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Nanocage-based $\{\text{In}_2\text{Tm}_2\}$ -organic framework for efficiently catalyzing the cycloaddition reaction of CO_2 with epoxides and Knoevenagel condensation†

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High density active sites and chemical stability for prepared MOFs are the prerequisites for their industrial applications, which prompted us to synthesize cluster-based metal-organic compounds. The combination of $[\text{In}_2\text{Tm}_2(\mu_2\text{-OH})_2(\text{CO}_2)_{10}(\text{H}_2\text{O})_2]$ clusters ($\{\text{In}_2\text{Tm}_2\}$) and the functional ligand 2,6-bis(2,4-dicarboxylphenyl)-4-(4-carboxylphenyl)pyridine (H_5BDPC) produced an extremely stable nanoporous skeleton of $\{(\text{Me}_2\text{NH}_2)_2[\text{In}_2\text{Tm}_2(\text{BDPC})_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_2]\cdot 2\text{DMF}\cdot 3\text{H}_2\text{O}\}_n$ (**NUC-56**), whose inner surface is functionalized by Lewis acidic and basic groups of metal centers, $\mu_2\text{-OH}$ groups and $\text{N}_{\text{pyridine}}$ atoms. To the best of our knowledge, **NUC-56** is a rarely reported planar-cluster-based $\{\text{In}_2\text{Ln}_2\}$ -organic framework, which possesses an excellent confined pore environment with high porosity, large specific surface area and abundant co-existing Lewis acid and base sites. Consequently, **NUC-56a** exhibited a good catalytic performance for the cycloaddition reaction of various epoxides with CO_2 and the Knoevenagel condensation reaction of different aldehydes and malononitrile under mild conditions. Therefore, this study can provide some guidance for the precise design of practical MOFs with excellent catalytic, stability and regeneration performances through the participation of rare earth ions.

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Introduction

Metal organic frameworks (MOFs), as a new type of porous inorganic-organic hybrid crystalline materials constructed from the exquisite combination of metal ions/clusters and diverse organic ligands, have attracted tremendous attention due to their desirable structural properties including adjustable pore size, high porosity, multiple active sites, and tailorable architectures, which have led to a wide range of applications, such as gas adsorption and separation, fluorescence sensing and heterogeneous catalysis.^{1–7} To date, there are relatively few reports on the applications of heterometallic frameworks due to the lack of mature synthetic regulation strategies. However, it has been proven that the introduction of a second metal ion in the framework is a valuable project to enhance the gas capture capacity and catalytic performance of MOFs because of the synergistic effect of two metal ions in the absence of specific mechanism processes.^{8–10} Therefore, the self-assembly of heterometallic MOFs with microchannels and extremely

exposed active sites is particularly challenging, but can be achieved by carefully designing organic ligands, reasonably configuring different metal ions and finely controlling the growth environment.^{11,12}

In addition, with the continuous expansion of industrial production and excessive use of fossil fuels, carbon dioxide (CO_2) emissions have increased at a rate of 4% per year, resulting in serious air pollution and greenhouse effect.^{13–19} However, from the perspective of resource utilization, CO_2 serves as one of the richest C1 resources on Earth with the advantages of large reserves, safety, non-toxicity and low price. Thus, converting CO_2 into valuable chemicals has strategic significance of environmental friendliness and sustainability.^{20–23} Accordingly, it is significant for the sustainable development of society to implement strategies of CO_2 capture and storage/sequestration (CCS), which have prompted the innovative preparation of functional microporous MOF-based materials.^{24–26} At present, the method for the preparation of cyclic carbonates by cycloaddition reaction using CO_2 and epoxides is consistent with the concept of “green preparation theory” and “atomic economy principle”. Also, carbonate products are widely used in lithium battery electrolytes, textiles, chemical industry, pharmaceuticals and preparation of functional polymers because of their excellent properties including high boiling point and solubility, low toxicity and

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degradability.^{27–29} Nevertheless, owing to the thermodynamic stability of CO₂, cycloaddition reactions usually demand a high reaction temperature and pressure. Thus, to overcome this disadvantageous problem, various homogeneous and heterogeneous catalysts have been developed to drive the reaction process. Among them, homogeneous catalysts have some drawbacks, such as difficult separation between catalyst and product, high energy consumption, and poor economic performance.^{30–32} Therefore, based on the above-mentioned problems, a variety of heterogeneous catalysts (ionic liquids, carrier solids, metal complexes, *etc.*) have been developed. However, solid heterogeneous catalysts usually need harsh conditions because they lack accessible surface area and exposed active sites to fully activate CO₂ molecules. Thus, it is of great significance to explore innovative heterogeneous catalysts with excellent stability, cyclic performance, and high activity to promote the reaction under mild conditions.^{33–36} Thus far, MOFs have been widely used in the field of heterogeneous catalysis due to their permanent porosity, adjustable pore structure, large specific surface area, multiple reaction active sites and excellent ability to adsorb CO₂.^{37–41} In-MOFs account for a small proportion of the reported MOFs although they are based on the most common SBUs, for instance, [In(CO₂)_n], [In₃O(CO₂)_n(OH₂)_n], and [In(O/OH)]_n and sporadic heterometallic clusters of {InM₂}, {In₂M₂}, {In₃Ln}, and {In₃Ln₂}.^{42–50} Nevertheless, the outstanding catalytic performance from the high-level p-orbitals of the In³⁺ ion provides motivation for scientists to pursue a superior indium-organic frame. In addition, Ln-MOFs have attracted increasing attention because of their high chemical stability and catalytic ability for most organic reactions, which should be attributed to the powerful positive charge of Ln^{III} cations and abundant vacant electron orbitals.^{51,52} However, promising heterometallic MOFs based on the combination of rare earth ions and In³⁺ ions are rarely reported.

In view of the considerations discussed above, the multifunctional ligand of 2,6-bis(2,4-dicarboxylphenyl)-4-(4-carboxylphenyl)pyridine (H₅BDCP) was reacted with In³⁺ and Tm³⁺ for the successful synthesis of a highly stable channel-based heterometallic {In₂Tm₂}-organic framework of {[In₂Tm₂(BDCP)₂(μ₂-OH)₂(H₂O)₂·2DMF·3H₂O]}_n (NUC-56) with excellent water resistance, thermal stability and a series of structural advantages, which rendered it an outstanding heterogeneous catalyst to boost cycloaddition reactions. Moreover, it also simultaneously exhibited efficient catalytic ability in the Knoevenagel condensation of aldehydes and malononitrile.

Experimental

Preparation of NUC-56 and NUC-56a

A sample of Tm₂O₃ (0.10 mmol), In(NO₃)₃·5H₂O (0.10 mmol) and H₅BDCP (0.08 mmol) in 10 mL solvent of DMF and H₂O (v:v = 8:2) with one drop of concentrated HNO₃ was heated in a Teflon-lined stainless-steel vessel at 110 °C for 2 days. The

cube crystals were collected by filtration after cooling, and the yield of crystals based on the H₅BDCP ligand was 53%. Anal. calcd for NUC-56 (C₄₀H₂₆N₃O₁₇InTm): C, 24.64; H, 2.36; N, 3.81 (%). Found: C, 24.60; H, 2.40; N, 3.77 (%). FT-IR (KBr pellet, cm⁻¹, Fig. S3†): 3750 (m), 2923 (w), 1857 (w), 1552 (w), 1500 (m), 1469 (m), 1415 (s), 1456 (s), 1089 (vs), 1014 (s), 921 (m), 858 (s), 819 (s), 777 (vs), 682 (m), 657 (m).

Results and discussion

Crystal structure description

Single-crystal X-ray diffraction analysis showed that NUC-56 crystallizes in a monoclinic system with the *C2/m* space group and exhibits a microporous three-dimensional framework of {[In₂Tm₂(BDCP)₂(μ₂-OH)₂(H₂O)₂·4DMF·3H₂O]}_n with coplanar [In₂Tm₂(μ₂-OH)₂(CO₂)₁₀(H₂O)₂] clusters as the basic building units (Fig. 1a and Fig. S1†). Astonishingly, NUC-56 is a planar-cluster-based {In₂Ln₂}-organic framework, whose inner surface is functionalized by abundant coexisting Lewis acid–base sites of In³⁺, Tm³⁺, μ₂-OH and N_{pyridine} atoms. Moreover, it is noteworthy that the {In₂Tm₂} clusters exist in a coplanar configuration and NUC-56 is synthesized by the structurally oriented ligand of BDCP^{5–}, forming a highly distorted connection mode, which resulted in the maximum exposure of the open metal sites of In³⁺ and Tm³⁺ and μ₂-OH. Therefore, the successful construction of NUC-56 offers a valuable technique for the synthesis of deeply functionalized common In-MOFs by introducing rare earth ions, which potentially have wider applicability in various catalysis fields.

Regarding the detailed internal links in NUC-56, there is a half Tm³⁺ ion, a half In³⁺ ion, a half BDCP^{5–}, two half μ₂-OH and two half associated H₂O in the asymmetric unit. The Tm(1) and In(1) ions are firstly bridged by two μ₂-η¹:η¹ α-carboxyl groups from two phenyl rings arranged on the 2- and 6-position of pyridine in one BDCP^{5–} to form a binuclear unit of [InTm(CO₂)₂] (Fig. 1a), which are further connected by one μ₂-OH group, leaving a unit of [InTm(μ₂-OH)(CO₂)₂]. Also, *via* the symmetry extension, two [InTm(μ₂-OH)(CO₂)₂] units are each bridged by four μ₂-η¹:η¹ γ-carboxyl groups from four phenyl rings arranged on the 2- and/or 6-position of pyridine of the BDCP^{5–} ligand to form a 2D layer with the initial quadrangular [In₂Tm₂(μ₂-OH)₂(CO₂)₈(H₂O)₂] clusters as nodes, in which each adjacent Tm³⁺ and In³⁺ are bridged by two μ₂-η¹:η¹ carboxyl groups, and each In³⁺ is saturated by one associated water molecule. Furthermore, each Tm³⁺ ion in the [In₂Tm₂(μ₂-OH)₂(CO₂)₈(H₂O)₂] SBU is further cheated by one γ-carboxyl group on the 4-position of the phenyl ring from the upper and lower planes to form a 3D anionic skeleton with the formation of a complete cluster of [In₂Tm₂(μ₂-OH)₂(CO₂)₁₀(H₂O)₂] (Fig. 1d). In conclusion, each tetranuclear heterometallic {In₂Tm₂} cluster is supported by ten carboxyl groups from eight deprotonated BDCP^{5–} linkers. It is worth mentioning that the eight {In₂Tm₂} clusters are each woven together to generate elliptical nanocages (aperture *ca.* 14.1 Å) (Fig. 1c) with their functionalized inner surface decorated by the coex-

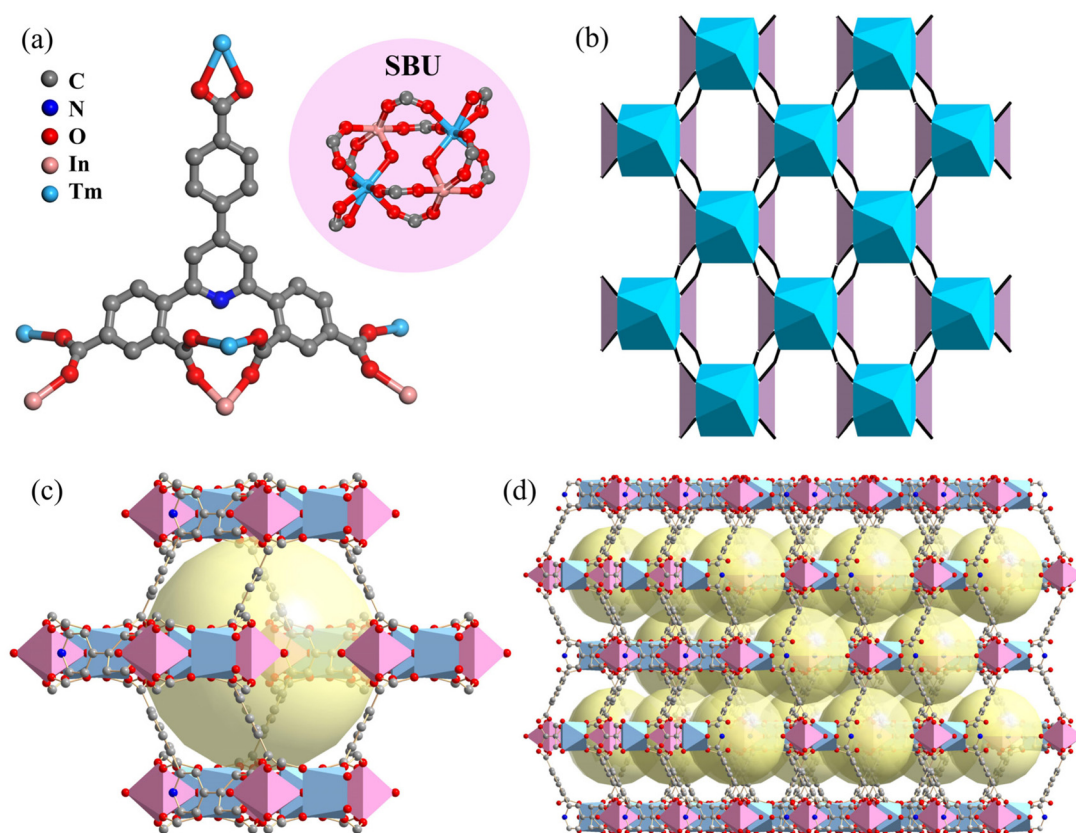


Fig. 1 Coplanar $[\text{In}_2\text{Tm}_2(\mu_2\text{-OH})_2(\text{CO}_2)_{10}(\text{H}_2\text{O})_2]$ cluster and the coordination environment of BDCP^{5-} ligand (a). Topology network with the Schläfli symbol of $\{4^{12}.6^{12}.8^4\}\{4^6\}_2$ of **NUC-56** (b). $\{\text{In}_2\text{Tm}_2\}$ cluster-shaped nanocage of **NUC-56** (c). 3D framework of **NUC-56** featured by oval nanocages (d).

isting Lewis acid and base sites. Besides, the H_5BDCP ligand has the two unique advantages, *i.e.*, spatial self-regulation and metal-cluster-orientation. Because the triaxial angle-adjustable planar H_5BDCP ligand enables three carboxylphenyl groups to rotate freely around the pyridine to obtain a more dynamic structure and the two α -carboxyl groups in the BDCP^{5-} ligand play a structure-oriented role, causing the other carboxyl groups to grab other metal ions to form binuclear or polynuclear metal-cluster nodes, **NUC-56** possesses excellent characteristics.

From a topological viewpoint, with BDCP^{5-} and $\{\text{In}_2\text{Tm}_2\}$ SBUs being seen as 4 and 8-c nodes, respectively, **NUC-56** can be simplified as a novel 3D (4-c) $_2$ (8-c) topology with the Schläfli symbol of $\{4^{12}.6^{12}.8^4\}\{4^6\}_2$ analyzed by TOPOS40, as shown in Fig. 1b.

Analysis of physicochemical properties

As shown in Fig. S2,[†] the PXRD pattern of **NUC-56** and the simulated pattern derived from the single-crystal X-ray data are consistent, proving its phase purity. In addition, the PXRD modes show that **NUC-56** has high water and chemical stability, which was proved by soaking it in water for 7 days at room temperature, 72 h in boiling water, and 7 h in water with a pH in the range of 2 to 12, as shown in Fig. S6 and S7.[†] The

thermal stability of the as-prepared **NUC-56** and **NUC-56a** samples was tested through thermogravimetric analysis experiment (TGA) in the temperature range of 25–800 °C (Fig. S5[†]), which showed a weight loss of ~5.4% (calcd 5.0%) from 25 °C to 100 °C, corresponding to the loss of free H_2O molecules. Next, the second loss of ~23.5% (calcd 22.0%) corresponded to the loss of solvent and associated H_2O molecules from 100 °C to 400 °C. Finally, **NUC-56** was stable up to 450 °C with insignificant further weight loss observed, demonstrating its outstanding thermal stability.

Gas adsorption behaviour

To measure the permanent porosity of **NUC-56a**, the newly-synthesized compound was firstly activated by immersing it in CH_3OH solvent for 3 days, and then heated under dynamic vacuum at 150 °C for 12 h, resulting in the de-solvated **NUC-56a** with abundant open metal active sites on the inner wall of its porous channels. Notably, the skeleton of the activated sample could still maintain its excellent integrity, which is supported by the PXRD pattern (Fig. S4[†]). The N_2 adsorption isotherms of **NUC-56a** were measured at 77 K, as shown in Fig. S8.[†] The obtained results exhibited that **NUC-56a** exhibited the reversible classical Type-I isotherm, confirming that **NUC-56** had microporous characteristics. The BET and

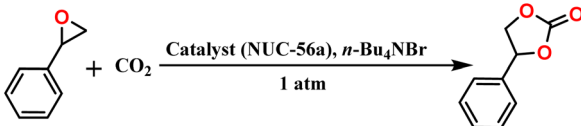
Langmuir surface area were $807 \text{ m}^2 \text{ g}^{-1}$ and $914 \text{ m}^2 \text{ g}^{-1}$, respectively. Furthermore, the aperture distribution measurement showed that its pore size ranged from 8.1 to $14.3 \text{ \AA}$, which illustrates that there were inhomogeneous micro-porous channels in the framework (Fig. S9†).^{53–55} Furthermore, **NUC-56a** also offered the maximum uptake capacity of CO_2 with a value of $90.8 \text{ cm}^3 \text{ g}^{-1}$ at 273 K and $53.5 \text{ cm}^3 \text{ g}^{-1}$ at 298 K (Fig. S10†). To explain the binding force between CO_2 and **NUC-56a**, the isosteric heat of CO_2 adsorption (Q_{st}) determined from the Clausius–Clapeyron equation was calculated to be 28.2 kJ mol^{-1} at zero loading (Fig. S11†).^{56–59}

The distribution of acidic and basic sites in the **NUC-56** catalyst was evaluated by TPD (temperature-programmed desorption) technology, as shown in Fig. 2. In the NH_3 -TPD profile, three groups of ammonia desorption peaks appeared in the temperature range of 100–450 °C, indicating that the NH_3 desorption is from the Lewis acid sites.^{60,61} According to the amount of ammonia desorbed (the integral area of NH_3 -TPD), it is obvious that the amount of stronger Lewis acid sites is greater than weak Lewis basic sites (Fig. 2a). Similarly, it can be seen from the CO_2 -TPD profile in Fig. 2b that Lewis basic sites also exist on the surface of the **NUC-56** catalyst. Also, the number of stronger basic sites is larger than that of weaker basic sites. The TPD results indicate that Lewis acid–base sites exist on the surface of **NUC-56** simultaneously, which is helpful to improve its catalytic performance.

Catalytic cycloaddition of CO_2 and epoxides

Motivated by the features of **NUC-56a** including high stability, large CO_2 sorption capacity, accessible microporous channels, and coexisting high-density Lewis acid and base sites (In^{3+} and Ln^{3+} , $\text{N}_{\text{pyridine}}$ atoms and $\mu_2\text{-OH}$ groups), its heterogeneous catalysis of the cycloaddition reaction was evaluated by using styrene oxide (SO) as a model substrate under solvent-free and mild conditions. Further studies on the reaction temperature, time and catalyst dosage were carried out to optimize the reaction conditions. As described in Table 1, only a few of the reac-

Table 1 Cycloaddition reaction of CO_2 with styrene oxide under various conditions^a

					
Entry	NUC-56a (mol%)	<i>n</i> -Bu ₄ NBr (mol%)	Temp. (°C)	Time (h)	Yield ^b (%)
1	0.05	0	rt	48	7
2	0	1	rt	48	5
3	0.05	1	rt	48	23
4	0.05	1	35	48	39
5	0.05	1	45	48	66
6	0.05	1	55	48	89
7	0.05	1	65	48	96
8	0.05	2	65	48	99
9	0.05	3	65	36	87
10	0.05	4	65	24	92
11	0.05	5	65	12	95
12	0.06	5	65	12	96
13	0.07	5	65	12	98
14	0.08	5	65	10	97
15	0.09	5	65	8	96
16	0.10	5	65	7	98
17	0.10	0	65	7	58
18	0	5	65	7	43

^a Reaction conditions: 20 mmol styrene oxide, solvent free, CO_2 (1 atm). ^b The *n*-dodecane was internal standard and checked by ¹H NMR and GC-MS spectroscopy.

tion substrates could be converted to the target product at 7% yield in the presence of 0.05 mol% **NUC-56a** at ambient temperature. In contrast, 5% yield was observed when only 1 mol% co-catalyst of *n*-Bu₄NBr as a catalyst was introduced for the cycloaddition reaction, as shown in entry 2. However, when 0.05 mol% of **NUC-56a** and 1 mol% of co-catalyst of *n*-Bu₄NBr were introduced in the cycloaddition reaction under the same reaction conditions, the product yield significantly increased to 23%, indicating that the cycloaddition reaction was

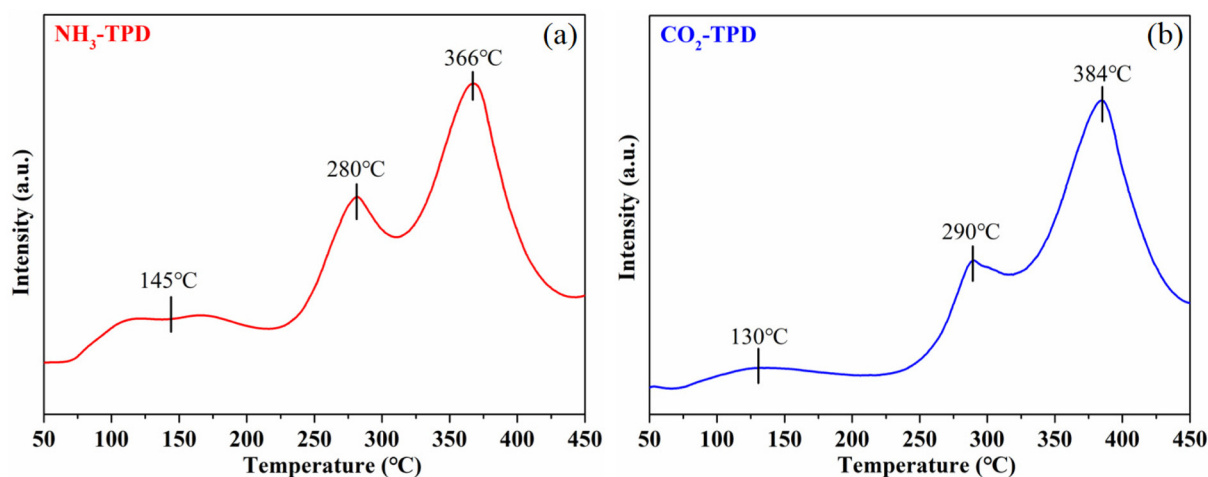


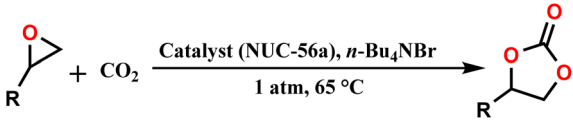
Fig. 2 NH_3 -TPD (a) and CO_2 -TPD (b) profiles of **NUC-56**.

completed by the synergistic catalysis of **NUC-56a** and *n*-Bu₄NBr (entry 3). Besides, with an increase in temperature, the conversion rate increased rapidly with high yield, and when the temperature reached 65 °C, the yield of styrene carbonate (SC) reached 96%, implying that the optimum reaction temperature should be set at 65 °C (entries 4–7). Furthermore, the influence of *n*-Bu₄NBr dosage on the SC yield was investigated. As shown in entries 8–11, as the amount of co-catalyst *n*-Bu₄NBr increased from 1 mol% to 5 mol%, the time taken to produce almost the same yield of SC gradually decreased from 48 h to 12 h. Consequently, the influence of **NUC-56a** dosage was discussed, and the data exhibited that the reaction time was reduced from 12 h to 7 h with the **NUC-56a** dosage from 0.06 to 0.10 mol%, exhibiting that the amount of catalyst has a significant influence on the reaction rate (entries 12–16). In addition, a set of control experiments conducted at 65 °C for 7 h using only 5.0 mol% *n*-Bu₄NBr or 0.10 mol% **NUC-56a** as a new catalytic system exhibited a significant reduction in yield, indicating that the combination of **NUC-56a** and *n*-Bu₄NBr played a very important role in the catalytic process (entries 17 and 18). Thus, it was concluded from the above investigations that the optimum catalytic conditions are 0.10 mol% **NUC-56a**, 5 mol% *n*-Bu₄NBr, 1 atm CO₂, 65 °C and 7 h. As shown in Table S3,† compared with some reports on MOF-based catalytic systems, it is noteworthy that the combination of **NUC-56a** and *n*-Bu₄NBr showed an excellent catalytic effect due to the structural advantages of **NUC-56a**, including high CO₂ adsorption capacity, plentiful Lewis acid and base sites and stable structure.

Inspired by the high catalytic efficiency of **NUC-56a**, epoxides with different substituents were selected to investigate the catalytic universality and size-selectivity under the optimal reaction conditions. As summarized in Table 2, all the selected epoxides with different electronic effects and distinctive steric hindrance were favorably transformed into the corresponding cyclic carbonates with a yield of more than 96%, which were certified by ¹H NMR spectroscopy (Fig. S12–19†). Apparently, the epoxides with strong electron-withdrawing groups (–F, –CF₃, –Cl, and –C=C) and small steric hindrance were almost entirely converted to the desired products because they could contact the reaction active sites without hindrance and electron-withdrawing groups caused a reduction in the electron density of oxygen atoms, which facilitated the critical step of ring opening (Table 2, entries 1–4 and 6).^{62,63} For entries 5 and 7, although the product molecules of 2-ethyloxirane and oxiran-2-ylmethanol had a smaller size than the channel widow of **NUC-56a**, the yield still decreased slightly, which can be attributed to the fact that the substituent groups possessed a notable electron-donating feature.^{64,65} However, the slightly lower yield of styrene carbonate proved that the microporous windows of **NUC-56a** had extremely adverse effects on the large-scale transport of large substrate molecules, reflecting that styrene oxide could not be efficiently reactivated in the catalytic sites.⁶⁶

The recyclability and heterogeneity of a heterogeneous catalyst are key factors for its practical application in organic syn-

Table 2 The cycloaddition reactions of CO₂ with various epoxides with **NUC-56a** as the catalyst^a

					
E. ^b	Epoxides	Products	Yield ^c (%)	TOF ^d	TON ^e
1			99	142	990
2			99	141	990
3			99	141	990
4			98	140	980
5			97	138	970
6			98	140	980
7			97	138	970
8			96	137	960

^a Reaction conditions: substrate (20 mmol), *n*-Bu₄NBr (5 mol%), **NUC-56a** catalyst (0.10 mol%, based on the active {In₂Tm₂} cluster), CO₂ (1 atm), 65 °C, 7 h. ^b E.: Entry. ^c The internal standard was *n*-dodecane and checked by GC-MS spectroscopy. ^d TOF = turnover frequency. ^e TON (turnover number) = mole of product/mole of catalyst.

thesis, which prompted us to perform hot leaching and recycling experiments using **NUC-56a** under the optimum conditions. Primarily, the **NUC-56a** catalyst involved in the model reaction was removed by centrifugation after 3 h. The observed SC yield of 63.0% did not change significantly as the reaction time was extended, indicating that **NUC-56a** did not liberate the metal cations and possessed typical heterogeneity (Fig. S23†). Subsequently, the recyclability of **NUC-56a** was evaluated in ten cycle experiments. After each reaction, **NUC-56a** was recovered by centrifugation, washed with strongly polar DMF solvent and the volatile acetone solvent, and dried under vacuum at 120 °C for 5 h. Subsequently, the recovered **NUC-56a** was reused for the next run in the same case. As depicted in Fig. 3, the tenth run gave the yield of SC of 95% with the selectivity remaining over 97%, proving that **NUC-56a** possessed outstanding catalytic ability and superior recoverability. The PXRD and FT-IR profiles of the recycled catalyst used for 10 times were in accordance with the freshly synthesized catalyst. However, there was no significant change in the N₂ adsorption-desorption isotherms, confirming the good stability during the reactions (Fig. S20–S22†). Also, the filtrate

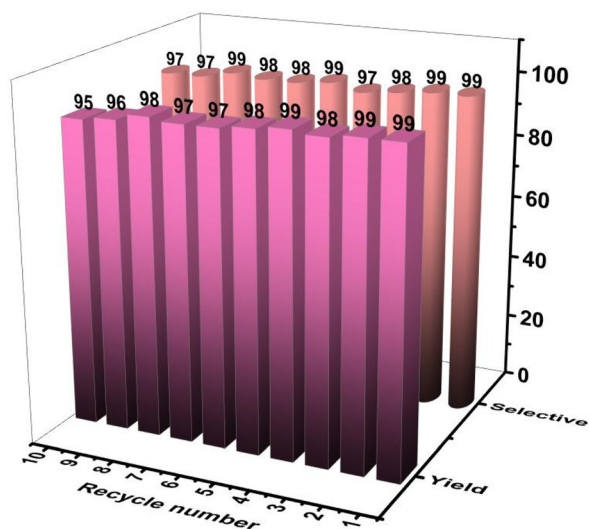


Fig. 3 Recyclability study for catalytic activities of NUC-56a in cycloaddition reaction.

obtained after removing the catalyst was tested by ICP-OES (inductively coupled plasma atomic emission spectrometry) technology, which displayed a negligible quantity of In^{3+} (0.020%) and Tm^{3+} (0.024%) (Table S5†). Thus, the above-mentioned results suggest that NUC-56a is an extremely stable and highly efficient heterogeneous catalyst in the field of chemical fixation CO_2 , and has great application prospects.

Therefore, based on the relevant references combined with the excellent characterization and catalytic performance of NUC-56a, the plausible catalytic mechanism for the cycloaddition is exhibited in Fig. 4.^{67–71} Firstly, the cycloaddition reaction began with the O atom of epoxide being activated by the Lewis acidic In^{3+} and Tm^{3+} sites to form In/Tm-epoxide adducts, resulting in the instability of the ternary rings. Subsequently, the Br^- ions released from the co-catalyst of $n\text{-Bu}_4\text{NBr}$ launched an affinity attack on the C atom with less

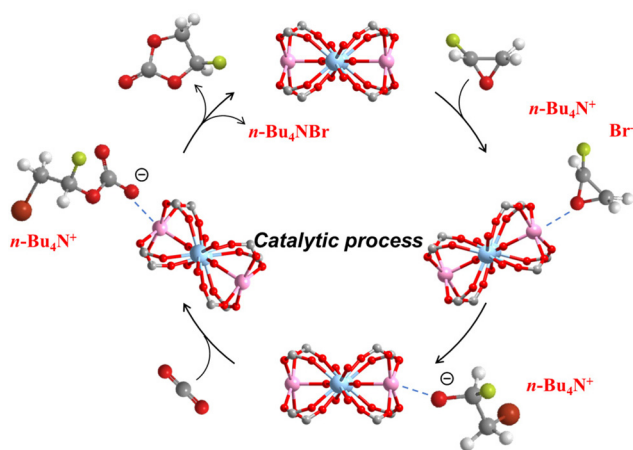


Fig. 4 Proposed reaction mechanism of catalytic cycloaddition reaction.

steric hindrance to produce the main intermediates of alkyl-carbonate anions, whose O^- atoms served as a nucleophilic reagent to react with CO_2 in the pores, generating the carbonate ester as the secondary intermediate. Finally, a closed-loop process was performed to end the reaction, accompanied by the release of NUC-56a and Br^- to participate in the next reaction process.

Catalytic activity of NUC-56a on Knoevenagel condensation

Benefiting from the large number of open Lewis acid-base sites of In^{3+} , Tm^{3+} , $\text{N}_{\text{pyridine}}$ atoms and $\mu_2\text{-OH}$ groups in its nanoporous channels, NUC-56a, as a perfect bifunctional heterogeneous catalyst, could be implemented to catalyze Knoevenagel condensation. As shown in Table 3, in a typical catalytic reaction, benzaldehyde and malononitrile were both introduced in a flask and slowly stirred for 36 h at room temperature under the condition of no NUC-56a. Consequently, the reaction process was continuously monitored by thin layer chromatography (TLC), and only 2% yield was obtained after 36 h, proving that the catalytic reaction hardly occurred the without NUC-56a catalyst, which could be seen as the blank control group for comparison with entry 2. Subsequently, 0.1 mol% NUC-56a was introduced as the catalyst with all the other conditions the same (entry 2). Surprisingly, it was found that the yield of 2-benzylidenemalononitrile in entry 2 (29%) was significantly higher than entry 1, indicating that NUC-56a had a certain promotion effect on the Knoevenagel condensation reaction. In addition, as revealed in entries 2–6, the effect of temperature on the reaction was gradually explored by increments of 10 °C, and the yield reached 99% when the Knoevenagel condensation reaction occurred at 65 °C. Setting 65 °C as the optimal reaction temperature, the influencing factor of the dose of NUC-56a on the reaction was further evaluated. As shown in entries 6–9, when the dose range of

Table 3 Schematic sketch of Knoevenagel condensation using substrates of benzaldehyde and malononitrile^a

Entry	NUC-56a (mol%)	Time (h)	<i>T</i> (°C)	Yield ^b (%)
1	0	36	25	2
2	0.1	36	25	29
3	0.1	36	35	47
4	0.1	36	45	72
5	0.1	36	55	93
6	0.1	36	65	99
7	0.2	24	65	99
8	0.3	12	65	98
9	0.4	8	65	99
10	0.4	2	65	67
11	0.4	4	65	92
12	0.4	6	65	98

^a Reaction conditions: malononitrile (20 mmol), benzaldehyde (10 mmol), ethanol 3 mL. ^b The internal standard was *n*-dodecane and checked by GC-MS spectroscopy.

NUC-56a increased from 0.1 to 0.4 mol%, the reaction efficiency greatly improved, as evidenced by the high yield obtained in a shorter time. Therefore, the optimal conditions were determined to be 10 mmol benzaldehyde, 20 mmol malononitrile, 0.4 mol% **NUC-56a**, 65 °C and 6 h. Notably, compared with the reported MOFs used as Knoevenagel condensation catalysts, the reaction catalyzed by **NUC-56a** exhibited excellent yield and high TON value, which saved more time and conformed to the principle of green chemistry (Table S6†). Additionally, as illustrated in Fig. S24,† the activating energy of the Knoevenagel condensation reaction calculated using Arrhenius equation was 41.4 kJ mol⁻¹.^{72,73}

To investigate the effect of different substituents and steric hindrance on the catalytic performance of Knoevenagel condensation, a series of aldehyde derivatives was selected as reactants to carry out the Knoevenagel condensation under the optimal conditions. As shown in entries 2–5 of Table 4, the Knoevenagel condensation reaction of malononitrile with benzaldehyde derivatives substituted with different electron-withdrawing groups (–NO₂, –F and –Br) led to 99% yield, indicating that the electron-withdrawing groups may play a beneficial role in the catalytic process. However, the substrates with electron-donating groups of –CH₃ had a slightly negative impact on the reaction conversion process, showing a decrease in yield (Table 4, entries 5 and 6). Amazingly, the substrate of 3,4-dimethyl benzaldehyde showed an obviously low yield,

which should be attributed to its large molecular size affecting the transport effect of the molecules and the contact opportunity with the reaction sites, as shown in entry 6. All the ¹H HMR spectra of the Knoevenagel condensation products are shown in Fig. S25–S30.†

Moreover, repeatability is an important factor in the practical application of heterogeneous catalysts. After each model reaction of Knoevenagel condensation, **NUC-56a** was separated by centrifugation, washed with DMSO and acetone, and dried under vacuum. As shown in Fig. 5, the recycled **NUC-56a** could maintain its catalytic performance with the yield and selectivity of over 95% even after reuse for ten times. Furthermore, the PXRD profile of **NUC-56a** after ten cycles well matched with the as-synthesized sample, indicating the retention of the initial frame structure during the reaction (Fig. S31†). Alternatively, the FT-IR spectra and the N₂ adsorption-desorption isotherms of the recycled samples used for ten cycles are in accordance with the original crystals, further proving the stability of the reused **NUC-56a** (Fig. S32 and S33†), respectively. Moreover, the supernatant obtained after removing the catalyst was tested by ICP-OES, showing that a negligible quantity of In³⁺ and Tm³⁺ ions leaked from **NUC-56a** (Table S8†). Furthermore, the conducted hot filtration experiments proved that **NUC-56a** owned typical heterogeneity because the model reaction was close to stagnation after removing the catalyst by filtration after 3 h (Fig. S34†).

According to the structural features and composition of **NUC-56a** and the related catalytic systems recorded in the literature, the reaction mechanism of Knoevenagel condensation in the presence of **NUC-56a** was proposed, as shown in Fig. 6.^{74–80} Firstly, the active sites of In³⁺, Tm³⁺, and μ₃-OH ions contact with the O atoms of the aldehyde groups by van der Waals force or hydrogen bonds, weakening the C=O bonds, and then the carbonyl carbon of malononitrile is acti-

Table 4 The Knoevenagel condensation reaction of aldehyde derivatives containing different groups^a

$\text{R}-\text{C}_6\text{H}_4-\text{CHO} + \text{NC-CN} \xrightarrow[\text{Ethanol (3 mL)}]{\text{Catalyst (NUC-56a)}} \text{R}-\text{C}_6\text{H}_4-\text{CH}=\text{C}(\text{CN})_2$					
E. ^b	Substrate	Products	Yield ^c (%)	TOF ^d	TON ^e
1			99	41	248
2			99	41	248
3			99	41	248
4			99	41	248
5			93	39	234
6			88	36	220

^a Reaction condition: catalyst **NUC-56a** (0.4 mol%, based on the active {In₂Tm₂} cluster), malononitrile (20 mmol), aldehyde derivatives (10 mmol), ethanol 3 mL, 6 h, 65 °C. ^b E.: Entry. ^c Calculation of yield based on GC-MS and ¹H NMR. ^d TOF = turnover frequency. ^e TON (turnover number) = mole of product/mole of catalyst (based on the {In₂Tm₂} cluster).

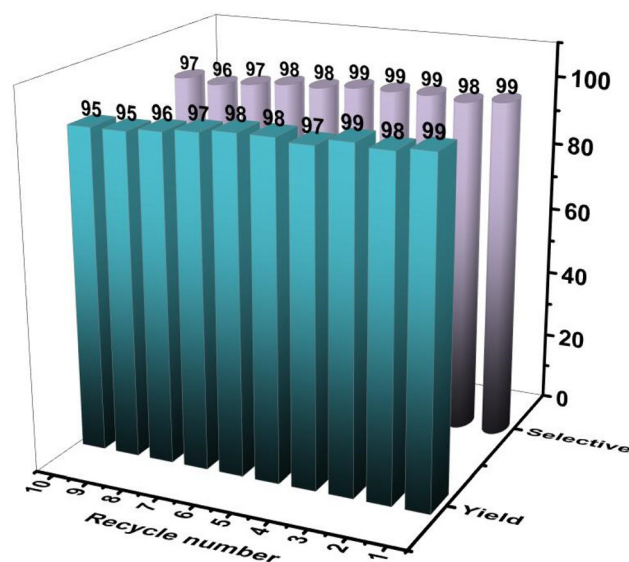


Fig. 5 Recyclability study for catalytic activities of **NUC-56a** in Knoevenagel condensation reaction.

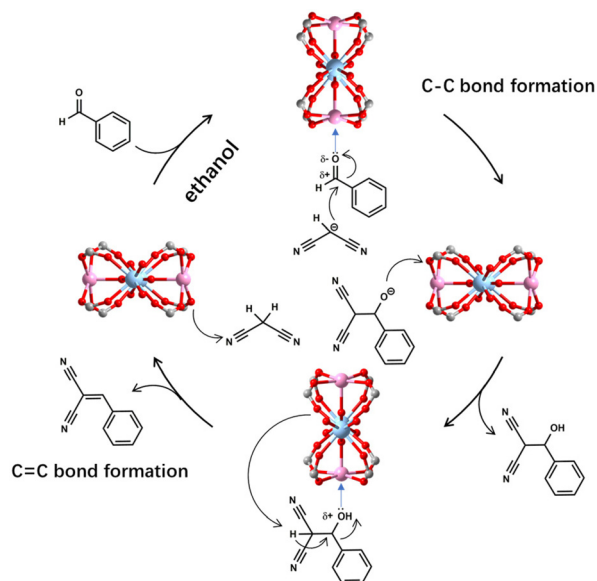


Fig. 6 Proposed reaction mechanism of catalytic Knoevenagel condensation reaction.

vated by the N-pyridine atom to form an active imine intermediate. The imine intermediate tends to undergo a Knoevenagel condensation reaction with the weakened C=O bond of aldehyde. Finally, with the release of water molecules, the product of benzylidenemalonitrile is generated.

Conclusions

The solvothermal self-assembly of In^{3+} , Tm^{3+} and H_5BDP led to the formation of an extremely stable microporous framework of $\{(\text{Me}_2\text{NH}_2)_2[\text{In}_2\text{Tm}_2(\text{BDP})_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_2]\cdot 2\text{DMF}\cdot 3\text{H}_2\text{O}\}_n$ (NUC-56) possessing an excellent confined pore environment with large specific surface area, high porosity, and abundant co-existing Lewis acid and base sites of In^{3+} , Tm^{3+} , $\mu_2\text{-OH}$ and $\text{N}_{\text{pyridine}}$ atoms, which are built based on the undocumented heterometallic clusters of $[\text{Tm}_2\text{In}_2(\mu_2\text{-OH})_2(\text{CO}_2)_{10}(\text{H}_2\text{O})_2]$. Due to the excellent characteristics of NUC-56a, it showed outstanding stability and excellent catalytic activity for the cycloaddition reactions and Knoevenagel condensation reactions under mild chemical conditions. Thus, this work exhibits that the intervention of high-coordinated rare-earth ions in MOF-based catalysts can realize excellent catalysis, stability and regenerative behaviour, meeting the requirements of long-term stability for the industrial application of these materials.

Author contributions

Hongxiao Lv: conceptualization, writing – original draft, methodology, data curation. Hongtai Chen: formal analysis, investi-

gation. Tuoping Hu: performance testing. Xiutang Zhang: supervision, writing – review & editing, project administration.

Conflicts of interest

All authors express that they have no conflict of interest.

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