Supporting Information

Two novel Ln_8 clusters bridged by CO_3^{2-} and effectively converting CO_2 into oxazolidinones and cyclic carbonates

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Experimental Section

Materials and methods

Triethanolamine was obtained from Sigma-Aldrich Co. Ltd., lanthanide salts ($Nd(NO_3)_3 \cdot 6H_2O$, $Sm(NO_3)_3 \cdot 6H_2O$) were obtained from Energy Chemical Co. Ltd., Aladdin Co. Ltd., acetonitrile and triethylamine were commercially purchased from Sigma-Aldrich Co. Ltd.. All chemical reagents and solvents used in synthetic studies were obtained from commercial sources, of reagent grade, and employed without further purification.

Physical measurements

Elemental analyses data (C, H, and N) were obtained on a PerkinElmer 2400 analyzer. The FT–IR spectra data were recorded via a PerkinElmer FT-IR spectrophotometer using KBr pellets from 4000 to 400 cm^{-1}. PXRD were performed on a Rigaku Ultima IV instrument at room temperature with the scan speed of 10° min^{-1} and the scan range of 2θ from 5–50° through Cu Kα radiation (λ = 1.54056 Å). TGA analyses data were collected on Perkin-Elmer TGA 4000 analyzer with the heating rate 10 ℃ / min form 30 to 800 °C under air atmosphere. UV−vis spectra were measured on JASCOV-570 spectrophotometer at room temperature. ^1H NMR spectra were collected on a Bruker spectrometer in $CDCl_3$ at 400 MHZ. The XPS data was collected on a Kratos Axis Ultra DLD multi-technique X-ray spectrometer. (ICP) tests were carried out by an ICP-9000(N+M). High resolution mass spectrum was performed on a Thermo Fisher Trace 1300 +ISQ LT instrument.

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Catalytic Experiment of CO_2 with aziridines.

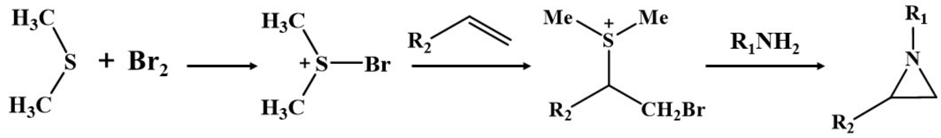
In a typical experiment, cluster **1** (30 mg) was ground and put into a 10 mL autoclave equipped with a magnetic stir bar. Then 1-ethyl-2-phenylaziridine (294.4 mg, 2.0 mmol) and tetrabutylammonium bromide (TBAB) (32.2 mg, 0.1 mmol) were also added into the reaction tube. Then the autoclave was capped under 1 MPa CO_2 and stirred at 70 °C for 10 h. Afterwards, the mixture was dissolved in CH_2Cl_2. The yield of corresponding oxazolidinones were determined by ^{1}H NMR and 1,3,5-trimethoxy-benzene is used as internal standard. To explore the recycling performance, the catalyst of cluster was collected centrifugally after each reaction, washed with methanol and dried completely for the next cycle.

Catalytic Experiment of CO_2 with styrene oxide.

CO_2, 25 mg cluster, 2 mmol styrene oxide and 3mol % mol TBAB were added into Schlenk tube and stirred at 80 ºC for 12 h. Then 2 mL dichloromethane was added to reactor and the mixture was purified by column chromatography. By 1,3,5-trimethoxybenzene using as internal standard, the yield was calculated by ^{1}H NMR spectroscopy. To explore the recycling performance, the catalyst of cluster was collected centrifugally after each reaction, washed with methanol and dried completely for the next cycle.

Synthesis of aziridines

At first, liquid bromine (0.2 mol) is added to dried dichloromethane (40 mL). At 0 °C, the mixture above was dropwise added to a mixture which consists of 0.2 mol dimethyl sulfide and 40 mL dichloromethane. Orange solid A was obtained after reacting for 12 h. Then A is washed with ethyl ether. Afterwards, 160 mmol styrene was dropwise added into a round-bottom flask containing160 mL acetonitrile and 160 mmol A at 0 °C. White solid B was obtained after reacting for 12 h and washing with acetonitrile and drying. At last, different amines (20-50 mmol) were added to the aqueous solution containing 10 mmol B. After reacting for 12 h at room temperature, 20 mL saturated NaCl solution was added and extracted with diethyl ether (3×20 mL) three times. The organic phase was dried by anhydrous $MgSO_4$ overnight. The substrates were obtained by rotary evaporation.



Scheme S1 Synthesis of aziridines.

Table S1 Selected bond lengths (Å) and angles (°) for cluster **1**[a]

Bond lengths			
Nd(3)-O(7)	2.355(5)	Nd(3)-O(23)#1	2.572(5)
Nd(3)-O(20)	2.554(6)	Nd(3)-O(4)	2.454(5)
Nd(3)-O(9)	2.381(5)	Nd(3)-O(19)	2.552(5)
Nd(3)-O(8)	2.559(5)	Nd(3)-O(12)	2.537(5)
Nd(3)-N(3)	2.676(6)	Nd(3)-N(7)	2.987(7)
Nd(2)-O(7)	2.320(5)	Nd(2)-O(23)#1	2.916(5)
Nd(2)-O(16)	2.576(6)	Nd(2)-O(4)	2.572(5)
Nd(2)-O(3)	2.303(6)	Nd(2)-O(6)	2.534(6)
Nd(2)-O(24)#1	2.543(5)	Nd(2)-N(2)	2.716(7)
Nd(2)-O(17)	2.966(8)	Nd(2)-O(5)	2.516(6)
Nd(4)-O(23)#1	2.685(5)	Nd(4)-O(22)#1	2.487(5)
Nd(4)-O(22)	2.502(5)	Nd(4)-N(4)	2.653(8)
Nd(4)-O(1)	2.326(5)	Nd(4)-O(9)	2.395(5)
Nd(4)-O(12)	2.470(5)	Nd(4)-O(11)	2.559(5)
Nd(4)-O(10)	2.607(5)	Nd(1)-O(23)#1	2.572(5)
Nd(1)-O(14)	2.572(6)	Nd(1)-O(4)	2.474(5)
Nd(1)-O(3)	2.365(6)	Nd(1)-O(1)	2.354(5)
Nd(1)-O(13)	2.577(5)	Nd(1)-O(2)	2.521(6)
Nd(1)-O(12)	2.552(5)	Nd(1)-N(5)	2.991(7)
Nd(1)-N(1)	2.684(7)		
Bond Angels			
O(7)-Nd(3)-O(23)#1	70.96(16)	O(7)-Nd(3)-O(20)	147.03(19)
O(7)-Nd(3)-O(4)	71.17(17)	O(7)-Nd(3)-O(9)	107.25(18)
O(7)-Nd(3)-O(19)	129.15(18)	O(7)-Nd(3)-O(8)	80.99(19)
O(7)-Nd(3)-O(12)	130.76(17)	O(7)-Nd(3)-N(3)	67.52(19)
O(7)-Nd(3)-N(7)	143.52(18)	O(23)#1-Nd(3)-N(3)	107.02(18)
O(23)#1-Nd(3)-N(7)	139.90(17)	O(20)-Nd(3)-O(23)#1	139.77(17)

O(20)-Nd(3)-O(8)	68.48(19)	O(20)-Nd(3)-N(3)	87.5(2)
O(20)-Nd(3)-N(7)	25.09(19)	O(4)-Nd(3)-O(23)#1	63.50(16)
O(4)-Nd(3)-O(20)	127.11(18)	O(4)-Nd(3)-O(19)	78.12(18)
O(4)-Nd(3)-O(8)	103.96(18)	O(4)-Nd(3)-O(12)	76.43(16)
O(4)-Nd(3)-N(3)	138.26(18)	O(4)-Nd(3)-N(7)	102.61(19)
O(9)-Nd(3)-O(23)#1	70.68(17)	O(9)-Nd(3)-O(20)	81.10(18)
O(9)-Nd(3)-O(4)	131.96(17)	O(9)-Nd(3)-O(19)	123.37(18)
O(9)-Nd(3)-O(8)	123.57(19)	O(9)-Nd(3)-O(12)	69.67(17)
O(9)-Nd(3)-N(3)	68.32(19)	O(9)-Nd(3)-N(7)	103.05(19)
O(19)-Nd(3)-O(23)#1	127.78(17)	O(19)-Nd(3)-O(20)	49.84(19)
O(19)-Nd(3)-O(8)	68.18(19)	O(19)-Nd(3)-N(3)	125.11(19)
O(19)-Nd(3)-N(7)	24.76(19)	O(8)-Nd(3)-O(23)#1	151.64(17)
O(8)-Nd(3)-N(3)	64.1(2)	O(8)-Nd(3)-N(7)	65.35(19)
O(12)-Nd(3)-O(23)#1	61.63(15)	O(12)-Nd(3)-O(20)	82.20(18)
O(12)-Nd(3)-O(19)	76.48(17)	O(12)-Nd(3)-O(8)	143.54(17)
O(12)-Nd(3)-N(3)	137.79(18)	O(12)-Nd(3)-N(7)	78.84(17)
O(7)-Nd(2)-O(23)#1	65.20(16)	O(7)-Nd(2)-O(16)	94.7(2)
O(7)-Nd(2)-O(4)	69.60(17)	O(7)-Nd(2)-O(6)	74.4(2)
O(7)-Nd(2)-O(24)#1	76.56(19)	O(7)-Nd(2)-N(2)	94.8(2)
O(7)-Nd(2)-O(17)	127.70(19)	O(7)-Nd(2)-O(5)	149.4(2)
O(23)#1-Nd(2)-O(17)	99.20(18)	O(16)-Nd(2)-O(23)#1	114.44(16)
O(16)-Nd(2)-N(2)	119.6(2)	O(16)-Nd(2)-O(17)	44.35(19)
O(4)-Nd(2)-O(23)#1	57.24(14)	O(4)-Nd(2)-O(16)	164.07(19)
O(4)-Nd(2)-N(2)	66.37(18)	O(4)-Nd(2)-O(17)	144.86(18)
O(3)-Nd(2)-O(7)	128.36(19)	O(3)-Nd(2)-O(23)#1	66.13(18)
O(3)-Nd(2)-O(16)	120.5(2)	O(3)-Nd(2)-O(4)	70.47(19)
O(3)-Nd(2)-O(6)	154.0(2)	O(3)-Nd(2)-O(24)#1	83.4(2)
O(3)-Nd(2)-N(2)	97.9(2)	O(3)-Nd(2)-O(17)	76.2(2)
O(3)-Nd(2)-O(5)	78.3(2)	O(6)-Nd(2)-O(23)#1	139.08(19)
O(6)-Nd(2)-O(16)	61.35(19)	O(6)-Nd(2)-O(4)	114.57(18)
O(6)-Nd(2)-O(24)#1	117.5(2)	O(6)-Nd(2)-N(2)	64.5(2)
O(6)-Nd(2)-O(17)	100.3(2)	O(24)#1-Nd(2)-O(23)#1	47.66(15)
O(24)#1-Nd(2)-O(16)	67.50(18)	O(24)#1-Nd(2)-O(4)	104.77(16)
O(24)#1-Nd(2)-N(2)	169.7(2)	O(24)#1-Nd(2)-O(17)	59.77(19)
N(2)-Nd(2)-O(23)#1	123.58(18)	N(2)-Nd(2)-O(17)	130.5(2)
O(5)-Nd(2)-O(23)#1	144.2(2)	O(5)-Nd(2)-O(16)	79.8(2)
O(5)-Nd(2)-O(4)	115.00(19)	O(5)-Nd(2)-O(6)	76.7(3)

O(5)-Nd(2)-O(24)#1	126.7(2)	O(5)-Nd(2)-N(2)	63.4(2)
O(5)-Nd(2)-O(17)	67.3(2)	O(22)#1-Nd(4)-O(23)#1	50.49(15)
O(22)-Nd(4)-O(23)#1	110.18(15)	O(22)#1-Nd(4)-O(22)	61.26(18)
O(22)-Nd(4)-N(4)	120.00(19)	O(22)#1-Nd(4)-N(4)	171.9(2)
O(22)-Nd(4)-O(11)	67.61(17)	O(22)#1-Nd(4)-O(11)	123.07(18)
O(22)-Nd(4)-O(10)	70.23(17)	O(22)#1-Nd(4)-O(10)	108.01(18)
N(4)-Nd(4)-O(23)#1	129.70(19)	O(1)-Nd(4)-O(23)#1	69.48(16)
O(1)-Nd(4)-O(22)#1	87.64(18)	O(1)-Nd(4)-O(22)	96.80(18)
O(1)-Nd(4)-N(4)	100.0(2)	O(1)-Nd(4)-O(9)	133.42(17)
O(1)-Nd(4)-O(12)	72.03(18)	O(1)-Nd(4)-O(11)	74.85(19)
O(1)-Nd(4)-O(10)	149.54(18)	O(9)-Nd(4)-O(23)#1	68.52(16)
O(9)-Nd(4)-O(22)	115.84(17)	O(9)-Nd(4)-O(22)#1	80.92(17)
O(9)-Nd(4)-N(4)	91.7(2)	O(9)-Nd(4)-O(12)	70.61(16)
O(9)-Nd(4)-O(11)	146.8(2)	O(9)-Nd(4)-O(10)	76.00(17)
O(12)-Nd(4)-O(23)#1	60.85(15)	O(12)-Nd(4)-O(22)#1	111.20(15)
O(12)-Nd(4)-O(22)	167.34(16)	O(12)-Nd(4)-N(4)	69.0(2)
O(12)-Nd(4)-O(11)	113.59(17)	O(12)-Nd(4)-O(10)	122.44(17)
O(11)-Nd(4)-O(23)#1	143.78(18)	O(11)-Nd(4)-N(4)	62.3(2)
O(11)-Nd(4)-O(10)	74.71(19)	O(10)-Nd(4)-O(23)#1	140.47(17)
O(10)-Nd(4)-N(4)	66.6(2)	O(23)#1-Nd(1)-O(14)	138.90(18)
O(23)#1-Nd(1)-O(13)	130.55(17)	O(23)#1-Nd(1)-N(5)	142.08(18)
O(23)#1-Nd(1)-N(1)	106.7(2)	O(14)-Nd(1)-O(13)	49.74(18)
O(14)-Nd(1)-N(5)	24.69(19)	O(14)-Nd(1)-N(1)	85.6(2)
O(4)-Nd(1)-O(23)#1	63.23(15)	O(4)-Nd(1)-O(14)	130.16(17)
O(4)-Nd(1)-O(13)	81.56(17)	O(4)-Nd(1)-O(2)	103.64(18)
O(4)-Nd(1)-O(12)	75.77(16)	O(4)-Nd(1)-N(5)	106.43(18)
O(4)-Nd(1)-N(1)	137.9(2)	O(3)-Nd(1)-O(23)#1	71.63(18)
O(3)-Nd(1)-O(14)	145.76(19)	O(3)-Nd(1)-O(4)	71.29(19)
O(3)-Nd(1)-O(13)	130.0(2)	O(3)-Nd(1)-O(2)	79.0(2)
O(3)-Nd(1)-O(12)	131.03(17)	O(3)-Nd(1)-N(5)	142.9(2)
O(3)-Nd(1)-N(1)	67.0(2)	O(1)-Nd(1)-O(23)#1	71.14(17)
O(1)-Nd(1)-O(14)	78.02(19)	O(1)-Nd(1)-O(4)	132.06(17)
O(1)-Nd(1)-O(3)	108.1(2)	O(1)-Nd(1)-O(13)	121.14(19)
O(1)-Nd(1)-O(2)	123.67(19)	O(1)-Nd(1)-O(12)	70.11(17)
O(1)-Nd(1)-N(5)	100.3(2)	O(1)-Nd(1)-N(1)	68.4(2)
O(13)-Nd(1)-N(5)	25.13(18)	O(13)-Nd(1)-N(1)	122.5(2)
O(2)-Nd(1)-O(23)#1	150.31(18)	O(2)-Nd(1)-O(14)	70.4(2)

O(2)-Nd(1)-O(13)	67.5(2)	O(2)-Nd(1)-O(12)	144.74(19)
O(2)-Nd(1)-N(5)	65.4(2)	O(2)-Nd(1)-N(1)	63.9(2)
O(12)-Nd(1)-O(23)#1	61.42(15)	O(12)-Nd(1)-O(14)	83.08(18)
O(12)-Nd(1)-O(13)	77.67(17)	O(12)-Nd(1)-N(5)	80.80(18)
O(12)-Nd(1)-N(1)	138.3(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+2, -z+1

Table S2 Selected bond lengths (Å) and angles (°) for cluster **2**[a]

Bond lengths			
Sm(2)-O(15)	2.538(6)	Sm(2)-O(5)	2.333(6)
Sm(2)-O(4)	2.370(6)	Sm(2)-O(23)	2.537(6)
Sm(2)-O(10)	2.427(6)	Sm(2)-O(22)	2.524(7)
Sm(2)-O(6)	2.548(6)	Sm(2)-N(2)	2.662(8)
Sm(2)-N(8)	2.956(8)	Sm(2)-O(2)	2.505(6)
Sm(4)-O(15)	2.913(6)	Sm(4)-O(5)	2.294(6)
Sm(4)-O(10)	2.567(6)	Sm(4)-O(11)	2.520(7)
Sm(4)-O(12)	2.490(8)	Sm(4)-O(18)	2.541(7)
Sm(4)-N(4)	2.707(8)	Sm(4)-O(14)	2.526(6)
Sm(4)-O(8)	2.281(7)	Sm(1)-O(15)	2.652(6)
Sm(1)-O(4)	Sm(1)-O(4)	Sm(1)-O(7)	2.307(7)
Sm(1)-O(13)	2.478(6)	Sm(1)-O(13)#1	2.485(6)
Sm(1)-O(3)	2.535(7)	Sm(1)-O(1)	2.569(7)
Sm(1)-O(2)	2.465(6)	Sm(1)-N(1)	2.623(10)
Sm(3)-O(15)	2.537(6)	Sm(3)-O(20)	2.539(7)
Sm(3)-O(10)	2.449(6)	Sm(3)-O(7)	2.330(6)
Sm(3)-O(19)	2.556(6)	Sm(3)-O(9)	2.507(7)
Sm(3)-N(7)	2.970(8)	Sm(3)-N(3)	2.667(9)
Sm(3)-O(2)	2.525(6)	Sm(3)-O(8)	2.355(7)
Bond Angels			
O(15)-Sm(2)-O(6)	151.3(2)	O(15)-Sm(2)-N(2)	107.6(2)
O(15)-Sm(2)-N(8)	140.2(2)	O(5)-Sm(2)-O(15)	71.2(2)
O(5)-Sm(2)-O(4)	107.5(2)	O(5)-Sm(2)-O(23)	129.1(2)
O(5)-Sm(2)-O(10)	71.8(2)	O(5)-Sm(2)-O(22)	146.3(2)
O(5)-Sm(2)-O(6)	80.5(2)	O(5)-Sm(2)-N(2)	67.8(2)
O(5)-Sm(2)-N(8)	143.3(2)	O(5)-Sm(2)-O(2)	131.1(2)
O(4)-Sm(2)-O(15)	70.9(2)	O(4)-Sm(2)-O(23)	123.1(2)
O(4)-Sm(2)-O(10)	132.7(2)	O(4)-Sm(2)-O(22)	80.3(2)

O(4)-Sm(2)-O(6)	124.3(2)	O(4)-Sm(2)-N(2)	68.5(2)
O(4)-Sm(2)-N(8)	102.6(2)	O(4)-Sm(2)-O(2)	70.1(2)
O(23)-Sm(2)-O(15)	128.0(2)	O(23)-Sm(2)-O(6)	67.7(2)
O(23)-Sm(2)-N(2)	124.3(2)	O(23)-Sm(2)-N(8)	25.0(2)
O(10)-Sm(2)-O(15)	64.21(19)	O(10)-Sm(2)-O(23)	77.5(2)
O(10)-Sm(2)-O(22)	127.2(2)	O(10)-Sm(2)-O(6)	102.6(2)
O(10)-Sm(2)-N(2)	139.0(2)	O(10)-Sm(2)-N(8)	102.3(2)
O(10)-Sm(2)-O(2)	76.17(19)	O(22)-Sm(2)-O(15)	139.9(2)
O(22)-Sm(2)-O(23)	50.5(2)	O(22)-Sm(2)-O(6)	68.8(2)
O(22)-Sm(2)-N(2)	86.1(2)	O(22)-Sm(2)-N(8)	25.5(2)
O(6)-Sm(2)-N(2)	64.4(2)	O(6)-Sm(2)-N(8)	65.2(2)
N(2)-Sm(2)-N(8)	105.7(3)	O(2)-Sm(2)-O(15)	61.86(18)
O(2)-Sm(2)-O(23)	76.2(2)	O(2)-Sm(2)-O(22)	82.6(2)
O(2)-Sm(2)-O(6)	143.1(2)	O(2)-Sm(2)-N(2)	138.3(2)
O(2)-Sm(2)-N(8)	78.8(2)	O(5)-Sm(4)-O(15)	64.84(19)
O(5)-Sm(4)-O(10)	69.9(2)	O(5)-Sm(4)-O(11)	75.1(2)
O(5)-Sm(4)-O(12)	150.3(3)	O(5)-Sm(4)-O(18)	95.2(3)
O(5)-Sm(4)-N(4)	95.8(3)	O(5)-Sm(4)-O(14)	76.8(2)
O(10)-Sm(4)-O(15)	57.20(16)	O(10)-Sm(4)-N(4)	67.1(2)
O(11)-Sm(4)-O(15)	139.3(2)	O(11)-Sm(4)-O(10)	115.6(2)
O(11)-Sm(4)-O(18)	61.3(2)	O(11)-Sm(4)-N(4)	65.0(3)
O(11)-Sm(4)-O(14)	117.5(2)	O(12)-Sm(4)-O(15)	144.2(3)
O(12)-Sm(4)-O(10)	116.3(2)	O(12)-Sm(4)-O(11)	76.5(3)
O(12)-Sm(4)-O(18)	78.4(3)	O(12)-Sm(4)-N(4)	64.1(3)
O(12)-Sm(4)-O(14)	124.8(3)	O(18)-Sm(4)-O(15)	114.1(2)
O(18)-Sm(4)-O(10)	164.7(2)	O(18)-Sm(4)-N(4)	119.7(2)
N(4)-Sm(4)-O(15)	124.2(2)	O(14)-Sm(4)-O(15)	47.57(18)
O(14)-Sm(4)-O(10)	104.70(18)	O(14)-Sm(4)-O(18)	67.2(2)
O(14)-Sm(4)-N(4)	170.7(2)	O(8)-Sm(4)-O(15)	65.9(2)
O(8)-Sm(4)-O(5)	128.2(2)	O(8)-Sm(4)-O(10)	71.0(2)
O(8)-Sm(4)-O(11)	154.5(3)	O(8)-Sm(4)-O(12)	78.6(3)
O(8)-Sm(4)-O(18)	118.7(3)	O(8)-Sm(4)-N(4)	98.8(3)
O(8)-Sm(4)-O(14)	81.8(3)	O(4)-Sm(1)-O(15)	68.90(19)
O(4)-Sm(1)-O(13)#1	116.3(2)	O(4)-Sm(1)-O(13)	81.7(2)
O(4)-Sm(1)-O(3)	146.7(3)	O(4)-Sm(1)-O(1)	76.1(2)
O(4)-Sm(1)-O(2)	70.8(2)	O(7)-Sm(1)-O(15)	69.5(2)
O(7)-Sm(1)-O(4)	133.8(2)	O(7)-Sm(1)-O(13)#1	96.2(2)

O(7)-Sm(1)-O(13)	87.6(2)	O(7)-Sm(1)-O(3)	74.4(2)
O(7)-Sm(1)-O(1)	149.1(2)	O(7)-Sm(1)-O(2)	71.9(2)
O(7)-Sm(1)-N(1)	99.8(3)	O(13)#1-Sm(1)-O(15)	110.06(18)
O(13)-Sm(1)-O(15)	50.99(18)	O(13)-Sm(1)-O(13)#1	60.7(2)
O(13)#1-Sm(1)-O(3)	67.6(2)	O(13)-Sm(1)-O(3)	122.5(2)
O(13)-Sm(1)-O(1)	107.7(2)	O(13)#1-Sm(1)-O(1)	70.2(2)
O(13)-Sm(1)-N(1)	172.2(3)	O(13)#1-Sm(1)-N(1)	120.4(2)
O(3)-Sm(1)-O(15)	143.4(2)	O(3)-Sm(1)-O(1)	74.8(2)
O(3)-Sm(1)-N(1)	62.6(3)	O(1)-Sm(1)-O(15)	140.8(2)
O(1)-Sm(1)-N(1)	67.0(3)	O(2)-Sm(1)-O(15)	60.74(18)
O(2)-Sm(1)-O(13)	111.62(18)	O(2)-Sm(1)-O(13)#1	166.7(2)
O(2)-Sm(1)-O(3)	113.3(2)	O(2)-Sm(1)-O(1)	123.1(2)
O(2)-Sm(1)-N(1)	68.8(2)	N(1)-Sm(1)-O(15)	129.4(2)
O(15)-Sm(3)-O(20)	139.0(2)	O(15)-Sm(3)-O(19)	130.3(2)
O(15)-Sm(3)-N(7)	142.1(2)	O(15)-Sm(3)-N(3)	107.5(2)
O(20)-Sm(3)-O(19)	50.1(2)	O(20)-Sm(3)-N(7)	25.1(2)
O(20)-Sm(3)-N(3)	84.6(3)	O(10)-Sm(3)-O(15)	63.94(19)
O(10)-Sm(3)-O(20)	129.8(2)	O(10)-Sm(3)-O(19)	80.6(2)
O(10)-Sm(3)-O(9)	101.9(2)	O(10)-Sm(3)-N(7)	105.6(2)
O(10)-Sm(3)-N(3)	138.7(3)	O(10)-Sm(3)-O(2)	75.42(19)
O(7)-Sm(3)-O(15)	71.2(2)	O(7)-Sm(3)-O(20)	77.7(2)
O(7)-Sm(3)-O(10)	132.7(2)	O(7)-Sm(3)-O(19)	120.9(2)
O(7)-Sm(3)-O(9)	125.0(2)	O(7)-Sm(3)-N(7)	100.2(2)
O(7)-Sm(3)-N(3)	68.7(3)	O(7)-Sm(3)-O(2)	70.4(2)
O(7)-Sm(3)-O(8)	108.3(2)	O(19)-Sm(3)-N(7)	25.2(2)
O(19)-Sm(3)-N(3)	122.0(3)	O(9)-Sm(3)-O(15)	149.8(2)
O(9)-Sm(3)-O(20)	70.9(3)	O(9)-Sm(3)-O(19)	67.2(2)
O(9)-Sm(3)-N(7)	65.3(3)	O(9)-Sm(3)-N(3)	64.5(3)
O(9)-Sm(3)-O(2)	144.0(2)	O(2)-Sm(3)-O(15)	61.60(18)
O(2)-Sm(3)-O(20)	83.3(2)	O(2)-Sm(3)-O(19)	77.1(2)
O(2)-Sm(3)-N(7)	80.7(2)	O(2)-Sm(3)-N(3)	138.9(2)
O(8)-Sm(3)-O(15)	71.9(2)	O(8)-Sm(3)-O(20)	145.2(2)
O(8)-Sm(3)-O(10)	72.0(2)	O(8)-Sm(3)-O(19)	130.0(2)
O(8)-Sm(3)-O(9)	78.5(3)	O(8)-Sm(3)-N(7)	142.6(3)
O(8)-Sm(3)-N(3)	67.2(3)	O(8)-Sm(3)-O(2)	131.3(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z+1

Table S3 The geometry analysis by SHAPE 2.0 for clusters **1** and **2**.

$Nd1^{III}$	***C_4v*JCSAPR**	***C_4v*CSAPR**	***D_3h*JTCTPR**	***D_3h*TCTPR**	***C_s*MFF**
	2.846	1.841	4.071	1.885	2.460
$Nd2^{III}$	***O_h*CU**	***D_4d*SAPR**	***D_2d*TDD**	***C_2v*BTPR**	***T_d*TT**
	3.375	5.208	3.019	5.051	4.106
$Nd3^{III}$	***C_4v*JCSAPR**	***C_4v*CSAPR**	***D_3h*JTCTPR**	***D_3h*TCTPR**	***C_s*MFF**
	2.895	1.955	4.115	2.052	2.579
$Nd4^{III}$	***C_4v*JCCU**	***C_4v*CCU**	***C_4v*CSAPR**	***C_2v*HH**	***C_s*MFF**
	3.877	3.588	7.691	3.831	5.968
$Sm1^{III}$	***C_4v*JCCU**	***C_4v*CCU**	***C_4v*CSAPR**	***C_2v*HH**	***C_s*MFF**
	3.962	3.611	7.578	3.833	5.857
$Sm2^{III}$	***C_4v*JCSAPR**	***C_4v*CSAPR**	***D_3h*JTCTPR**	***D_3h*TCTPR**	***C_s*MFF**
	2.685	1.766	3.910	1.901	2.452
$Sm3^{III}$	***C_4v*JCSAPR**	***C_4v*CSAPR**	***D_3h*JTCTPR**	***D_3h*TCTPR**	***C_s*MFF**
	2.644	1.658	3.876	1.761	2.237
$Sm4^{III}$	***O_h*Cube**	***D4d*SAPR**	***D_2d*TDD**	***C_2v*BTPR**	***T_d*TT**
	3.268	5.181	2.949	5.175	3.984

JCSAPR-9=Capped square antiprism J10; **CSAPR-9**=Spherical capped square antiprism; **JTCTPR-9**=Tricapped trigonal prism J51; **TCTPR-9**=Spherical tricapped trigonal prism; **MFF-9=**Muffin; **JCCU-9=**Capped cube J8; **CCU-9=**Spherical-relaxed capped cube; **HH-9**=Hula-hoop. **CU-8=**Cube; **SAPR-8** = Square antiprism; **TDD-8** = Triangular dodecahedron; **BTPR-8** = Biaugmented trigonal prism; **TT-8=**Triakis tetrahedron.

Table S4 Reported Ln–based complexes as catalysts for the cycloaddition reactions of CO_2 with 1-ethyl-2-phenylaziridine under mild conditions.

Cat. (%)	Co–cat.	P_{CO_2} / MPa	T / °C	Time / h	Y / %	Ref
{[Cu_2(BCP)(H_2O)$_2$]·3DMF$_n$	TBAB	2	100	12	＞99	1
Zn-MOF	TBAB	2	70	12	＞99	2
{Cu_4(CuTBCPPP)(H_2O)$_4$}$_n$	TBAB	2	100	10	＞99	3
{[$NH_2(CH_3)_2$][In(CPT)$_2$]·3CH_3CN·3DMA}$_n$	TBAB	2	70	10	99	4
{[Cu_2(L_4^-)(H_2O)$_2$]·3DMF·2H_2O}$_n$	TBAB	0.5	60	12	98	5
{[Ni(DCTP)]·6.5DMF}$_n$	TBAB	2	70	10	95	6
{[Zn(H_2O)($C_5H_7NO_4$)]·H_2O}$_n$	TBAB/H_2O	1	r.t.	24	94	7
{[$H_2N(CH_3)_2$]$_3$[Zn_3(BTB)$_2$(5-atz)$_3$]·3EtOH·3H_2O·3DMF}$_n$	TBAB	1	70	10	94	8
{[Co_2(XN)$_2$(IPA)$_2$]·2H_2O}$_n$	TBAB	1	30	10	89	9
Cluster **1**	TBAB	1	70	10	94	This Work
Cluster **2**	TBAB	1	70	10	92	This Work

Table S5 Reported Ln–based complexes as catalysts for the cycloaddition reactions of CO_2 with styrene oxide under mild conditions.

Cat. (%)	Co–cat.	P_{CO_2}	T /	Tim	Y / %	Ref

		/bar	℃	e / h		
$\{[Eu(BTB)(phen)]\cdot 4.5DMF\cdot 2H_2O\}_n$	TBAB	1	80	12	68	10
3d–4f MOF	TBAB	1	70	12	77	11
$Zn^{II}{}_2Nd^{III}{}_2L_4$	TBAB	1	80	14	88	12
Tb–BDC	TBAB	1	60	12	89	13
$Zn^{II}{}_2Yb^{III}{}_2L_4$	TBAB	1	80	14	90	12
Tb_4 MOF	TBAB	1	60	12	95	14
Yb–mesocate	TBAB	1	120	2.5	95	15
$[Dy_7(CDA)_6(HCOO)_3(\mu_3\text{-}OH)_6(H_2O)_8]_n$	TBAB	1	80	12	98	16
$\{[Ni_3Th_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(IN)_{12})(H_2O)_{12}]\cdot(OH)_6\cdot 5DMF\cdot 2H_2O\}_n$	TBAB	1	70	12	＞99	17
Cluster **1**	TBAB	1	80	12	97	This Work
Cluster **2**	TBAB	1	80	12	96	This Work

Table S6 The ICP results of cluster **1** after recycling (filter liquor).

Compounds	Nd^{3+}
Cluster **1** after catalytic recycling (filter liquor)	0.20 %

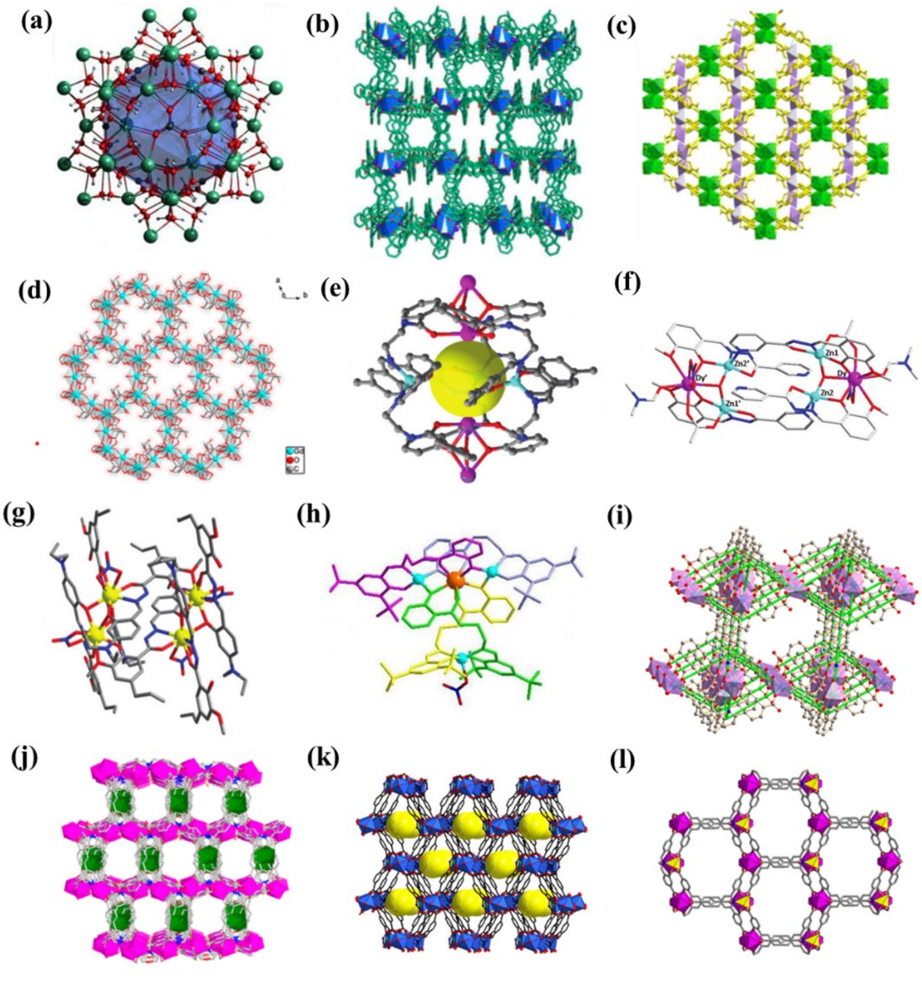


Fig.S1 The structures of recently reported representative complexes as catalyst for the reaction of CO_2 and epoxides. (a) $\{[Ln_3(\mu_6\text{-}CO_3)(\mu_3\text{-}OH)_6]OH\}_n$;[18] (b) $\{[Eu(BTB)(phen)]\cdot 4.5DMF\cdot 2H_2O\}n$;[10] (c) $\{[TbZn(BPDC)_2(\mu_2\text{-}H_2O)Cl(H_2O)_3]\cdot 5H_2O\cdot 0.5DMA\}_n$;[19] (d) $[Ln_7(CDA)_6(HCOO)_3(\mu_3\text{-}OH)_6(H_2O)_8]_n$;[16] (e) $Ln_4Zn_3L_6$;[20] (f) $[Ln_2Zn_4(\mu_3\text{-}OH)_2L_4(AcO)_2(NO_3)_2(DMF)_2]\cdot 2(CH_3OH)$;[21] (g) $[Ln_4L_6(NO_3)_4]\cdot 4(MeCN)$;[22] (h) Zn_3LnL_4;[23] (i) $\{(Me_2NH_2)[Tm_3(BDCP)_2)(H_2O)_3]\cdot 4DMF\cdot H_2O\}_n$;[24] (j) $[Tm_2(BDCP)_2]\cdot 3DMF\cdot 3H_2O\}_n$;[25] (k) $\{[Tb_4(BDCP)_2(\mu_2\text{–}OH)_2]\cdot 3DMF\cdot 5H_2O\}_n$;[26] (l) $\{[CoYb(BDCP)(H_2O)]\cdot 3DMF\cdot 3H_2O\}_n$;[27]

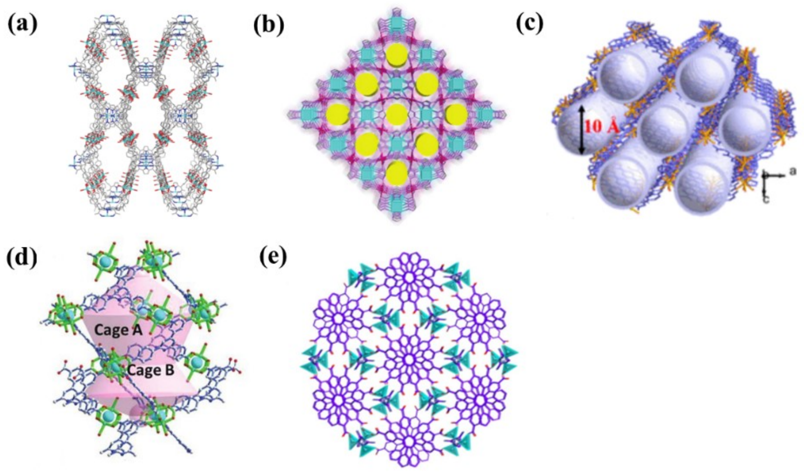


Fig.S2 The structures of recently reported representative complexes as catalyst for the reaction of CO_2 and aziridines. (a) MMPF-10;[3] (b) $\{[K_{1.2}Na_{2.8}ZnI_8(HL)_{12}]\cdot 4H_2O\}_n$;[28] (c) $\{[Cu_2(BCP)(H_2O)_2]\cdot 3DMF\}_n$;[29] (d) $\{[NH_2(CH_3)_2][In(CPT)_2]\cdot 3CH_3CN\cdot 3DMA\}_n$;[4] (e) $\{[H_2N(CH_3)_2]_3[Zn_3(BTB)_2(5\text{-}atz)_3]\cdot 3EtOH\cdot 3H_2O\cdot 3DMF\}_n$.[8]

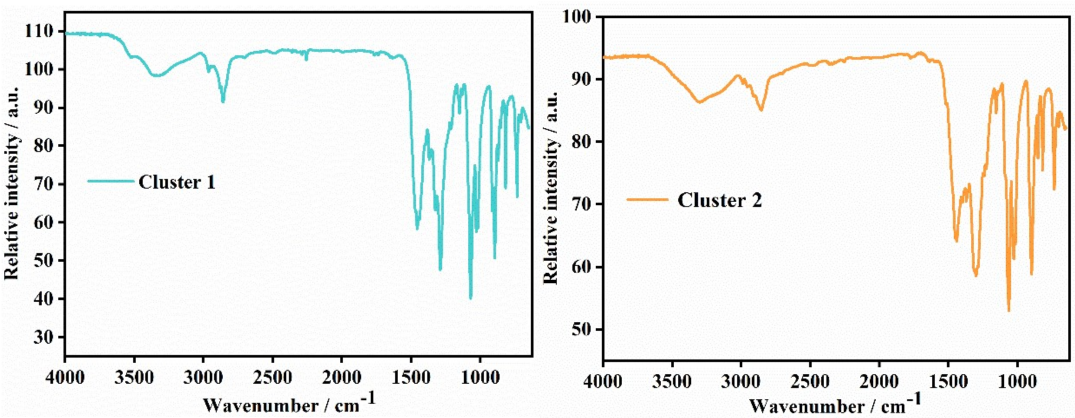


Fig. S3 The IR spectra clusters **1** and **2**.

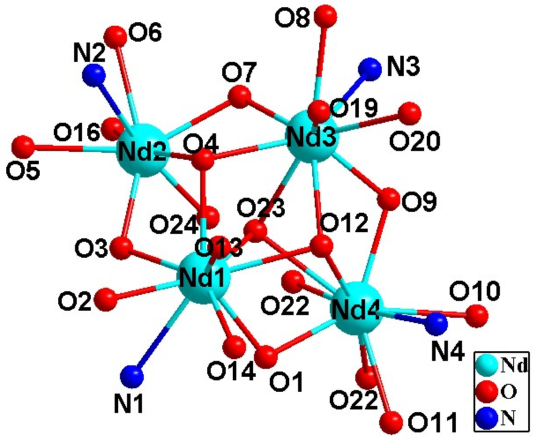


Fig. S4 The coordinate atom labels of central Nd(III) ions in cluster **1**.

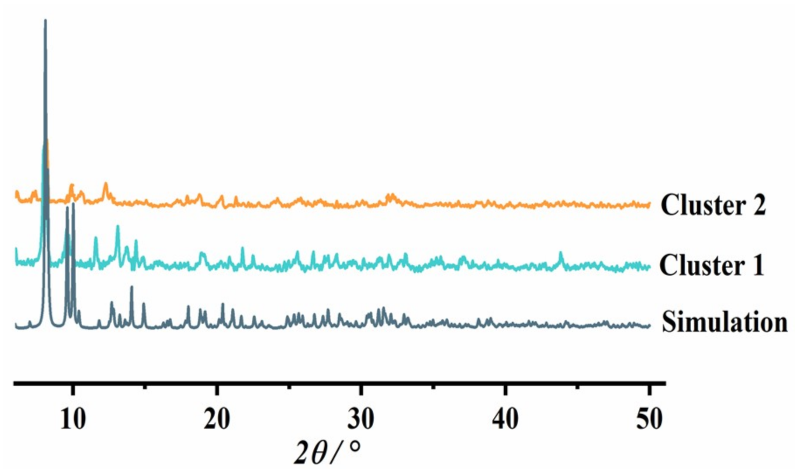


Fig. S5 The PXRD of clusters **1** and **2**.

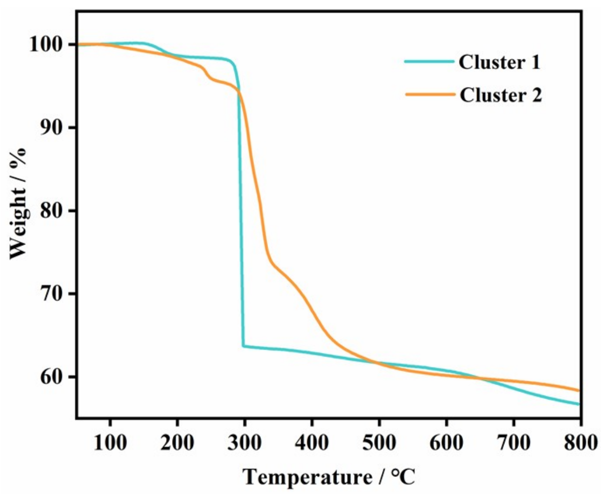


Fig. S6 The TGA curves of clusters **1** and **2**.

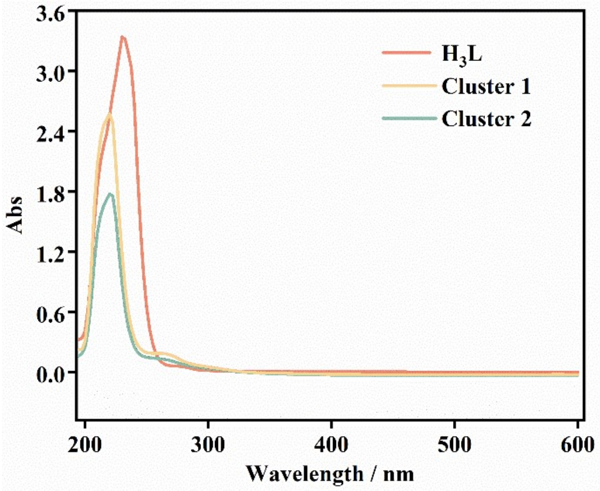


Fig. S7 The The UV-vis spectra of clusters **1**, **2** and H_3L ligand.

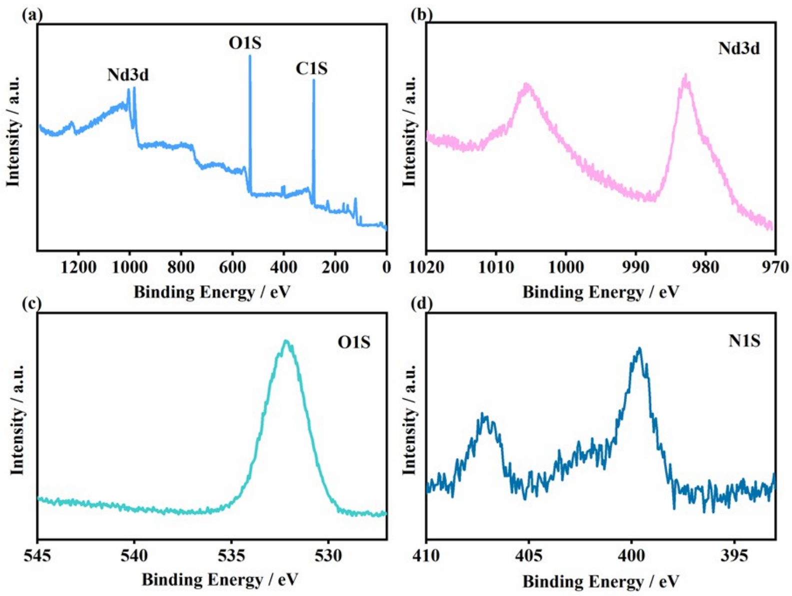


Fig. S8 XPS spectra of cluster **1**. (a) Full spectrum, (b) Nd 4d, (c) O 1s, and (d) N1s spectrum.

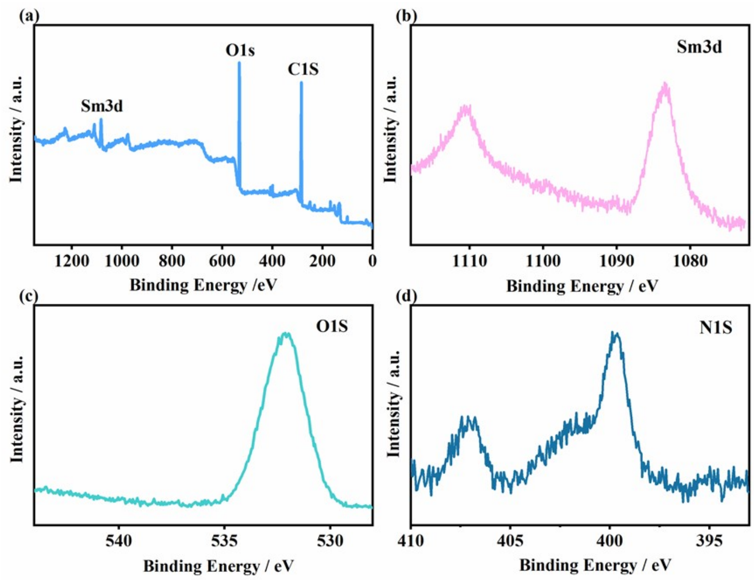


Fig. S9 XPS spectra of cluster **2**. (a) Full spectrum, (b) Sm 4d, (c) O 1s, and (d) N1s spectrum.

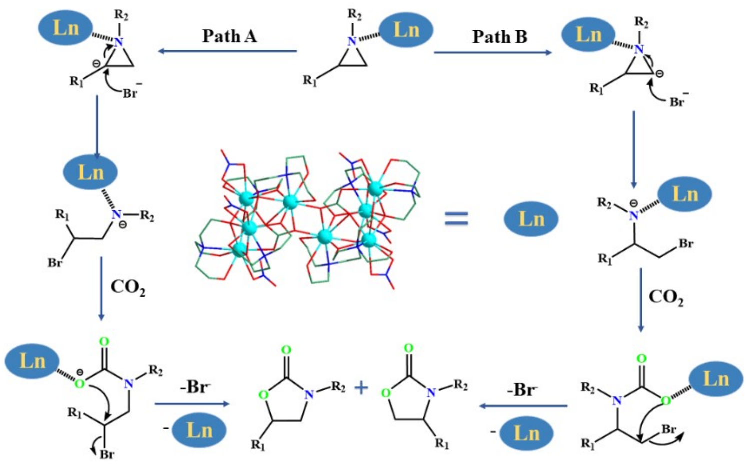


Fig. S10 A possible mechanism for catalyzed reaction.

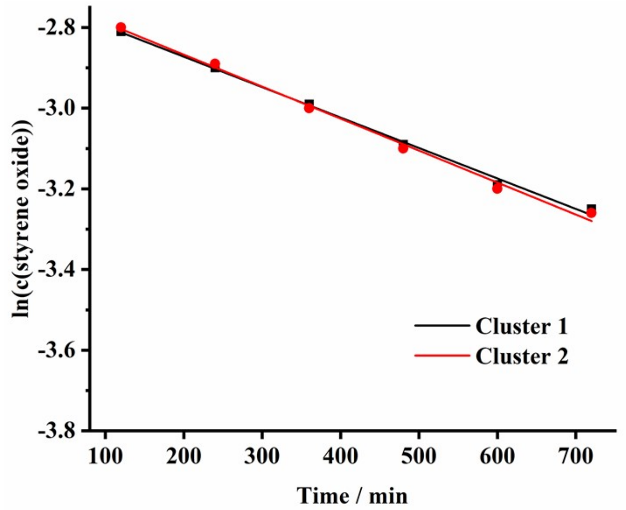


Fig. S11 The kinetic study for clusters **1** and **2** in the reactions.

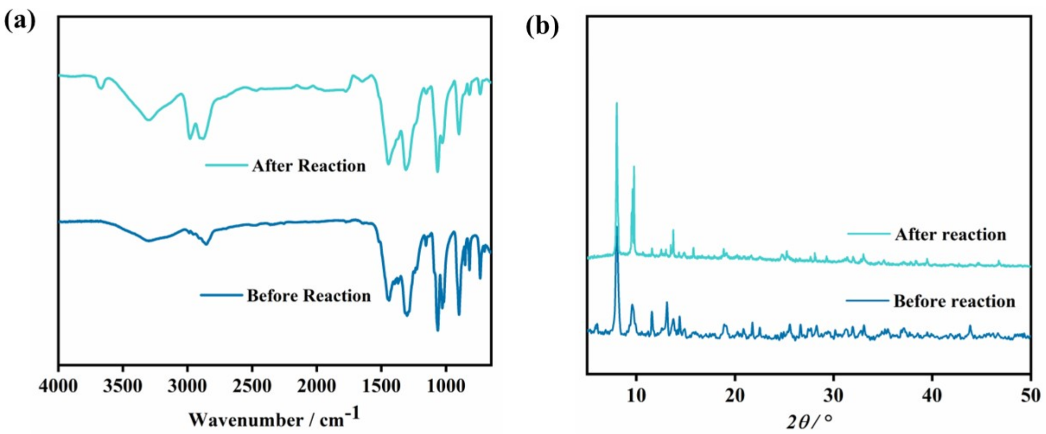


Fig. S12 The IR spectra and PXRD of cluster **1** after recycled reaction of CO_2 and styrene oxide.

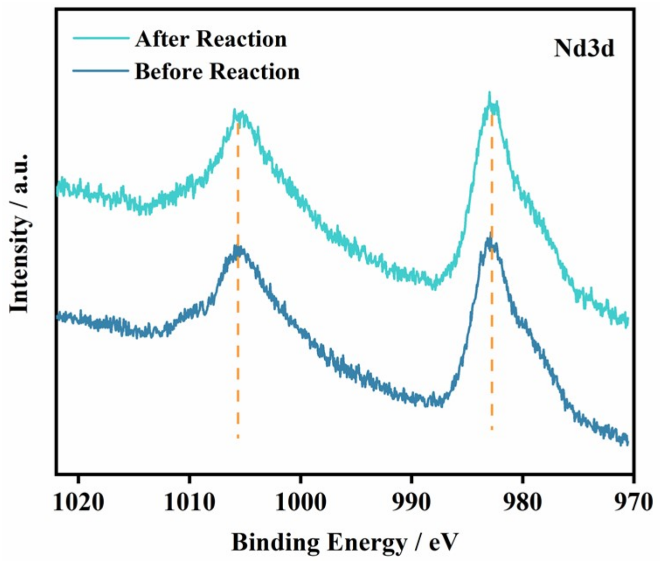


Fig. S13 The XPS of cluster **1** for the reaction of CO_2 and styrene oxide.

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