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6s-3d $\{Ba_3Zn_4\}$ -Organic Framework as an Effective Heterogeneous Catalyst for Chemical Fixation of CO₂ and Knoevenagel Condensation Reaction

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ABSTRACT: The exquisite combination of Ba^{2+} and Zn^{2+} with the aid of 2,4,6tri(2,4-dicarboxyphenyl)pyridine (H₆TDP) under the condition of solvothermal selfassembly generates one highly robust $[Ba_3Zn_4(CO_2)_{12}(HCO_2)_2(OH_2)_2]$ -organic framework of { $[Ba_3Zn_4(TDP)_2(HCO_2)_2(OH_2)_2]$ ·7DMF·4H₂O}_n (**NUC-27**), in which adjacent 2D layers are interlaced via hydrogen-bonding interactions to form a 3D skeleton with peapod-like channels and nano-caged voids. It is worth emphasizing that both Ba^{2+} and Zn^{2+} ions in **NUC-27** display the extremely low coordination modes: hexa-coordinated [Ba(1)] and tetra-coordinated [Ba(2), Zn(1), and Zn(2)]. Furthermore, to the best our knowledge, **NUC-27** is one scarcely reported 2Dbased nanomaterial with an unprecedented Z-shaped hepta-nuclear heterometallic cluster of $[Ba_3Zn_4(CO_2)_{12}(HCO_2)_2(OH_2)_2]$ as SBUs, which not only has plentiful low-coordinated open metal sites but also has the excellent physicochemical properties including omni-directional opening pores, ultrahigh porosity, larger specific surface area, and the coexistence of Lewis acid-base sites. Just as expected, thanks to its rich



active metal sites and pyridine groups as strong Lewis acid-base roles, completely activated NUC-27 displays high catalytic efficiency on the chemical transformation of epoxides with CO_2 into cyclic carbonates under mild conditions and effectively accelerates the reaction process of Knoevenagel condensation.

INTRODUCTION

Metal-organic frameworks (MOFs), as a class of burgeoning hybrid materials, have been widely investigated in the area of heterogeneous catalysts. Meanwhile, in order to improve their catalytic activity, the current hot research topic has been gradually characterized by developing corresponding two-dimensional (2D) MOFs catalytic materials.¹⁻⁶ Two-dimensional nanomaterials, as an more intriguing subclass of MOFs, have better performance because of their obviously inherent advantages including well-off open metal sites, omni-directional opening pores and ultrahigh porosity, larger specific surface area, and high electrical conductivity, which render them the excellent physicochemical properties along with the most promising applications in the fields of energy conversion, luminescence, photocurrent switching, etc.⁷⁻¹⁰ Compared to conventional three-dimensional MOFs, the enhanced catalytic activity of two-dimensional MOFs is responsible for the abundant active sites, higher density crystal defects, and exchangeable coordination sites.¹¹⁻¹⁴

 CO_2 could be widely used for human beings in the fields of electronics industry, medical research and clinical diagnosis, refrigeration, etc.^{15–18} However, excessive emission of CO_2 from modern enterprises and motorized tools has created a problem of serious global warming.^{17–22} Therefore, it becomes an urgent issue to develop a sustainable enrichment technology

for CO₂, by which the focused fundamental research on the chemical cycloaddition of CO₂ with epoxides into high valueadded alkyl carbonates is demonstrated to satisfy the green development stratagem of energy conservation and environ-mental protection.²³⁻²⁷ MOF-based materials can serve as an excellent heterogeneous catalyst because of their good recyclability and easy product separation. Although the achieved experimental data for the high catalytic efficiency dedicated by a large amount of MOFs is intriguing, the realization of application on an industrial scale still poses a challenge because of extensive requirements including stability, recyclability, the enterprise's total cost, etc. Up to this day, only a few reported MOFs make the chemical transformation of CO₂ simpler, saving energy, minimizing wastage, avoiding the use of toxic organic solvents, and reducing environmental pollution in mild conditions, which demonstrate that the indepth study is necessary for realizing the industrialization of MOF catalysts.^{28–31}

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In addition, almost all documented studies demonstrate that the catalytic performance on the chemical fixation of CO_2 is greatly dominated by the constituents of employed MOFs, especially the geometry of metal ion coordination and the properties of metal ions.^{32–35} Our previous researches exhibited that heavy metal cations possess the excellent capabilities of wider coordination number and stronger hard Lewis acidity because of their larger ionic radius and higher charge density, which entitle them to the favorable congenital factors for concentrating and catalyzing the cycloaddition of CO₂ molecules by acknowledged polarization behavior.³⁶⁻³⁹ However, up to now, the MOFs constructed from the alkaline cation of barium are scarcely reported, which may be due to that the highly multivariate coordination number and fuzzy directionality usually result in nonporous highly interpenetrating frameworks under the self-assembly conditions.^{40,41} So, in order to realize the high catalytic efficiency and the application in multiple fields, the well-proven effective strategy of introducing heavy metal cations as nodes into MOFs will undoubtedly receive more and more attention.⁴²⁻⁴

In view of the above-mentioned discussions, the favorable cations of Ba^{2+} and Zn^{2+} are employed to assemble heterometallic SBUs-based frameworks under the solvothermal conditions in the presence of the bifunctional 2,4,6-tri(2,4-dicarboxyphenyl)pyridine (H₆TDP) ligand. Here, we report one novel two-dimensional heterometallic–organic framework of { $[Ba_3Zn_4(TDP)_2(HCO_2)_2(OH_2)_2]$ ·7DMF·4H₂O}_n (NUC-27). Furthermore, adjacent 2D layers in NUC-27 are interlaced to each other via rich hydrogen-bonding interaction around protruded ZnO₃(OH₂) units to form peapod-like channels with excellent physicochemical properties including omni-directional opening pores, ultrahigh porosity, larger specific surface area, and the coexistence of Lewis acid-base sites.

EXPERIMENTAL SECTION

Preparation of NUC-27. A mixture of anhydrous zinc chloride (0.014 g, 0.10 mmol), barium chloride (0.021 g, 0.10 mmol), and H₆TDP (0.057 g, 0.10 mmol) was added into a mixed solvent including 3.0 mL of DMF, 3.0 mL of EtOH, 1.5 mL of H₂O, and 0.1 mL of concentrated HNO₃ solution. This obtained suspension was further magnetically stirred for 30 min to form a homogeneous solution and then sealed in a 25 mL Teflon-lined stainless steel vessel at 130 °C for 72 h. Colorless crystals were obtained by cooling gradually to room temperature with a yield of 90% on account of H₆TDP. Anal. Calcd for NUC-27 ($C_{81}H_{85}Ba_3N_9O_{41}Zn_4$): C, 38.70; H, 3.14; N, 5.01 (%). Found: C, 38.63; H, 3.21; N, 5.09 (%). IR (KBr pellet, cm⁻¹): 3448 (vs), 2932 (s), 1665 (s), 1553 (m), 1393 (s), 1255 (v), 1097 (m), 788 (m), 736 (w), 665 (m), 475 (w).

Catalytic Experiment Operation. Newly synthesized NUC-27 crystals were first immersed into low-boiling methanol for 3 days while the methanol was replaced three times in 1 day at ambient temperature. Then, the samples were collected and the same operation above was applied using dichloromethane to replace methanol. Finally, the obtained crystals of NUC-27 were dried in a vacuum drying oven at 120 °C for 10 h. The catalytic coupling of CO2 and epoxides was performed in a 25 mL stainless clave under the solvent-free conditions of 1 atm CO₂ gas, 2% mmol heterogeneous catalyst NUC-27 (based on the Zn center), and tetrabutylammonium bromide (n-Bu₄NBr, 4 mol %). After reaction, the heterogeneous catalyst of NUC-27 was recovered by simple centrifugation separation, followed by cleaning with strong polar solvent of DMF and volatile dichloromethane in turn. For the Knoevenagel condensation reaction, in a model reaction, 20 mmol of benzaldehydes and 10 mmol of malononitrile were added into 3 mL of ethanol in the presence of activated NUC-27 as catalyst, and

then the mixture was transferred into a magnetically stirred roundbottom quartz flask. The catalyst after reaction completion was retrieved using the same method above. For these two kinds of catalytic reactions, the conversion rate, the yield of the product, and the selectivity were monitored by gas chromatography mass spectrometry (GC-MS), and the transformed products were determined by ¹H NMR spectroscopy.

RESULT AND DISCUSSION

Description of the Crystal Structure. Single-crystal XRD analysis exhibits that NUC-27 crystallizes in the monoclinic system with $P2_1/n$ space group, and the asymmetric unit consists of two crystallographically independent barium ions (Ba(1) and Ba(2)), two zinc ions (Zn(1) and Zn(2)), one TDP⁶⁻ ligand, one formate anion, and one associated water molecule. In NUC-27, Ba(1) and Zn(1) are exquisitely spanned together by six carboxyl groups to form one undocumented heterometallic SBUs of $[BaZn_2(CO_2)_6]$. While, Ba(2) and Zn(2) are bridged via another three carboxyl groups to generate one new kind of binuclear SBUs of $\{BaZn(CO_2)_3(OH_2)\}$. Such two kinds of SBUs are further unified to form unprecedented Z-shaped hepta-nuclear clusters of $[Ba_3Zn_4(CO_2)_{12}(HCO_2)_2(OH_2)_2]$, which are further propagated by the organic skeletons of TDP⁶⁻ ligands into two-dimensional layers. Moreover, adjacent 2D layers are interlaced to each other via protruded $ZnO_3(OH_2)$ units along with rich hydrogen-bonding interactions to form a highly robust 3D network, in which nano-caged voids with the diameter of 13.7 Å are shaped by 8 $\{Ba_3Zn_4(CO_2)_{12}(HCO_2)_2\}$ $(OH_2)_2$ } SBUs and 12 TDP^{6-} ligands. In view of a threedimensional perspective, there are three kinds of channels with the same window size of 8.6×6.9 Å. It is worth emphasizing that both Ba^{2+} and Zn^{2+} ions in NUC-27 display the extremely low coordination modes: hexa-coordinated [Ba(1)] and tetracoordinated [Ba(2), Zn(1), and Zn(2)], which render the host framework a promising heterogeneous catalyst for various important catalytic process.

As for its detailed internal links, first, Ba(1) ion is chelated by six α -carboxyl groups from two TDP⁶⁻ ligands with the coordination mode of μ_2 - η^1 : η^1 , by which Zn(1) and Zn(1#) are further spanned together to form one trinuclear $\{BaZn_2\}$ unit. In detail, Ba(1) and Zn(1) (or Zn(1#)) are linked by three $\mu_2 \eta^1: \eta^1 \alpha$ -carboxyl groups from two separate TDP⁶⁻ ligands. Furthermore, Zn(1) and Zn(1#) are separately coordinated by one formate anion. Thus, with the aid of six μ_2 - η^1 : η^1 carboxyl groups from two TDP⁶⁻ ligands and two formate anions, Ba(1), Zn(1), and Zn(1#) are exquisitely spanned together to form one undocumented $[BaZn_2(CO_2)_6]$ SBU (Figure S1b). The alkaline earth ion of Ba(1) is located in a heavily distorted octahedron coordination geometry, which is completed by six carboxyl oxygen atoms with Ba(1)-O bond distances in the rang of 2.599(8)-2.687(5) Å, much smaller than the documented normal region of 2.710-2.989 Å. Such should be ascribed to the combination pattern of $[BaZn_2(CO_2)_6]$, which is bonded together by six carboxyl groups of two symmetrical TDP⁶⁻ ligands. Furthermore, it is worth mentioning that Ba(1) ion exhibits the unexpected exposure, which could be verified from its large bond angles of 97.48-107.3°. And meanwhile, in view of common coordination numbers (7, 8, and 10) in documented Ba-based MOFs, hexa-coordinated Ba2+ is extremely scarce. While, Ba(2) and Zn(2) are spanned together to form one binuclear {BaZn- $(CO_2)_3(OH_2)$ unit with the help of three $\mu_2 - \eta^1 : \eta^1 \beta$ -carboxyl



Figure 1. The coordination environment of TDP^{6-} ligand and the structural details of $\{Ba_3Zn_4(CO_2)_{12}(HCO_2)_2(OH_2)_2\}$ SBUs (a); the 2D sheet of **NUC-27** (b); the hydrogen bonded 3D framework of **NUC-27** featured by edging-sharing nanocages (pink polyhedron = Ba^{II} ; blue polyhedron = Zn^{II} ; H atoms are omitted for clarity) (c).

Scheme 1. Schematic Diagram of the Assembling Procedure of Hydrogen Bonded 3D Network Featured by Podiform Channels^a



^{*a*}Green wave line, hydrogen bond; purple ball, pore area.

groups stationed on 4-position of pyridine from three separate TDP^{6-} ligands, among which Zn(2) is simultaneously coordinated by one aqueous molecule (Figure S1b). Ba(2) is further coordinated by the above-mentioned formate anion with the coordination mode of $\mu_2 - \eta^1 : \eta^1$, which acts as a reinforcing plug by linking to Zn(1) and Ba(2) throughout the whole framework. Thus, the above two kinds of SBUs are combined into undocumented Z-shaped heptanuclear clusters of $\{[BaZn(CO_2)_3(OH_2)](HCO_2)[BaZn_2(CO_2)_6](HCO_2) [BaZn(CO_2)_3(OH_2)]$ (abbreviated as $\{Ba_3Zn_4(CO_2)_{12}$ - $(HCO_2)_2(OH_2)_2$ }, Figure 1a), which are further expanded into one two-dimensional structure with the aid of a TDP⁶⁻ ligand (Figure 1b). Beyond expectation, Ba(2) ion adopts a trigonal pyramidal coordination configuration with Ba(2)-O bond distances in the rang of 2.695(7)-2.761(6) Å (Figure S1a), which renders Ba(2) ion in a state of extreme openness, undoubtedly being competent to the task of catalyzing the cycloaddition of epoxides and CO₂ as Lewis acid sites in view of the recognized reaction mechanism. Moreover, for Zn(1)and Zn(2), although their coordination modes are slightly different, their tetra-coordination modes make them strong Lewis acid sites, serving as another kind of efficient catalytic sites.

In addition, it is worth emphasizing that these twodimensional layers in NUC-27 are further stacked into one 3D supramolecular nanoporous architecture through hydrogen-bonding association (Figure 1c and Scheme 1). The potential solvent area volume is calculated by PLATON to be 3285 Å³ (58.8% of unit cell volume). Furthermore, it is noteworthy that the assembling procedure of the hydrogen bonded 3D network exhibits that hydrogen-bonding interactions between interlaced adjacent 2D layers generate a seldom reported podiform semi-closed structure with a slightly symmetric interlace to comply with intermolecular repulsion. Such an impressive interlayer precipitation model provides continuous edge-shared semi-enclosed nanocages with omnidirectional open windows. As shown in Figure S1d, each six TDP⁶⁻ ligands and four $\{Ba_3Zn_4(CO_2)_{12}(HCO_2)_2(OH_2)_2\}$ SBUs in a single 2D layer make up a hemispherical shell, which is further sutured by hydrogen bonds $(O(1w)-H(1w)\cdots N(1))$, C(5)-H(5)···O(1w), C(5)-H(5)···O(12), and C(15)-H(15)··· O(12)) among adjacent layers to form an unprecedented nanocage structure with the diameter of 13.7 Å (Figure S1e). In the meantime, nanocage-embedded channels with the window size of 8.6 \times 6.9 Å² exist along three axial directions. The detailed information on hydrogen bonding is concluded in Table S3.

In addition, it is worthy of note that the successful construction of NUC-27 demonstrates that H₆TDP is one productive ligand with very strong coordination ability. Despite the strong acid reaction conditions, deprotonation behavior for all carboxyl groups could take place in the process of crystal formation, and each TDP⁶⁻ ligand serves as a μ_4 -bridge to connect four {Ba₃Zn₄(CO₂)₁₂(HCO₂)₂(OH₂)₂} clusters. In NUC-27, six carboxyl groups of TDP⁶⁻ display the single coordination mode of μ_2 - η^1 : η^1 , which is completely different from previously discovered mixed modes, such as $\mu_1-\eta^1$: η^1 , bridged $\mu_2-\eta^1$: η^1 , and chelated+bridged $\mu_2-\eta^2$: η^1 . In view of our speculation, different kinds of metal combinations not only lead to different host metal–organic frameworks but also lead

to different coordination modes of organic ligands along with their own torsion regulation. In NUC-27, the brand-new coordination patterns to metal ions of Ba^{2+} and Zn^{2+} result in severe torsion angles between branched phenyl rings and dominant pyridine with the twist angles of 51.4°, 87.9°, and 53.0°, which confirm that conjugated polycarboxylate ligands are the best choice to construct porous functional MOFs.

In respect of the topological structure of NUC-27, defining the trigeminal TDP⁶⁻ ligand, $[BaZn_2(CO_2)_6]$, and $[BaZn-(CO_2)_3(OH_2)]$ SBUs as topological nodes, the final hostframework should be simplified into one novel 3-nodal 4connected two-dimensional sheet with the Schläfli symbol of $\{3.6^4.7\}_4\{3^2.6^2.7^2\}$ shown in Figure S1c.

Water Resistance of NUC-27. Owing to the relative weak coordination bond of metal—organic framework materials, they are prone to hydrolyze in an aqueous environment. Therefore, the low water resistance keeps most of the MOFs from being widely applied. To test the water resistance of NUC-27, various aquatic systems were conducted including normal temperature water and boiling water. As shown in Figure S3, PXRD patterns after different water treatments are in line with the as-synthesized one, which excludes the structural collapse and reflects the strong water tolerance of NUC-27. Structurally, the internal environment of the nanochannel of NUC-27 could be adjusted by a heterometallic doping strategy, leaving a strong hydrophobic inner surface.³³

Gas Adsorption Studies. A fully activated sample of NUC-27 was obtained by solvent exchange and vacuum drying for 12 h; the activation temperature was determined by the TGA analysis (Figure S2) to ensure complete removal of water molecules. The integrity of the solvent-removing sample of NUC-27 was identified by PXRD analysis, revealing a well consistence with that of the original NUC-27 sample as illustrated in Figure S4. To assess the permanent pore characteristic of guest-free NUC-27, a cryogenic nitrogen adsorption isotherm was collected at 77 K shown in Figure S5. A classical type-I sorption isotherm was observed with the BET surface area of 1078 m^2/g and the pore distribution ranging 6.5-14.3 Å. As can be seen in Figure S6, furthermore, the adsorption behaviors of NUC-27 towards CO2 were investigated under 273 and 298 K. The steeply increasing uptakes in the low-pressure region of 0-0.1 bar indicate the high affinity of the NUC-27 framework to CO₂ molecules. With increasing the pressure, the adsorption capacity inclines to be saturated and observed at 85.6 and 64.8 cm^3/g , respectively. The isosteric heat of adsorption (Q_{st}) was employed to quantify the binding force between CO2 and the NUC-27 framework, As shown in Figure S7, the Q_{st} value calculated by a virial method slightly increased with the increase of uptake amount, indicating the energy distribution is relative homogeneous for the inner surface of NUC-27. The Qst value at zero loading was observed to be 31.5 kJ/mol, which is comparable to that of a previously reported MOFsbased sorbent with a large adsorption capacity of CO_2 .³⁴⁻⁴⁴

Catalytic Coupling of CO₂ and Epoxides. On account of these characteristics including highly exposed metal cations, highly partitioned pore channels, large specific surface area, and good trapping performance of CO_2 , the catalytic efficiency of **NUC-27** was testified for chemical transformation of CO_2 with epoxides under comparatively mild conditions into cyclic carbonates, which have been viewed as a bifunctional reaction for synergistically solving the energy crisis and reducing the amount of greenhouse gases.^{42–44} As illustrated in Table 1, 1,2-

Table 1. Catalytic Coupling of CO_2 with Propylene Oxide under Various Conditions^{*a*}

| ٩ | $>_{+ co_2}$ | Catalyst (NUC-27), <i>n</i> -Bu ₄ NI 1 atm | Br | | ⊳ |
|-------|-------------------|---|--------|-------|------------------------|
| entry | NUC-27 (mol %) | <i>n</i> -Bu ₄ NBr (mol %) | T (°C) | t (h) | yield (%) ^b |
| 1 | 2 | 0 | rt | 12 | 17 |
| 2 | 0 | 2.5 | rt | 12 | 49 |
| 3 | 2 | 2.5 | rt | 12 | 64 |
| 4 | 2 | 2.5 | 30 | 12 | 71 |
| 5 | 2 | 2.5 | 40 | 12 | 78 |
| 6 | 2 | 2.5 | 50 | 12 | 90 |
| 7 | 2 | 2.5 | 60 | 12 | 99 |
| 8 | 2 | 5.0 | 60 | 2 | 42 |
| 9 | 2 | 5.0 | 60 | 4 | 70 |
| 10 | 2 | 5.0 | 60 | 6 | 89 |
| 11 | 2 | 5.0 | 60 | 8 | 99 |

"Reaction conditions: propylene oxide (20 mmol), CO_2 (1 atm), solvent free. ^bThe conversion rate and reaction yield are checked by GC–MS spectroscopy.

epoxypropane was selected as a model to explore the influence of different reaction conditions on the conversion of propylene oxide with CO_2 into the targeted propylene carbonate. During the whole experimental process, the amount of NUC-27 was set at 2 mol %. Entry 1 in Table 1 exhibits that the yield in the presence of only solvent-free NUC-27 was less than 17% at room temperature, and the co-catalyst of *n*-Bu₄NBr with the similar reaction conditions led to a 49% yield (entry 2). However, as shown in entry 3, by simultaneously employing 2 mol % NUC-27 and 2.5 mol % Bu₄NBr, the yield could reach 64%, which proved that NUC-27 and *n*-Bu₄NBr possessed the completely different catalytic efficiency for the second-order reaction of cycloaddition from epoxides with CO2. Furthermore, with the temperature being enhanced every 10 °C, the vield accordingly increased with the final yield of 99% at 60 °C after 12 h (entry 7). However, under the conditions that the quantity of co-catalyst n-Bu₄NBr was doubled and NUC-27 was constant, the yield at 60 °C within 8 h could quickly ascend to 99% (entry 11). Compared to recently documented MOFs-based catalysts (Table S6), NUC-27 displayed the better catalytic performance, which should be attributed to the higher concentration of CO₂ around the referential polarized sites in the void channels of the host framework devoted by these intrinsic characteristics of active metal sites (Zn^{II} and Ba^{II}), uncoordinated pyridine and carboxyl oxygen atoms, and unimpeded void space.45,46

Under established optimal reaction conditions including 20 mmol of epoxide, 2 mol % **NUC-27**, 5 mol % *n*-Bu₄NBr, and 1 atm CO₂ at 60 °C within 8 h, a series of epoxide derivatives with typical substitutes were employed to check the catalytic universality of **NUC-27** and the effect of substituents on the reaction. Just as demonstrated in Table 2, activated **NUC-27** possessed the significant catalytic activity to the chemical transformation of selected epoxies into corresponding carbonates with the yield of above 95% under the set reaction conditions except for styrene oxide with a relatively high boiling point of 194 °C, which maybe limited its activity agility and consequently reduced the final yield at the low temperature of 60 °C. The compassion for entries of 2 and 3 exhibited that an epoxide with one electron-withdrawing

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Table 2. Catalytic Coupling of CO_2 and Various Epoxides under Optimal Reaction Conditions^a



^{*a*}Reaction conditions: epoxide substrates (20 mmol), NUC-27 catalyst (2 mol %, based on the Zn metal center), n-Bu₄NBr (5 mol %), CO₂ (1 atm), solvent free, 60 °C, 8 h. ^{*b*}The conversion rate and reaction yield are checked by GC–MS spectroscopy. ^{*c*}TON (turnover number) = mole of product/mol of catalyst.

group was more likely to proceed the cycloaddition reaction, which should be ascribed to that the electron absorption effect could effectively reduce the electron density of propylene oxide. Furthermore, the comparison between entries of 1-4 and 5 clearly displayed that the steric hindrance has a greatly adverse influence on the cycloaddition reaction, which was in accordance with the documented similar reactions catalyzed by porous MOFs (Table S4).⁵¹⁻⁵³ The reason from our speculation was that large substituents on epoxides not only affect the convenience of their access to nanocages but also affect the opportunity to contact with active sites. Thus, within the specified time, the corresponding yield for the substrates with larger substituents was relatively low. Moreover, compared to reported porous MOF-based catalysts, MOF-205(S),⁴¹ MMCF-2,⁴⁴ and Hf-Nu-1000,⁴⁷ NUC-27 exhibited the faster catalytic efficiency, which should be ascribed to the contribution of $\{Ba_3Zn_4(CO_2)_{12}(HCO_2)_2(OH_2)_2\}$ units on the surface of the channel on the basis of the clarified reaction mechanism.⁵¹ During the testified reaction process, the principle of catalysis is to reduce the reaction energy level and accelerate the reaction process by polarizing the reactants of epoxides and CO₂. Therefore, the research on NUC-27 set a benchmark that it is most effective for metal cations contained in porous MOFs to protrude into the position where the reaction substrates could be easily hit, by which the high catalytic activity of an emerged catalyst could be achieved.

The post-treatment including recovery and cyclic utilization for one emerged catalyst is one of the most important factors for evaluating its practical application except for the excellent catalytic performance. Thus, the 10-fold amplification reaction based on the optimal conditions with 1,2-epoxypropane as substrate by employing 500 mg of NUC-27 was repeated for five times, during which NUC-27 was recycled by filtration after each cycle and directly reused for the next cycle. When the fifth cycle was over, the recovered sample of NUC-27 was cleansed with dichloromethane and consequently vacuumdried. ICP analysis revealed that only trace amounts of Ba(II) $(\approx 0.037\%)$ and Zn(II) $(\approx 0.019\%)$ ions were detected from the reaction filtrate, which includes the leaching effect of the host framework. Furthermore, just as shown in Figure S8, these principal peaks of the PXRD data for recovered NUC-27 were in accordance with the ones determined by unused activated NUC-27, implying the high chemical stability and excellent reusability. Moreover, it should be noted that the catalytic effect of NUC-27 was almost the same within these five cycles. which was confirmed by the transformation yield, shown in Figure S9. For the further hot filtration experiment, the catalytic reaction immediately ceased when removing the catalyst during the catalytic process, while the reaction could continue in the presence of catalyst (Figure S10), revealing the heterogeneous nature of NUC-27.

The catalytic coupling of CO_2 with alkyl epoxides into carbonates prompted by specific catalysts involves three consecutive steps including ring-opening of epoxide, nucleophilic addition of CO_2 , and cycle closure. Thus, one inferential mechanism for the catalytic reaction by **NUC-27** is exhibited in Figure 2. First, guest molecules of epoxide and CO_2



Figure 2. Proposed reaction mechanism of coupling epoxides with CO_2 catalyzed by NUC-27.

stationed in the channels of NUC-27 were simultaneously polarized by exposed Lewis acidic and basic sites on the wall. Then anions of bromide from n-Bu₄NBr initiated one nucleophilic attack on the α -carbon atoms of propylene oxide to form the anionic intermediates of bromoalkoxide weakly coordinated with metal sites, just like bats hanging from branches. Under such circumstances, bromoalkoxide will easily fulfill the nucleophilic addition reaction with the polarized "touch porcelain" molecules of CO₂ to form the alkylcarbonate salts, which were prone to display closed-loop behavior to offer the five-membered ring carbonates.

Catalytic Knoevenagel Condensation Performance. The coexistence of bifunctional Lewis acid-base sites uniformly located in the nanocages makes activated **NUC-27** a promising heterogeneous catalyst for Knoevenagel condensation reaction.^{48–51} In a typical reaction, the substrates of benzaldehyde (10 mmol) and malononitrile (20 mmol) were selected as model reactants to define the optimal reaction conditions. As can be seen in Table 3, initially, the condensation reaction was Table 3. Catalytic Knoevenagel Condensation Reaction from Substrates of Benzaldehyde and Malononitrile^{*a*}

| | O + CN | Catalyst (NI ethanol (3 | JC-27) mL) | |
|-------|---------------|----------------------------|------------------|------------------------|
| entry | NUC-27 (mmol) | time (h) | temperature (°C) | yield (%) ^b |
| 1 | 0 | 1 | 60 | 4 |
| 2 | 0.01 | 1 | 60 | 63 |
| 3 | 0.02 | 1 | 60 | 91 |
| 4 | 0.03 | 1 | 60 | 99 |
| 5 | 0.03 | 1 | rt | 34 |
| 6 | 0.03 | 1 | 30 | 52 |
| 7 | 0.03 | 1 | 40 | 84 |
| 8 | 0.03 | 1 | 50 | 92 |
| | | | | |

^{*a*}Reaction conditions: benzaldehyde (10 mmol), malononitrile (20 mmol), ethanol (3 mL). ^{*b*}The reaction yield is checked by GC–MS spectroscopy.

nearly stagnant without any catalyst (entry 1); only a trace amount of 2-benzylidenemalononitrile was detected. In contrast, the yield of desired product could soar to 63% within 1 h in the presence of 0.01 mmol NUC-27 at 60 °C (entry 2), which indicates that the NUC-27 as bifunctional catalyst plays a crucial role in the Knoevenagel condensation reaction. Furthermore, when increasing the catalyst amount to 0.03 mmol, the yield of 2-benzylidenemalononitrile product could reach 99% (entry of 4). In order to further probe into the interfering factors in the process of catalytic reaction, the reaction temperature was set from room temperature to 50 °C in the presence of 0.03 mmol of catalyst. As shown in entries 5-8, the conversion rate increases from 34% to 92% with increasing the temperature, implying that reaction temperature is directly related to the yield of product. Hence, the above three steps concluded the following: the Knoevenagel condensation reaction of 10 mmol of benzaldehyde and 20 mmol of malononitrile could be efficiently accomplished in the presence of 0.03 mmol of NUC-27 catalyst at 60 °C.

To further investigate the catalytic generality of NUC-27, a series of aldehyde derivatives with different substituents and molecular sizes (Table S5) were explored under optimal reaction conditions shown in Table 4. The results revealed that NUC-27 displayed moderate catalytic effect on all six reaction substrates, while slight differences and rules still could be found: (i) electron-deficient substituents (F-, Cl-, and NO_2 -) with the benzaldehyde are more active than the electron-rich substituents (MeO- and Me-); (ii) the conversion rate increased along with electron-withdrawing ability, enhancing of electron-deficient substituents, that is, $NO_2 - > F - > Cl - .^{49,50}$ Therefore, understandably, the MeOwith the strongest electron-donating nature among them gave the lowest conversion rate of 91%. On the other hand, the nonaromatic hexahydro-benzaldehyde was selected to further check the catalytic universality as shown in entry 7. The conversion rate was observed to be 94%, which surpasses most of the MOFs-based catalysts and verifies that NUC-27 could efficiently catalyze a broad range of aldehydes including aromatic and nonaromatic types.

Recyclability as a measure of the catalyst applicability was further evaluated. In a typical experiment, by repeatedly using **NUC-27** for the Knoevenagel condensation reaction under optimal reaction conditions in five cycles, the catalyst can be easily recovered by centrifugation. The collected catalyst was Table 4. Knoevenagel Condensation Reaction of Aldehyde Derivatives with Different Groups a



"Reaction conditions: aldehyde derivatives (10 mmol), malononitrile (20 mmol), NUC-27 (0.03 mmol, based on the Zn metal center), ethanol (3 mL), 1 h, 60 °C. ^bThe reaction yield is checked by GC–MS spectroscopy. ^cTON (turnover number) = moles of products/mol of catalyst.

further washed with DMF and acetone in turn to make sure that the attached reactants are completely removed. As shown in Figure S12, the conversion rate was obtained over 95% for each cycle, which shows a successive good catalytic effect of NUC-27. After the recycled catalytic experiment, only a negligible amount of Zn(II) ($\approx 0.028\%$) and Ba(II) ($\approx 0.041\%$) was determined by ICP analysis. In combination with the PXRD pattern, it could keep its original shape after the catalytic process (Figure S11), confirming the strong skeleton stability of the catalyst during the process of Knoevenagel condensation reactions. Furthermore, a hot filtration experiment was employed to determine the heterogeneous nature of NUC-27. As illustrated in Figure S13, the catalytic reaction could complete within 1 h, whereas, in the parallel experiment, the reaction was almost stagnant after removing the catalyst, proving the pure heterogeneous nature of NUC-27.

On account of the coexistence of Lewis acid-base sites of NUC-27, $^{50-53}$ the hypothetical catalytic mechanism of the Knoevenagel condensation reaction should be summarized as follows: First, the exposed metal ions (Zn(II) and Ba(II)) as Lewis acidic sites will interact and polarize the carbonyl oxygen on the benzaldehyde, thus enhancing the electrophilicity of the carbonyl carbon atom to easily receive the attack from malononitrile (Figure 3). It should be noted that the Lewis acid sites could promote the deprotonation of the cyano group in malononitrile. Then, the carbonyl group from the aldehyde contacts with the carbanion to form an intermediate (C–C bond formation), followed by rearrangement and dehydration, and the desired benzylidenemalononitrile was formed (C=C bond formation).



Figure 3. Proposed catalytic mechanism of Knoevenagel condensation reaction catalyzed by NUC-27.

CONCLUSIONS

In summary, the hydrothermal self-assembly of Ba²⁺ and Zn²⁺ generates one 6s-3d nano-caged heterometallic material of $\{[Ba_3Zn_4(TDP)_2(HCO_2)_2(OH_2)_2]\cdot 7DMF\cdot 4H_2O\}_n$ (NUC-27), in which two kinds of undocumented heterometallic SBUs of $[BaZn_2(CO_2)_6]$ and $\{BaZn(CO_2)_3(OH_2)\}$ are combined into one intriguing Z-shaped hepta-nuclear cluster of $[Ba_3Zn_4(CO_2)_{12}(HCO_2)_2(OH_2)_2]$ via the connection of two formate anions. Owing to the unique hydrogen bonded peapod-like channels and the coexistence of Lewis acid-base sites, NUC-27 displays high catalytic efficiency on the chemical transformation of alkyl epoxides with CO₂ into cyclic carbonates under mild conditions. In the meantime, by taking NUC-27 as a bifunctional heterogeneous catalyst, Knoevenagel condensation could be effectively accelerated. This work demonstrates that the schematization and assembly of functional 2D heterometallic MOFs could be more productive for enhancing the catalytic efficiency on various chemical transformations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03736.

Crystallographic data and refinement parameters of NUC-27, selected bond lengths and angles, the TGA curves of as-synthesized and activated sample of NUC-27, PXRD patterns of NUC-27 after water treatment, N₂ absorption/desorption isotherms of NUC-27 at 77 K (PDF)

Accession Codes

CCDC 2046852 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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