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# Combination of dimensional reduction and active site addition strategies for preparing unique {RE<sub>9</sub>}-cluster-based MOFs: efficient CO<sub>2</sub> fixation and Knoevenagel condensation†

The current application of porous catalytic materials for organic synthesis is always confined to comparatively simple small substrates because of the diffusion barrier. Therefore, in this study, dimensional reduction and active site addition strategies were employed for preparing unique porous {RE<sub>9</sub>}-clusterbased metal-organic frameworks (MOFs)  $\{[Me_2NH_2]_4[RE_9(pddb)_6(\mu_3-O)_2(\mu_3$ rare-earth  $OH_{12}(H_2O)_{1.5}(HCO_2)_3] \cdot 6.5DMF \cdot 11H_2O)_n$  (MOF-RE, RE = Tb, Y, and Dy) with high-density multiple active sites. It was found that MOF-RE are rare {RE9}-based two-dimensional (2D) networks including triangularnanoporous (1.3 nm) and triangular-microporous (0.8 nm) channels decorated by abundant Lewis acidbase sites (open RE(III) sites and N<sub>pyridine</sub> atoms) on the inner surface. As anticipated, due to the coexistence of Lewis acid-base sites, activated samples exhibited better catalytic activity (a yield of 96%, and a TON value of 768 for styrene oxide) than most previously reported 3D MOF materials for the cycloaddition of CO<sub>2</sub> and multifarious epoxides under moderate conditions. Moreover, as a heterogeneous catalyst, MOF-Tb, has excellent catalytic performance (with a TON value of 396 for benzaldehyde) for the Knoevenagel condensation reaction of malononitrile and aldehydes with high catalytic stability and recoverability. In addition, both reactions possessed high turnover numbers and frequencies. These dimensional reduction and active site addition tactics may permit the exploitation of new nanoporous MOF catalysts based on rare-earth clusters for useful and intricate organic conversions.

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#### Introduction

One of the most important concerns facing all nations on Earth is global climate change, as the main greenhouse gas, carbon dioxide ( $\mathrm{CO}_2$ ) has contributed various severe ecological issues, such as sea level rise and climate change, raising concerns for  $\mathrm{CO}_2$  capture and utilization technology. <sup>1-4</sup> The current efficient methods of using  $\mathrm{CO}_2$  to create valuable complexes may not only significantly reduce the amount of  $\mathrm{CO}_2$  in the environment but also help humanity economically,

making them one of the most advantageous options.<sup>5-7</sup> Since

cyclic carbonates are a type of extensively utilized chemical

and chemical raw material, it has been discovered that produ-

cing cyclic carbonates synthetically from epoxides and CO2 is

Metal-organic frameworks (MOFs) containing different polynuclear metal-oxo clusters are unique porous crystalline materials with widespread promise for sensing, heterogeneous catalysis and gas storage/separation.<sup>15–21</sup> Recent studies have exhibited that polynuclear cluster-based rare-earth (RE) MOFs possess exceedingly high stability and abundant catalytic active sites, <sup>22–24</sup> in which the catalytic efficiency for CO<sub>2</sub> con-

among the most effective ways to solve environmental issues and realize resource utilization. Nevertheless, CO<sub>2</sub> conversion typically involves synergistic catalysis with numerous active sites. Numerous efforts have been made to date to study promising heterogeneous catalysts. Although some are regarded as advantageous, including zeolites, activated carbon, metal oxides and organic polymers, they typically call for high catalytic loadings and harsh conditions, resulting in relatively low yields and conversions with poor recyclability due to the scarcity of catalytic sites.

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version and Knoevenagel condensation could be greatly accelerated by the synergistic effect of activated metal ions (Lewis acid sites, LASs) and nucleophilic groups (Lewis base sites, LBSs).25,26 However, the accessibility of these RE-MOF materials to sterically demanding substrates is limited by expanding and stabilizing the active sites. Since the substrates cannot easily reach internal LASs, RE-MOFs perform poorly with larger substrates or complex reactions. 27,28 It is essential to design functional ligands and precisely build RE-microporous MOFs with a high specific surface area and access to multiple active sites via an in situ function-oriented synthesis strategy to extract the catalytic ability of polynuclear clusterbased RE-MOFs to the greatest extent.

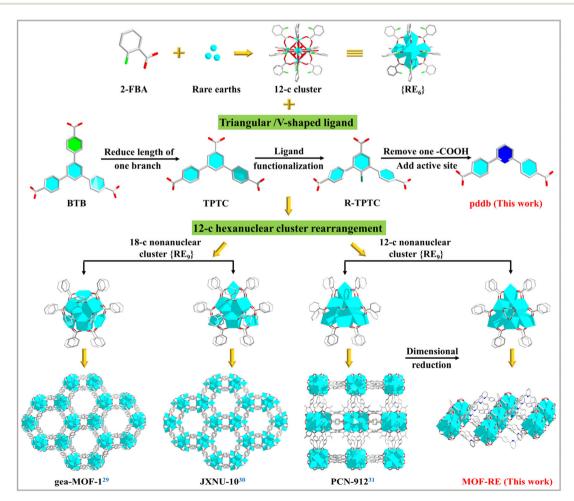
In light of the previous discussion on the standard of functional RE-MOFs as heterogeneous catalysts, this work thoroughly studied the effect of the topological structures of RE-MOFs on the catalytic activity and revealed dimensional reduction and active site addition methods to enhance catalytic reactivity through permitting unrestricted access to Lewis acid-base sites in two-dimensional (2D) MOFs (Scheme 1).29-31 These strategies can accurately predict the structures of MOFs, so as to achieve the regulation of the catalytic performance.

a series of unique porous 2D RE-MOFs  ${[Me_2NH_2]_4[RE_9(pddb)_6(\mu_3-O)_2(\mu_3-OH)_{12}(H_2O)_{1.5}(HCO_2)_3] \cdot 6.5DMF}$  $11H_2O_{ln}$  (MOF-RE; RE = Tb, Y and Dy) with {RE<sub>9</sub>} clusters as secondary building units (SBUs) are successfully prepared from  $C_2$ symmetry V-shaped 2,6-bis(4'-carboxyl-phenyl)pyridine (H2pddb) under solvothermal conditions. Notably, MOF-RE have high densities of quantified open metal sites (OMSs) acting as LASs and uncoordinated pyridines as LBSs, all of which are exposed in open channels. Benefiting from these active sites, MOF-RE exhibits excellent catalytic efficiencies for CO2 transformation with high yields, turnover numbers (TONs), and turnover frequencies (TOFs) compared to those of many reported 3D MOF materials. Moreover, they have excellent catalytic properties for Knoevenagel condensations via the synergistic effects of the LASs and LBSs.

## Results and discussion

#### Description of the crystal structure

The reaction of rare-earth salts (RE = Tb, Dy, and Y) with H<sub>2</sub>pddb in a mixed solution (DMF/H<sub>2</sub>O) in the presence of HNO<sub>3</sub> and 2-fluorobenzoic acid (2-FBA) gave hexagonal crystals



Scheme 1 Different polynuclear cluster-based rare-earth MOFs formed by the {RE<sub>9</sub>} clusters and functional connectors.

Table 1 Crystal data and structure refinements for MOF-RE

| Complex                                 | MOF-Tb                         | MOF-Y                         | MOF-Dy                        |
|---|--------------------------------|-------------------------------|-------------------------------|
| Empirical formula                       | $C_{117}H_{69}N_6O_{45.5}Tb_9$ | $C_{117}H_{69}N_6O_{45.5}Y_9$ | $C_{117}H_{69}N_6O_{45.5}D_5$ |
| Formula mass                            | 3717.06                        | 3086.97                       | 3749.28                       |
| Crystal system                          | Hexagonal                      | Hexagonal                     | Hexagonal                     |
| Space group                             | $P6_3/mmc$                     | P6 <sub>3</sub> /mmc          | $P6_3/mmc$                    |
| $a[\mathring{A}]$                       | 22.5962(4)                     | 22.5233(11)                   | 22.6331(9)                    |
| a [Å]<br>b [Å]                          | 22.5962(4)                     | 22.5233(11)                   | 22.6331(9)                    |
| c [Å]                                   | 22.7452(5)                     | 22.7551(15)                   | 22.6392(11)                   |
| α [ ο ]                                 | 90                             | 90                            | 90                            |
| $\beta$ $\circ$                         | 90                             | 90                            | 90                            |
| ,<br>γ [o]_                             | 120                            | 120                           | 120                           |
| V [Å <sup>3</sup> ]                     | 10 057.5(4)                    | 9997.1(12)                    | 10 043.4(9)                   |
| Z                                       | 2                              | 2                             | 2                             |
| $D_{\rm calcd}$ . [g cm <sup>-3</sup> ] | 1.227                          | 1.026                         | 1.240                         |
| $\mu  [\mathrm{mm}^{-1}]$               | 3.173                          | 2.634                         | 3.357                         |
| F[000]                                  | 3524                           | 3056                          | 3542                          |
| $\theta$ [ $\circ$ ]                    | 2.071-25.349                   | 2.072-25.385                  | 2.078-25.380                  |
| Reflections collected                   | 34 562/3409                    | 64 794/3391                   | 66 446/3411                   |
| GOOF                                    | 1.050                          | 1.061                         | 1.041                         |
| $R^{a,b}$ indices $[I > 2\sigma(I)]$    | $R_1 = 0.0261$                 | $R_1 = 0.0419$                | $R_1 = 0.0270$                |
| . ()3                                   | $WR_2 = 0.0648$                | $WR_2 = 0.1209$               | $wR_2 = 0.0730$               |
| R indices (all data)                    | $R_1 = 0.0331$                 | $R_1 = 0.0590$                | $R_1 = 0.0336$                |
| ,                                       | $WR_2 = 0.0680$                | $WR_2 = 0.1303$               | $wR_2 = 0.0766$               |

of MOF-RE. The presence of 2-FBA as a structure guiding agent is an essential condition for the assembly of the polynuclear cluster-based MOFs. The MOF-RE crystallize in a primitive hexagonal  $P6_3/mmc$  space group (Table 1) and are 2D porous networks. Remarkably, they possess unique polynuclear rare-earth-carboxylate clusters, *i.e.*, a 12-c nonanuclear [RE<sub>9</sub>( $\mu_3$ -O)<sub>2</sub>( $\mu_3$ -OH)<sub>12</sub>(O<sub>2</sub>C-)<sub>12</sub>(H<sub>2</sub>O)<sub>1.5</sub>(HCO<sub>2</sub>)<sub>3</sub>] core, in which formates are produced by the breakdown of DMF molecules.<sup>32</sup>

The  $[RE_9(\mu_3-O)_2(\mu_3-OH)_{12}(O_2C-)_{12}(H_2O)_{1.5}(HCO_2)_3]$  cluster has a threefold symmetry and is composed of nine RE ions arrayed in a {RE<sub>9</sub>} tricapped trigonal prism, according to detailed research of the nonanuclear cluster (Fig. S1a†). In contrast to the triangular planes of the tetragonal pyramids of the RE<sub>9</sub> tricapped trigonal prism, which are each capped by a μ<sub>3</sub>-OH, the two triangular planes of the central RE<sub>6</sub> trigonal prism are each capped by a  $\mu_3$ -O (Fig. S1b†). The six RE1 ions are each coordinated with eight O atoms: two from carboxylate moieties of two separate pddb2- connecters and four from four μ<sub>3</sub>-OH, and another two coordination sites are composed of O atoms from one  $HCO_2^-$  ligand and a  $\mu_3$ -O (O1) (Fig. S2a†). The remaining three RE2 cations are each coordinated with nine O atoms: a terminal H2O molecule, four µ3-OH and four carboxylate O from four independent pddb2- ligands (Fig. S2a†). The nonanuclear  $[RE_9(\mu_3\text{-O})_2(\mu_3\text{-OH})_{12}]$  cluster is created by twelve  $\mu_3$ -OH and two  $\mu_3$ -O connecting nine RE elements (Fig. 1a) and is terminated through twelve carboxylates from twelve independent pddb<sup>2-</sup> linkers to generate a 12-connected  $[RE_9(\mu_3-O)_2(\mu_3-OH)_{12}(O_2C-)_{12}]$  SBU. As the extension point of the  $[RE_9(\mu_3-O)_2(\mu_3-OH)_{12}(O_2C-)_{12}]$  core, C atoms from the carboxylate groups of twelve independent pddb<sup>2-</sup> linkers are arranged into a hexagonal prism, which conforms to the d6R vertex diagram of a 12-connected node. There are three H<sub>2</sub>O molecules and three extra HCO<sub>2</sub> bridging linkers

coordinated with the RE ions to form a nonanuclear [RE<sub>9</sub>( $\mu_3$ -O)<sub>2</sub>( $\mu_3$ -OH)<sub>12</sub>(O<sub>2</sub>C-)<sub>12</sub>(H<sub>2</sub>O)<sub>1.5</sub>(HCO<sub>2</sub>)<sub>3</sub>] cluster (Fig. 1a).

In the structure of MOF-RE, the pddb<sup>2-</sup> ligands adopt a bidentate bridging mode to connect two adjacent nonanuclear clusters (Fig. S2b†) to form 2D anionic layers with triangularmicroporous (~0.8 nm) and triangular-nanoporous (~1.3 nm) channels (Fig. 1b-d). The 2D infinite layers are stacked along the c axis with an average interlayer spacing of 11.37 Å (Fig. 1e and i). Notably, there are honeycomb-like hexagonal channels with a diameter of  $\sim$ 1.3 nm along the c axis, which are full of protonated [Me<sub>2</sub>NH<sub>2</sub>]<sup>+</sup> cations (Fig. 1f). The porosity computed by PLATON is ~56.1% of the overall crystal volume after excludsolvents. Topologically, the  $[RE_9(\mu_3-O)_2(\mu_3-$ OH)<sub>12</sub>(O<sub>2</sub>C)<sub>12</sub>(H<sub>2</sub>O)<sub>1.5</sub>(HCO<sub>2</sub>)<sub>3</sub>] clusters and ligands may act as 12-connected nodes and linear rods, respectively, and the whole structure can be represented as a 12-connected skeleton (Fig. 1g and h).

#### Gas adsorption studies

**MOF-Tb** was chosen as a representative for thorough studies due to its isomorphism. The freshly synthesized sample was vacuum-dried at 200 °C for 4 h prior to the sorption test to obtain the activated sample, **MOF-Tba**. The thermogravimetric analysis (TGA) curve was used to explore the activation temperature (Fig. S5†). Simultaneously, the framework integrality of activated **MOF-Tba** was verified *via* the powder X-ray diffraction (PXRD) pattern (Fig. S3†). A 77 K N<sub>2</sub> adsorption experiment was performed to confirm the pore properties of **MOF-Tba** (Fig. 2a), indicating that it possesses a traditional type-I adsorption isotherm as well as high Langmuir (825.33 m<sup>2</sup> g<sup>-1</sup>) and Brunauer–Emmett–Teller (BET) surface areas (560.35 m<sup>2</sup> g<sup>-1</sup>). The pore size distribution acquired through fitting the 77 K N<sub>2</sub>-sorption isotherm using nonlocal density functional

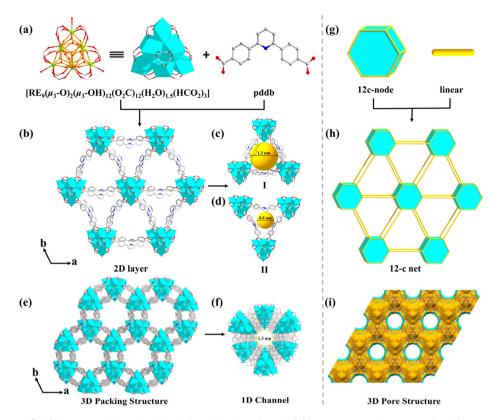


Fig. 1 (a and g) Types of {RE<sub>9</sub>} cluster and ligand and their simplifications; (b and h) 2D structure and corresponding 12-connected net of MOF-RE; (c and d) different channels along the c axis; (e and f) 3D supramolecular arrangement with 1D hexagonal channels; (i) view of the porous structure of MOF-RE.

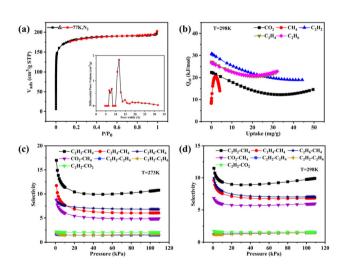


Fig. 2 (a) N<sub>2</sub> sorption isotherm at 77 K (inset displays the pore size distribution); (b) gas  $(C_2H_n, CO_2 \text{ and } CH_4)$  adsorption heat  $Q_{st}$  for MOF-Tba. Adsorption selectivities of MOF-Tba at 273 K (c) and 298 K (d) calculated using IAST for equimolar mixtures of C2Hn/CH4, CO2/CH4,  $C_2H_2/C_2H_n$  and  $C_2H_2/CO_2$ .

theory is consistent with the pore diameter provided by X-ray crystal data (Fig. 2a).

The latent application of MOF-Tba for CO2 and light hydrocarbon (CH<sub>4</sub> and C<sub>2</sub>H<sub>n</sub>) sorption (Fig. S6 and  $7^{\dagger}$ )/separation (Fig. 2c and d) has been carefully examined because of its inherent perpetual porosity and channel circumstances. The results displayed that the loading capacity of C2H2 in MOF-Tba is higher than that of other gases, demonstrating the maximum interaction between C<sub>2</sub>H<sub>2</sub> and the framework. The sorption enthalpies  $(Q_{st})$  were determined using the virial approach to establish the adsorption affinity between the five gases and skeleton more accurately (Fig. 2b and Fig. S8†). The  $Q_{\rm st}$  of **MOF-Tba** to  $C_2H_2$  (37.6 kJ mol<sup>-1</sup>) is higher than that of  $CO_2$  (22.4 kJ mol<sup>-1</sup>),  $C_2H_4$  (27.2 kJ mol<sup>-1</sup>),  $C_2H_6$  (26.7 kJ mol<sup>-1</sup>), and CH<sub>4</sub> (8.6 kJ mol<sup>-1</sup>) under zero coverage, which agrees with the measured adsorption amount. Moreover, the possibility of separating CH<sub>4</sub> from light hydrocarbons was studied by ideal solution adsorbed theory (IAST) for binary equimolar mixtures (Fig. S9 and 10†).33 The selectivities for CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> over CH<sub>4</sub> at 1 bar and 298 K are 5.9, 9.8, 6.8 and 7.0, respectively (Fig. 2c), making MOF-Tba an exceptional sorbent for effectively removing CO2/C2 light hydrocarbons from natural gas.

### Catalytic performance for CO2 conversion

Considering that MOF-Tba has the advantages of solventaccessible nanoscale channels, high specific surface area and abundant coexisting Lewis acid-base sites ([Tb<sub>9</sub>(μ<sub>3</sub>-O)<sub>2</sub>(μ<sub>3</sub>- $OH)_{12}(O_2C)_{12}(H_2O)_{1.5}(HCO_2)_3$ ] clusters and  $N_{pyridine}$  atoms), it was employed as an effective heterogeneous catalyst for the cyclo-addition of  $CO_2$  and epoxy complexes (Scheme S1†). Our previous study<sup>34</sup> has shown that the catalysts were not recycled and exhibited poor activity due to the lack of high-density active sites when selecting the pddb ligand itself and physical mixture of the rare-earth metal-pddb ligand to catalyze this reaction. Therefore, this study conducted a range of control experiments based on styrene oxide, determined ideal reaction conditions, such as time, temperature, and catalyst dosage and identified products through  $^1H$  NMR spectroscopy (Fig. S14–25†).

Entry 1 (Table 2) displays that when MOF-Tba (0.05 mol%) was added as a catalyst, only a small amount of product with a yield of 5% was detected within 12 h. In addition, only a slight conversion (10%) could be observed under the cocatalyst of n-Bu<sub>4</sub>NBr (1 mol%) alone, as shown in entry 2. Nevertheless, the yield was tremendously improved to 29% (entry 3) when MOF-Tba (0.05 mol%) and n-Bu<sub>4</sub>NBr (1 mol%) were concurrently introduced to the reaction, suggesting that MOF-Tba and n-Bu<sub>4</sub>NBr synergistically activated the second-order reaction of CO<sub>2</sub> and epoxides. Increasing the temperature was used to demonstrate that one of the key factors was temperature for influencing the reaction outcome, as shown in entries 4 and 5. Furthermore, entries 6and 7 examined and listed the effect of the cocatalyst n-Bu<sub>4</sub>NBr dosage, which demonstrated that the quantity of the cocatalyst had a clear impact on the reaction rate. The yield increased to 95% when 5 mol% n-Bu<sub>4</sub>NBr cocatalyst was added. The amount of MOF-Tba was increased because the practical application of the catalyst will be severely hampered by the 12 h reaction time. Styrene oxide could be converted into 4-phenyl-1,3-dioxolan-2-one more rapidly, as described in entries 8-10. In conclusion, it was found that the ideal reaction conditions are 0.125 mol% MOF-Tba catalyst, 5 mol% n-Bu<sub>4</sub>NBr cocatalyst, 60 °C and 6 h. In addition, we performed a detailed analysis of the <sup>1</sup>H NMR spectrum for entry 10, confirming that no by-products were generated during the reaction (Fig. S19†).

The catalytic universality of MOF-Tba was further evaluated utilizing a range of propylene oxide derivatives with distinct substituents and steric hindrance under determined ideal reaction circumstances (Table 3). The outcomes indicated that

Table 2 Cycloaddition of  $CO_2$  with styrene oxide under different conditions<sup>a</sup>

| Entry | MOF (mol%) | <i>n</i> -Bu <sub>4</sub> NBr (mol%) | <i>T</i> (°C) | t (h) | Yield <sup>b</sup> (%) |
|-------|------------|--------------------------------------|---------------|-------|------------------------|
| 1     | 0.05       | 0                                    | 25            | 12    | 5                      |
| 2     | 0          | 1                                    | 25            | 12    | 10                     |
| 3     | 0.05       | 1                                    | 25            | 12    | 32                     |
| 4     | 0.05       | 1                                    | 40            | 12    | 54                     |
| 5     | 0.05       | 1                                    | 60            | 12    | 78                     |
| 6     | 0.05       | 3                                    | 60            | 12    | 86                     |
| 7     | 0.05       | 5                                    | 60            | 12    | 95                     |
| 8     | 0.075      | 5                                    | 60            | 10    | 94                     |
| 9     | 0.1        | 5                                    | 60            | 8     | 95                     |
| 10    | 0.125      | 5                                    | 60            | 6     | 96                     |

<sup>&</sup>lt;sup>a</sup> Reaction conditions: solvent-free, styrene oxide (20 mmol), and CO<sub>2</sub> (1 atm). <sup>b</sup> The product yield was determined by <sup>1</sup>H NMR.

there was some regularity in how different substituents affected the yield. It can be seen from the comparison of entries 1 and 2 that the epoxy complexes with electron-withdrawing groups (-Br and -Cl) could improve the efficiency of the cycloaddition reaction, and the yield could reach more than 99%, the reason for which is that the electron-withdrawing group may decrease the electron density of ethylene oxide. 35,36 In contrast, electron-donating groups had a disadvantageous impact on this process, as in entry 3.37,38 Furthermore, entries 4-6 exhibited a significant decrease in the conversion of epoxide with bulky substituents, confirming the idea that big substituents restrict the mobility of substrate molecules. 39-42 Table S1† lists information about the molecular sizes of all epoxide derivatives. Additionally, the TON of MOF-Tba for styrene oxide was notable compared to most reported TON values for MOF catalysts (Table S2†), which was likely attributable to the profitable contribution of {Tb<sub>9</sub>} clusters and abundant N<sub>pyridine</sub> groups in the channels.

The actual organic synthesis industry depends heavily on the stability and recyclability of catalysts;<sup>43</sup> hence, additional tests were conducted about hot leaching, recovery, and recycling of MOF-Tba. First, the recycling stability of MOF-Tba for the cyclization reaction of CO2 with styrene oxide was studied under the determined ideal reaction conditions. The conversion of styrene oxide was nearly unchanged for five cycles by the recovered catalyst MOF-Tba (Fig. S11†). Meanwhile, the PXRD pattern of the recovered MOF-Tba sample after five experiments was essentially matched with the newly formed one, showing that the MOF-Tba catalyst maintained the stability of the framework (Fig. S12†). Afterward, inductively coupled plasma (ICP) analysis was then used in leaching experiments. As a result, the recovered filtrate included just a little quantity of Tb(III) ions (0.015%), further demonstrating the stability of MOF-Tba in the organic reaction. Furthermore, a thermal filtration experiment was carried out, and the results showed that the reaction hardly happens when the catalyst is filtered out (Fig. S13†), meaning that MOF-Tba possessed a heterogeneous nature.

The probable catalytic mechanism can be deduced from prior MOF-related literature, <sup>44–47</sup> and the distinctive structural characteristics of **MOF-Tba**, including high specific surface area, functional channel, and plentiful {Tb<sub>9</sub>} clusters (Fig. 3). First, the epoxide rapidly diffuses into the **MOF-Tba** catalyst and makes weak contact with its exposed metal sites in a confined environment. Then, the nucleophilic attack of less-obstructed carbon atoms in the epoxide by the Br<sup>-</sup> anion released by *n*-Bu<sub>4</sub>NBr promotes the formation of the alkylcarbonate anion. Subsequently, polarized CO<sub>2</sub> molecules tend to undergo nucleophilic addition reactions with alkylcarbonate anions to generate alkylcarbonate salt. Finally, the ring closure behavior results in the production of cyclic carbonate and liberation of catalysts.

#### Catalytic performances for Knoevenagel condensation

Knoevenagel condensation is a classical C-C bond coupling reaction, and its reaction mechanism involves the covalent

Table 3 Cycloaddition of CO<sub>2</sub> with epoxides under optimal conditions<sup>a</sup>

| Entry | Epoxide | Product | $Yield^{b}$ (%) | $TON^c$ | $\mathrm{TOF}^d\left(\mathbf{h}^{-1}\right)$ |
|-------|---------|---------|-----------------|---------|--|
| 1     | O Br    | Ļ       | >99             | 792     | 132  |
| 2     | Åa      | o Br    | >99             | 792     | 132  |
| 3     |         |         | 96              | 768     | 128  |
| 4     | گ_°~~   | والم    | 96              | 768     | 128  |
| 5     |         |         | 96              | 768     | 128  |
| 6     |         | , L     | 95              | 760     | 127  |

 $<sup>^</sup>a$  Reaction conditions: solvent-free, epoxides (20 mmol), n-Bu<sub>4</sub>NBr (5 mol%), Tb-MOF catalyst (0.125 mol%), CO<sub>2</sub> (1 atm), 60 °C, and 6 h.  $^b$  Yield was determined by  $^1$ H NMR.  $^c$  TON = [product (mmol)]/[catalyst (mmol)].  $^d$  TOF = TON/time.

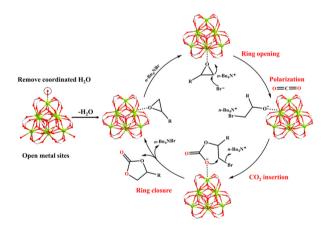


Fig. 3 Proposed mechanism of CO<sub>2</sub> conversion catalyzed by MOF-Tba.

C=C bond formed by the carbonyl group combining with the methylene group activated via both electron-withdrawing moieties. 40-42,48 Pharmaceuticals and fine compounds are frequently synthesized using this process. Recent research has proven that active metal centers (LASs) and nucleophilic moieties (LBSs) in porous MOFs could work together to significantly speed up the Knoevenagel reaction. 49-52 Therefore, more research was done on active porous MOF-Tba to catalyze the Knoevenagel condensation (Scheme S2†).

Initially, perfect reaction conditions were studied with benzaldehyde and malononitrile as substrates in the presence of desolvated MOF-Tba as a heterogeneous catalyst, as seen in

Table 4 and Fig. S29-31.† Entry 1 shows that only trace 2-benzylidenemalono-nitrile (3%) was produced at 25 °C without the catalyst MOF-Tba, whereas when MOF-Tba (0.1 mol%) was introduced, a yield of 38% was generated within 2 h (entry 2), indicating that the reaction could scarcely be carried out without the catalyst. The conversion of the substrate increased progressively when all other factors governing the reaction were held constant, and only the catalyst dosage was increased (entries 3 and 4). At 25 °C, the yield was 85% when the MOF-Tba dosage was raised to 0.25 mol% (entry 5). The reaction substrate was virtually entirely converted as the temperature rose from 25 °C to 60 °C in parallel investigations using 0.25 mol% MOF-Tba (entries 6 and 7), demonstrating that

Table 4 Knoevenagel condensation from substrates of benzaldehyde and malononitrile<sup>a</sup>

| Entry | MOF-Tba (mol%) | Time (h) | T (°C) | Yield <sup>b</sup> (%) |
|-------|----------------|----------|--------|------------------------|
| 1     | 0              | 2        | 25     | 3                      |
| 2     | 0.1            | 2        | 25     | 38                     |
| 3     | 0.15           | 2        | 25     | 58                     |
| 4     | 0.2            | 2        | 25     | 76                     |
| 5     | 0.25           | 2        | 25     | 85                     |
| 6     | 0.25           | 2        | 40     | 93                     |
| 7     | 0.25           | 2        | 60     | 99                     |
| 8     | 0.25           | 1.5      | 60     | 95                     |
| 9     | 0.25           | 1        | 60     | 88                     |
| 10    | 0.25           | 0.5      | 60     | 65                     |

<sup>a</sup> Reaction conditions: malononitrile (20 mmol), benzaldehyde (10 mmol). <sup>b</sup> The product yield was determined by <sup>1</sup>H NMR.

temperature was one of the crucial elements in the condensation reaction. Additionally, the connection between the conversion with reaction time was examined under the reaction environments of 0.25 mol% MOF-Tba at 60 °C (entries 8-10). It can be seen from the above results that the ideal reaction conditions were 0.25 mol% MOF-Tba, 60 °C, and 2 h when the ratio of malononitrile to aldehyde was 2:1.

Based on aforementioned discoveries, we chose several aldehyde derivatives with various substituents and steric hindrance (Table S3†) to confirm the MOF-Tba catalyst's suitability for the Knoevenagel condensation reaction, and the outcomes are displayed in Table 5 and Fig. S32-38.†

Entries 2-4 show that the conversion efficiency of benzaldehyde with electron-drawing groups (-F, -Br, and -NO<sub>2</sub>) surpassed 99%, whereas the catalytic yield was slightly decreased due to the presence of the electron-donating groups (-CH<sub>3</sub> and -CH<sub>2</sub>CH<sub>3</sub>) (entries 5 and 6), indicating that the electron-donating moieties greatly inhibit the Knoevenagel condensation reaction. Additionally, the conversion efficiency clearly reduced as the molecular size and steric hindrance of the substrate increased (entry 7). Remarkably, benzaldehyde had a TON value of 396, which was much higher than the majority of previously documented MOF catalysts (Table S4†).

The best experimental conditions were used to study the stability and recyclability of MOF-Tba. The utilized MOF-Tba catalyst was recovered and repeatedly cleaned with DMF after each reaction. Over 97% of 2-benzylidenemalono-nitrile was produced after five repetitions of the process using MOF-Tba, which retained excellent catalytic activity (Fig. S26†). Furthermore, the PXRD peaks of gathered MOF-Tba demonstrated that the host framework remained unchanged, suggesting the great stability of the microporous heterogeneous catalyst (Fig. S27†). Following the catalytic recycling experiment, leached homogenous Tb(III) was monitored by ICP analysis as well. The probability of leaching metal ions from the MOF-Tba network during Knoevenagel condensation was ruled out when trace Tb(III) of 0.018% was found in the filtrate. Under optimal reaction circumstances, a heat filtration test was conducted to confirm the heterogeneous nature of MOF-Tba. The solid catalyst was filtered out after the reaction had been going on for 0.5 hours. Since the conversion rate barely altered (Fig. S28†), the heterogeneous nature of MOF-Tba was further supported.

Fig. 4 implies a likely catalytic reaction mechanism based on relevant published studies<sup>53-59</sup> and structural characteristics of MOF-Tba. First, the carbonyl oxygen of the aldehyde

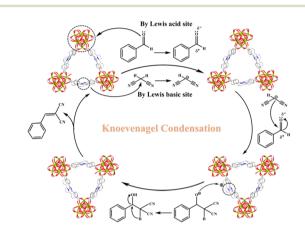


Fig. 4 Proposed mechanism for Knoevenagel condensation by MOF-Tba.

Table 5 Knoevenagel condensation reaction of aldehyde derivatives under optimal conditions

| Entry | Substrate | Product             | Yield <sup>b</sup> (%) | $TON^c$ | $TOF^{d}\left(h^{-1}\right)$ |
|-------|-----------|---------------------|------------------------|---------|------------------------------|
| 1     | Ç, 0      | CY CN               | >99                    | 396     | 198                          |
| 2     | , O       | , N                 | >99                    | 396     | 198                          |
| 3     | Br        | F                   | >99                    | 396     | 198                          |
| 4     | 02/N      | Br CN               | >99                    | 396     | 198                          |
| 5     |           | O <sub>2</sub> N CN | 98                     | 384     | 192                          |
| 6     |           |                     | 94                     | 372     | 186                          |
| 7     |           |                     | 87                     | 348     | 174                          |

<sup>&</sup>lt;sup>a</sup> Reaction conditions: aldehyde derivatives (10 mmol), malononitrile (20 mmol), catalyst MOF-Tba (0.25 mol%), 2 h, 60 °C. <sup>b</sup> The yield was calculated by <sup>1</sup>H NMR. <sup>c</sup> TON = [product (mmol)]/[catalyst (mmol)]. <sup>d</sup> TOF = TON/time.

group made a weak interaction with the exposed Tb(III) sites of **MOF-Tba**, converting its carbon atom into a positive carbon center and initiating the reaction. Simultaneously,  $N_{pyridine}$  atoms as the LBSs caused the carbonyl carbon of malononitrile to polarize into a negative center. Second, a covalent bond was formed between two carbon atoms with opposing electric charges, resulting in an imine intermediate. Finally, the recombination of intramolecular electrons combined with the release of  $H_2O$  molecules and the used catalyst resulted in the formation of the product benzylidenemalononitrile.

### Conclusions

Research Article

A series of 2D {RE<sub>9</sub>}-cluster-based rare-earth **MOF-RE** with Lewis acid-base dual functional sites were designed and synthesized by dimensional reduction and active site addition strategies. As expected, they benefited from high-density active sites and had exceptional catalytic properties for the chemical fixation of CO<sub>2</sub> with epoxides under moderate conditions, together with satisfactory catalytic efficiencies for Knoevenagel condensation. These strategies proposed in this work not only provide a new method for the preparation of nanoporous cluster-based RE-MOFs with various catalytic activities but also lay a foundation for the research of the catalytic mechanism.

#### Conflicts of interest

There are no conflicts to declare.

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