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An excellently stable heterovalent copper–organic framework based on  $Cu_4I_4$ and  $Cu(COO)_2N_2$  SBUs: The catalytic performance for  $CO_2$  cycloaddition reaction and Knoevenagel condensation reaction

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PII:	S1387-7003(20)30422-6
DOI:	https://doi.org/10.1016/j.inoche.2020.107940
Reference:	INOCHE 107940
To appear in:	Inorganic Chemistry Communications
Received Date:	28 March 2020
Revised Date:	9 April 2020
Accepted Date:	11 April 2020



Please cite this article as: F. Jin, An excellently stable heterovalent copper–organic framework based on  $Cu_4I_4$  and  $Cu(COO)_2N_2$  SBUs: The catalytic performance for  $CO_2$  cycloaddition reaction and Knoevenagel condensation reaction, *Inorganic Chemistry Communications* (2020), doi: https://doi.org/10.1016/j.inoche. 2020.107940

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An excellently stable heterovalent copper-organic framework based on  $Cu_4I_4$  and  $Cu(COO)_2N_2$  SBUs: The catalytic performance for  $CO_2$  cycloaddition reaction and Knoevenagel condensation reaction

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### Abstract

A novel 3D heterovalent Cu-based MOF,  $[Cu_2Cu_4I_4(ANA)_4(DMF)_4]_n$  (denoted as complex 1), was successfully designed and synthesized by the self-assembly of CuI and 5-aminonicotinic acid (HANA) under the solvothermal synthesis. The prepared sample has the fascinating structure and was analysed in detail by lots of testing methods. Due to the excellent stability and various catalytic sites, this material can catalyse CO<sub>2</sub> cycloaddition reaction and Knoevenagel condensation reaction; meanwhile, complex 1 has outstanding recyclability and keep catalytic performance at least four cycles.

*Keywords*: heterovalent copper-organic framework; heterogeneous catalyst; stability; CO<sub>2</sub> cycloaddition reaction; Knoevenagel condensation reaction.

Metal-organic frameworks (MOFs) are a rapidly developing inorganic-organic hybrid crystals,<sup>[1-3]</sup> which have been attracted a lot of interest due to their plentiful structures and potentially actual applications, such as gas sorption/separation,<sup>[4-6]</sup> immobilizing enzyme,<sup>[7,8]</sup> luminescence sensor,<sup>[9-11]</sup>, optical device,<sup>[12-14]</sup> and heterogeneous catalysis<sup>[15,16]</sup>. Contrast to traditional materials, MOFs have various unique properties and merits, especially structural diversity, designability, and modification.<sup>[17-19]</sup> From the previous researches, MOFs can be well designed and synthesized by the coordination assembly of various metal ions/clusters and organic ligands.<sup>[20-23]</sup> Meanwhile, diverse factors from internal and external environments all can affect the crystal textures, such as pH value, temperature, pressure, template, solvent, and countervailing anion.<sup>[24-27]</sup> Also, organic linkers play a vital role in the preparation of MOFs, especially linkers with multifarious coordination sites of N and O donors, because they are able to provide a variety of self-assembly configurations with metal nodes to generate fascinating structures with unique properties.<sup>[28-30]</sup> Recently, MOFs based on metal halides (especially copper(I) halides) as secondary building unit (SBU) have been attracted lots of considerable attentions due to their attractive structures and functional properties.<sup>[31-33]</sup> CuI-based SBUs offer a series of geometrically diverse

structural motifs, including the dimeric rhomboid  $[Cu_2I_2]$ , the tetrameric cubane-like  $[Cu_4I_4]$ , the hexagonal-prism-shaped  $[Cu_6I_6]$ , the zigzag  $[Cu_xI_y]_n$  chain, *etc*.<sup>[34-37]</sup> CuI can be implemented as the metal source to construct MOFs, which is not only attributed to the formation of various  $Cu_xI_y$  clusters but also the easy conversation of  $Cu^{2+}$  ions from  $Cu^+$  ions in air by the oxidation process in suit.<sup>[38]</sup>  $Cu^{2+}$  ions are easy to coordinate with  $-COO^-$  to form  $Cu(CO_2)_n$  SBUs;<sup>[39]</sup> meanwhile,  $Cu^+$  and  $I^-$  ions can be linked with N donors to generate much more stable  $[Cu_xI_y]_n$  SBUs.<sup>[40-44]</sup> It is significantly important to implement suitable building linkers to synthesize heterovalent copper–organic frameworks with fascinating textures and excellent properties. Hence, organic linkers containing pyridine and –COOH are good candidates to assemble with CuI to construct such MOFs.

According to the above discussions, we chose a 5-aminonicotinic acid (HANA) as the organic linker, which has pyridine, carboxylic acid, and amino functional group. CuI is the metal source to coordinate with HANA to prepare MOFs. Herein, a novel three-dimensional (3D) heterovalent Cu–organic framework based on Cu<sub>4</sub>I<sub>4</sub> and Cu(COO)<sub>2</sub>N<sub>2</sub> SBUs, formula as  $[Cu_2Cu_4I_4(ANA)_4(DMF)_4]_n$  (complex 1), was successfully prepared under the solvothermal approach. The as-synthesized 1 possesses a fascinating structure, which was analysed in detail by various testing methods. By virtue of the excellent stability and lots of catalytic sites, complex 1 is a heterogeneous catalyst for the CO<sub>2</sub> cycloaddition reaction and Knoevenagel condensation reaction. In addition, complex 1 owns the remarkable recyclability and retains the catalytic performance at least four cycles.

From the single crystal X-ray diffraction analysis, it evidently shows that complex **1** belongs to the  $I4_1/a$  space group of the tetragonal system. As shown in Fig. 1a, the asymmetrical unit of complex **1** has a half Cu atom, another Cu atom, one I atom, one ANA<sup>-</sup> bridging organic linker, and a terminated DMF molecular. The ANA<sup>-</sup> bridging linker has only one coordination fashion as  $\mu_3$ - $\eta^1$ :  $\eta^1$ :  $\eta^1$  to connect with three Cu atoms by pyridine, carboxylic acid, and amino functional groups (Fig. 1b). Notably, Cu(COO)<sub>2</sub>N<sub>2</sub> SBU can be found in complex **1** and the Cu<sup>2+</sup> ion exists in this SBU,

which is attributed to the oxidation of  $Cu^+$  in air (Fig. 1c). On the other hand, the  $Cu^+$  in  $Cu_4I_4$  SBU can coordinate with four N donors of pyridines from four ANA<sup>-</sup> bridging linkers (Fig. 1d). The structure clearly illustrates that the heterovalent Cu–organic framework is successfully prepared as expected. Finally,  $Cu(COO)_2N_2$  and  $Cu_4I_4$  SBUs can be further connected with each other by these ANA<sup>-</sup> linkers to construct a novel 3D framework (Fig. 1e).



Fig. 1 (a) The asymmetrical unit; (b) the coordination mode of organic linker; (c, d) the coordination environments of  $CuO_3N_2$  and  $Cu_4I_4$ ; and (e) viewing of the 3D structure in complex 1 (all H atoms are removed for clarity).

As displayed in Fig. 2a, the thermogravimetric (TG) data of experimental complex **1** obviously can keep a platform and no any weight loss before ~250 °C, but a significant weight loss can be found after increasing the heating temperature due to losing the coordinated DMF molecules. Finally, the main skeleton collapses after the temperature increases to ~520 °C. From the powder X-ray diffraction (PXRD) patterns of fresh as-synthesized sample, these characteristic peaks are consistent well with those of simulated patterns to prove the pure phase and uniformity (Fig. 2b). To further estimate the stability, the as-synthesized samples were immersed in air for one month, in water for one week at room temperature, after heating at 250 °C for one week, and in pH aqueous solutions of pH = 3 and 13 at room temperature for one day, respectively. Also, the corresponding PXRD patterns clearly show that the skeleton can be kept very

well after treating with these conditions. The result illustrates complex **1** has the excellent physicochemical stability.



**Fig. 2** (a) The TG data of as-synthesized complex 1; and (b) the PXRD profile of simulated and experiment complex 1 after treating with various conditions.

Benefit from the excellent stability and various metal sites as Lewis acid sites, complex 1 may be used as a potential heterogeneous catalyst for chemical fixation of CO<sub>2</sub> and epoxides to cyclic carbonates.<sup>[45-50]</sup> The prepared crystals were dried in air for 1 day before processing catalytic reactions. Epoxides (20 mmol), n-Bu<sub>4</sub>NBr (0.3 mmol), and complex 1 (100 mg) were putted in a high-pressure reaction with 1 MPa CO<sub>2</sub>, which was heated at 80 °C for 8 hours. The product of cyclic carbonate can be calculated by the GC measurement with *n*-dodecane as the additive internal standard. Catalytic results are all listed in Table 1. As seen in entries 1 and 2, the individual component for epoxypropane and CO<sub>2</sub> only show the low yields of complex 1 (~11%) or n-Bu<sub>4</sub>NBr (~19%), respectively. However, a higher catalytic yield of >99% can be detected by using complex 1 and *n*-Bu<sub>4</sub>NBr in the reaction system (entry 3). The results show that this CO<sub>2</sub> cycloaddition reaction almost can't be efficiently catalysed by itself and can fully react in the presence of complex 1 and *n*-Bu<sub>4</sub>NBr because of their synergistically catalytic effect of metal centres as catalytic sites in complex 1 and *n*-Bu<sub>4</sub>NBr as cocatalysis. To investigate the catalytic performance for different epoxides, complex 1 and *n*-Bu<sub>4</sub>NBr were both used to catalyse these reactions at the same reaction condition.

#### Journal Pre-proofs

The yield of epichlorohydrin and CO<sub>2</sub> can react completely (entry 4), but the other catalytic yields obviously decrease to ~93%, ~87%, and ~72% for 1,2-epoxy-3-allyloxypropane, benzyl phenylglycidyl ether, and *tert*-butyl glycidyl ether, respectively (entries 5, 6 and 7), which may be attributed to the increasing molecule sizes and different electronic effects of functional groups.<sup>[51-53]</sup> To estimate the recyclability of complex 1, the cyclic sample can well keep the catalytic ability for chemical transformation of epoxypropane and CO<sub>2</sub> at least four cycles (entry 8 and Fig. 3a). The PXRD pattern of complex 1 after reusing four times is consistent well with that of pristine complex 1 to prove the excellent stability of complex 1 in the successive catalytic experiments (Fig. 3b).

Table 1. The catalytic yields of CO<sub>2</sub> and various epoxides.

	R	CO <sub>2</sub>		
Entry	Catalyst	Epoxide	Product	Yield %
1	complex 1			11
2	<i>n-</i> Bu₄NBr			19
3	complex <b>1</b> + <i>n</i> - Bu <sub>4</sub> NBr			>99



Fig. 3 Reusability (a) and PXRD pattern (b) of complex 1.

According to the previous reported MOFs for catalyzing this reaction,[54-58] the

#### Journal Pre-proofs

assumptive reaction can be deduced as follows: Firstly, this reaction is caused by the interaction between the O atom in epoxide ring and the metal site in complex 1. Subsequently, the epoxide ring will be attacked by Br<sup>-</sup> anion from *n*-Bu<sub>4</sub>NBr to open the ring. At the same time, the O anion can quickly react with  $CO_2$  as C1 source to synthesize an ionic alkycarbonate intermediate. Finally, the targeted cyclic carbonates will be obtained from alkycarbonate anions by the cyclization process. Nevertheless, the accurate mechanism is still far beyond our understanding nowadays.

Due to various N atoms in complex 1, the resultant sample may be used as a Lewis basic catalysis for Knoevenagel condensation reaction. [59-70] After the as-synthesized samples were dried in air before the reaction, complex 1 (100 mg) was added in a toluene solution (5 mL) containing substrates with different functional groups (1.0 mmol) and malononitrile (1.05 mol). The above reaction was heated at 100 °C in an oil bath for 10 hours under slowly stirring. The catalytic result was tested and calculated by the GC approach. The catalytic yield of 2-benzylidenemalononitrile can reach up as high as >99% after 10 hours (entry 1 of Table 2); however, this reaction has very low catalytic performance ( $\sim 9\%$ ) without complex 1. The catalytic result obviously illustrates that complex 1 can efficiently catalyze this catalytic reaction (entry 2). Different substrates with various functional groups were explored and investigated to further evaluate the relationship between the structures of substrates and the corresponding catalytic performances. The -F and -NO2 groups have the electronwithdrawing effect, which both have high catalytic yields as high as >99% (entries 3) and 4 of Table 2). When the functional groups are substituted by other functional groups, the catalytic performance has totally different catalytic yield. As seen in entries 5 and 6, the yields obviously reduce to 90% of only one electron donor –OMe group (entry 5) and 83% (entry 6) of two –OMe groups, respectively. Based on the catalytic yields, it shows that the electron effect of functional groups on substrates will directly affect the catalytic performance. Meanwhile, the reusability of complex 1 is also an important factor to estimate this heterogeneous catalyst. As seen in entry 7 and Fig. 4b, complex 1 can catalyze the Knoevenagel condensation by using benzaldehyde as the substrate model, which can keep the catalytic yield at least four times. The result shows that

complex **1** has the greatly potential application for the Knoevenagel condensation with excellent reusability.



 Table 2. Catalytic yields of Knoevenagel condensations by using complex 1.

<sup>[</sup>a] Reaction conditions: substrates with various functional groups (1.0 mmol), malononitrile (1.05 mol), and catalyst (100 mg) were added in toluene (5 mL) at 100  $^{\circ}$ C for 10 hours. [b] The same reaction conditions as in [a], but without the catalyst. [c] The recyclability test after four cycles.



Fig. 4 (a) The reusability and (b) the PXRD pattern of complex 1 for this catalytic reaction.

In conclusion, a 3D excellently stable heterovalent copper–organic framework based on  $Cu_4I_4$  and  $Cu(COO)_2N_2$  SBUs is successfully designed and synthesized by the solvothermal synthesis. The prepared sample can be used as a bifunctional heterogeneous catalyst for chemical fixation of  $CO_2$  and epoxide, and Knoevenagel condensation reaction. Especially, the excellent stability of complex 1 can be used to continuously catalyse both reactions at least four cycles.

### **Appendix A. Supplementary data**

The experiments are listed in the supporting information. The CCDC reference number is 1992434.

## Acknowledgements

This research did not receive any specific funding.

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#### **Graphical Abstract-Pictogram**



This work exhibits an excellently stable heterovalent copper–organic framework based on  $Cu_4I_4$  and  $Cu(COO)_2N_2$  SBUs, which can catalyse the CO<sub>2</sub> cycloaddition reaction and Knoevenagel condensation reaction with preferable recyclability.

Highlights

- 1. A 3D heterovalent Cu–organic framework based on  $Cu_4I_4$  and  $Cu(COO)_2N_2$  SBUs was successfully designed and synthesized.
- 2. The resultant sample can catalyse the CO<sub>2</sub> cycloaddition reaction and Knoevenagel condensation reaction.
- 3. Complex 1 has the remarkable stability and recyclability at least four cycles.

#### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



Feng Jin: Supervision and writing this article.