Supporting Information

# Amide-functionalized heterometallic helicate cages as highly efficient catalysts for CO<sub>2</sub> conversion under mild condition<sup>†</sup>

Li Wang,<sup>a,b</sup> Ruilian Zhang,<sup>a</sup> Qingxin Han,<sup>a,c</sup> Cong Xu,<sup>a</sup> Wanmin Chen,<sup>a</sup> Huan Yang,<sup>a</sup> Guoshu Gao,<sup>a</sup> Wenwu Qin<sup>a</sup> and Weisheng Liu<sup>a</sup>\*

a. Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province and State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Special Function Materials and Structure Design, Ministry of Education, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, China.

b. College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an 710065, P.R. China

c. Institute for Biomass and Function Materials, College of Bioresources Chemical and Materials Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China \*Corresponding author. E-mail: liuws@lzu.edu.cn.

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#### 1. Characterization data of H<sub>2</sub>L and catalysts

**Materials and Methods.** The infrared spectra were recorded on a Burker VERTEX 70 FTIR spectrometer using KBr pellets in the 400-4000cm<sup>-1</sup> region. The steadystate luminescence spectra, were determined on a FLSP 920 fluorescence spectrometer (Edinburgh Instruments, UK) at room temperature on solid-state samples.



Figure S1. IR of  $H_2L$ , complexes 1 and 2



Figure S2. Normalized excitation and emission spectra of the recycled catalyst 1 in the solid state

#### 2. Crystallography data

Crystal data were collected on a Bruker FRAMBO diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) at 290 K. Data reduction was accomplished by the Bruker SAINT program. Multi-scan absorption corrections were applied by using the program SADABS. Structures were solved by direct methods and refined by a full matrix least-squares technique based on F<sup>2</sup> using the Olex2 1.2 program. (CCDC number: 1841341 and 1841342 for **1** and **2**, respectively)

	1	2			
Empirical formula	$Zn_{3}Nd_{4}C_{114}H_{126}N_{24}O_{42}$	$Zn_{3}Eu_{4}C_{114}H_{126}N_{24}O_{42}$			
Formula weight	3277.45	3308.33			
<i>T</i> /K	290.83(10)	290.83(10)			
Crystal system	trigonal	trigonal			
Space group	<i>R-3c</i>	<i>R-3c</i>			
a/Å	17.8928(5)	17.8497(5)			
b/Å	17.8928(5)	17.8497(5)			
c/Å	69.099(2)	68.762(2)			
$\alpha$ /°	90	90			
$eta$ / $^{\circ}$	90	90			
$\gamma/^{\circ}$	120	120			
V/Å <sup>3</sup>	19158.4(12)	18973.1(12)			
Ζ	6	6			
$D_{calc}/{ m Mg}~{ m m}^{-3}$	1.704	1.737			
<i>F</i> (000)	9864.0	9936.0			
$\theta$ range for data collection	6.982 to 57.712 °	6.992 to 51.986°			
Data/restraints/parameters	5402/18/285	4145/18/285			
Goodness-of-fit on $F^2$	1.007	1.033			
Final <i>R</i> indices [I>2sigma (I)] <sup>a</sup>	$R_1$ =0.0489, $wR_2$ =0.0974	$R_1$ =0.0420, $wR_2$ =0.0826			
<i>R</i> indices (all data) <sup>b</sup>	$R_1$ =0.1179, $wR_2$ =0.1244	$R_1$ =0.0825, $wR_2$ =0.1018			
Largest diff. peak/hole/e. Å-3	1.97/-0.81	1.80/-0.99			
${}^{a}R_{1} = \Sigma   F_{o}  -  F_{c}   / \Sigma  F_{o} ; {}^{b}wR_{2} = \Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})2]^{1/2}$					

 Table S1. Crystal data and structure refinement parameters for complexes 1 and 2

1					
Nd1-04	2.364(4)	Nd1-02 <sup>2</sup>	2.520(4)	Nd2-05 <sup>2</sup>	2.494(4)
Nd1-041	2.364(3)	Nd1-02	2.519(4)	Nd2-06	2.502(4)
Nd1-04 <sup>2</sup>	2.364(3)	$Nd1-02^{1}$	2.520(4)	$Nd2-06^{2}$	2.501(4)
Nd1-01 <sup>2</sup>	2.573(4)	$Nd2-04^{2}$	2.458(4)	$Nd2-06^{1}$	2.501(4)
Nd1-01	2.573(4)	Nd2-04	2.458(4)	Zn1-N3 <sup>3</sup>	1.998(5)
Nd1-011	2.573(4)	$Nd2-04^{1}$	2.458(4)	Zn1-N3	1.998(5)
Nd1-N1 <sup>1</sup>	2.976(5)	Nd2-05	2.494(4)	Zn1-07 <sup>3</sup>	1.905(4)
Nd1-N1 <sup>2</sup>	2.976(5)	$Nd2-05^{1}$	2.494(3)	Zn1-07	1.905(4)
Nd1-N1	2.976(5)				

Table S2. Selected bond lengths (Å) for complex 1

<sup>1</sup>1-Y,1+X-Y,+Z; <sup>2</sup>+Y-X,1-X,+Z; <sup>3</sup>2/3-Y+X,4/3-Y,-1/6-Z

2					
Eu1-01	2.476(4)	Eu1-03 <sup>2</sup>	2.330(4)	Eu2-04	2.472(4)
Eu1-01 <sup>1</sup>	2.477(5)	Eu1-03	2.330(4)	Eu2-03 <sup>2</sup>	2.418(4)
Eu1-01 <sup>2</sup>	2.477(5)	Eu1-03 <sup>1</sup>	2.330(4)	Eu2-03	2.418(4)
Eu1-02 <sup>2</sup>	2.545(4)	Eu2-05 <sup>1</sup>	2.457(4)	Eu2-031	2.418(4)
Eu1-021	2.545(4)	Eu2-05 <sup>2</sup>	2.457(4)	Zn1-06 <sup>3</sup>	1.910(4)
Eu1-02	2.545(4)	Eu2-05	2.457(4)	Zn1-06	1.910(4)
Eu1-N1 <sup>2</sup>	2.940(6)	Eu2-04 <sup>2</sup>	2.472(4)	Zn1-N3 <sup>3</sup>	1.994(5)
Eu1-N1 <sup>1</sup>	2.940(6)	Eu2-041	2.472(4)	Zn1-N3	1.994(5)
Eu1-N1	2.940(6)				

# Table S3. Selected bond lengths (Å) for complex 2

<sup>1</sup>1-Y, +X-Y, +Z; <sup>2</sup>1+Y-X, 1-X, +Z; <sup>3</sup>4/3-X, 2/3-X+Y, 7/6-Z

Supplementary Structural Figures.



**Figure S3** M and P enantiomers extracted from the structure of complex **1** (H atoms, coordinated nitrates, solvent molecules and phenyl were omitted for clarity.)



**Figure S4.** Complex 1: a. single strand of helicate; b. Coordination polyhedron of Nd<sup>3+</sup>; c. Coordination polyhedron of Zn<sup>2+</sup>. (<sup>1</sup>1-Y, +X-Y,+Z; <sup>2</sup>1+Y-X,1-X,+Z; <sup>3</sup>4/3-X,2/3-X+Y,7/6-Z)



**Figure S5.** Complex **2**: a. single strand of helicate; b. Coordination polyhedron of Eu<sup>3+</sup>; c. Coordination polyhedron of Zn<sup>2+</sup>. ( <sup>1</sup>1-Y, +X-Y,+Z; <sup>2</sup>1+Y-X,1-X,+Z; <sup>3</sup>4/3-X,2/3-X+Y,7/6-Z)

## 3. Catalysis Details

**Table S4**. Representative homogeneous and heterogeneous catalysts with high TOF used for the synthesis of cyclic carbonates.

Cat.	Co-cat.	Catalyst/Epoxide	Р	Т	Tim	Conversions	TOF	Ref
		(Mole ratio)	(MPa)	(°C)	e	(%)	(h <sup>-1</sup> )	
					(h)			
Zn(OPO) <sub>2</sub>	TBAB	(propylene epoxide)	3	120	1	46	18400	1
	(0.9)	1:40000						
Zn-CMP	TBAB	(propylene epoxide)	3	120	1	29	11600	2
	(0.9)	1:40000						
Zn-porphyrin	-	(1,2-Epoxyhexane)	1.7	160	1	79	26333	3
		1:33333						
Al-aminotriphenolate	PPN-Br	(1,2-Epoxyhexane)	1	90	2	36	36000	4
		1:200000						
Mg-porphyrin	-	(1,2-Epoxyhexane)	1.7	120	1	36	12000	5
		1:33333						
1	TBAB	(styrene oxide)	1	120	1	61	24400	This
	(0.5)	1:40000						work
-	TBAB	(styrene oxide)	1	120	1	19	-	This
	(0.5)	1:40000						work

**Table S5**. Synthesis of cyclic carbonate via insertion of  $CO_2$  to epichlorohydrin catalysed by catalyst **1** under ambient condition.

Entry	Cat. (%)	Co-cat. (%)	T(°C)	P(bar)	Time(h)	Conversions(%)
1	-	TBAB(1)	r.t	10	24	9
2	-	TBAB(2)	r.t	10	24	12
3	-	TBAB(3.6)	r.t	10	24	18
4	1	TBAB(3.6)	r.t	1	24	83

Reaction conditions: 10 mmol epoxide, 0.125 mol % catalyst, 1-3.6 mol % TBAB, r,t, 24 h, 1-10 atm; Conversions were determined by <sup>1</sup>H NMR analysis. Selectivity of cyclic carbonates were all >99%.

**Table S6**. Time-course studies of catalysts **1** of cycloaddition reaction started with excessive styrene oxide (50 mmol), catalyst (0.001 mmol), **TBAB** (0.08 mmol), 120 °C and 1 MPa CO<sub>2</sub>. After a time interval, the small aliquot of the supernatant reaction mixture was taken out when the pressure of CO<sub>2</sub> decreased to 0.7 MPa, then purged CO<sub>2</sub> to 1 MPa again and heated to 120 °C. The conversions were calculated by <sup>1</sup>H NMR.

Round	Total time	Conversion/%
1	1	21
2	2.5	45
3	4.5	67
4	7.5	79
5	12	88
6	18	99



Figure S6. Histogram of the conversions of excessive styrene oxide using complex 1understandardconditions.

4. Characterization data and NMR Spectra





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