New \textit{rht}-Type Metal–Organic Frameworks Decorated with Acylamide Groups for Efficient Carbon Dioxide Capture and Chemical Fixation from Raw Power Plant Flue Gas

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Supporting Information

ABSTRACT: The combination of carbon dioxide capture and chemical fixation in a one-pot process is attractive for both chemists and governments. The cycloaddition of carbon dioxide with epoxides to produce cyclic carbonates is an atomic economical reaction without any side products. By incorporating acylamide to enhance the binding affinity toward CO$_2$, new \textit{rht}-type metal–organic frameworks (MOFs) with (3, 28) and (3, 24) connected units were constructed. Zn-NTTA with two types of dinuclear paddlewheel building blocks—\{Zn$_2$(OOC$^-$)$_4$\} and \{Zn$_2$(OOC$^-$)$_3$\}. The high uptake of CO$_2$ (115.6 cm$^3$·g$^{-1}$) and selectivity over N$_2$ (30:1) at 273 K indicated that these MOFs are excellent candidates for postcombustion CO$_2$ isolation and capture. The MOFs feature high catalytic activity, rapid dynamics of transformation and excellent stability with turnover number (TON) values up to 110 000 per paddlewheel unit after $5 \times 6$ rounds of recyclability, demonstrating that they are promising heterogeneous catalysts for CO$_2$ cyclo-addition to value-added cyclic carbonates. The cycloaddition of epoxides with wet gases demonstrated that the catalyst activity was not affected by moisture, and the indices of the PXRD patterns of the bulk samples filtered from the catalytic reaction revealed that the crystallinities were maintained. The combination of the selective capture and catalytic transformation in one-pot enables the use of a negative-cost feedstock—raw power plant flue gas without any separation and purification—revealing the broad prospects of such MOFs for practical CO$_2$ fixation in industry.

KEYWORDS: \textit{rht}-type metal–organic frameworks, carbon dioxide capture, chemical fixation, cycloaddition, mixed gas, cyclic carbonates

INTRODUCTION

Carbon dioxide (CO$_2$) is an inexpensive, nontoxic, and abundant renewable C1 source.\textsuperscript{1,2} It should also be considered a raw material resource and a business opportunity rather than a waste product with a disposal cost.\textsuperscript{3} Increasing amounts of low-cost and relatively pure carbon dioxide will soon be available from plants for carbon sequestration and storage, and thus, carbon dioxide is a potential feedstock with nearly zero or even negative cost for conversion to fuels, useful carbonates and chemicals.\textsuperscript{3,5} From the perspectives of green chemistry and atomic economy, the cycloaddition of carbon dioxide to an epoxide to produce cyclic carbonates is quite promising because the incorporation of carbon dioxide into these chemicals does not generate any side products.\textsuperscript{6–9} In particular, porous frameworks offer many advantages over both homogeneous and nonporous heterogeneous catalysts in terms of their ease of recovery and their shape and size selectivity.\textsuperscript{10,11} The possibility of combining carbon dioxide capture and chemical fixation is attractive because it would allow the direct use of carbon dioxide from plants without further separation and purification from other gases and the production of large quantities of chemical products using small quantities of catalysts.

Metal–organic frameworks (MOFs), which are also known as porous coordination polymers, are porous crystalline solids generated by the association of metal-containing secondary building units and multitopic organic linkers through strong bonds.\textsuperscript{12,13} Because of their unique attributes, open structures with periodic dual compositions, and amenability to bottom-up assembly into a desired framework, these frameworks have emerged as very promising materials for heterogeneous catalysis over the past few decades.\textsuperscript{14,15} Specifically, their high surface area, large pores and absence of framework interpenetration make \textit{rht}-type frameworks ideal prototypical platforms for the development of novel large pores for carbon
dioxide capture and chemical fixation. The \( rht \)-type MOFs comprise large, highly symmetric 24-connected polyhedra of linked \( M_2(\text{carboxylate})_4 \) paddlewheel clusters, and the insertion of acylamide groups into the symmetric ligand linking the three 1,3-benzenedicarboxylate moieties significantly enhances the carbon dioxide binding affinity and uptake. Because this type of framework exhibits a high density of open coordinated metal ion sites and these active sites are positioned to orient well toward the center of the polyhedron, the incorporation of metal ions with strong Lewis acidity within these decorated frameworks may enhance the interactions between the active sites and substrates. Thus, they may potentially catalyze the coupling reaction of epoxides with carbon dioxide under mild conditions.

Inspired by advances in homogeneous catalysts with high activity and heterogeneous catalysts with excellent selectivity, herein, we report the synthesis and catalytic properties of (3, 28)-connected and (3, 24)-connected isoreticular MOFs, referred to as Zn-NTTA and Cu-NTTA, that were designed from triangular acylamide-bridging hexacarboxylate linkers, \( \text{H}_2\text{NTTA} \) \( (5,5^\prime,5^\prime^-\{(4,4^\prime,4^\prime^-\text{ntiltiltris(benzoyl)}) \text{tris}(\text{azanediyl})\}) \text{trisphosphoric acid} \), for the cycloaddition of carbon dioxide using raw power plant flue gas. We envisioned that the well-positioned acylamide groups and the catalytic sites within the large-pores of the MOFs would combine carbon dioxide capture and chemical fixation without the need for further separation and purification (Scheme 1). These MOFs’ excellent activity toward the cycloaddition of carbon dioxide with a total turnover number as high as 110 000 suggests that this new approach is quite promising and has broad prospects for practical applications in industry using a negative-cost feedstock—raw power plant flue gas—to produce cyclic carbonates.

**Experimental Section**

*Reagents and Syntheses.* All chemicals were of reagent-grade quality, obtained from commercial sources and used without further purification. All epoxides were purchased from Energy Chemical and distilled in a nitrogen atmosphere from \( \text{CaH}_2 \) prior to use. Carbon dioxide (99.995%) and mixed gas were purchased from the Dalian Institute of Special Gases and used as received.

**Instrumentation.** Elemental analyses of C, H and N were performed using a Vario EL III elemental analyzer. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using KBr pellets on a JASCO FT/IR-430. Powder X-ray diffraction (PXRD) measurements were obtained on a Rigaku D/Max-2,400 XRD instrument with a sealed Cu tube (\( \lambda = 1.54178 \) Å). Thermogravimetric analyses were performed on a Mettler-Toledo TGA/SDTA851 instrument and recorded under \( \text{N}_2 \) or air after 14 equilibrations at 100 °C followed by a ramp of 10 °C min\(^{-1} \) up to 800 °C. Confocal laser scanning microscopy (CLSM) was performed using an Olympus Fluoview FV1000 with \( \lambda_{	ext{exc}} = 635 \) nm. The bright-field images and confocal images of the obtained samples were scanned at \( \lambda_{	ext{em}} = 650-750 \) nm and excited at 635 nm using a 405/488/635 nm filter. Laser Raman spectra were recorded in a Horiba Jobin-Yvon LabRAM HR Evolution Raman spectrometer. The \( \text{N}_2 \) adsorption/desorption isotherms were measured volumetrically using a Micromeritics ASAP 2020 surface area analyzer up to saturated pressure at 77 K. Gravimetric CO\(_\text{2} \) adsorption/desorption measurements were performed on an IGA-003 gravimetric adsorption instrument (Hiden-Iscoha, UK) over the 0–1 bar range at 273 and 298 K. Scanning electron microscopy (SEM) images were taken with a Nova NanoSEM 450 microscope.

**Synthesis of the Ligand.** The organic linker \( \text{H}_2\text{NTTA} \) was prepared according to the literature and characterized by IR, \( \text{H}^\text{n} \) nuclear magnetic resonance (NMR), \( \text{C}^\text{13} \) NMR, and mass spectrometry (MS). Two grams (4.6 mmol) of 4,4,4′-tricarboxyphenylamine chlorides was added to a solution of 4.17 g (23.0 mmol) of 5-amino isophthalic acid and 2.05 mL (14.72 mmol) of triethylamine in 80 mL of acetone. The mixture was stirred for 16 h, and then, 500 mL of water was added. After filtration, the solid was washed with acetone, water, methanol, and finally, ether. Yield = 3.3 g, 83%. FT-IR spectrum (KBr, cm\(^{-1} \)): 3416 (br, s), 3078 (br, s), 1705 (vs), 1595 (vs), 1550 (s), 1431 (m), 1323 (m), 1185 (vs), 1278 (vs), 1247 (s), 1186 (m), 762 (m), 668 (m), 597 (w). \( \text{H}^\text{n} \) NMR (dimethyl sulfoxide (DMSO)-\( d_6 \), \( \delta \) ppm): 10.56 (s, 3H, NH), 8.68 (s, 6H, ArH), 8.22 (s, 3H, ArH), 8.07–8.04 (d, \( J = 8.06 \) Hz, 6H, ArH), 7.27–7.25 (d, \( J = 7.26 \) Hz, 6H, ArH). \( \text{C}^\text{13} \) NMR (DMSO-\( d_6 \), \( \delta \) ppm): 166.80, 164.91, 149.16, 139.27, 132.26, 129.36, 124.95, 123.57. High-performance liquid chromatography (HPLC)-MS: m/z calcd. for \( \text{C}_{45}\text{H}_{30}\text{N}_{4}\text{O}_{15} \): 866.17, 433.08, found: 865.2 [M-H]\(^{-}\), 432.2 [M-H]\(^{2-}\).
Synthesis of Zn-NTTA. A mixture of H₂NTTA (17 mg, 0.02 mmol) and Zn(NO₃)₂·6H₂O (29.7 mg, 0.1 mmol) was dissolved in 6 mL of mixed solvent containing N, N-dimethylformamide (DEF) and ethanol in a screw-capped vial. The resulting mixture was kept in an oven at 100 °C for 3 days. After cooling the oven to room temperature, light-yellow, block-shaped single crystals were separated, washed with dimethylformamide (DMF) and dried naturally at room temperature. The reaction yield based on the weight of the solvent-free material was approximately 60% relative to H₂NTTA. Anal. Calcd for Zn₆C₉₀N₈O₆₂.₅H₁₁: C, 45.95; H, 3.63; N, 5.36%. Found: C, 46.30; H, 3.70; N, 5.19%. IR (KBr): 3385 (br, s), 1621 (s), 1554 (s), 1503 (s), 1432 (s), 1372 (s), 1217 (vs), 1185 (vs), 1103 (s), 844 (w), 781 (m), 724 (m) cm⁻¹.

Synthesis of Cu-NTTA. H₂NTTA (17 mg, 0.02 mmol) and Cu(NO₃)₂·3H₂O (24 mg, 0.1 mmol) were dissolved in 2 mL of DMF containing 300 μL of HNO₃ producing octahedron-shaped green crystals. The reaction yield based on the weight of the solvent-free material was approximately 70% relative to H₂NTTA. Anal. Calcd for Cu₆C₉₀N₈O₆₂.₅H₁₁: C, 46.36; H, 4.11, N 6.69%. Found: C, 47.24; H, 4.13; N, 6.64%. IR (KBr): 3430 (br, s), 1661 (vs), 1592 (s), 1502 (s), 1432 (s), 1382 (s), 1237 (m), 1100 (m), 775 (m), 729 (w), 663 (w) cm⁻¹.

Crystallography. The crystallographic data of Zn-NTTA and Cu-NTTA were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using the SMART and SAIN'T programs. Routine Lorentz polarization and multiscan absorption correction were applied to the intensity data. Their structures were determined, and the heavy atoms were identified from successive full-matrix least-squares refinements on F² and Fourier synthesizes. Except for the disordered carbon and oxygen atoms, the non-hydrogen atoms of the ligand backbones were refined anisotropically. Except for the solvent water, the coordinated water molecules, and hydroxide ions, hydrogen atoms were fixed geometrically at calculated positions and allowed to ride on the parent non-hydrogen atoms. The hydrogen atoms of the ligand water molecules could not be located, but they are included in the formula.

For the crystal data of Zn-NTTA, to enhance the stability of the refinement, the acylamide group and benzene ring were disordered and split into two parts. Several constraints, including fixing the bond distances of these disordered atoms, were used. The geometrical constraints of idealized regular polygons were used for the benzene rings, and the thermal parameters on adjacent atoms in the two molecules were restrained to be similar. In the refinement of the crystal data of Cu-NTTA, the acylamide group and benzene ring were disordered into two parts. The bond distances of the benzene molecules were also fixed to the ideal geometrical shape, and the thermal parameters on adjacent atoms in the two molecules were restrained to be similar. The crystallographic data are summarized in Table 1.

Catalytic Pretreatment. The catalysts were first soaked in acetonitrile solution (24 h) for guest molecule exchange, and then, they were fully dried in a vacuum oven (100 °C, 2 h) to eliminate the acetonitrile molecules.

Dye Uptake. Before the dye uptake experiments, Zn-NTTA was first soaked in an acetonitrile solution (24 h) for guest molecule exchange and fully dried in a vacuum oven (100 °C, 12 h) to eliminate the acetonitrile molecules. Then, the dried Zn-NTTA (3 mg) crystals were soaked overnight in a DMF solution of 2′,7′-dichlorofluorescein dye (24 mM, 2 mL) in a constant temperature oscillation incubator. The resulting crystals were washed thoroughly with DMF to remove any dye from the surfaces of the crystals until the solution become colorless, and then, they were dried naturally at room temperature. The dried samples were dissociated with concentrated hydrochloric acid, and the resultant clear solution with a light olivine color was diluted to 1 mL and adjusted to a pH of 10. The absorption experiment was performed using an ultraviolet (UV)-vis spectrophotometer. The concentration of 2′,7′-dichlorofluorescein dye was determined by comparing the UV–vis absorption with a standard curve.

Gas Adsorption Studies. The N₂ (99.999%) adsorption/desorption isotherms were measured volumetrically using a Micromeritics ASAP 2020 surface area analyzer up to saturated pressure at 77 K. Before the analysis, Cu-NTTA was soaked in acetonitrile for 3 days, and the acetone was refreshed every 8 h. Then, approximately 100 mg of acetonitrile-exchanged sample was charged into a sample tube and activated at 100 °C for 15 h using the “outgas” function of the surface area analyzer. The resulting mass of dried material was approximately 75 mg. To collect the relative pressure (P/P₀) accurately at each data point, the saturation pressure Pₛ was monitored and measured throughout the analysis of the gases by a dedicated saturation pressure transducer. The specific surface areas were determined using the Brunauer–Emmett–Teller (BET) and Langmuir equations from the N₂ sorption data. For the Langmuir surface areas, the entire set of adsorption data was used. The gravimetric CO₂ adsorption measurement was performed on an IGA-003 gravimetric adsorption instrument (Hiden-Isoschema, UK) over the 0–1 bar range at 273 and 298 K. Prior to the sorption measurement, the same evacuation procedures used for the low-pressure gas sorption measurements were performed with sample quantities of approximately 100 mg; roughly 70 mg of fully desolvated sample was obtained. At each pressure, the sample mass was monitored until equilibrium was reached (within 25 min).

Laser Raman Spectroscopy. The crystals of Cu-NTTA were placed in a vacuum, and after the introduction of 1 MPa of CO₂, Raman spectroscopy measurements were collected using a solid-state 785 nm laser. A laser power of 5% was used to avoid sample degradation under the laser beam during the Raman measurements.

CLSM. The crystals of Zn-NTTA were soaked in a DMF solution of methylene blue dye, and experiments were conducted using the same procedure as for the experiments of dye uptake. The bright field images and confocal images of the obtained samples were scanned at λₑm = 650–750 nm and exited by 635 nm through a 405/488/635 nm filter.

Preparation of Zn-NTTA@ (1a) and Zn-NTTA@ (2a). Zn-NTTA was first soaked in acetonitrile solution (24 h) for guest molecule exchange and fully dried in a vacuum oven (100 °C, 2 h) to eliminate the acetonitrile molecules. Crystals of Zn-NTTA@ (1a) were obtained by soaking the treated Zn-NTTA (0.05 mmol) in a glycidyl phenyl ether solution (10 mmol) for 24 h. Zn-NTTA@ (2a) was obtained by soaking the treated Zn-NTTA (0.05 mmol) in a styrene oxide solution (10 mmol) for 24 h.

### Table 1. Crystallographic and Structural Refinement Data

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**RESULTS AND DISCUSSION**

**Synthesis and Characterization of Zn- and Cu-MOFs.** The solvothermal reaction of H$_2$NTTA and Zn(NO$_3$)$_2$·6H$_2$O generated cube-shaped, light-yellow Zn-NTTA crystals of Zn$_2$(NTTA)$_3$·(H$_2$O)$_2$·(OH)$_2$ in 60% yield. Elemental and PXRD analyses revealed that the bulk sample consisted of a pure single phase (Figure S6). The single X-ray crystal structure revealed that the Zn-NTTA crystallizes in space group Fm$ar{3}$m and that two types of dinuclear inorganic paddlewheel molecular building blocks were present in the crystal structure. Type I consisted of two zinc ions exhibiting the expected square pyramidal geometry \{Zn$_2$(OOC$^-$)$_4$(H$_2$O)$_2$\}$_2$ with each coordinated to three oxygen atoms of four carboxylates and one axial water molecule (ZnO$_5$). Type II consisted of two zinc ions arranged in a triangular pyramidal geometry \{Zn$_2$(OOC$^-$)$_3$(OH)$_2$\}, with each coordinated to three oxygen atoms of three carboxylates and one axial hydroxide ion; this structure is unprecedented among similar ligands (Figure 1a). The carboxyl groups of the 24 isophthalate moieties from the organic ligands connect 6 Zn$_2$(OOC$^-$)$_4$ and 8 Zn$_2$(OOC$^-$)$_3$ paddlewheel units together to form an ideal tetrahedron hexahedron (tetra-H$_6$) (Figure 1b), and three of these units are connected by an organic linker to create a (3,28)-connected isoreticular rht-type framework (Figure 2a). The three-dimensional (3D) framework can be viewed as packing the following three types of polyhedral in a 1:2:1 ratio: a tetrahedronhexahedron (tetra-H$_6$, yellow), a truncated tetrahedron (T-T$_d$, violet) and a truncated octahedron (T-O$_b$, royal blue). Whereas the vertexes of T-T$_d$ and T-O$_b$ are 4 \{Zn$_2$(OOC$^-$)$_3$\} paddlewheel units and 6 \{Zn$_2$(OOC$^-$)$_4$\} paddlewheel units, respectively, each truncated triangular face of T-T$_d$ or T-O$_b$ is fully occupied by one ligand (Figure 2b). The diameters of the spheres representing the voids inside these polyhedra are ca. 16.0, 15.6, and 19.0 Å, respectively, resulting in a large solvent-accessible volume (79.7%) and low density (0.454 g cm$^{-3}$) (Figure 1c, d).

The solvothermal reaction of Cu(NO$_3$)$_2$·3H$_2$O with H$_2$NTTA resulted in Cu-NTTA in 70% yield. The single X-ray crystal structure revealed that Cu-NTTA crystallizes in the space group Fm$ar{3}$m. In this structure, 24 isophthalate moieties from ligands connect 12 \{Zn$_2$(OOC$^-$)$_4$\} paddlewheel units to form a metal–organic cuboctahedron (cub-$O_6$), with three of the units connected by an organic linker to afford a noninterpenetrated (3, 24)-connected net that exhibits the same topology as the prototypical rht-type MOF (Figure 3b, Figure S5). The overall structure consists of three polyhedra [cuboctahedron (cub-$O_6$), truncated tetrahedron (T-T$_d$), and truncated octahedron (T-O$_b$)] packed in a 1:2:1 ratio (Figure 3a). The inner sphere diameters for the cub-$O_6$, T-T$_d$, and T-O$_b$ are 15.8, 15.6, and 24.0 Å, respectively. The free volume in fully desolvated Cu-NTTA is approximately 74%, as determined by PLATON.

N$_2$-adsorption/desorption measurements were performed at 77 K after the activation process. The results revealed a
reversible Type I isotherm, which is characteristic of microporous materials. The BET surface area, calculated in the pressure range of $0.03 - 0.109$ $p/p_0$, was found to be $3931 \text{ m}^2\text{g}^{-1}$ (Figure S10), and the total pore volume was $1.27 \text{ cm}^3\text{g}^{-1}$ (Figure 4a). The enhancement of the affinity toward CO$_2$ depends strongly on the polarizing strength of the functional groups. The polarity of the pore surface of Cu-NTTA is greatly enhanced by the -NH–CO- functionality. Because of the enhanced pore surface polarity, the CO$_2$ uptake by Cu-NTTA was as high as $115.6 \text{ cm}^3\text{g}^{-1}$ at $273 \text{ K}$ and $65.5 \text{ cm}^3\text{g}^{-1}$ at $298 \text{ K}$ and 800 mmHg. As shown in Figure 4b, the CO$_2$ uptake at 800 Torr and 298 K for Cu-NTTA is 35 times greater than that of N$_2$. The initial slopes of the CO$_2$- and N$_2$-adsorption isotherms were calculated, and the ratios of these slopes were

Figure 2. (a) (3,28)-connected isoreticular rht-type framework of Zn-NTTA. (b) View of the three types of polyhedra in Zn-NTTA. Spheres represent the void space within the three types of polyhedra (tetra-$H_b$ yellow; T-$T_b$ violet; and T-$T_{10}$ royal blue). Water molecules and H atoms have been omitted for clarity.

Figure 3. Structure of Cu-NTTA. (a) View of the three types of polyhedra in Cu-NTTA. Spheres represent the void space within the three types of polyhedra (cub-$O_b$ blue; T-$T_{10}$ orange; and T-$O_b$ bright green). (b) The typical cuboctahedron (cub-$O_b$). Copper, carbon, nitrogen and oxygen are shown in green, gray, blue, and red, respectively. Hydrogen and solvent molecules were omitted for clarity.

Figure 4. (a) N$_2$-adsorption isotherm (77 K) for Cu-NTTA; (b) adsorption isotherms for CO$_2$ (squares) and N$_2$ (stars) at 273 (black) and 298 K (red). Filled and open symbols represent adsorption and desorption branches, respectively.
used to estimate the adsorption selectivity for CO2 over N2 (Figures S11 and S12). On the basis of these data, the calculated CO2/N2 selectivities were 30:1 at 273 K and 21:1 at 298 K.48

The Raman spectra of the MOFs in a vacuum and after the introduction of 1.0 MPa of CO2 showed peaks at 1,388 cm$^{-1}$, further supporting that CO2 molecules were adsorbed within the MOFs (Figure 5). The −CO-NH- groups in channels are postulated to not only enhance the reaction rate by increasing the concentration of CO2 substrate around the reactive center but also increase the electron cloud density of activated CO2, thereby enabling the formation of the cyclic carbonate ring.51

Dye-uptake studies were performed by soaking Zn-NTTA in a DMF solution containing 2′,7′-dichlorofluorescein. Zn-NTTA exhibits remarkable color changes after taking up 2′,7′-dichlorofluorescein and methylene blue dyes, and these changes can be easily observed with the naked eye (Figure S13). The experiments indicated a quantum uptake equivalent to 5.4% of the weight of the MOFs (Figure 6, left). CLSM of the methylene blue-adsorbed crystals revealed a blue fluorescence response52 that can be assigned to methylene blue (Figure 6, right). The uniform distribution of the dye molecules throughout the crystals suggests that the dyes penetrated deeply into the channels rather than remaining on the external surface.53 These results demonstrate the ability of Zn-NTTA to adsorb organic substrates within its open channels. The high surface areas and large pore volumes of the MOFs make them promising candidates for CO2 capture and sequestration technology.54

**Studies on the Cycloaddition of Carbon Dioxide and Epoxides.** Our catalytic experiments were focused on the cycloaddition of carbon dioxide and epoxides. The reaction of 1a and 2a with CO2 at 0.1 MPa was utilized to investigate the catalytic performance of the different catalysts. The yields of the cyclic carbonates were calculated by 1H NMR. Zn-NTTA exhibits highly efficient catalytic activity for the cycloaddition of 1a with CO2 at 0.1 MPa and 353 K, giving a yield of 61.7%. When the reactant was 2a, the yield was only 20.7%. MOF-150 produced similar results under the same conditions but with yields of only 51.3 and 19.6% for 1a and 2a, respectively.55

Similarly, the catalytic performances of Cu-NTTA and HKUST-1 were studied for the coupling reactions of epoxides with CO2 under the same conditions. Cu-NTTA and HKUST-1 had slight differences with these two types of substrates (yields of 35 and 28.3% for 1a and 24.5 and 23.4% for 2a) (Figure 7). Zn-NTTA and MOF-150 exhibited greater activities with 1a than Cu-NTTA and HKUST-1. We reasoned that the total catalytic efficiency for the cycloaddition of carbon dioxide under mild conditions is primarily attributable to both the activity of the catalytic sites and the dynamics of the
substrate and product transformation during the heterogeneous reaction.

As shown in Figure 8, the emerging peaks at 1040 cm\(^{-1}\) in the IR spectrum between Zn-NTTA, free epoxides and Zn-NTTA@ (1a), which correspond to the characteristic peaks of \(\nu_{\text{C}^{-}\text{O}^{-}\text{C}}\), and the obvious shifts of the \(^1\)H NMR spectrum of Zn-NTTA@ (1a) relative to that of the free 1a suggested the adsorption and activation of the 1a in the MOF channels. The cooperative weak interactions enforced the spatial proximity between the adsorbed substrates and the zinc ions, further enhancing the compatibility between the activated intermediates of the coupling reactions. The open zinc ions in the pores of Zn-NTTA can serve as Lewis acid catalytic sites to activate the epoxy ring through the oxygen atom of the epoxide and as charge-dense binding sites that capture carbon dioxide because of their compatible quadrupole moment and polarizability.57,58 Furthermore, the incorporation of acylamide groups into the decorated MOFs enhanced the CO\(_2\) fixation. From a mechanistic perspective, the reaction is initiated by Br\(^{-}\) generated from TBABr, which attacks the less-hindered methylene C atom of the epoxide to open the epoxy ring.59,60 The activated epoxide intermediate reacts with activated carbon dioxide to yield a cyclic carbonate with high efficiency and selectivity.

The stability of the catalyst is also an important indicator in the study of catalytic reactions. The catalyst stability in the cycloaddition reaction at higher temperature and pressure was investigated. In a typical experiment, the reactions were conducted in an autoclave reactor using the epoxide (20 mmol) with carbon dioxide purged to 1.0 MPa in a solvent-free environment at 373 K. In the presence of 0.3 mmol of TBABr, the loading of 0.25 mol % ratio of Zn-NTTA (based on a paddlewheel unit) resulted in an almost complete conversion (yield ~98\%) within 8 h (Figure 9a, Table S2 and Figure S16). The turnover frequency (TOF) was approximately 2000 per mole of catalyst per hour.

When the reactant was styrene oxide, the yield was approximately 94\% after 24 h under the same conditions (Table S3 and Figure S17). The introduction of oxiran-2-ylmethoxy or a methoxy group to the phenyl ring resulted in yields of approximately 97 and 82\% of the respective products under the same reaction conditions (Table 2). Loading excessive glycidyl phenyl ether (87.5 mmol) with the same quantity of Zn-NTTA (5 \(\mu\)mol, based on a paddlewheel unit) resulted in an initial TOF of up to approximately 7000 per mole of paddlewheel unit per hour. With the size of the microcrystals reduced to 5 \(\mu\)m by grinding Zn-NTTA and Cu-NTTA crystals, the reaction of 1a with CO\(_2\) giving the same conversion to that of the as-synthesized materials at the same conditions (Figure S20). It seems that the size of the crystals did not dominate the catalysis directly.

Cycloaddition of CO\(_2\) to Epoxides Using Mixed Gas. Coal-burning electric power plants are a major source of carbon dioxide accumulation in the Earth’s atmosphere.61 The exhaust from coal-fired power stations is a mixture that is approximately 14\% carbon dioxide, 80\% nitrogen, and 6\% oxygen.62 The capture and separation of carbon dioxide from power plant flue gas represents a large proportion of the total cost of carbon capture and storage. Additionally, the temperature of these waste gases is very high.63 We adopted a mixed gas without
further separation and purification from other gases as the carbon dioxide source without altering any other conditions (373 K, 20 mmol of epoxides, 0.3 mmol of TBABr, and Zn-NTTA (5 μmol, based on a paddlewheel unit)). In a typical experiment, the mixture was discharged, and fresh mixed gas was purged to maintain the pressure of the system every hour. The yield of carbonate was 87.3% and 43.8%, and no other byproducts were observed after 8 h (Figure 7 and Figure S19). These results are comparable with those obtained under mild conditions (0.1 MPa of pure carbon dioxide). Thus, the use of the mixed gas (1.0 MPa, with a partial pressure of carbon dioxide of approximately 0.1 MPa) did not reduce the catalyst activity and demonstrated that the separation and purification of CO₂ are not required.

A typical composition of coal-fired flue gas comprises 12.5—12.8% CO₂, 6.2% H₂O, 4.4% O₂, 50 ppm of CO, 420 ppm of NOₓ, 420 ppm of SO₂, and 76.0—77.0% N₂. In terms of the cyclo-addition of epoxides with CO₂, the effect of the trace gases (CO, NOₓ, SO₂) and N₂ can be ignored. Perhaps the most influence over the reaction is O₂ and H₂O. For the practical use of this catalyst in industry, the cycloaddition of epoxides with wet gases was investigated. In a typical experiment, the reactions were conducted in an autoclave reactor using the 1a (20 mmol) and H₂O (100 μL) with carbon dioxide or mixed gases purged to 1.0 MPa and then reacted at 373 K for 8 h. As shown in Figure 10, the catalyst activity was not affected by moisture, and the indices of the PXRD patterns of the Zn-NTTA and Cu-NTTA bulk samples filtered from the catalytic reaction revealed that the crystallinities were maintained (Figures S21 and S22). Because raw power plant flue gas is always considered to be a negative-cost feedstock, the combination of selective capture and catalytic transformation enables the use of power plant flue gas without any separation and purification for CO₂ chemical fixation; thus, this material

Table 2. Catalyzed Coupling of Epoxides with Carbon Dioxide

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Zn-NTTA</th>
<th>Cu-NTTA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield (%)</td>
<td>TON</td>
<td>Yield (%)</td>
</tr>
<tr>
<td>1</td>
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<td>3920</td>
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<tr>
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<td>2560</td>
<td>56.3</td>
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<tr>
<td>3</td>
<td>97.2</td>
<td>3880</td>
<td>97.4</td>
</tr>
<tr>
<td>4</td>
<td>82.5</td>
<td>3300</td>
<td>89.4</td>
</tr>
</tbody>
</table>

“Reaction conditions: epoxide (20 mmol), catalyst (5 μmol, based on a paddlewheel unit), and TBABr (0.3 mmol) under carbon dioxide (1 MPa), 373 K, and 8 h. The yields were determined by 1H NMR analysis.” Under common conditions, but without the epoxide (10 mmol).
has broad prospects for practical application in the chemical industry.

Recyclability is an essential feature of any catalyst considered for use in industrial applications. Because of the small amount of catalyst used in a reaction, the unavoidable loss of the catalyst will decrease the yield after each reaction. Thus, experiments were performed using large excesses of 1a (87.5 mmol) and Zn-NTTA (5 μmol, based on a paddlewheel unit) while maintaining the pressure of the system (from 0.4 to 1.0 MPa) through the addition of carbon dioxide. No other reaction conditions were altered. A small aliquot of the supernatant reaction mixture was analyzed by 1H NMR to calculate the reaction yields. The catalyst was filtered and washed with dichloromethane after 12 h of reaction. Then, fresh 1a (87.5 mmol) and cocatalyst TBABr (0.3 mmol) were added, and the system was purged with carbon dioxide to 1.0 MPa; this process was repeated five times. These time-course and recycling experiments resulted in a total product amount of approximately 282 mmol and total turnover number (TON) and recycling experiments resulted in a total product amount of 110,000 per mole of catalyst per paddlewheel unit after 30 rounds. These time-course and recycling experiments resulted in a total product amount of 110,000 per mole of catalyst per paddlewheel unit after 30 rounds.

Figure 10. Cycloaddition of epoxides with wet gases. Reaction conditions: 1a (20 mmol), H2O (100 μL), catalyst (5 μmol, based on a paddlewheel unit), and TBABr (0.3 mmol) under carbon dioxide or mixed gas (1.0 MPa) at 373 K for 8 h.

In summary, a new rh-type MOF with two types of dinuclear paddlewheel building blocks—{Zn2(OOC−)4} and {Zn2(OOC−)3}—was created by incorporating an acylamide-functionalized linker. We subsequently used these MOFs to combine efficient carbon dioxide capture and chemical fixation within a one-pot catalytic reaction. The NH–CO groups within the MOFs enhanced the CO2 uptake amounts and the selectivity for CO2 over N2, making the MOFs excellent candidates for postcombustion carbon capture. These MOFs feature high catalytic activity, rapid dynamics of the substrate-to-product transformation, and excellent stability, with TON values up to 110,000 per paddlewheel unit after 30 rounds. Thus, they are promising heterogeneous catalysts for CO2 cycloaddition to value-added cyclic carbonates. The combination of selective capture and catalytic transformation in a one-pot reaction enables using a negative-cost feedstock—raw power plant flue gases—without any separation and purification, revealing the broad prospects for the practical application of CO2 chemical fixation in the chemical industry.

## CONCLUSIONS

In summary, a new rh-type MOF with two types of dinuclear paddlewheel building blocks—{Zn2(OOC−)4} and {Zn2(OOC−)3}—was created by incorporating an acylamide-functionalized linker. We subsequently used these MOFs to combine efficient carbon dioxide capture and chemical fixation within a one-pot catalytic reaction. The NH–CO groups within the MOFs enhanced the CO2 uptake amounts and the selectivity for CO2 over N2, making the MOFs excellent candidates for postcombustion carbon capture. These MOFs feature high catalytic activity, rapid dynamics of the substrate-to-product transformation, and excellent stability, with TON values up to 110,000 per paddlewheel unit after 30 rounds. Thus, they are promising heterogeneous catalysts for CO2 cycloaddition to value-added cyclic carbonates. The combination of selective capture and catalytic transformation in a one-pot reaction enables using a negative-cost feedstock—raw power plant flue gases—without any separation and purification, revealing the broad prospects for the practical application of CO2 chemical fixation in the chemical industry.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b13928.

- 1H NMR and 13C NMR, XRD, gas adsorption studies, and catalysis details (PDF)
- Crystallographic information file for Zn-NTTA (CIF)
- Crystallographic information file for Cu-NTTA (CIF)

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**Author Contributions**

X.Y.G., J.F.B., and C.Y.D. conceived and designed the experiments. X.Y.G. and C.H. performed the experiments. C.H., J.F.B., and C.Y.D. contributed materials and analysis tools. X.Y.G., J.F.B., and C.Y.D. cowrote the paper. All authors discussed the results and commented on the manuscript.

**Notes**

The authors declare no competing financial interest.

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