**. As for **1-H**, the conversion of propylene oxide to propylene carbonate decreased to 54% (Entry 7). This result strongly suggested the importance of the -NH<sub>2</sub> group towards CO<sub>2</sub> coupling with epoxides. What's more, we assume that the high activity of **1-NH<sub>2</sub>** for the reaction maybe benefit from a synergistic effect. Therefore the test was performed. Seen from entry 17, no activity was observed when aniline was used as catalyst. Single Ligand 1 only afforded low activity (53%) (Entry 14) for the reaction, but their combination gave conversion of 83% (Entry 18) under the same reaction conditions, implying the strong synergistic effect between them.

To make clear whether in the presence of -OH or -COOH group would also responsible for the catalysis. -NH<sub>2</sub> was replaced by -OH/-COOH forming catalyst **1-OH** and **1-COOH**. Compared with the other catalysts, the material **1-OH** and **1-COOH** despite having both acid and basic sites, showed rather low conversion (40% and 37%), even less than that of catalyst **1-H**. Aim to make clear whether there was space effect, an inactive organic group -NO<sub>2</sub> was chosen replacing of -OH/-COOH fixed at the hole wall. **1-NO<sub>2</sub>** gained almost the same conversation with **1-H**, which proved there was no space effect. It

seemed that the existence of -COOH weakened the catalytic performance for this reaction. We suppose maybe -OH/-COOH surely have participated in the reaction by activating epoxide as reported, then possibly the strong acid site impeded desorption of the product exhibiting a low yield<sup>[35]</sup>. The accurate reason need our further investigation.

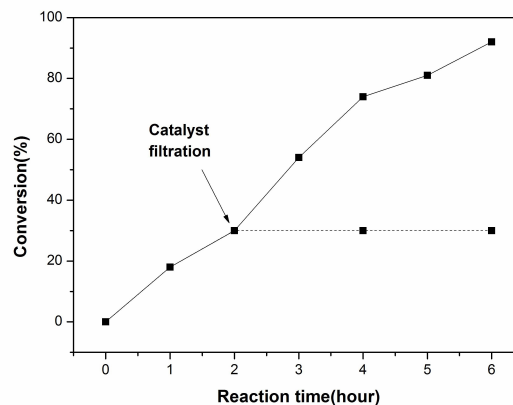


Figure 4. Cycloaddition of CO<sub>2</sub> to propylene oxide in the presence of **1-NH<sub>2</sub>**.

Reaction conditions: PO 3.5ml, P(CO<sub>2</sub>) 3MPa, catalyst 0.07mmol, Temperature 100 °C

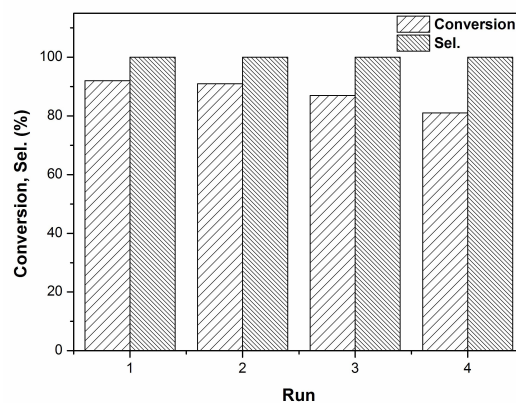


Figure 5. The recyclability of **1-NH<sub>2</sub>** for the cycloaddition reaction.

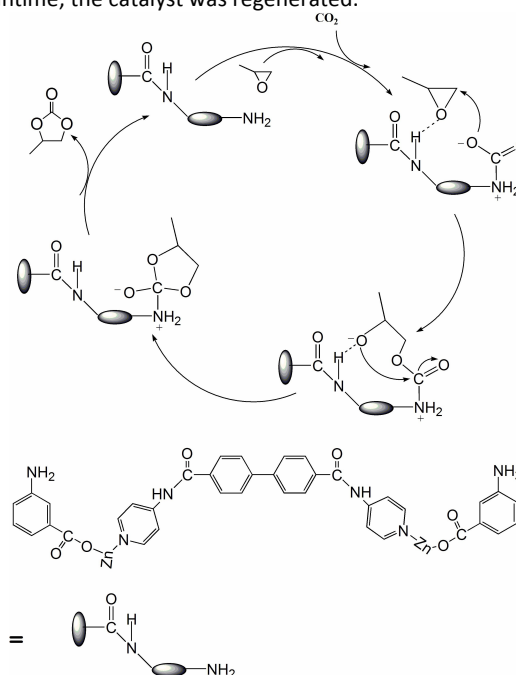
Reaction conditions: PO 3.5ml, P(CO<sub>2</sub>) 3MPa, catalyst 0.07mmol, Temperature 100 °C, time 6 h.

A filtering experiment was performed to test the stability of **1-NH<sub>2</sub>** in the reaction system. Remove the catalyst after the reaction proceeded for 2 h, further heat the filtrate at the same temperature with the same CO<sub>2</sub> pressure. The composition was monitored at given time intervals. Result was shown in figure 4, obviously no more propylene carbonate was produced, which means a true heterogeneous catalysis. The recycling of catalyst was investigated to further prove the constancy of the catalyst activity. For each cycle, the used catalyst was separated by filtration, washed with methanol to remove the products adhering to the surface of the catalyst, dried at 130 °C under vacuum, and then reused directly for the next run. The activities of the reused **1-NH<sub>2</sub>** catalyst were summarized in Figure 5. In each run the selectivity remained constant and the conversion was with a minimal reduction since, at the end of the forth cycle the value was 81%, respectively, 11% lower than initial value. Moreover, the catalytic activity remained between TOF = 97–110 h<sup>-1</sup>. Powder X-ray diffraction (PXRD)

patterns suggest that **1-NH<sub>2</sub>** sample after the fourth cycle of catalytic reactions retains good crystallinity without significant degradation in structural integrity (Figure 2). These results indicated that **1-NH<sub>2</sub>** had good stability and capacity of being reused for the CO<sub>2</sub> cycloaddition reaction.

The most surprising aspect of the title catalyst is the catalytic reaction proceeded in the absence of co-catalysts. We summarized all the MOFs catalysts reported in the literature for the same reaction. As listed in Table 2, they always need the assistance of co-catalyst for the reaction. We assumed that the MOFs could absorb the reactants and activate the epoxide ring via hydrogen bonds. Meanwhile CO<sub>2</sub> was activated by the co-catalyst such as quaternary ammonium. However, **1-NH<sub>2</sub>** was functionalized by two types of organic groups, acylamide and -NH<sub>2</sub> groups, which might play synergistic effect for the activation of epoxide ring and CO<sub>2</sub>. Therefore, based on the results, as well as those of the present work [21, 35-36], a plausible mechanism for this chemical fixation reaction of CO<sub>2</sub> was suggested showing the synergistic effect (Scheme 1). This mechanism insists that both -NH<sub>2</sub> and acylamide group have the same importance when the reaction takes place. First, through hydrogen bond, the acylamide group with oxygen atom of epoxide resulted in polarization of the epoxide C-O bonds and forming an active propylene oxide. Simultaneously, CO<sub>2</sub> was activated by -NH<sub>2</sub> (the primary amine) forming carbamate anion<sup>[36]</sup>. Then, carbonate anion attacks the less hindered β-carbon atom of the active propylene oxide, which opens the epoxide ring furnishing

ring-opened intermediate. The resulting anion attacks the carbonyl carbon intramolecularly, ring closed forming propylene carbonate. In meantime, the catalyst was regenerated.



Scheme 1 Proposed possible mechanism for the CO<sub>2</sub> cycloaddition reaction catalyzed by **1-NH<sub>2</sub>**

Table 1 Cycloaddition of CO<sub>2</sub> to PO catalyzed by different catalysts

Entry	Catalyst	Time (h)	Temperature (°C)	PCO <sub>2</sub> (MPa)	Conversion (%)	Selectivity (%)	TOF <sup>a</sup>
1	<b>1-NH<sub>2</sub></b>	6	100	2	18	82	22
2	<b>1-NH<sub>2</sub></b> (1st)	6	100	3	92	>99	110
3	<b>1-NH<sub>2</sub></b>	6	80	3	60	>99	72
4	<b>1-NH<sub>2</sub></b>	6	90	3	79	>99	94
5	<b>1-NH<sub>2</sub></b>	6	110	3	92	>99	110
6	<b>1-NH<sub>2</sub></b>	9	100	3	92	>99	73
7	<b>1-H</b>	6	100	3	54	>99	65
8	<b>1-OH</b>	6	100	3	40	>99	48
9	<b>1-NO<sub>2</sub></b>	6	100	3	53	>99	63
10	<b>1-COOH</b>	6	100	3	37	>99	44
11	<b>1-NH<sub>2</sub></b> (2ed)	6	100	3	91	>99	109
12	<b>1-NH<sub>2</sub></b> (3rd)	6	100	3	87	>99	104
13	<b>1-NH<sub>2</sub></b> (4th)	6	100	3	81	>99	97
14 <sup>b</sup>	Ligand 1	6	100	3	53	>99	---
15	H <sub>2</sub> aip	6	100	3	0	---	---
16 <sup>b</sup>	Ligand 1 + H <sub>2</sub> aip + Zn(NO <sub>3</sub> ) <sub>2</sub>	6	100	3	39	>99	---
17	aniline	6	100	3	0	---	---
18	Ligand 1 + aniline	6	100	3	83	>99	---

Reaction conditions: PO(3.5mL), catalyst(0.07mmol)

<sup>a</sup> TOF: mole of product/mole of catalyst/hour

<sup>b</sup> Ligand 1: L(N<sup>4</sup>,N<sup>4'</sup>-di(pyridin-4-yl)biphenyl-4,4'-dicarboxamide)

## Journal Name



## ARTICLE

Table 2. Comparison with synthesis of PC from CO<sub>2</sub> and PO reaction catalyzed by MOFs

Entry	MOF	Co-catalyst	Pressure (MPa)	Temperature (°C)	Time(h)	Yield (%)	Ref.
1	MOF-5	<i>n</i> -Bu <sub>4</sub> NBr	6	50	4	98	15
2	Hf-NU-1000	<i>n</i> -Bu <sub>4</sub> NBr	1atm	25	26	100	16
3	Cr-MIL-101	TBABr	0.8	25	24	82	17
4	Fe-MIL-101	TBABr	0.8	25	24	95	37
5	MOF-505	<i>n</i> Bu <sub>4</sub> NBr	1atm	25	48	48	38
6	HKUST-1	<i>n</i> Bu <sub>4</sub> NBr	1atm	25	48	49	38
7	MMPF-9	<i>n</i> Bu <sub>4</sub> NBr	1atm	25	48	87	38
8	PCN-224(Co)	<sup>n</sup> Bu <sub>4</sub> NCl	2	100	4	42	39
9	Ni(salphen)-MOF	NBu <sub>4</sub> Br	2	80	4	80	40
10	<b>1-NH<sub>2</sub></b>	none	3	100	6	92	Present work

## 4. Conclusions

MOFs with different functional groups exhibiting different catalytic activities for the synthesis of propylene carbonate from propylene oxide and CO<sub>2</sub>. The catalytic activities of **1-OH** and **1-COOH** containing hydroxyl and carboxyl groups were lower than that of **1-H** instead. Getting rid of the space effect which was proved by **1-NO<sub>2</sub>** replacing of inactive group (-NO<sub>2</sub>), maybe it was because the the strong acid sites impeded desorption of the product. **1-NH<sub>2</sub>** worked as an excellent self-supported catalyst for the reaction with conversion of 92%. The imultaneous presence of both -NH<sub>2</sub> and acylamide group promoted the conversion via synergetic effect. Furthermore, the catalyst could be easily separated, recovered and reused for four times with a minimal loss of its original catalytic activity.

## Acknowledgements

This work was supported by the National Natural Science Foundations of China (No.21561020 and No. 21261017) and Jiangxi Province (No. 20122BAB213003, 20132BAB203009, 20132BAB213004 and 20133ACB20001), the Foundation of Educational Department of Jiangxi province (No. GJJ13112).

## Notes and references

- 1 T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara and T. Maeshima, *Chem. Commun.*, 1997, 1129–1130.
- 2 (a) P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998; (b) M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T. E. Müller, *ChemSusChem.*, 2011, **4**(9), 1216–1240.
- 3 T. Sakakura, K. Kohno, *Chem. Commun.*, 2009, **11**, 1312–1330.
- 4 W. L. Dai, B. Jin, S. L. Luo, X. B. Luo, X. M. Tu, C. T. Au, *J. Mol. Catal. A: Chem.*, 2013, **378**, 326–332.
- 5 N. Aoyagi, Y. Furusho, T. Endo, *Tetrahedron Lett.*, 2013, **54**(51), 7031–7034.
- 6 Z. Wu, X. Yu, E. Liu, *ChemCatChem.*, 2013, **5**, 1328–1333.
- 7 T. Cao, L. T. Sun, Y. Shi, L. Hua, R. Zhang, L. Guo, W. W. Zhu, Z. S. Hou, *Chin. J. Catal.*, 2012, **33**, 416–424.
- 8 M. Sankar, T. G. Ajithkumar, G. Sankar, P. Manikandan, *Catalysis Communications*, 2015, **59**, 201–205.
- 9 C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. W. Kleij, *J. Am. Chem. Soc.*, 2013, **135**(4), 1228–1231.
- 10 F. Ahmadi, S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. M. Baltork, A. R. Khosropour, *Polyhedron.*, 2012, **32**, 68–72.
- 11 E. J. Doskocil, *J. Phys. Chem. B*, 2005, **109**, 2315–2320.
- 12 R. Srivastava, D. Srinivas, P. Ratnasamy, *Catal. Lett.*, 2003, **91**, 133–139.
- 13 H. Yasuda, L. N. He, T. Takahashi, *Appl. Catal. A: Gen.*, 2006, **298**, 177–180.
- 14 Y. B. Xiong, H. Wang, R. M. Wang, Y. F. Yan, B. Zheng, Y. P. Wang, *Chem. Commun.*, 2010, **46**, 3399–3401.

## ARTICLE

Journal Name

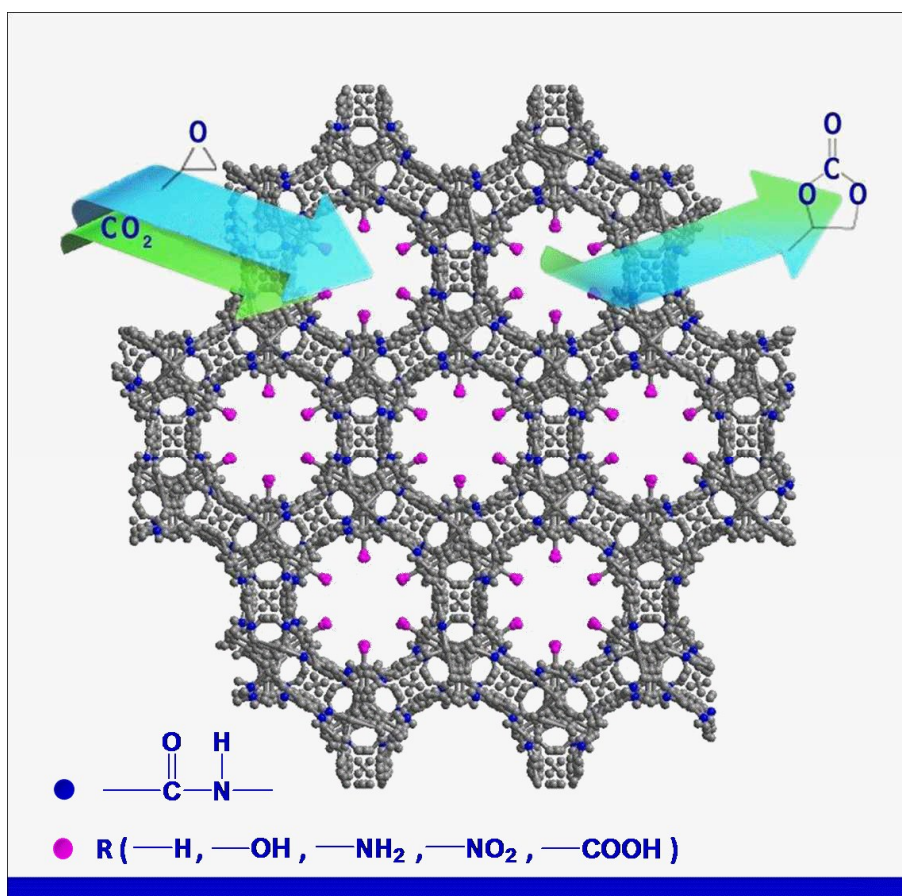
- 15 J. L. Song, Z. F. Zhang, S. Q. Hu, T. B. Wu, T. Jiang, B. X. Han, *GreenChem.*, 2009, **11**, 1031-1036.
- 16 M. H. Beyzavi, R. C. Klet, S. Tussupbayev, J. Borycz, N. A. Vermeulen, C. J. Cramer, J. F. Stoddart, J. T. Hupp, and O. K. Farha, *J. Am. Chem. Soc.*, 2014, **136**(45), 15861–15864.
- 17 O. V. Zalomaeva, A. M. Chibiryaev, K. A. Kovalenko, O. A. Kholdeeva, B. S. Balzhinimaev, V. P. Fedin, *Journal of Catalysis*, 2013, **298**, 179-185.
- 18 J. Ma, J. L. Liu, Z. F. Zhang, B. X. Han, *Green Chem.*, 2012, **14**, 2410–2420.
- 19 Y. Zhao, J. S. Tian, X. H. Qi, Z. N. Han, Y. Y. Zhuang, L. N. He, *Journal of Molecular Catalysis A: Chemical*, 2007, **271**(1-2), 284-289.
- 20 M. Sankar, N. H. Tarte, P. Manikandan, *Applied Catalysis A: General*, 2004, **276**, 217-222.
- 21 S. D. Lee, B. M. Kim, D. W. Kim, M. I. Kim, K. R. Roshan, M. K. Kim, Y. S. Won, D. W. Park, *Applied Catalysis A: General*, 2014, **486**, 69-76.
- 22 Z. Z. Yang, L. N. He, C. X. Miao, S. Chanfreau, *Adv. Synth. Catal.*, 2010, **352**(13), 2233-2240.
- 23 Y. M. Shen, W. L. Duan, M. Shi, *Eur. J. Org. Chem.*, 2004, **14**, 3080-3089.
- 24 L. Han, H. Q. Li, S. J. Choi, M. S. Park, S. M. Lee, Y. J. Kim, D. W. Park, *Applied Catalysis A: General*, 2012, **429-430**, 67-72.
- 25 R. C. Luo, X. T. Zhou, Y. X. Fang, H. B. Ji, *Carbon*, 2015, **82**, 1-11.
- 26 J. Sun, S. J. Zhang, W. G. Cheng, J. Y. Ren, *Tetrahedron Lett.*, 2008, **49**, 3588-3591.
- 27 J. Sun, L. J. Han, W. G. Cheng, J. Q. Wang, X. P. Zhang, S. J. Zhang, *ChemSusChem.*, 2011, **4**, 502–507.
- 28 W. L. Dai, L. Chen, S. F. Yin, W. H. Li, Y. Y. Zhang, S. L. Luo, C. T. Au, *Catal. Lett.*, 2010, **137**, 74–80.
- 29 D. F. Ji, X. B. Lu, R. He, *Applied Catalysis A: General*, 2000, **203**, 329–333.
- 30 M. Tu, R. J. Davis, *J. Catal.*, 2001, **199**, 85-89.
- 31 C. Chen, J. Zhang, G. H. Li, P. Shen, H. C. Jin, N. Zhang, *Dalton Trans.*, 2014, **00**, 1-7.
- 32 F. Luo, M. S. Wang, M. B. Luo, G. M. Sun, Y. M. Song, P. X. Li, G. C. Guo, *Chem. Commun.*, 2012, **48**, 5989–5991.
- 33 W. L. Dai, L. Chen, S. F. Yin, W. H. Li, Y. Y. Zhang, S. L. Luo, C. T. Au, *Catal. Lett.*, 2010, **137**, 74–80.
- 34 L. F. Xiao, F. W. Li, J. J. Peng, C. G. Xia, *J. Mol. Catal. A: Chem.*, 2006, **253**, 265–269.
- 35 J. Kim, S. N. Kim, H. G. Jang, G. Seo, W. S. Ahn, *Applied Catalysis A: General*, 2013, **453**, 175-180.
- 36 R. Srivastava, D. Srinivas, P. Ratnasamy, *Microporous and Mesoporous Materials*, 2006, **90**, 314-326.
- 37 O. V. Zalomaeva, N. V. Maksimchuk, A. M. Chibiryaev, K. A. Kovalenko, V. P. Fedin, B. S. Balzhinimaev, *Journal of Energy Chemistry*, 2013, **22**, 130-135.
- 38 W. Y. Gao, Y. Chen, Y. H. Niu, K. Williams, L. Cash, P. J. Perez, L. Wojtas, J. F. Cai, Y. S. Chen, S. Q. Ma, *Angew. Chem. Int. Ed.*, 2014, **53**(10), 2615-2619.
- 39 D. W. Feng, W. C. Chung, Z. W. Wei, Z. Y. Gu, H. L. Jiang, Y. P. Chen, D. J. Darensbourg, H. C. Zhou, *J. Am. Chem. Soc.*, 2013, **135**(45), 17105-17110.
- 40 Y. W. Ren, Y. C. Shi, J. X. Chen, S. R. Yang, C. R. Qi, H. F. Jiang, *RSC Adv.*, 2013, **3**, 2167-2170.

## Graphical and textual abstract

### Isomorphic MOFs functionalized by free-standing acylamide and organic groups serving as self-supported catalysts for CO<sub>2</sub> cycloaddition reaction

Lili Song, Chao Chen,\* Xiangbin Chen, Ning Zhang\*

*Institute of Applied Chemistry, College of Chemistry, Nanchang University, Nanchang, Jiangxi 330031, P. R. China; Fax: +86 791 83969514; Tel: +86 791 83779427; E-mail: chaochen@ncu.edu.cn (C. Chen), nzhang.ncu@163.com (N. Zhang)*



MOFs exhibited different catalytic activities dependent on the organic groups decorated on the pore wall, which played synergistic catalytic effect.