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# Postsynthetic ionization of an imidazole-containing metal–organic framework for the cycloaddition of carbon dioxide and epoxides†

Jun Liang,<sup>ab</sup> Rui-Ping Chen,<sup>a</sup> Xiu-Yun Wang,<sup>a</sup> Tao-Tao Liu,<sup>a</sup> Xu-Sheng Wang,<sup>a</sup> Yuan-Biao Huang<sup>\*a</sup> and Rong Cao<sup>\*ab</sup>

A bifunctional imidazolium functionalized zirconium metal–organic framework (Zr-MOF), (I<sup>+</sup>)Meim-UiO-66 (2), was successfully prepared from the imidazole-containing Zr-MOF Im-UiO-66 (1) by a post-synthetic modification (PSM) method. It was found that the crystal size and pore features of the imidazole-containing 1 could be tuned at the nanoscale. The bifunctional MOF 2, containing Brønsted acid sites and iodide ions, was shown to be an efficient and recyclable heterogeneous catalyst for the cycloaddition of carbon dioxide (CO<sub>2</sub>) with epoxides, without the use of any co-catalyst, at ambient pressure. The solvent-free synthesis of the cyclic carbonate from CO<sub>2</sub> and an epoxide was monitored by *in situ* Fourier transform infrared spectroscopy (FT-IR) and an acid/base synergistic catalysis mechanism was proposed. We hope that our strategy provides an effective approach for the introduction of functional *N*-heterocyclic groups into MOFs for potential applications.

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## Introduction

The conversion of greenhouse carbon dioxide (CO<sub>2</sub>), as a renewable C1 synthon, into value-added chemicals such as cyclic carbonates, is one of the hot topics in the field of catalysis.<sup>1</sup> However, due to the inert nature of CO<sub>2</sub>, finding a chemical fixation process with a high efficiency is still a great challenge.<sup>2</sup> Up to now, various homogeneous catalysts including quaternary ammonium complexes,<sup>3</sup> alkali metal salts,<sup>4</sup> ionic liquids,<sup>5</sup> and metal–organic complexes<sup>2a,6</sup> have been applied to the cycloaddition of CO<sub>2</sub> with epoxides into cyclic carbonates. However, homogeneous catalysts often suffer from laborious and expensive purification processes, whereas the use of porous heterogeneous catalysts could overcome the product–catalyst separation problem.<sup>7</sup>

Recently, metal–organic frameworks (MOFs), as a class of porous crystalline compounds composed of metal nodes and organic linkers, have shown workable applications in gas adsorption and catalysis due to their chemical and composition tunabilities as well as their permanent porosities and large

surface areas.<sup>8,9</sup> Although a few MOF catalysts have been utilized for the coupling reactions of CO<sub>2</sub> with epoxides, most of them are efficient only under high pressure conditions or with co-catalysts, such as organic bases and organic salts, which are uneconomical and complicated.<sup>10</sup> Thus the synthesis of porous MOF materials with efficient catalytic sites, which can be used for the conversion of CO<sub>2</sub> without a co-catalyst at atmospheric pressure is highly desirable. As is known, imidazoliums have been employed as efficient catalysts for the cycloaddition reaction of CO<sub>2</sub>.<sup>5e,11</sup> Despite that, a handful of imidazolium-based MOFs have been synthesized *via* pre-synthetic strategies, although none of them have been utilized for the chemical fixation of CO<sub>2</sub>.<sup>12</sup> Furthermore, *N*-heterocyclic functional groups such as imidazole (im) and imidazolium could enhance the “CO<sub>2</sub> capture” capability due to the weak interactions between the CO<sub>2</sub> molecule and the nitrogen atom.<sup>6,13</sup> However, it remains a challenge to obtain porous and stable MOFs with free imidazole groups through avoiding undesirable coordination with metal nodes in direct synthesis.<sup>14</sup> In particular, UiO-66,<sup>15b</sup> as an archetype of a 12-connected Zr-based MOF, is among the most stable and tunable MOFs due to its high valence metal-oxide clusters (Zr<sub>6</sub>) and its variable connectivity.<sup>15</sup> UiO-66 derivatives are typically constructed from Zr<sub>6</sub> clusters and linear dicarboxylic linkers, and the produced open Brønsted-acid sites (Zr–OH/Zr–OH<sub>2</sub>) could enhance the acidic catalysis by decreasing the number of linkers.<sup>16</sup> Thus, we hope that the isoreticular synthesis of imidazole-containing UiO-66 could pave the way towards imidazolium functionalized MOFs, which can be employed as bifunctional catalysts containing Brønsted-

<sup>a</sup>State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, University of Chinese Academy of Sciences Fujian, Fuzhou, 350002, P. R. China. E-mail: rcao@fjirsm.ac.cn; Fax: +86 591 8379 6710

<sup>b</sup>Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China

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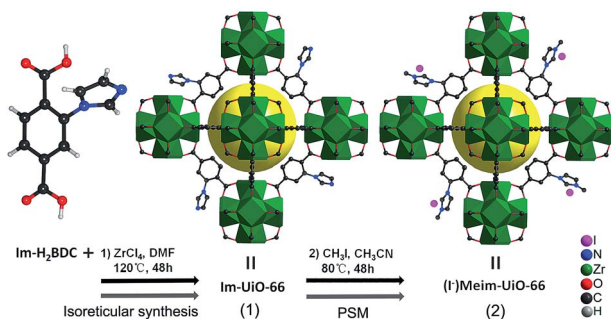
acid sites and halogen anions for carbon dioxide capture and synergistic conversion.<sup>17</sup>

Herein, we first synthesized a bifunctional imidazolium decorated Zr-MOF, (I<sup>-</sup>)Meim-UiO-66 (**2**), *via* isoreticular synthesis and a post-synthetic modification (PSM) method.<sup>18</sup> Interestingly, **2** is shown to be an efficient and recyclable heterogeneous catalyst for the cycloaddition of CO<sub>2</sub> with epoxides, without the use of any co-catalyst, at ambient pressure. As shown in Scheme 1, a delicate linear linker, 2-(imidazol-1-yl)-terephthalic acid (Im-H<sub>2</sub>BDC), was selected in order to construct imidazolium-Zr-MOF efficiently (for details, see Fig. S1†).

## Results and discussion

### Syntheses and characterizations of Im-UiO-66 (**1**) and (I<sup>-</sup>)Meim-UiO-66 (**2**)

Initially, Im-UiO-66 (**1**) was readily synthesized in 75% yield by the solvothermal reaction of an equimolar mixture of Im-H<sub>2</sub>BDC·HCl and ZrCl<sub>4</sub> in DMF at 120 °C for 48 h. The powder X-ray diffraction (PXRD) patterns of the resultant solid matched well with the calculated pattern of UiO-66 (Fig. 1a), which indicated that the two compounds had similar topological structures (Fig. S5†).<sup>15b</sup> Interestingly, the obtained uniform small nanocrystals (20–30 nm) of Im-UiO-66 (**1**) were able to facilitate contact with the substrate and enhance the catalysis (Fig. 1c and S6†).<sup>9c</sup> The framework of **1** was chemically stable in aqueous sodium hydroxide and hydrochloric acid conditions (pH = 1–14), as confirmed by the PXRD patterns collected for each sample (Fig. S7†). Furthermore, **1** had a Brunauer–Emmett–Teller (BET) surface area of 538 m<sup>2</sup> g<sup>-1</sup> (Fig. 1e and Table S1†). Notably, **1**, which contained imidazole groups, indeed showed a higher CO<sub>2</sub> adsorption uptake (5.85 wt%) than UiO-66 (3.39 wt%) at room temperature (Fig. 1f). In order to further investigate the structural features and active components of this framework, **1** was measured by CO<sub>2</sub>-TPD and NH<sub>3</sub>-TPD, which revealed the existence of a large amount of medium Lewis basic sites (free imidazole groups) and acid sites (probably Brønsted-acid (Zr–OH/Zr–OH<sub>2</sub>) sites of defect Zr<sub>6</sub> nodes)<sup>18</sup> in **1** (for details, see Fig. S8†).



Scheme 1 Syntheses of **1** and **2** *via* reticular chemistry and by a PSM method, respectively. Green polyhedra: Zr<sub>6</sub> clusters. Yellow ball: micropores. Only part of the linkers are shown for clarity.

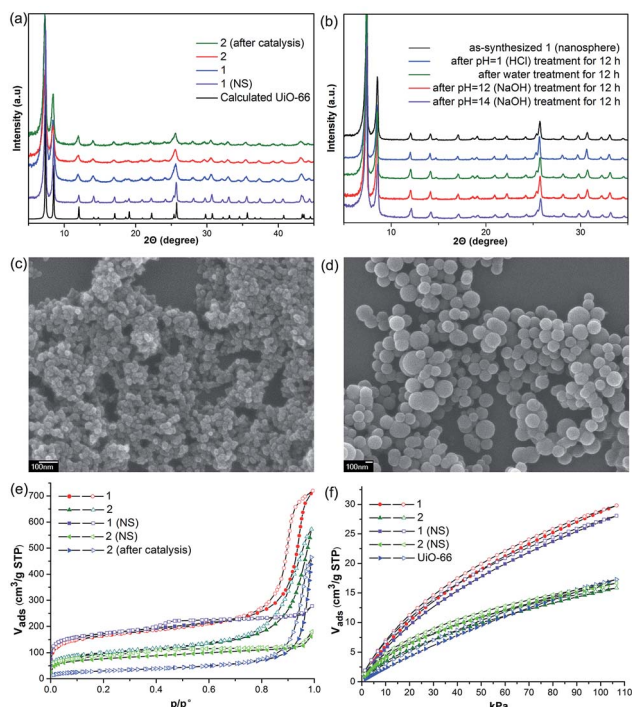


Fig. 1 (a) PXRD of **1**, **1** (nanosphere, NS), **2** and **2** after catalysis. (b) The PXRD patterns of **1** (NS) after treatment with different aqueous solutions. The SEM images of (c) as-synthesized nanoparticles of **1** and (d) nanoparticles of **1** (NS). Scale bar: 100 nm. (e) N<sub>2</sub> sorption isotherms for **1**, **2**, **1** (nanosphere, NS) and **2** (NS) at 77 K. (f) CO<sub>2</sub> sorption isotherms for **1**, **2**, **1** (NS), **2** (NS) and UiO-66 at 298 K. Solid symbols denote adsorption, open symbols denote desorption ( $P/P^0$  = partial pressure).

The successful synthesis of robust **1** with uncoordinated imidazole groups prompted us to implement a post-synthetic functionalization of **1** with methyl iodide (Scheme 1). The PXRD pattern indicated that the targeted **2** retained its original framework integrity (Fig. 1a). To determine the degree of methyl-modification of **1**, <sup>1</sup>H NMR analyses were performed after the digestion of **2** in DMSO-*d*<sub>6</sub> and HF (Fig. S9†), and indicated that *ca.* 75% of the imidazole groups were converted to imidazolium, based on the molar ratio of the (I<sup>-</sup>)Meim-BDC<sup>2-</sup> and Im-BDC<sup>2-</sup> linkers. The formation of **2** was further confirmed by mass spectra, FT-IR and solid <sup>13</sup>C NMR (Fig. S10 and S11†). Compared with the <sup>13</sup>C NMR spectrum of **1**, the <sup>13</sup>C NMR spectrum of **2** showed a unique peak at 36.0 ppm, which was ascribed to the methyl carbon in the framework (Fig. 2).<sup>19</sup> Energy dispersive spectroscopy (EDS) images (Fig. S12†) confirmed the homogeneous distribution of the iodide throughout the interior of the **2** crystals. After incorporation of the methyl groups, **2** still exhibited a high BET surface area of 328 m<sup>2</sup> g<sup>-1</sup> (Fig. 1e) and a good CO<sub>2</sub> adsorption uptake of 3.1 wt% at room temperature (Fig. 1f). The zero-coverage adsorption enthalpies for CO<sub>2</sub> at 298 K were 27.4 and 44.2 kJ mol<sup>-1</sup> for **1** and **2**, respectively (Fig. S13†). The  $Q_{st}$  value of **1** was higher than that of most metal azolate frameworks (MAFs) but slightly lower than that of nitrogen rich IFMC-1 (30.7 kJ mol<sup>-1</sup>).<sup>15b</sup> On the other hand, the  $Q_{st}$  value of **2** containing imidazolium groups was moderate, which surpassed that of most reported





Table 1 Cycloaddition of CO<sub>2</sub> with epoxides, catalyzed by 2<sup>a</sup>

Entry	Substrate	Product	Conversion <sup>b</sup> [%]	Selectivity <sup>b</sup> [%]
1			100	93
2			92	81
3			76	92
4			46	71
5			77	62
6			61	38
7			38	34

<sup>a</sup> Reaction conditions: epoxide (10 mmol), 2 (50 mg, 0.052 mmol), CO<sub>2</sub> (0.1 MPa), 393 K, *t* = 24 h. <sup>b</sup> Determined by GC-MS.

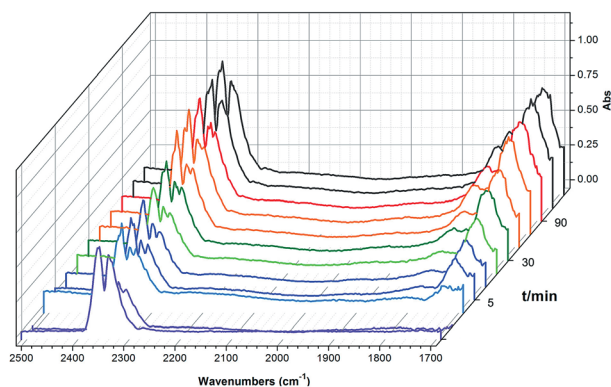
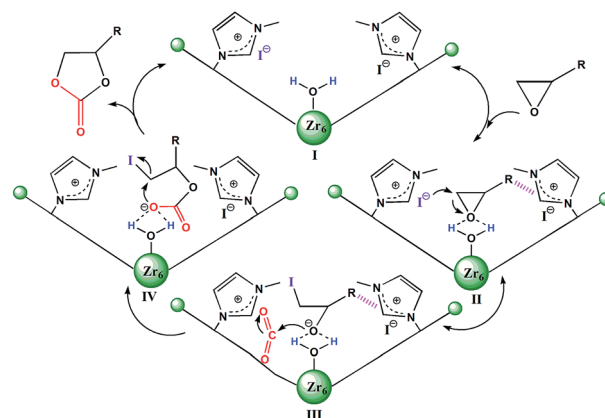


Fig. 3 *In situ* FT-IR spectra of the synthesis of chloropropene carbonate catalyzed by 2 at 100 °C under an atmospheric dilute CO<sub>2</sub>/N<sub>2</sub> gas mixture. IR absorption of 2 is subtracted for clarity.



Scheme 2 Plausible mechanism of 2 catalyzed cycloaddition reaction of CO<sub>2</sub> with epoxides. The hashed bonds represent π···π, cationic···π or hydrogen bonding interactions.

framework to form a complex ionic catalyst that self-catalyzes the reaction based on a similar mechanism.<sup>18b</sup>

To examine the scope of the substrates for the cycloaddition reaction of CO<sub>2</sub>, other epoxides were studied under optimal conditions. As shown in Table 1, the epoxide allyl glycidyl ether gave a high conversion (92%) and a satisfactory carbonate selectivity (>81%) (Table 1, entry 2). However, phenyl glycidyl ether afforded a moderate conversion (76%) and a high selectivity (>92%) (Table 1, entry 3). In contrast, the chain epoxides propylene oxide, 1,2-epoxyhexane and 1,2-epoxyoctane gave a moderate to low epoxide conversion and selectivity (Table 1, entries 5–7). We ascribed the higher carbonate selectivity of the aromatic epoxides over those of the chain epoxides to the possible π···π, cationic···π and hydrogen bonding interactions

between the aromatic substrates and the catalyst frameworks (Table 1, entries 2–4).

Separation of the catalyst from the reaction mixture is easily carried out by centrifugation. This allows the catalyst to be recycled six times for use in the cycloaddition reaction of epichlorohydrin with CO<sub>2</sub>, without a noticeable loss in activity (Table S6 and Fig. S21†), despite the fact that the BET surface area of 2 decreases to 109 m<sup>2</sup> g<sup>-1</sup> after catalysis (Fig. 1e). The decreased surface area without sacrifice of the activity of 2 indicated that the active sites on the external surfaces could effectively promote the catalytic reaction. Additionally, the PXRD pattern of 2 after catalysis is in agreement with that of synthesized 2 (Fig. 1a), which demonstrates that the catalyst framework is retained.



## Conclusion

In summary, we have successfully synthesized a bifunctional porous imidazolium functionalized Zr-MOF, (I<sup>-</sup>)Meim-UiO-66, *via* isoreticular synthesis and a PSM method. This new MOF can serve as an efficient heterogeneous catalyst towards the capture and coupling of CO<sub>2</sub> with epoxides at ambient pressure, without a co-catalyst, under mild conditions. It was found that the smaller particles of **2** led to a higher catalytic activity towards CO<sub>2</sub> fixation than that of nanosphere **2** (NS). Considering the high stabilities, hierarchical pores and modifiable features of **1** and **1** (NS), it is expected that more functional materials based on Im-UiO-66 will be explored in the future.<sup>20</sup>

## Experimental section

Imidazole-containing Zr-MOFs: nanocrystals of Im-UiO-66 (**1**) were prepared by adding Im-H<sub>2</sub>BDC·HCl·H<sub>2</sub>O (57 mg), ZrCl<sub>4</sub> (47 mg) and acetic acid (1.2 mL) successively into 5 mL of DMF. The mixture was sonicated sufficiently before being transferred into an autoclave. The autoclave was heated at 393 K for 48 h. The resultant gel was centrifuged and washed repeatedly with DMF and methanol to yield **1**. Nanospheres of Im-UiO-66 were synthesized in a similar way: Im-H<sub>2</sub>BDC·HCl·H<sub>2</sub>O (57 mg), Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O (86 mg) and acetic acid (2 mL) were successively added into 3 mL of DMF. The mixture was sonicated sufficiently before being transferred into an autoclave. Imidazolium functionalized Zr-MOFs: Im-UiO-66 (0.346 g) was stirred and refluxed in a CH<sub>3</sub>CN (15 mL) suspension of methyl iodide (0.5 mL) for 48 h. The precipitate was collected and washed with CH<sub>3</sub>CN, MeOH and ether before drying under vacuum to yield (I<sup>-</sup>)Meim-UiO-66 (**2**).

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