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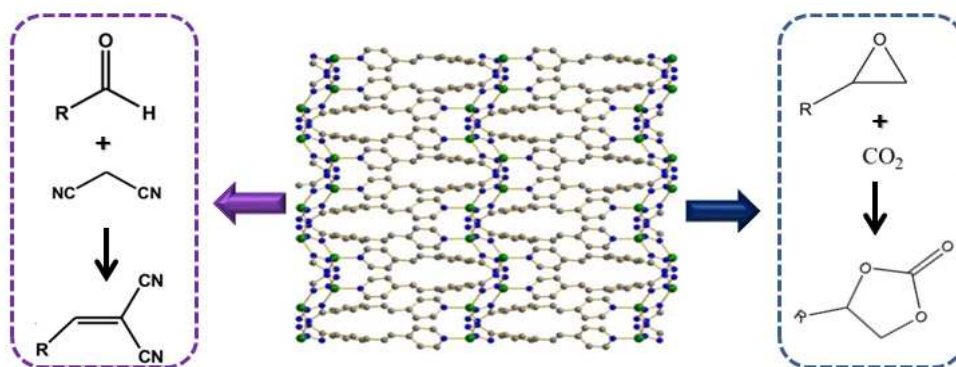
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Graphical Abstract



A 3D Cu(II)-based MOF was successfully synthesized and used as a heterogeneous catalyst for the CO₂ cycloaddition reaction and Knoevenagel condensation reaction.

Synthesis, crystal structure and catalytic property of a highly stable 3D Cu(II)-organic framework

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Abstract

A three-dimensional (3D) Cu(II)-based MOF, [CuL·Cl]_n (namely complex **1**), was successfully generated through the in-situ reaction of CuCl₂, NaN₃, and 4-(4-cyanostyryl)pyridine. Notably, –CN and N₃[−] can directly react to form a tetrazolate group during the crystal growth process. This reaction was further proved by single crystal X-ray diffraction data. Thanks to the excellent stability, various N-donors as Lewis basic sites and Cu(II) centres as Lewis acid sites, the as-made complex **1** has a potential application as a bifunctional heterogeneous catalyst for the CO₂ cycloaddition reaction and Knoevenagel condensation reaction. In addition, complex **1** has the excellent recyclability for both reactions at least six cycles.

Keywords: In situ reaction; heterogeneous catalyst; CO₂ cycloaddition reaction; Knoevenagel condensation reaction; recyclability.

1. Introduction

Recently, metal–organic frameworks (MOFs) [1,2] are organic-inorganic hybrid crystalline materials, which have been developed rapidly thanks to their various structures and greatly potential applications in small gas sorption [3-5], bio-carrier [6,7], luminescent detector [8-10], optical device [11,12], and catalysis [13,14]. Compared with other solid materials, MOFs have lots of unique features, including structural diversity, designability, multifunctional site, and adjustability [15-17]. Taking into account of some previous reports, diversiform MOFs can be tuned and constructed by rationally choosing metal centres and organic building blocks with various coordination sites to achieve excellent properties [18-20]. Among all properties, MOFs exhibit greatly potential applications as heterogeneous catalysts for many catalytic reactions because of their catalytic centres, including Lewis acid sites (open metal site) [21-23], Brønsted acidic sites (–COOH and –OH) [24-26], and Lewis basic sites (–NH₂) [27-29]. However, the poor stability of MOFs greatly limits the development of these materials as heterogeneous catalysts in practical applications. Up to now, some useful approaches have been developed to enhance the stability of

MOFs to expand their real usability, such as surface hydrophobic coating, soft and hard acid base theory, multi-wall and high connected multicore structure [30-32]. Bridging organic linkers have significantly important influences for the structures and properties of MOFs. Most attentions have been still focused on carboxylic acid organic ligands due to their excellent coordination abilities and easy preparation of MOFs [33,34]. On the other hand, another sort of linkers focuses on the heterocyclic nitrogen rings (pyridine, imidazole, triazole, and tetrazole) in the assemble process of MOFs with transition metals [35-38]. Compared with the carboxylic acid linkers, such linkers are always difficult to prepare MOFs, but the as-synthesized MOFs always have the excellent stability. In addition, the free N-donors and metal centers in MOFs can be served as Lewis basic sites and Lewis acid sites for different catalytic reactions [39-41]. Hence, it is a significant change to construct highly stable MOFs based on organic linkers with various N-donors to investigate their catalytic applications.

Based on the above discussion, we chosen an organic linker 4-(4-cyanostyryl)pyridine with pyridine and cyano groups as a bridging linker to assemble with Cu(II) and NaN_3 . The cyano group can react with N_3^- to generate tetrazole groups in suit, which was further assembled with Cu(II) to construct MOFs. As we expect, a novel three-dimensional (3D) Cu(II)-organic framework, $[\text{CuL}\cdot\text{Cl}]_n$ (namely complex **1**), has been successfully prepared *via* the solvothermal reaction; meanwhile, the tetrazole groups are found in the structure of complex **1**. The as-prepared sample was detailly characterized and analysed by lots of testing methods. More importantly, complex **1** exhibits the excellent catalytic performance for the CO_2 cycloaddition reaction and Knoevenagel condensation reaction with the outstanding recyclability.

2. Experimental

2.1. Materials and general methods

All chemicals and solvents were purchased and used directly. Powder X-ray diffraction (PXRD) patterns were carried out on a Bruker D8 GADDS from 5° to 40° .

Thermogravimetric analyses (TGA) data were measured on a TGA Q500 under N₂ from room temperature to 800 °C. The catalytic yield was obtained on a Thermo Fisher Trace ISQ GC/MS. Elemental analysis of C, H and N was performed on a CE-440 analyzer (Leeman Laboratories).

2.2. Synthesis of complex **1**

CuCl₂ (0.1 mmol), NaN₃ (0.1 mmol), and 4-(4-cyanostyryl)pyridine (0.1 mmol) were all added in a mixture solution of ethanol (1.2 mL) and H₂O (2.8 mL) and carefully sealed in a Teflon-lined steel. The mixture was putted and heated at 165 °C for 4 days. Then, it was cooled slowly to room temperature at a decreasing rate of 5 °C h⁻¹. Finally, blue crystals with high quality were collected and washed with ethanol. These crystals were dried in air with the yield of 61% based on the linker. Anal. Calc. (%) for C₁₄H₁₀CuN₅: C, 53.85; H, 3.21; N, 22.44. Found: C, 54.01; H, 3.26; N, 22.39.

2.3. Single crystal X-ray diffraction of complex **1**

Single crystal X-ray diffraction of complex **1** was measured on a Bruker SMART CCD diffractometer with Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation. The structure of complex **1** can be well solved by using *SHELXL*-2015 [42,43] in the *OLEX2* program [44]. All non-H atoms were added by the anisotropic parameters. The crystal data and structure refinement of complex **1** are summarized in Table 1.

2.4. The Knoevenagel condensation reaction

In a typical catalytic reaction, benzaldehyde with different substitutional groups (1.00 mmol) and malononitrile (1.05 mmol) were both dissolved in toluene (4 mL) in a reaction bottle with complex **1** (100 mg). The reaction mixture was heated in an oil bath at 100 °C for 4 hours under slowly stirring. The catalytic yields can be calculated by using the GC method with biphenyl as an internal standard substance.

2.5. The CO₂ cycloaddition reaction

In a typical reaction, epoxides (10 mmol), *n*-Bu₄NBr (0.35 mmol), and complex **1** (100 mg) were all added in a high-pressure reaction equipment with CO₂ (1 MPa) at 100 °C for 8 hours. The yields of cyclic carbonates can be obtained by the GC approach with *n*-dodecane as an internal standard.

Table 1. Crystal data and structure refinement.

Sum formula	C ₁₄ H ₁₀ CuN ₅
Formula weight	311.82
Crystal system	monoclinic
Space group	<i>P</i> 21/ <i>c</i>
<i>a</i> (Å)	13.4232(12)
<i>b</i> (Å)	9.1569(9)
<i>c</i> (Å)	10.1126(9)
α (°)	90
β (°)	99.916(2)
γ (°)	90
Volume (Å ³)	1224.4(2)
<i>Z</i>	4
<i>D</i> _x (g cm ⁻³)	1.692
<i>M</i> _u (mm ⁻¹)	1.779
<i>N</i> _{ref}	2621
<i>R</i> (int)	0.0336
Goodness-of-fit on F ²	1.045
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0885, 0.0875
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0467, 0.0915

3. Results and discussion

3.1. Structural description for complex **1**

The as-synthesized crystals can be generated by mixing 4-(4-cyanostyryl)pyridine,

CuCl₂, and NaN₃ in a mixture solution of water and ethanol. The large single crystal of complex **1** with high-quality was used to collect the single crystal X-ray diffraction data, illustrating that it crystallized in the *P21/c* space group of the monoclinic system with the cell parameters of $a = 3.4232(12) \text{ \AA}$, $b = 9.1569(9) \text{ \AA}$, $c = 10.1126(9) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 99.916(2)^\circ$, $\gamma = 90^\circ$. The asymmetric structural unit of complex **1** has one Cu atom and an organic linker, which evidently exhibits the formation of tetrazole in this linker as the similar report [45] (Fig. 1a). Fig. 1b shows the coordination mode of the bridging linker as $\mu_4-\eta^1: \eta^1: \eta^1: \eta^1$ to connect with four Cu atoms by one pyridine and three N-donors from tetrazole rings. Each Cu atom links with four N-donors from three different tetrazole rings and one pyridine. Interestingly, all Cu atoms and tetrazole rings can generate a two-dimensional (2D) layer (Fig. 1c), which are further connected with each other by pyridine rings from linkers to finally construct a 3D structure. The 3D structure of complex **1** is shown in different directions (Figs. 1d-1f).

<Figure 1>

3.2. PXRD and thermal analysis

As displayed in Fig. 2a, the PXRD peaks of as-synthesized bulk samples were measured at room temperature, which are consistent well with those of the simulated pattern. The result clearly proves that the as-synthesized samples are purity as the obtained single structure. The TGA data of as-synthesized complex **1** indicates that the resultant sample has the outstanding stability before $\sim 300^\circ\text{C}$; meanwhile, the skeleton of complex **1** shows a rapid weight loss with the increasing of heating temperature (Fig. 2b). The TGA result shows that complex **1** has the excellent heating stability.

<Figure 2>

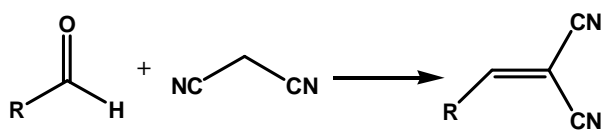
3.3. Catalytic properties

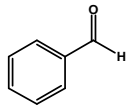
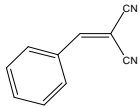
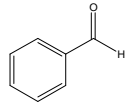
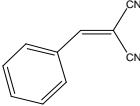
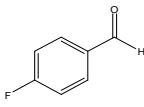
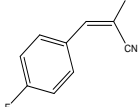
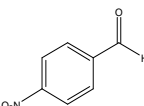
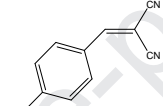
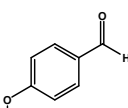
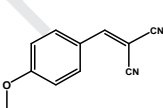
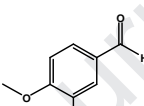
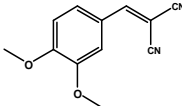
Thanks to lots of Lewis base sites in complex **1**, the as-synthesized sample may be investigated and applied as a basic catalyst for the Knoevenagel condensation reaction

[46-51]. Prior these catalytic reactions, as-synthesized **1** was soaked in fresh toluene for 1 hour, which was further filtered and dried in air. In the typical catalytic reaction, the benzaldehyde containing various substitutional groups (1.00 mmol) and malononitrile (1.05 mmol) were both dissolved in 4 mL toluene in a reaction bottle. The addition of complex **1** (100 mg) in the reaction system is considered as a catalyst. The reaction was heated in an oil bath at 100 °C for 4 hours under slowly stirring. The yields can be obtained by the GC method with biphenyl as an internal standard substance. All catalytic results in this work are summarized in Table 2. As seen in entry 1, the product yield of 2-benzylidenemalononitrile is higher than 99% within 4 hours. This reaction was further selected as a reaction mode to investigate the kinetic catalytic rate (Fig. 3). The catalytic result indicates that the catalytic reaction can be almost completely reacted after 4 hours at 100 °C. To evaluate the necessity of complex **1** for the reaction, the reaction will quickly stop once filtering complex **1** from the reaction system. In addition, the yield of this reaction is only 9% in the absence of complex **1** (entry 2). The control experiments illustrate that complex **1** is the necessary catalysis for the Knoevenagel condensation reaction. The catalytic substrates were expanded with different sizes and functional groups under the same reaction condition. It evidently exhibits that the catalytic results are also higher than 99% (entries 3 and 4), which is mainly attributed to the electron-withdrawing groups of -F and -NO₂ in aldehydes to facilitate the reaction. Contrastively, the aldehydes with the electron-donor and large size group of -OMe show lower catalytic yields to 88% and 81% for one -OMe group (entry 5) and two -OMe groups (entry 6), respectively. The catalytic performance is similar with some previous reports [46-51].

<Figure 3>

Table 2. All catalytic yields of different aldehyde reactants.



Entry	Substrate	Product	Yield (%)
1			>99
2			9
3			>99
4			>99
5			88
6			81

The stability and recyclability of complex **1** are both important factors for heterogeneous catalysts. After each reaction of benzaldehyde as the substrate, complex **1** can be easily re-collected by centrifuging at 8000 r·min⁻¹ for 2 minutes. The reused sample can be recovered after washing with toluene for 2 times. As seen in Fig. 4a, the catalytic yields of reused samples can be well kept even after recycling six times. The corresponding PXRD profile of complex **1** after reusing six times are well preserved to prove the high stability of complex **1** for this reaction (Fig. 4b).

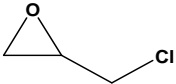
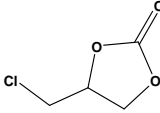
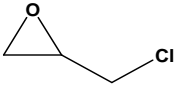
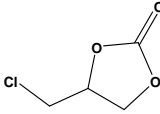
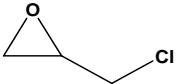
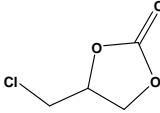
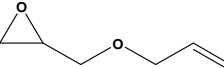
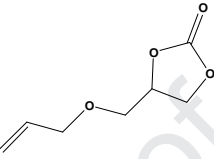
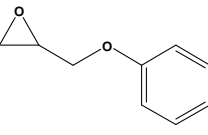
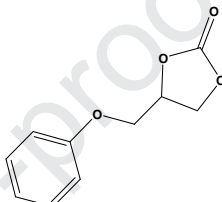
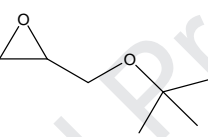
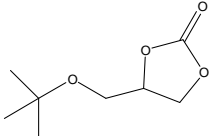

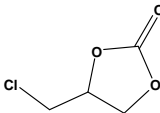
<Figure 4>

Because of the metal sites as Lewis acid catalytic centres, complex **1** can be considered as a potential heterogeneous catalyst for the CO₂ cycloaddition reaction with epoxides to form cyclic carbonates [52-62]. The prepared samples after washing

with CH₂Cl₂ were directly dried in air before the catalytic reaction of CO₂ and epoxides. The reaction condition is set as 1 MPa CO₂ at 100 °C for 8 hours by mixing epoxides (10 mmol), *n*-Bu₄NBr (0.35 mmol), and complex **1** (100 mg) in a high-pressure reaction equipment under slowly stirring. The yields of targeted cyclic carbonates can be calculated by the GC approach with *n*-dodecane as an internal standard substance. All catalytic results are concluded in Table 3. Only complex **1** or *n*-Bu₄NBr as the catalyst for epichlorohydrin and CO₂ has a very low catalytic yields of complex **1** (31%, entry 1) or *n*-Bu₄NBr (~9%, entry 2), displaying that they can't catalyse this CO₂ reaction by independent one. However, complex **1** is able to catalyse this reaction with a high yield of >99% with *n*-Bu₄NBr simultaneously (entry 3). All results claim that complex **1** and *n*-Bu₄NBr can catalyse this reaction by the synergy catalysis process. Different epoxides are selected as substrates for this CO₂ reaction. The yields gradually reduce to 91% (entry 4), 82% (entry 5), and 79% (entry 6) for 1,2-epoxy-3-allyloxypropane, benzyl phenylglycidyl ether, and tert-butyl glycidyl ether, which may be mainly ascribed to the different groups with different size and electronic effects [52-62]. The recyclability is also investigated by the reaction and the corresponding PXRD pattern. As shown in entry 7 and Fig. 5a, the catalytic performance of recollected samples can be well preserved for the chemical transformation of epichlorohydrin and CO₂ for six times. The PXRD pattern can well preserve the main diffraction peaks to illustrate the high stability of recycled complex **1** after the successive using six times (Fig. 5b).

Table 3. The yields of this CO₂ cycloaddition reaction with epoxides.

Entry	Catalyst	Epoxide	Product	Yield%

1	complex 1			31
2	<i>n</i> -Bu ₄ NBr			9
3	complex 1 + <i>n</i> -Bu ₄ NBr			>99
4	complex 1 + <i>n</i> -Bu ₄ NBr			91
5	complex 1 + <i>n</i> -Bu ₄ NBr			82
6	complex 1 + <i>n</i> -Bu ₄ NBr			79
7	Reused complex 1 + <i>n</i> -Bu ₄ NBr			>99

<Figure 5>

The assumptive catalytic mechanism can be deduced from the previous reports for this CO₂ fixating reaction (Fig. 6) [52-62]. This reaction can be caused by the weak interaction between O atoms in epoxide rings and Cu(II) sites in complex **1**. Epoxide rings will rapidly attacked by Br⁻ from *n*-Bu₄NBr to open the epoxide rings. Then, oxygen anions can be reacted with CO₂ to form the ionic alkylcarbonate intermediate. The cyclic carbonate product will generate by the cyclization process of the alkylcarbonate anion. However, the accurate mechanism is also significantly far beyond our research capabilities.

<Figure 6>

4. Conclusion

In summary, a 3D Cu(II)-organic framework based on 2D Cu-tetrazole layers can be constructed and served as a bifunctional heterogeneous catalyst for the Knoevenagel condensation reaction and chemical fixation of CO₂ with epoxides. Due to the excellent stability of complex **1**, it has the excellent stability and recyclability for both catalytic reactions at least six cycles.

Appendix A. Supplementary data

The luminescent spectra and crystal table are listed in the supporting information. The CCDC reference number is 1977907.

Acknowledgements

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Fig. 1. (a) The asymmetrical unit; (b) the coordination mode of this organic linker; (c) the 2D Cu(II)-based layer; and (d-f) the 3D structure of complex **1** (H atoms are removed for clarity).

Fig. 2. (a) The PXRD pattern of simulated (bottom, black) and as-synthesized complex **1** (up, red); and (b) the TGA curve of as-synthesized complex **1**.

Fig. 3. The kinetic catalytic rates of benzaldehyde as the substrate in complex **1** (black), after filtering complex **1** (blue), and without any catalyst (pink).

Fig. 4. Recyclability (a) and PXRD profiles (b) of complex **1**.

Fig. 5. The recyclability (a) and the corresponding PXRD profiles (b) of complex **1**.

Fig. 6. The assumptive catalytic mechanism for this CO₂ fixating reaction.

Synthesis, crystal structure and catalytic property of a highly stable 3D Cu(II)-organic framework

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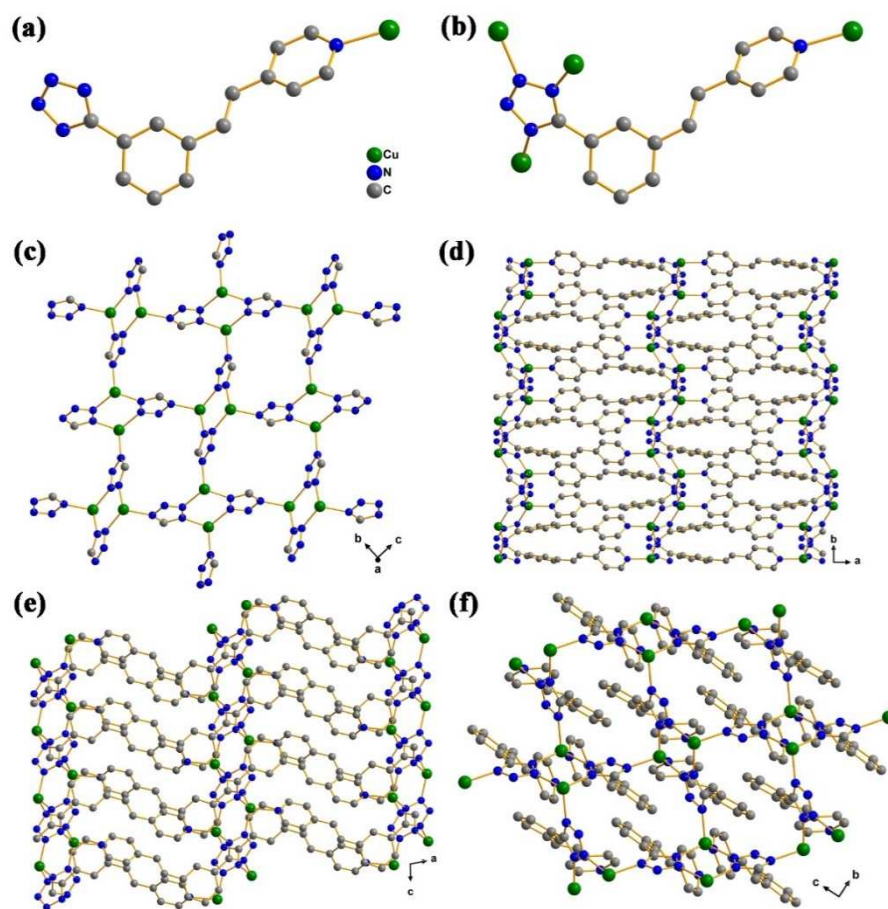


Figure 1

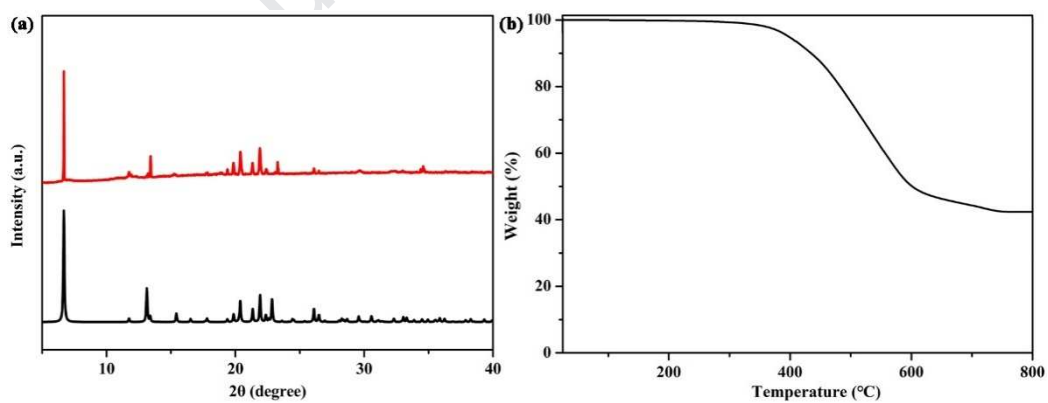


Figure 2

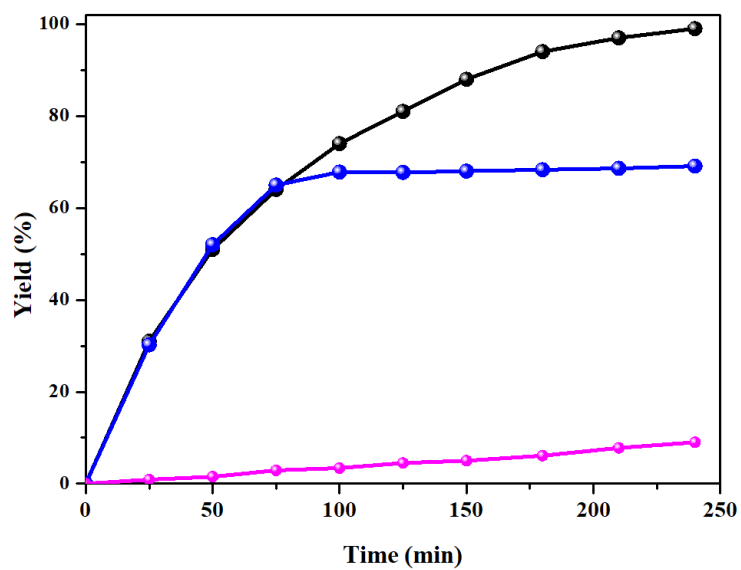


Figure 3

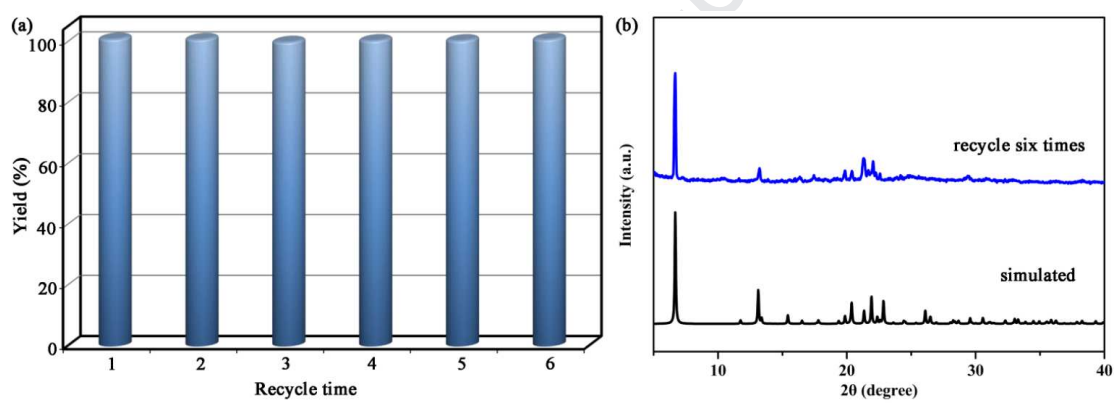


Figure 4

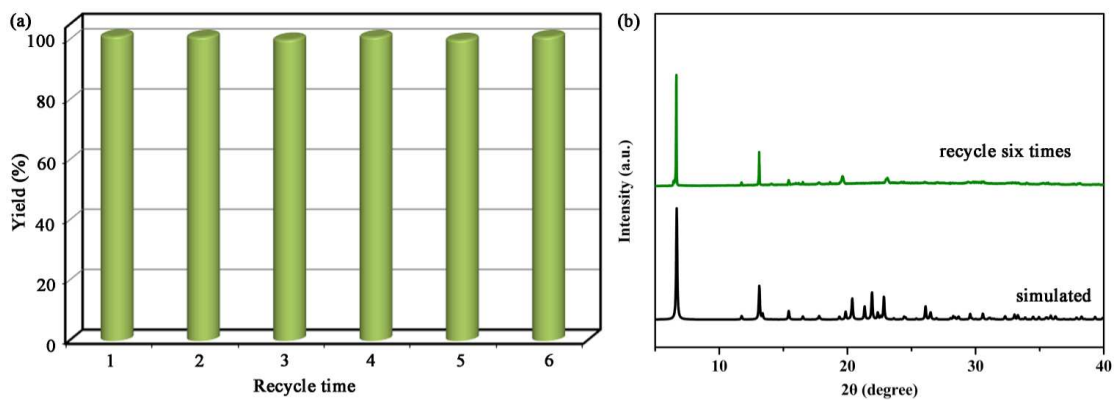


Figure 5

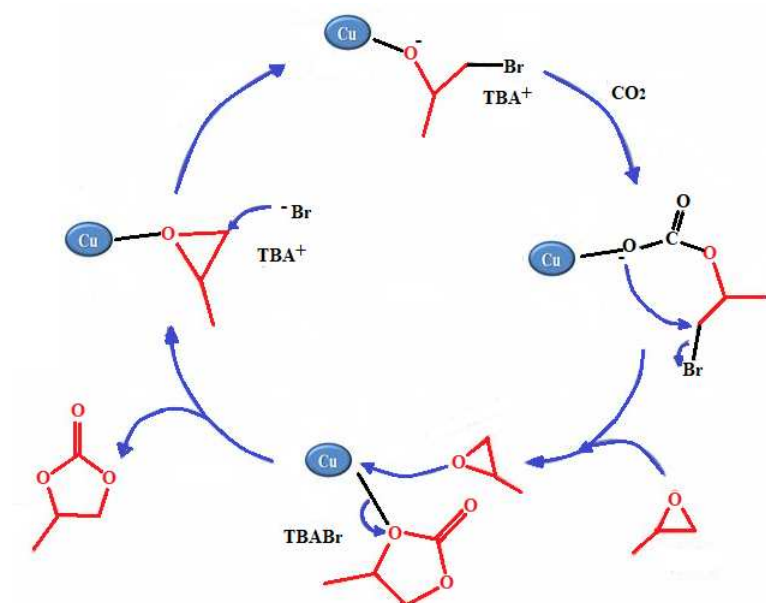


Figure 6

1. A Cu(II)-organic framework was successfully synthesized via the solvothermal reaction.
2. It can catalyse the Knoevenagel condensation reaction and chemical fixation of CO₂ with epoxides.
3. The as-synthesized sample has the excellent stability and recyclability.

Journal Pre-proof

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: