An uncommon multicentered Zn^I-Zn^I bonds-based MOF for CO_2 fixation with aziridines/epoxides

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Materials and methods.

All reagents and reactants were used directly in the experiment after being purchased by a commercial approach. All Powder X-ray diffractions and relevant thermos-diffractogram measurements were carried out on Ultima IV X-ray diffractometer using Cu-Kα radiation. The Elemental analysis (EA) of C, H and N was performed applying a Perkin-Elmer elemental analyzer. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos Axis Ultra DLD (delay-line detector) spectrometer equipped with a monochromatic Al-Kα X-ray source (1468.6 eV). Thermogravimetric analysis (TGA) was recorded on a Netzsch TG 209 TG-DTA analyzer in N_2 atmosphere from room temperature to 800 °C with a heating rate of 10 °C min^{-1}. Isotherm of CO_2 and N_2 was measured by a Quantachrome Autosorb-1 volumetric adsorption analyser. The metal content was recorded by inductively coupled plasma-atomic emission spectrometry (ICP-AES) atomic emission spectrometric analysis (IRIS Advantage). The electron paramagnetic resonance (EPR) measurement of **1** was done on a Bruker EMX-6/1 spectrometer in X-band, with a modulation frequency of 100 kHz and at room temperature. Variable-temperature magnetic susceptibilities were obtained on a Quantum Design MPMS-XL7 magnetometer. ^1H NMR spectra were recorded on a Bruker 300 or 400 spectrometer in $CDCl_3$ and $CDCl_3$ (7.26 ppm) was used as an internal reference.

Preparation of compound 1

The mixture of KC_4N_3 (0.1 mmol, 0.0128 g), NaN_3 (0.6 mmol, 0.0390 g), $Zn(NO_3)_2·6H_2O$ (0.3 mmol, 0.0892 g) and DMF (5 mL) were mixed in a 25 mL Teflon-lined stainless vessel, sealed and heated to 200 °C for 72 h in an oven and cooled down to 30 °C with the rate of 2.4 °C/h. Colorless polyhedral crystals were obtained and washed with ethanol. yield: 38% based on $Zn(NO_3)_2·6H_2O$. Anal. cald. (%) for $C_{12}H_{20}N_{48}O_4Zn_8K_{1.2}Na_{2.8}$ (Mr = 1535.17): C 9.40 H 1.29, N 43.86; Found: C 9.39, H 1.31, N 43.79. **Caution!** Owing to the potentially explosive nature of NaN_3, only a small amount of material should be used and handled with care!

Catalyzing reaction of CO_2 and aziridines

In a typical experiment, activated sample **1** (20 mg, 0.052 mmol) after being grinded was added into 10 mL autoclave with a magnetic stir bar, and substrate **1a** (294.4 mg, 2 mmol) and co-catalyst TBAB (32.4 mg, 0.1 mmol, 5 mol% relatives to **1a**) were put into the reaction tube.

Then the autoclave was capped under 2 MPa CO_2 and stirred for 12 h at a certain temperature. After the reaction, the mixture was dissolved in dry CH_2Cl_2, and the yield of corresponding oxazolidinones of 3-ethyl-5-phenyl-oxazolidin-2-one (**2a**) and 3-ethyl-4-phenyloxazolidin-2-one (**3a**) was determined by ^1H NMR analysis employing 1,3,5-trimethoxybenzene (42.1 mg, 0.25 mmol) as an internal standard.

Catalyzing reaction of CO_2 and epoxides

The mixture of activated catalyst **1** (10 mg, 0.026 mmol), substrate **A_1** (240.0 mg, 2 mmol) and co-catalyst TBAB (32.4 mg, 0.1 mmol, 5 mol% relatives to **A_1**) were added into the reaction tube equipped with CO_2 balloon. After the reaction, the mixture was dissolved in dry CH_2Cl_2 and the corresponding yield of cyclic carbonates **A_1** was determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene (42.1 mg, 0.25 mmol) as an internal standard.

Activation Reaction of aziridinesand CO_2

1a, **1a**/TBAB, **1a**/**1**, and **1a**/TBAB/**1** systems were performed in four Schlenk tubes capped to CO_2 balloons and stirred at 70 °C for 2 h, then the appropriate amount of samples were analyzed rapidly by ^1H NMR spectroscopy ($CDCl_3$).

Activation Reaction of epoxides and CO_2

A_1, **A_1**/TBAB, **A_1**/**1**, and **A_1**/TBAB/**1** systems were performed in four Schlenk tubes capped to CO_2 balloons, and stirred at 70 °C for 2 h, then the appropriate amount of samples were analyzed rapidly by ^1H NMR spectroscopy ($CDCl_3$).

X-Ray crystallography

Suitable polyhedral crystals of **1** were placed in a cooled N_2 gas stream at ~ 124 K for the crystallographic data collection on a SuperNova single crystal diffractometer equipped with graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å). Data reduction included absorption was performed by using the SAINT program.[1] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXS-97 and SHELXL-97 programs.[2] All the hydrogen atoms were placed geometrically and refined using a riding model. As for compound **1**, we used PLATON/SQUEEZE[3] to remove the diffraction from the solvent region. The number of isolated H_2O molecules was determined by TG analysis and elemental analysis.

Table S1. Crystals data and structure refinement for **1**.

Identification code	**1**
CCDC	1822099
Empirical formula	$C_{12}H_{20}N_{48}O_4Zn_8K_{1.2}Na_{2.8}$
Formula weight	1535.17
Temperature/K	123.60(14)
Crystal system	cubic
Space group	*Im-3*
a/Å	14.5713(7)
b/Å	14.5713(7)
c/Å	14.5713(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3093.8(4)
Z	24
$F(000)$	1427.0
Goodness-of-fit on F^2	1.569
Final R indexes [I>=2σ (I)]	$R_1 = 0.1208$, $wR_2 = 0.3717$
Final R indexes [all data]	$R_1 = 0.1399$, $wR_2 = 0.3923$

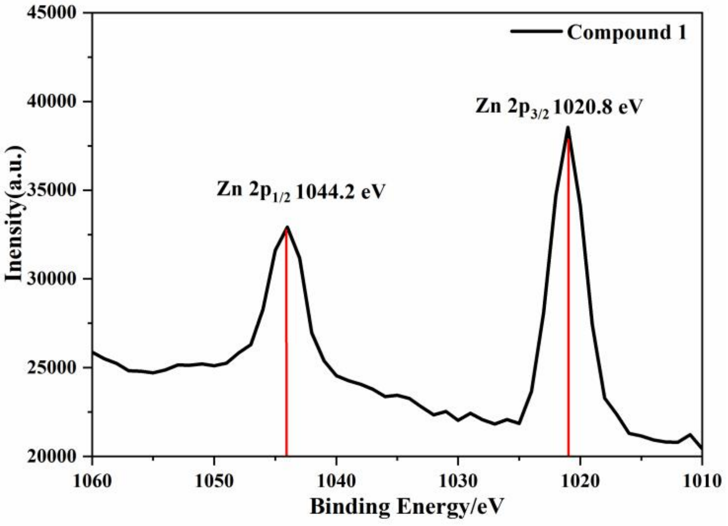
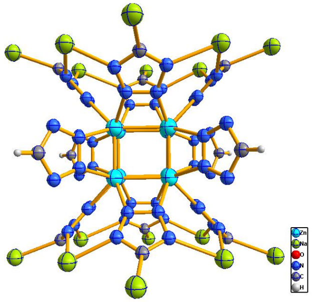
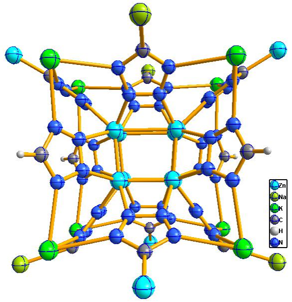
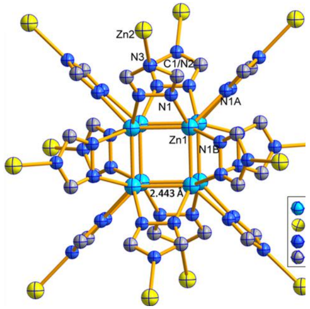
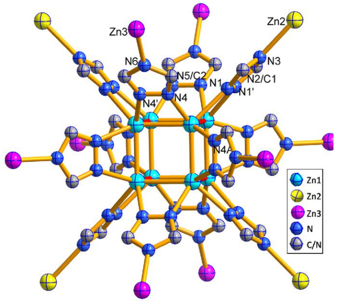
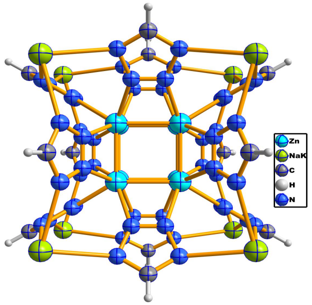


Fig. S1. XPS spectra of Zn in compound **1**, Zn 2p$_{1/2}$ and 2p$_{3/2}$.

Table S2. The detailed structural information of five cluster-based MOFs containing uncommon multicentered Zn^{I}-Zn^{I} bonds.

No.	**Zn_8-1**	**Zn_8-2**	**Zn_8-3**	**Zn_8-4**	**Compound 1**
Formula	$Na_{2.6}K_{1.4}\{[Na(DMF)]_8[Zn^{I}_8(HL)_4(L)_8]\}\cdot 8H_2O\cdot 2H_2L\cdot DMF$	$Na_3K_{2.33}\{K_4[Na(DMF)_3]_{1.33}[Zn^{II}Br]_{1.33}[Zn^{I}_8(HL)_4(L)_8]\}\cdot 2H_2O\cdot 2H_2L\cdot 4DMF$	$\{[Zn^{I}_8Zn^{II}_3(H_2O)_6(HL)_{12}](OH)_2\cdot 13H_2O\}_n$	$\{[Zn^{I}_8Zn^{II}_3(H_2O)_2(HL)_{12}](OH)_2\cdot 13H_2O\}_n$	$\{[K_{1.2}Na_{2.8}Zn^{I}_8(HL)_{12}]\cdot 4H_2O\}_n$
Crystal system	tetragonal	cubic	cubic	tetragonal	cubic
Space group	*I*4/*m*	*P*-43*m*	*Pm*-3*m*	*I*4/*mmm*	*Im*-3
a, *b*, *c*	13.9834(6), 13.9834(6), 18.9790(9)	18.43990(10), 18.43990(10), 18.43990(10)	11.1465(6), 11.1465(6), 11.1465(6)	11.0000(16), 11.0000(16), 21.000(4)	14.5713(7), 14.5713(7), 14.5713(7)
α, *β*, *γ*	90.00, 90.00, 90.00	90.00, 90.00, 90.00	90.00, 90.00, 90.00	90.00, 90.00, 90.00	90.00, 90.00, 90.00
Zn^{I}-Zn^{I} bond lengths (Å)	2.292, 2.4810	2.394, 2.766, 2.2713	2.443	2.412, 2.394	2.357
Zn_8-cluster					
Ref.	P. Cui, et.al., *Nat. Commun.*, 2015, **6**, 6331.	P. Cui, et.al., *Nat. Commun.*, 2015, **6**, 6331.	H. C. Hu, et.al., *Chem. Eur. J.*, 2018, **24**, 3683.	H. C. Hu, et.al., *Chem. Eur. J.*, 2018, **24**, 3683.	This work

HL = tetrazole monoanion

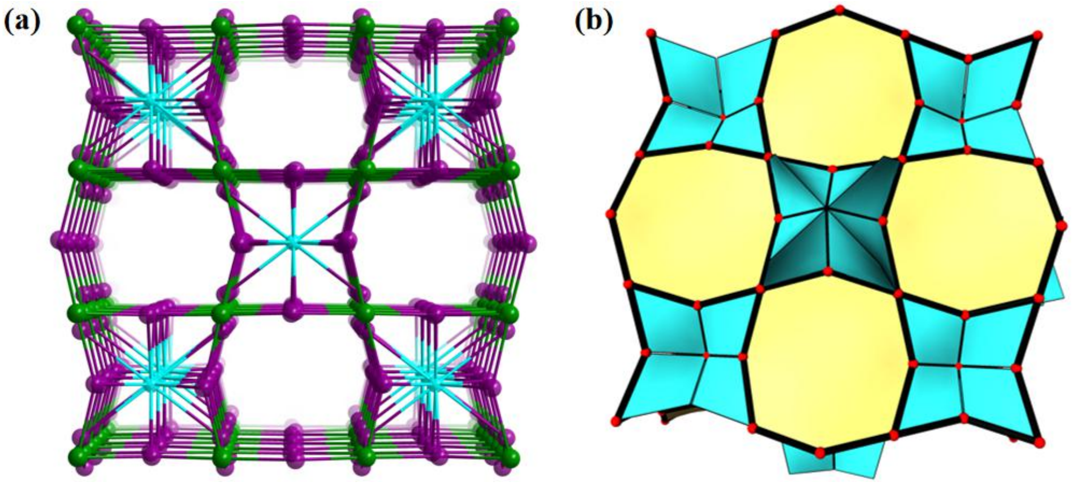


Fig. S2. (a) The topology of framework **1**, purple balls represent Zn_8-clusters, green balls represent K^+ and Na^+ ions, and turquoise balls represent tetrazole monoanions; (b) Tiling representations of **1**.

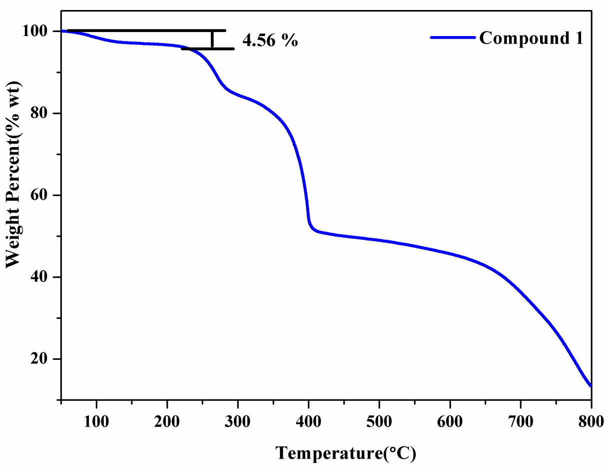


Fig. S3. Thermogravimetric analysis curves of **1**.

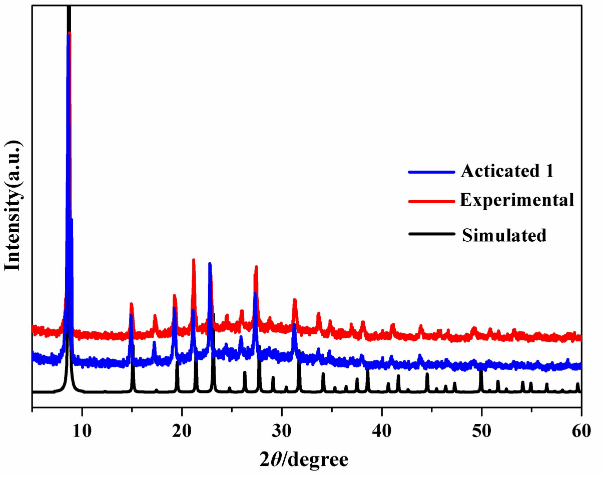


Fig. S4. The PXRD patterns of **1** and activated sample **1**.

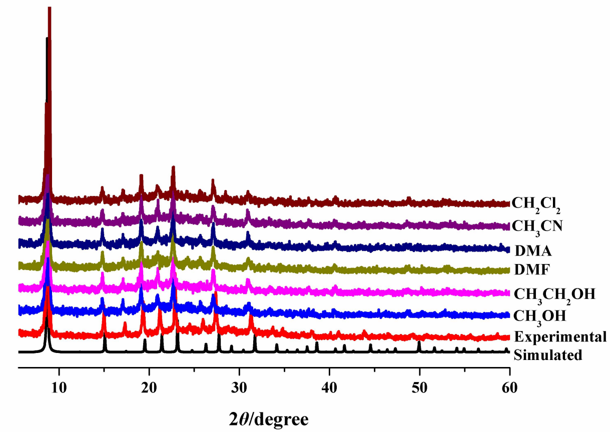


Fig. S5. The PXRD patterns of compound **1** after immersing in several common organic solvents.

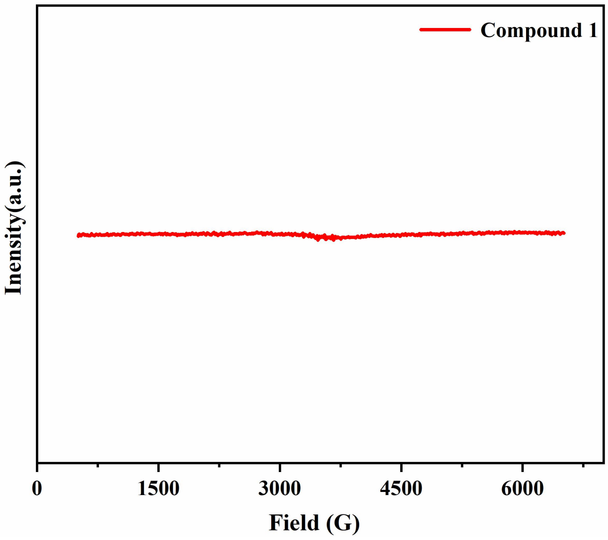


Fig. S6. EPR spectrum of **1**.

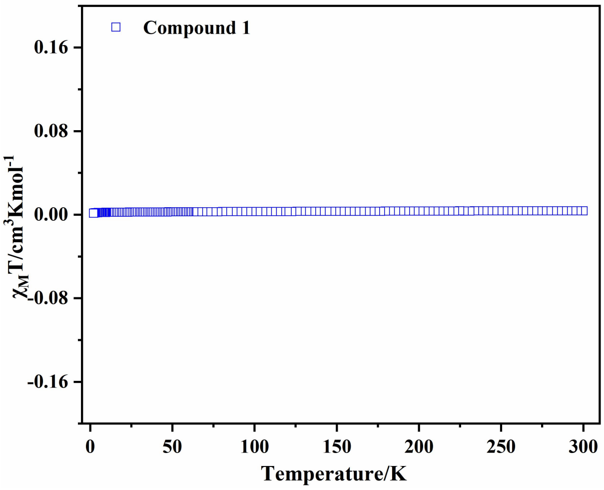


Fig. S7. Temperature dependence of magnetic susceptibilities of **1**.

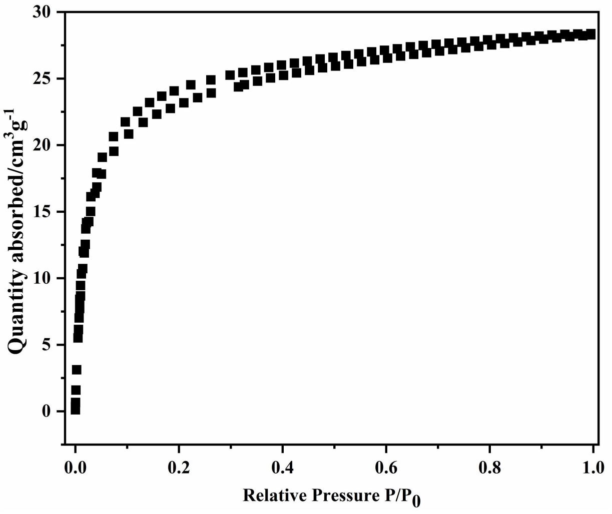


Fig. S8. CO_2 adsorption/desorption of the compound **1** (298 K).

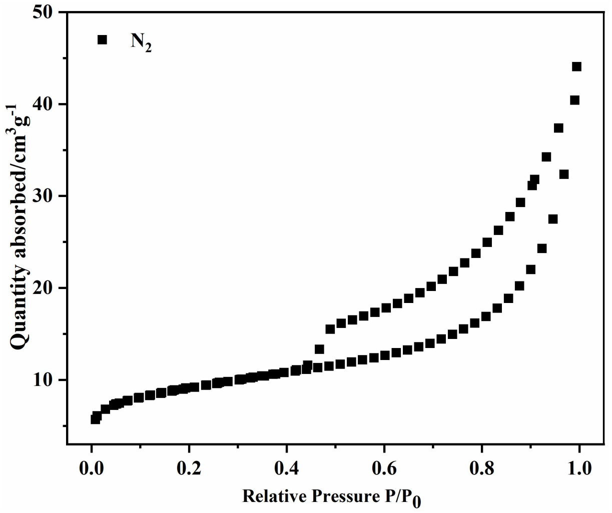
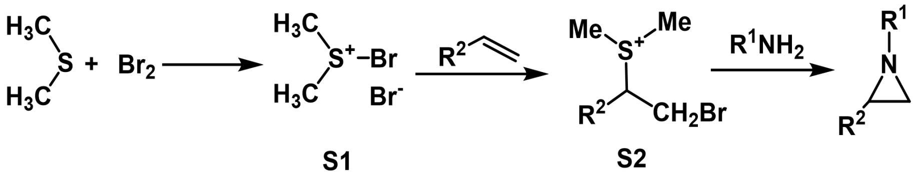


Fig. S9. N_2 adsorption-desorption isotherms of the compound **1**.

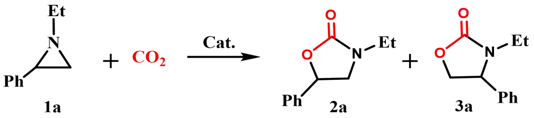
Preparation of aziridines. [4]

The aziridines were prepared as reported methods in previous works (**Scheme S1**).[4] Firstly, bromine (0.2 mol, 32.0 g) was dissolved in 40 mL dry CH_2Cl_2, then was slowly dropped over 30 min to 40 mL CH_2Cl_2 solution containing dimethyl sulfide (0.2 mol, 12.4 g) in the ice-salt bath. Light orange crystals of bromodimethyl sulfonium bromide (**S1**) were gradually generated during the adding process, and **S1** were completely obtained and collected by filtration. Yield: 80%. Secondly, **S1** (160 mmol, 35.56 g) was dissolved in 160 mL CH_3CN, then olefin (160 mmol) was slowly dropped into the solution. The mixture was stirred for 4 h after the addition of all the olefin. The white solid **S2** was gradually generated during the process, and was collected by filtration, dried under vacuum. Yield: 30 - 38.6%. Thirdly, **S2** (10 mmol) was added into 20 mL water at room temperature, then amine (20 - 50 mmol) was slowly added into the solution, and was stirred over 12 h. Then 20 mL of saturated brine was slowly dropped into the mixture. At last, the mixture extracted with diethyl ether (3 × 20 mL), dried with anhydrous Na_2SO_4 overnight and the solvent evaporated under reduced pressure. Thus, aziridines were obtained by distillation under reduced pressure. Yield: 85 - 100%.



Scheme S1. Preparation of aziridines.

Table S3. Cycloaddition reaction of CO_2 and 1-ethyl-2-phenylaziridine under various conditions.[a]



Entry	**1** (mg)	Temp. (°C)	Yield (%)[b]	Regio-sel[c]
1	20	30	74	93:7
2	20	50	>99	93:7
3	20	70	>99	98:2
4	20	100	>99	92:8
5[d]	20	100	87	90:10
6[e]	20	100	>99	92:8
7[f]	0	70	64	89:11
8[g]	0	70	33	98:2
9[h]	0	70	56	91:9
10[i]	0	70	71	98:2

[a] Reaction conditions: 1-ethyl-2-phenylaziridine (**1a**) (294.4 mg, 2.0 mmol), solvent-free, TBAB (32.4 mg, 0.1 mmol), CO_2 (2.0 MPa), 12 h, catalyst **1**; [b] Total yield of **2a** and **3a** determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard; [c] Molar ratio of **2a** to **3a**; [d] CO_2 (1.0 MPa); [e] TBAB (16.2 mg, 0.05 mmol), 2 MPa; [f] TBAB (32.4 mg, 0.1 mmol) and $Zn(OAc)_2$ (19.1 mg, 0.104 mmol); [g] TBAB (32.4 mg, 0.1 mmol) and $Zn(NO_3)_2$ (30.9 mg, 0.104 mmol); [h] TBAB (32.4 mg, 0.1 mmol) and $ZnSO_4$ (16.7 mg, 0.104 mmol); [i] TBAB (32.4 mg, 0.1 mmol) and $ZnCl_2$ (14.2 mg, 0.104 mmol).

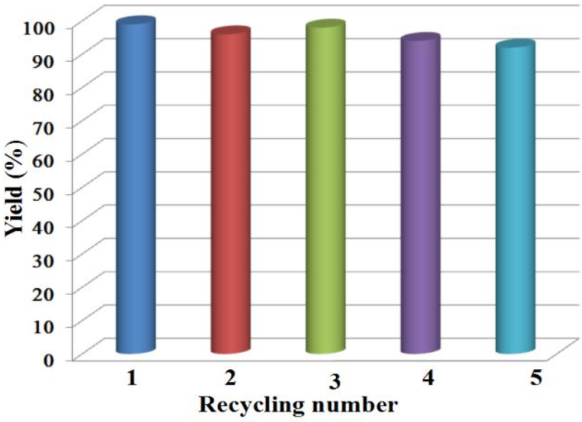


Fig. S10. Recycle tests of compound **1** for cycloaddition reaction of CO_2 and 1-ethyl-2-phenylaziridine.

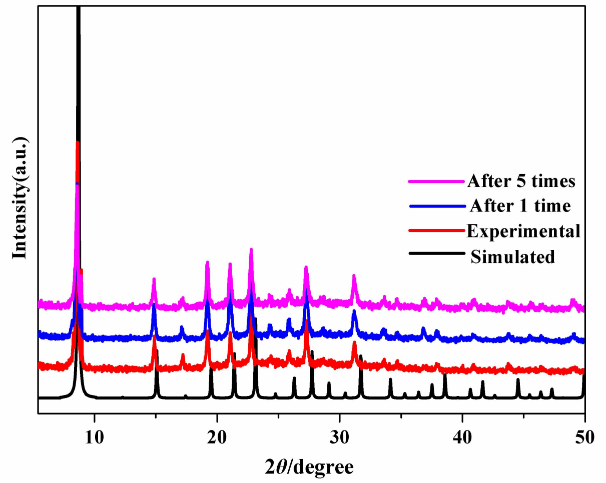


Fig. S11. The PXRD patterns of **1** after five cyclic cycloaddition reactions of CO_2 and 1-ethyl-2-phenylaziridine.

Table S4. The ICP-AES results of **1** after cyclic cycloaddition reaction of 1-ethyl-2-phenylaziridine and CO_2.

Sample	Zn^{2+} (%) (after the first time)	Zn^{2+} (%) (after the fifth time)
1	0.68	1.29

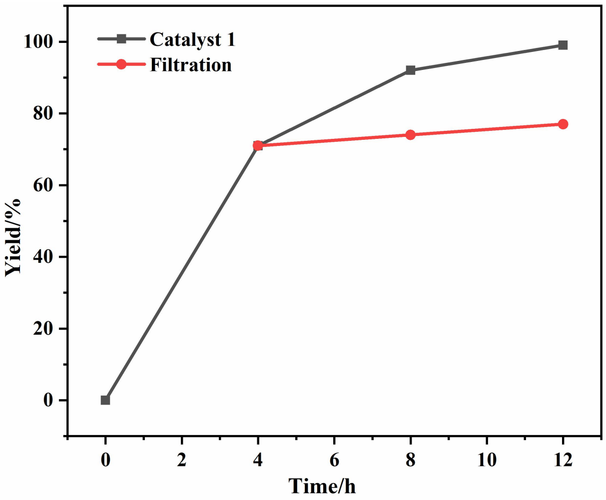
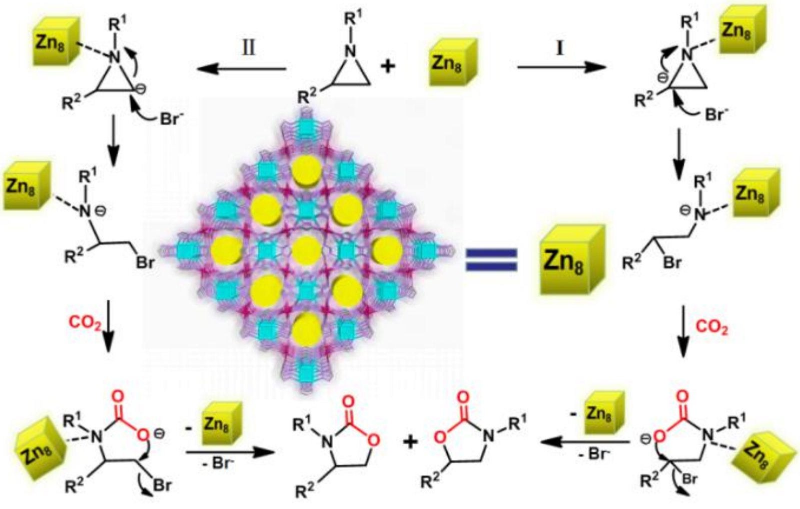


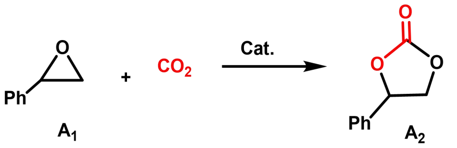
Fig. S12. Catalyst filtration test for the cycloaddition of 1-ethyl-2-phenylaziridine and CO_2.



Scheme S2. A representation of the tentatively proposed catalytic mechanism for the cycloaddition of CO_2 and aziridines into oxazolidinones catalyzed by **1** (L^+ = tetra-*n*-tertbutylammonium).

The cycloaddition of CO_2 and epoxides to form cyclic carbonates was also tested at mild reaction conditions. The reactions of CO_2 with phenylethylene oxide (**A_1**) under different conditions were tried to optimize the reaction. As shown in **Table S5**, ESI†, the optimized reaction temperature is 70 °C (entries 1-7, **Table S5**, ESI†). Then the absence of cocatalyst made the starting material be recovered quantitatively (entry 8, **Table S5**, ESI†). In addition, the yield of **A_2** decreased with the reduction of TBAB amount or without catalyst **1**, indicating cocatalyst TBAB and catalyst **1** have a synergistic effect on the reaction. When the reaction time is 9 h, the yield of **A_2** is only 74%. Thus, the optimized reactions are 70 °C under 0.1 MPa CO_2 balloon with **1** (10 mg) and TBAB (32.4 mg). After having established a cyclization protocol, the reactivity of various epoxides was examined to further explore the utility (**Table S6**, ESI†). Notably, several typical cyclic carbonates can be obtained in comparatively excellent yields, clearly manifesting **1** can catalyze cycloaddition reaction with relatively extensive epoxides.

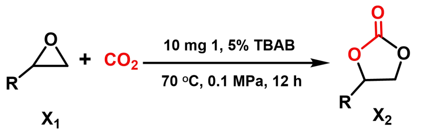
Table S5. Cycloaddition reaction of CO_2 and phenylethylene oxide under various conditions.[a]

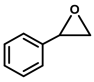
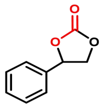
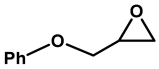
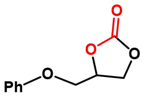
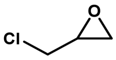
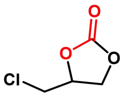
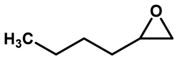
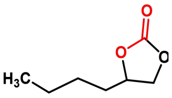
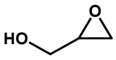
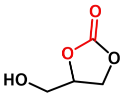


Entry	Catalyst **1** (mg)	TBAB (mg)	Temp. (°C)	Yield (%)[b]
1	10	32.4	30	24
2	10	32.4	40	39
3	10	32.4	50	36
4	10	32.4	60	75
5	10	32.4	70	99
6	10	32.4	80	99
7	10	32.4	90	99
8	10	0	70	0
9	10	16.2	70	86
10	0	32.4	70	56
11[c]	10	32.4	70	74
12[d]	0	32.4	70	82
13[e]	0	32.4	70	50
14[f]	0	32.4	70	78
15[g]	0	32.4	70	45

[a] Reaction conditions: Phenylethylene oxide (240.0 mg, 2.0 mmol), solvent-free, TBAB, CO_2 (0.1 MPa), 12 h, 10 mg catalyst **1** (loading based on metal center Zn, about 5.4 mol%); [b] Total yield of **A_2** determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard; [c] 9h; [d] TBAB (32.4 mg, 0.1 mmol) and $Zn(OAc)_2$ (9.5 mg, 0.054 mmol); [e] TBAB (32.4 mg, 0.1 mmol) and $Zn(NO_3)_2$ (15.5 mg, 0.054 mmol); [f] TBAB (32.4 mg, 0.1 mmol) and $ZnSO_4$ (8.4 mg, 0.054 mmol); [g] TBAB (32.4 mg, 0.1 mmol) and $ZnCl_2$ (7.1 mg, 0.054 mmol).

Table S6. Synthesis of various cyclic carbonates from CO_2 and epoxides by catalyst **1**.[a]



Entry	Substrates	Products	Yield (%)[b]
1	 **A1**		>99
2	 **B1**		99
3	 **C1**		99
4	 **D1**		99
5	 **E1**		65

[a] Reaction conditions: epoxides (2.0 mmol), solvent-free, 10 mg of catalyst **1** loading (based on metal center, about 2.7 mol%), TBAB (32.4 mg, 0.1 mmol), CO_2 (0.1 MPa), 12 h; [b] Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

For the practical application, the recyclable performance of catalyst **1** for the cycloaddition reaction of CO_2 with phenylethylene oxide also was explored (**Fig. S13**, ESI†). Catalyst **1** was separated from the reaction mixture by centrifugation and filtration, and then washed by dry CH_2Cl_2. The recycling tests show the catalytic activity keeps basically constant, and the PXRD patterns of sample **1** after five runs still keep well consistent with the original one (**Fig. S14**, ESI†). ICP-AES measurement of reaction filtrate after the first and the fifth recycling processes uncovered that only $< 3\%$ Zn^{2+} was observed (**Table S7**, ESI†), which further proved the stability of the basic framework in **1**. A catalyst filtration test for the cycloaddition of epoxides with CO_2 was also confirmed (**Fig. S15**, ESI†), the reaction rate dramatically decreased after removal of catalyst at 4 h, proving that **1** is a heterogeneous catalyst.

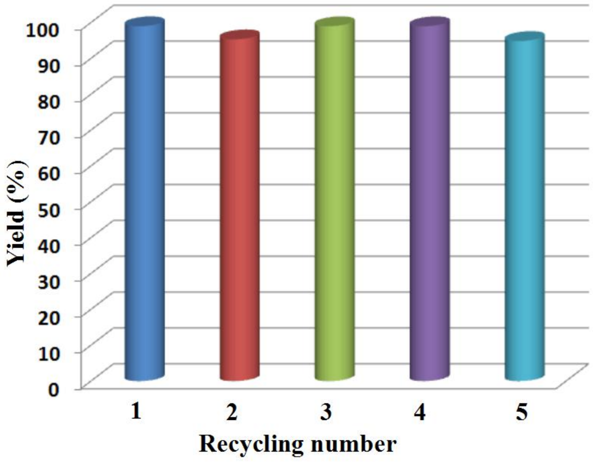


Fig. S13. Recycle tests with compound **1** for the cycloaddition reaction of CO_2 and phenylethylene oxide.

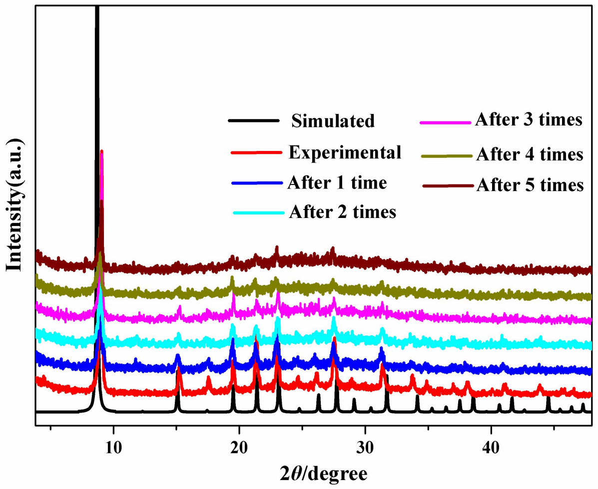


Fig. S14. The PXRD patterns of **1** after five times reactions of phenylethylene epoxide and CO_2.

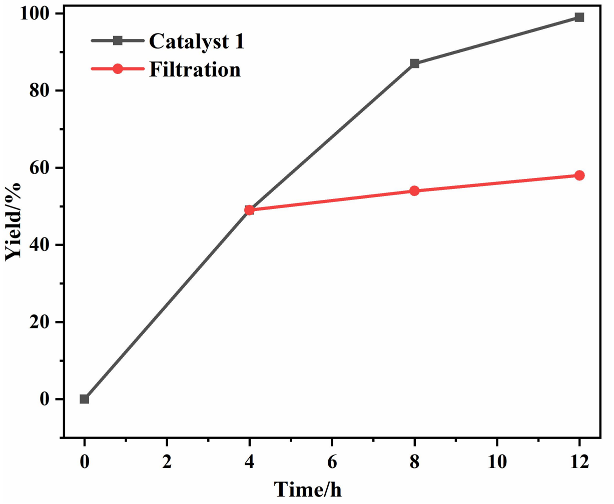


Fig. S15. Catalyst filtration test for the cycloaddition of phenylethylene epoxide and CO_2.

Table S7. The ICP-AES results of **1** after cyclic cycloaddition reaction of phenylethylene epoxide and CO_2.

Sample	Zn^{2+} (%) (after the first time)	Zn^{2+} (%) (after the fifth time)
1	2.23	1.96

To explore the substrate activation of catalyst **1**, ^1H NMR measurements of phenylethylene oxide after adding TBAB, **1** or **1**/TBAB were also carried out to monitor the activation of phenylethylene oxide molecules (**Fig. S16**, ESI†). In comparison with the spectroscopy of pure phenylethylene oxide, the spectra after adding **1**/TBAB exhibit broad and dwarf peaks of C-H (d ≈ 3.83, 3.10, 2.78 ppm), which suggests that phenylethylene oxide can be activated by **1**.[5] Based on previous results,[6] the reaction mechanism was explored. The different zinc sources such as $Zn(OAc)_2$, $Zn(NO_3)_2$, $ZnSO_4$ and $ZnCl_2$ (entries 12-15, **Table S5**, ESI†) were measured to prove the catalytic activity. The yield of $\mathbf{A_2}$ is less than that of catalyst **1**, which is originated from the interaction between Zn^{2+} and Br^- restricting the nucleophilicity of Br^-.[7] The catalyst **1** shows higher activity not only the enrichment ability of CO_2 and substrate molecules but also the constraint of interaction between Zn^{2+} and Br^-, thus more free Br^- can attack epoxides. A plausible mechanism is depicted as **Scheme S3**, ESI†: (a) Catalyst **1** can enrich epoxides and CO_2, and Lewis acidic zinc sites in **1** binding with O atoms of epoxides can activate substrates; (b) The less-hindered carbon atom of the activated epoxides is attacked free Br^-, resulting from the opening of the epoxide ring; (c) CO_2 reacts with O^- of the ring-opened intermediate to obtain alkylcarbonate salt; (d) O^- attacks carbon atom of the C-Br, and the corresponding product is obtained through intramolecular ring closure, thus, the cyclic carbonate is successfully obtained.

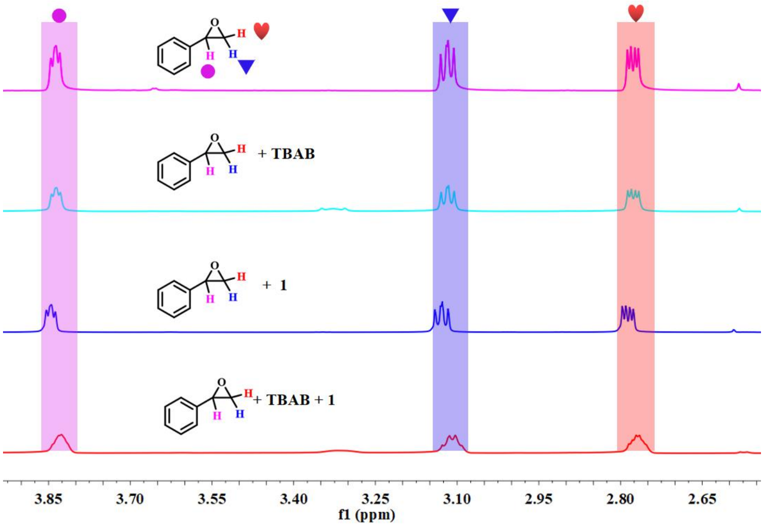
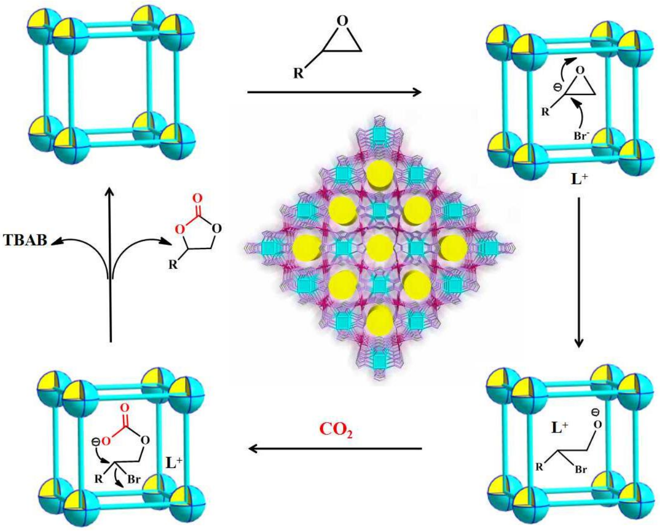


Fig. S16. Spectral changes on attempting activation of C-O bond by different systems (in $CDCl_3$).



Scheme S3. A representation of the tentatively proposed catalytic mechanism for the cycloaddition of CO_2 and epoxides into cyclic carbonates catalyzed by the catalyst **1** (L^+ = tetra-*n*-tertbutylammo-nium).

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