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# A Zinc Coordination Complex Mimicking Carbonic Anhydrase for CO<sub>2</sub> Hydrolysis and Sequestration

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S Supporting Information

ABSTRACT: Carbonic anhydrase (CA) mimicking is an effective and environmentally friendly strategy for carbon dioxide sequestration. Herein, we developed a nonanuclear CA-mimetic zinc coordination complex (1) which possesses a coordination environment similar to that of CA's catalytically active zinc sites. Complex 1 exhibited excellent reusability, solvent and thermal stability, and gram-scale synthesis, which are essential for practical applications. It was found that complex 1 exhibited outstanding catalytic performance that is much better in comparison to that of the popular CA-mimetic compound Zncyclen and comparable to that of the reported metal-organic frameworks (e.g., CFA-1). Moreover, we found that its catalytic activity can be significantly improved via OAc<sup>-</sup>/OH<sup>-</sup> exchange and particle size reduction treatment. This study provides important guidance for the design of highly efficient CA-mimetic materials.



# INTRODUCTION

Emission of carbon dioxide  $(CO_2)$  has led to severe climate problems such as an increase in earth's surface temperature due to the greenhouse effect.<sup>1</sup> Among the technologies utilized to mitigate CO<sub>2</sub> emissions, biological CO<sub>2</sub> sequestration by carbonic anhydrases (CA) has demonstrated great promise due to its environmentally friendly nature and outstanding catalytic efficiency in converting  $CO_2$  into  $HCO_3$ .<sup>2-5</sup> However, the application of CA is limited by its inherent deficiency such as high sensitivity to pH, low thermal and chemical stability, and high cost.<sup>6</sup> Although many efforts have been made to use solid porous materials to immobilize CA to improve its stability against perturbation environments and harsh conditions,<sup>7-</sup> this strategy still faces drawbacks such as low immobilization efficiency and unavoidable reduction of enzymatic activity. Thus, exploring new strategies to overcome these shortcomings is of great significance and urgently needed.

Biomimetic catalysis has emerged as an alternative of enzyme immobilization due to its high stability, recyclability, and cost efficiency. Biological CO<sub>2</sub> sequestration by CA mostly relies on the tetrahedral catalytic center in which the Zn ion coordinates with three histidine imidazole moieties and a single hydroxide ion. The catalytic mechanism of CO<sub>2</sub> sequestration by CA is the nucleophilic attack of a Znhydroxyl group toward CO2 and subsequent formation of bicarbonate anions.<sup>2,13</sup> An efficient strategy to mimic CA is to

construct Zn-based coordination complexes with the same Zn coordination environments as CA.<sup>14–17</sup> For instance, Kläui et al. reported the use of tris(imidazolyl)phosphane as a ligand to synthesize a variety of stable zinc coordination complexes to mimic CA.<sup>18</sup> Ichikawa's group also synthesized a Zn coordination complex for CA mimicking.<sup>19</sup> Our group has long focused on employing coordination complexes, especially metal-organic frameworks (MOFs), to mimic natural enzymes for advanced applications.<sup>20-22</sup> Recently, we demonstrated that a series of MOFs can mimic CA, and they exhibited excellent efficiency on CO<sub>2</sub> in situ conversion.<sup>6</sup> However, the small-scale synthesis and high cost hinder the further application of current CA-mimetic coordination complexes.

Herein, we developed a CA-mimetic coordination complex,  $[Zn_9(Me_2bta)_{12}(OAc)_6]$ ·3DMF (1; Me<sub>2</sub>bta = 5,6-dimethyl-1,2,3-benzotriazole), consisting of a nonanuclear Zn cluster in which the Zn atoms possess a coordination environment similar to the Zn active site in CA (Figure 1), and evaluated its CA-biomimetic activity and catalytic kinetics using model substrates and direct CO<sub>2</sub> conversion. Notably, this biomimetic coordination complex can be easily prepared on a gram scale. In addition, we found that OAc<sup>-</sup>/OH<sup>-</sup> exchange and

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**Figure 1.** (a) Coordination environment of the Zn active site in CA. (b) Nonanuclear Zn cluster of compound **1** in which the coordination geometry of the peripheral  $Zn_3$  with coordination environment similar to that of the active site in CA is shown.

particle size reduction treatment can significantly improve its catalytic activity.

# EXPERIMENTAL SECTION

Synthesis of  $[Zn_9(Me_2bta)_{12}(OAc)_6]$ -3DMF (1) and 1-nano. The zinc coordination compound  $[Zn_9(Me_2bta)_{12}(OAc)_6]$ -3DMF (1) was synthesized according to a procedure reported by Volkmer et al.<sup>23</sup> Zn(OAc)\_2·2H\_2O (0.102 g, 0.46 mmol) and Me\_2bta (0.614 g, 3.72 mmol) were dissolved in 10.0 mL of DMF, respectively. Then, these two solutions were mixed and stirred at room temperature for 30 min. After the solvent was slowly evaporated for 3 days, colorless and block-shaped crystals of 1 were filtered and dried under vacuum to remove DMF. Nanosized particles were obtained via grinding. The particle size of 1-nano was measured using a nanoparticle size analyzer.

**Preparation of 1\* and 1-nano\***. Compound 1\* and 1-nano\* were obtained via soaking 250 mg of 1 or 1-nano in 20.0 mL of NaOH solution (pH 9.0–10.0) for 2.5 h. The NaOH solution was replaced every 30 min.<sup>24,25</sup> The complex was collected by filtration, washed with water three times, and then dried at room temperature. About 15–20 mg samples of 1 and 1\* were digested in 0.5 mL of CF<sub>3</sub>COOH and gently heated until they completely dissolved. Subsequently, ~0.1 mL of DMSO- $d_6$  was added to the solution for <sup>1</sup>H NMR analysis (Figure S3).

Assay of Activities of Zinc Coordination Compounds. The activities of the catalysts were measured at 25 °C via monitoring the concentration changes of p-NP at 402 nm, which is a hydrolysis product of p-NPA and p-NPB. To draw a calibration curve of p-NP, various concentrations of p-NP (5-60  $\mu$ M) in HEPES buffer (50 mM, pH 8.0) including 1% acetonitrile and 10% DMF was scanned by a UV/vis/NIR spectrometer (Lambda 950). First, 2.67 mL of HEPES buffer (50 mM, pH 8.0) and 0.3 mL of zinc coordination compound (0.21  $\mu$ mol) which was dispersed in DMF were placed in a cuvette. Then, p-NPA (0.03 mL, 50 mM) or p-NPB (0.03 mL, 50 mM), dissolved in acetonitrile, was placed in the cuvette (the final molar percent of zinc coordination compound catalyst was 14%). The amount of hydrolysate p-NP was measured by a UV/vis/NIR spectrometer at 1 s intervals for 1800 s. Meanwhile, to study the effect of self-decomposition of p-NPA and p-NPB, a blank control without addition of zinc coordination compound was also studied under the same conditions.

**Reusability of Zinc Coordination Compounds.** The recyclability of zinc coordination compound for substrate hydrolysis was evaluated. *p*-NPA (0.5 mM) was added to 40.0 mL of HEPES buffer (50 mM, pH 8.0) containing 0.21  $\mu$ mol of catalyst. The reaction mixture was stirred at room temperature for 1 h to hydrolyze *p*-NPA. Subsequently, the zinc coordination compounds were separated and washed three times with deionized water by centrifugation. Zinc coordination compounds were dried at room temperature for the next catalytic cycle.

 $CO_2$  Hydration in the Change of pH Value. During the  $CO_2$  hydration process, bicarbonate ions and H<sup>+</sup> were generated to form an acidic solution. The change in pH value of the reaction solution was monitored by real-time detection. A 0.21  $\mu$ mol portion of catalyst

diffused in 1.5 mL of DMF was mixed with 13.5 mL of HEPES buffer (50 mM, pH 8.0). First,  $CO_2$  was introduced to the reaction system and the pH value of the solution was recorded at the same time. Finally, the reaction was stopped when the pH value stayed at a plateau.

 $CO_2$  Sequestration. Conversion of  $CO_2$  to  $CaCO_3$  was carried out to evaluate the  $CO_2$  sequestration, which was performed in 11.0 mL of a reaction solution containing 1.0 mL of DMF with 2.0 mg of catalyst, 5.0 mL of HEPES buffer with 400 mM CaCl<sub>2</sub>, and an additional 5.0 mL of 50 mM HEPES buffer (pH 8.0). The solution was stirred for 1 h with bubbling  $CO_2$  gas.  $CaCO_3$  was collected by centrifugation and then dried. Finally, the mass of formed CaCO<sub>3</sub> was weighed to calculate the yield.

#### RESULTS AND DISCUSSION

A colorless crystalline powder of 1 was afforded via slow evaporation of a reaction mixture of  $Me_2bta$  with zinc acetate dihydrate in DMF solvent at room temperature. The powder X-ray diffraction (PXRD) pattern of the as-synthesized compound agreed well with the simulated pattern of 1 (Figure 2a). In addition, an inverted fluorescence microscope (Figure



Figure 2. (a) PXRD patterns of 1, 1\*, 1-nano, and 1-nano\*. (b) Microscope image of 1. (c) TEM image of 1-nano. (d) TEM image of 1\*. (e) TEM image of 1-nano\*.

2b) showed colorless, block-shaped microscale crystals. Singlecrystal data revealed that compound 1 contains a nonanuclear cluster of  $[Zn_9L_{12}]^{6+}$  (L = 1,2,3-benzotriazolate). Notably, complex 1 can be easily synthesized on a gram scale in a onepot reaction, which surpasses reported CA-mimetic coordination complexes.<sup>2,26–29</sup> As shown in Figure 1b, Zn1 and Zn2 are the central metal atoms of 1 that are coordinated with six nitrogen atoms, while Zn3 is the peripheral metal atom that coordinates with three nitrogen atoms and one carboxylate oxygen atom. Compound 1 shows great potential to mimic CA for CO<sub>2</sub> sequestration, because the peripheral Zn3 atom possesses a coordination environment similar to that of the active Zn center in CA.

High stability toward various solvents, acids and bases, and thermal treatment is essential for biomimetic catalysts. We found that complex 1 showed high stability under harsh conditions such as organic solvents, high temperatures, and solutions with a broad spectrum of pH values. After 1 was soaked in DMF, methanol, ethanol, acetonitrile and HEPES buffer (50 mM, pH = 8.0), its PXRD patterns agreed with the simulated pattern (Figure S1a), indicative of its high stability. Meanwhile, PXRD data also showed that compound 1 can be stable in HEPES solutions at pH ranging from 4 to 12 (Figure S1b). In addition, the thermal stability of 1 was tested via heating at different temperatures (~80–200 °C). From PXRD results, we found complex 1 still can retain its crystallinity at Scheme 1. Hydrolysis Reactions of p-NPA and p-NPB



Figure 3. (a) Catalytic kinetic traces of different catalysts on hydrolysis of *p*-NPA. (b) Catalytic kinetic traces of different catalysts on hydrolysis of *p*-NPB. (c) 6 h conversion of *p*-NPA hydrolyzed by different catalysts. (d) Recyclability of 1-nano\* on hydrolysis of *p*-NPA for five cycles.

250 °C (Figure S1c). Moreover, thermogravimetric analysis (TGA) results showed that there were two distinct weight loss steps for 1. The first one was a 10% weight loss occurring at 40-140 °C that was attributed to the solvent molecules and then a 40% mass loss began around 400 °C. These results further indicated that complex 1 possessed good thermal stability (Figure S1d).

The biomimetic catalysis activity of complex 1 was first evaluated via monitoring the concentration change of pnitrophenol (p-NP) produced from the hydrolysis of pnitrophenylacetate (p-NPA) and p-nitrophenylbutyrate (p-NPB) (Scheme 1). In addition, a popular CA-mimetic compound, Zn-cyclen, was selected as a positive control.<sup>30-34</sup> Self-decomposition of *p*-NPA and *p*-NPB without addition of catalysts was set as the blank control. The catalysis results revealed that 1 exhibited good catalytic performance toward the hydrolysis of p-NPA and p-NPB (Figure 3a,b). For the hydrolysis of *p*-NPA, the initial rate of 1 is  $(3.0 \pm 0.26) \times 10^{-2}$  $\mu$ M/s, which is more than 3 times better than that of the blank reaction,  $(0.94 \pm 0.05) \times 10^{-2} \,\mu\text{M/s}$ , and much higher than that of Zn cyclen,  $(1.65 \pm 0.04) \times 10^{-2} \mu M/s$ . For the hydrolysis of p-NPB, the initial rate of 1 is  $(2.25 \pm 0.25) \times$  $10^{-2} \mu M/s$ , which is about 5-fold better than its selfdecomposition,  $(0.46 \pm 0.07) \times 10^{-2} \mu$ M/s, and also much higher than that of Zn-cyclen,  $(0.98 \pm 0.04) \times 10^{-2} \,\mu\text{M/s}$ .

Inspired by the structure of CA, we tried to exchange the acetate anions with hydroxide anions to further promote the catalytic activity of 1. It was found that hydroxide anions can

successfully replace the acetate anions via simply soaking 1 in NaOH solution (pH 10). PXRD (Figure 2a) and TEM (Figure 2d) analysis revealed that the formed 1\* did not show structural or morphology changes. The successful OAc<sup>-</sup>/OH<sup>-</sup> exchange (Figure S2a) was confirmed by the FTIR spectrum of 1 and 1\*. In the FTIR spectrum of complex 1, there is a strong band at 1669 cm<sup>-1</sup> assigned to the asymmetric stretching vibration of the coordinated acetate anions, but it is a weak response signal in the spectrum of  $1^*$ . Furthermore, the <sup>1</sup>H NMR spectrum of the digested complex 1\* showed almost no residue of acetate anions (Figure S3). After successful OAc<sup>-/</sup> OH<sup>-</sup> exchange, the initial rate of *p*-NPA hydrolysis was (4.59  $\pm$  0.29)  $\times$  10<sup>-2</sup>  $\mu$ M/s for 1\*, which is 1.5 times better than that of the untreated 1. Similarly, the initial rate of p-NPB hydrolysis for 1\*, (3.75  $\pm$  0.15)  $\times$  10<sup>-2</sup>  $\mu$ M/s, is also approximately 1.7 times better than that of 1. The results revealed the improved biomimetic catalysis due to the anionexchange strategy.

We further investigated whether the catalytic activity originated from the surface or inside of the complex 1. The  $CO_2$  adsorption isotherm collected at 195 K unveiled the nonporous structure of 1, which is consistent with the structural analysis. Thus, the catalytic reactions should occur on the surface of the material. Reducing the particle size could promote the catalytic activity due to increased material surface. We prepared nanosized particles (1-nano, ~160 nm) via grinding (Figure 2c and Figure S4a). The initial rates of *p*-NPA and *p*-NPB hydrolysis were increased to (4.39 ± 0.29) × 10<sup>-2</sup>



Figure 4. (a) Conversion of CO<sub>2</sub> evaluated via weighing the formed CaCO<sub>3</sub>. (b) Real-time monitoring of pH change for different compounds.

and (4.28  $\pm$  0.09) × 10<sup>-2</sup>  $\mu$ M/s for 1-nano, respectively, which are ~1.5 times better than those of the microsized 1 (~50  $\mu$ m, Figure 3a,b). These results revealed that reducing particle size could enhance the catalytic activity, because the increased particle surface allowed more active sites to contact with reaction substrates.

Finally, combining the OAc<sup>-</sup>/OH<sup>-</sup> exchange and particle size reduction treatment, we obtained a superior CAbiomimetic catalyst, 1-nano\*, which showed the best catalytic ability (Figure 2a). For the hydrolysis of p-NPA and p-NPB, the initial rates of reactions catalyzed by 1-nano\* were improved to  $(6.28 \pm 0.05) \times 10^{-2}$  and  $(5.51 \pm 0.09) \times 10^{-2}$  $\mu$ M/s, respectively, which are more than 2 times better than those of the untreated 1. Moreover, the catalytic activity of 1nano\* is comparable to that of the reported CA-biomimetic metal-organic framework CFA-1 (initial rate:  $6.42 \times 10^{-2}$  $\mu$ M/s). In addition, the conversion of *p*-NPA was also detected to illustrate the catalytic activity of biomimetic catalysts (Figure 3c). Notably, 1-nano\* showed the highest conversion of 70.7  $\pm$  1.1% after reaction for 6 h, while the conversions of blank control, Zn-cyclen, 1, 1-nano, and 1\* were 12.29  $\pm$ 0.4%,  $28.0 \pm 2.6\%$ ,  $53.8 \pm 4.4\%$ ,  $63.6 \pm 2.6\%$ , and  $66.9 \pm 2.9\%$ , respectively (Table S1). Furthermore, the recyclability of 1nano\* was also evaluated. We found that 1-nano\* still retained high catalytic activity after five consecutive catalysis cycles (Figure 3d). After five catalytic cycles, 1-nano\* still retained  $\sim$ 82% of the conversion of the first cycle. Moreover, the Zn salts  $(Zn(OAc)_2 \text{ and } Zn(OH)_2)$  and the physical mixtures of these Zn salts and the ligand were also selected as controls. There is no obvious catalytic activity for  $Zn(OAc)_2$ , while  $Zn(OH)_2$  cannot dissolve in the reaction solution and also showed no catalytic activity. We further mixed  $Zn(OAc)_2$  with Me<sub>2</sub>bta in solution and found that the mixture showed much lower catalytic activity in comparison to 1-nano\* (Figure S6). These results further indicated Zn centers with a coordination environment similar to that of to CA is crucial to the high catalytic activity.

Effectively eliminating  $CO_2$  is of great significance for CA's catalytic performance and application.<sup>35</sup> Thus, the conversion of  $CO_2$  into  $CaCO_3$  was conducted to evaluate the biomimetic applicability of compound **1**. The weight of formed  $CaCO_3$  converted from  $CO_2$  can be used to assess the  $CO_2$  hydration and sequestration efficiency. We observed that the weights of the formed precipitate generated by blank control, Zn-cyclen, **1**, **1\***, **1-nano** and **1-nano\*** are 21.4, 27.8, 36.9, 66.0, 71.8, and 79.4 mg, respectively (Figure 4a). SEM/EDX images and PXRD patterns proved that the formed precipitate after bubbling  $CO_2$  was  $CaCO_3$  (Figures S7 and S8). For **1-nano\***,

the weight of formed CaCO<sub>3</sub> is 2.6-fold higher than that of blank control. Moreover, the amount of CaCO<sub>3</sub> generated by 1-nano\* is higher than that generated by Co-BBP and Co-BBP@Tb-MOF, which were reported by Sahoo et al.<sup>36</sup> (Table S1). In addition, during the  $CO_2$  hydration process, bicarbonate ions and H<sup>+</sup> were generated to form an acidic solution. The pH change of the reaction solution was monitored by real-time detection. Catalysts (0.21  $\mu$ mol) were diffused in 15.0 mL of HEPES buffer (50 mM, pH 8.0) containing 10% DMF. The pH value of the solution was recorded and meanwhile CO<sub>2</sub> was introduced into the reaction system. Finally, the reaction was stopped when the pH value did not change. According to the real-time monitoring of pH change, the pH value rapidly dropped from 7.9 to 6.5 within 2 min in the presence of 1-nano\*. According to the pH change, we observed the order 1-nano\* > 1\*  $\approx$  1-nano  $\approx$  1 > Zncyclen > blank control, which is in agreement with the results for hydrolysis of p-NPA (Figure 4b). These results indicated that compound 1-nano\* showed the best catalysis effect on  $CO_2$  conversion.

## CONCLUSION

In conclusion, we demonstrated that a nonanuclear Zn coordination complex 1 possesses high CA-biomimetic catalytic activity, attributed to the similarity of its coordination environment to the zinc active centers in CA. Complex 1 can be easily prepared on a gram scale and had good thermal, solvent, and pH stability. The biomimetic catalytic activity of complex 1 was comprehensively studied via evaluation of hydrolysis of p-NPA and p-NPB and conversion of CO<sub>2</sub> into CaCO<sub>3</sub>. In order to improve the catalytic activity, except for using an OAc<sup>-</sup>/OH<sup>-</sup> exchange strategy, we also developed a new approach via reducing particle size to improve its catalytic efficiency. The formed 1-nano\* catalyst showed boosted catalytic activity, which is more than 2 times better than that of the untreated 1. Moreover, the biomimetic catalysts exhibited good reusability. This study paves a new avenue to design coordination complexes to mimic CA for CO<sub>2</sub> treatment. Moreover, new strategies have also been developed to promote solid material biomimetic efficiency.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01059.

Materials and general methods, PXRD, TEM images, TGA, <sup>1</sup>H NMR, particle size and SEM/EDX images (PDF)

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#### Notes

The authors declare no competing financial interest.

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