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# New Lanthanide (III) Coordination Polymers: Synthesis, Structural Features, and Catalytic Activity in CO<sub>2</sub> Fixation

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A new series of lanthanide coordination polymers formulated as  $[Ln(\mu-L)(\mu_3-L)(H_2O)]_nX_n$  (Ln/X = Er/Cl (1), Er/Br (2), Tm/Cl (3), Tm/Br (4), Yb/Cl (5), and Yb/Br (6); L = 1,3-bis(4-carboxyphenyl) imidazolium carboxylate(1+)) was solvothermally generated and fully characterized. Single-crystal X-ray diffraction analysis shows that all products possess isomorphous structures that are composed of cationic 1D double chains with encapsulated halide anions. From a topological perspective, such 1D chains can be classified as a binodal 3,5-connected net with a unique topology defined by the point symbol of  $(3.4^2)(3^2.4^2.5^3.6^2.7)$ . All products 1-6 feature a remarkable thermal stability and were applied as highly active heterogeneous catalysts for the coupling reactions between halogenated propylene oxides and CO<sub>2</sub> to give the corresponding cyclic carbonates. Reaction conditions, substrate and catalyst scope, and mechanistic features for this catalytic transformation were investigated. High products yields (up to 98%), elevated TONs (up to 3920) or TOFs (up to 326 h<sup>-1</sup>) were attained under mild reaction conditions. In addition, the catalyst 6 can be recycled at least eight times with no loss of catalytic activity.

# INTRODUCTION

Lanthanide coordination polymers (Ln-CPs) have emerged as an important class of compounds with various functional properties and applications, ranging from in chemical sensing,<sup>1</sup> <sup>2</sup> luminescence properties, <sup>3, 4</sup> gas storage and separation <sup>5-8</sup> and heterogeneous catalysis. <sup>9-17</sup> Among these, heterogeneous catalysis has attracted more attention because of the unique ff electron transition of lanthanide ions.<sup>18-20</sup>

As an inexpensive, nontoxic, and abundant renewable C1 source, CO<sub>2</sub> could be considered as an available pollutant resources used in organic synthesis aspect and the catalytic conversion of CO<sub>2</sub> into useful products became a hot issue in scientific research and environmental governance.<sup>21</sup> In this area, one of the most interesting directions of CO<sub>2</sub> conversion is the coupling reaction of CO<sub>2</sub> and epoxides to form cyclic carbonates, which is atomic-economic and having industrial value in important industrial intermediates synthesis.22-24 Using transition metal salts and related coordination

# compounds are common catalysts for the conversion of carbon dioxide into cyclic carbonates is very effective strategy in the past studies.<sup>25-28</sup> Compared with transition metal based catalysts, the lanthanide containing compounds can potentially have some advantages, because Ln<sup>3+</sup> ions can not only act as possible Lewis acidic sites and enhance catalytic activity, but also can show some intrinsic characteristics and rich coordination patterns.<sup>29-32</sup> In addition, the application of CPs as heterogeneous catalysts for coupling of CO<sub>2</sub> and epoxides to obtain cyclic carbonates can be considered as an interesting and good candidate for CO<sub>2</sub> fixation.

Until now, only a few CP or MOF catalysts have been reported for such a type of transformation, without showing a high efficiency in CO<sub>2</sub> conversion.<sup>31, 33-35</sup> Hence, the Ln CPs with stable metal-organic structures can be considered as good candidates for the  $CO_2$  fixation reactions.<sup>35-41</sup>

Based on the above background, we report herein a series of Ln CPs formulated as  $[Ln(\mu-L)(\mu_3-L)(H_2O)]_nX_n$  (Ln/X = Er/CI(1), Er/Br (2), Tm/Cl (3), Tm/Br (4), Yb/Cl (5), and Yb/Br (6); L = 1,3-bis(4-carboxyphenyl) imidazolium carboxvlate(1+)). Solvothermal synthesis, full characterization, structural and topological features, thermal stability, and catalytic properties of these products will be discussed in the present work.

# **EXPERIMENTAL SECTION**

All the materials were purchased from commercial sources and used without further purification. 1,3-Bis(4carboxyphenyl)imidazolium chloride  $(H_2L^+Cl^-)$  and 1,3-bis(4-

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carboxyphenyl)imidazolium bromide  $(H_2L^+Br^-)$  were synthesized following a literature protocol.<sup>42, 43</sup>

The single-crystal X-ray diffraction data were collected on a Bruker SMART 1000 CCD diffractometer operating at 48 kV and 30 mA by using a graphite-monochromated Mo-K $\alpha$  radiation source ( $\lambda$  = 0.71073 Å). An empirical absorption correction based on a comparison of redundant and equivalent reflections was applied by using SADABS. All structures were solved by direct methods using SHELXTL-2013<sup>44</sup> and refined by full-matrix least-squares cycles on F<sup>2</sup> via Olex2 program<sup>45</sup>. All the non-hydrogen atoms were refined anisotropically.

Topological analysis of metal-organic networks in the obtained compounds was performed using Topos software and applying a concept of a simplified underlying net.<sup>46, 47</sup> An underlying net can be generated by reducing the  $\mu_3$ -L and  $\mu$ -L moieties to their centroids and eliminating terminal H<sub>2</sub>O ligands. Connectivity of Er nodes via coordination bonds with  $\mu_3$ -L and  $\mu$ -L blocks was maintained.

X-ray powder diffraction data were collected on a PANalytical X'Pert Pro Diffractometer operated at 40 kV and 40 mA with Cu K $\alpha$  radiation ( $\lambda$ =1.5406Å). The steady-state luminescence spectra and lifetime measurements were measured on an Edinburgh Instruments FSL920 fluorescence spectrometer, with 450 W Xe arc lamp as the steady-state excitation source or Nd-pumped OPOlette laser as the excitation source for lifetime measurements. The quantum yields of the compounds in the solid state were determined according to an absolute method of Wrighton using an integrating sphere (150 mm diameter, BaSO<sub>4</sub> coating) from Edinburgh Instruments FLS920. The infrared spectra were recorded on a Burker VERTEX 70 FTIR spectrometer using the KBr pellets in the 400–4000 cm<sup>-1</sup> region.

#### Preparation of $[Er(\mu-L)(\mu_3-L)(H_2O)]_nCl_n$ (1).

A 20 mL vial was charged with  $ErCl_3 GH_2O$  (0.0095 g, 0.025 mmol),  $H_2L^*Cl^-$  (0.0172g, 0.05 mmol), N,N-dimethylacetamide (DMA, 2 mL) and distilled water (1 mL). After ultrasonic oscillation for 5 minutes, the mixture was heated at 85 °C for 24 h and then cooled to room temperature, resulting in the formation of light pink block crystals. These were filtered off, washed with ethanol, and dried at room temperature to give compound **1** in 76% yield based on Er(III). IR (KBr pellet, cm<sup>-1</sup>): 524 (m), 622 (m), 694 (m), 781 (s), 858 (w), 1134 (m), 1253 (m), 1336 (s), 1383 (s), 1550 (vs), 1618 (vs), 2930 (w), 3118 (w), 3481 (m). Elemental analysis: N 6.65%, C 49.05%, H 3.00%. (Calculated: N 6.71%, C 48.89%, H 2.90%).

#### Preparation of $[Er(\mu-L)(\mu_3-L)(H_2O)]_nBr_n$ (2).

The synthesis of **2** was similar to that of **1** except using  $ErBr_3$  (0.0102 g, 0.025 mmol) and  $H_2L^+Br^-$  (0.0195 g, 0.05 mmol) as starting materials. Compound **2** was obtained in 67% yield based on Er(III). IR (KBr pellet, cm<sup>-1</sup>): 522 (m), 622 (m), 781 (s), 858 (m), 1255 (m), 1338 (m), 1385 (s), 1547 (s), 1618 (s), 2930 (w), 3444 (m). Elemental analysis: N 6.22%, C 46.55%, H 2.70%. (Calculated: N 6.37%, C 46.42%, H 2.75%).

## Preparation of $[Tm(\mu-L)(\mu_3-L)(H_2O)]_nCl_n$ (3).

The synthesis of **3** was similar to that of **1** except using  $TmCl_{3}$ · $GH_{2}O$  (0.0116 g, 0.025 mmol) as a starting material. Compound **3** was obtained in 71% yield based on Tm(III). IR (KBr pellet, cm<sup>-1</sup>): 505 (m), 543 (m), 692 (m), 781 (vs), 858 (m), 1130 (m), 1253 (m), 1337 (vs), 1383 (s), 1552 (vs), 1616 (vs), 2924 (w), 3118 (w), 3435 (m). Elemental analysis: N 6.50%, C 48.63%, H 2.84%. (Calculated: N 6.69%, C 48.79%, H 2.89%).

## Preparation of $[Tm(\mu-L)(\mu_3-L)(H_2O)]_nBr_n$ (4).

The synthesis of **4** was similar to that of **1** except using TmBr<sub>3</sub> (0.0102 g, 0.025 mmol) and H<sub>2</sub>L<sup>+</sup>Br<sup>-</sup> (0.0195 g, 0.05 mmol) as starting materials. Compound **4** was obtained in 70% yield based on Tm(III). IR (KBr pellet, cm<sup>-1</sup>): 509 (w), 547 (w), 692 (w), 783 (s), 858 (m), 1134 (w), 1257 (m), 1338 (s), 1406 (vs), 1545 (vs), 1616 (vs), 2898 (w), 2950 (w), 3429 (w). Elemental analysis: N 6.18%, C 46.43%, H 2.69%. (Calculated: N 6.36%, C 46.33%, H 2.74%).

#### Preparation of $[Yb(\mu-L)(\mu_3-L)(H_2O)]_nCl_n$ (5).

The synthesis of **5** was similar to that of **1** except using  $YbCI_3 \cdot 6H_2O$  (0.0097 g, 0.025 mmol) as a starting material. Compound **5** was obtained in 68% yield based on Yb(III). IR (KBr pellet, cm<sup>-1</sup>): 511 (w), 547 (w), 697 (w), 781 (s), 860 (m), 1134 (w), 1255 (m), 1338 (s), 1406 (vs), 1548 (vs), 1616 (vs), 2927 (w), 3423 (w). Elemental analysis: N 6.42%, C 48.46%, H 2.84%. (Calculated: N 6.66%, C 48.55%, H 2.88%).

## Preparation of $[Yb(\mu-L)(\mu_3-L)(H_2O)]_nBr_n$ (6).

The synthesis of **6** was similar to that of **1** except using YbBr<sub>3</sub>·6H<sub>2</sub>O (0.0130 g, 0.025 mmol) and H<sub>2</sub>L<sup>+</sup>Br<sup>-</sup> (0.0195 g, 0.05 mmol) as starting materials. Compound **6** was obtained in 65% yield based on Yb(III). IR (KBr pellet, cm<sup>-1</sup>): 509 (w), 545 (w), 694 (m), 781 (s), 860 (m), 1130 (w), 1182 (w), 1257 (m), 1338 (s), 1410 (vs), 1545 (vs), 1618 (vs), 2920 (w), 3410 (w). Elemental analysis: N 6.10%, C 46.09%, H 2.68%. (Calculated: N 6.30%, C 45.91%, H 2.72%).

#### Catalytic studies.

The cycloaddition reactions under high temperature and pressure were carried out in 22 ml stainless steel reactor equipped with a magnetic stirrer. In these experiments, propylene oxide derivatives (10mmol), Compound **1-6** (0.01mmol) and Tetrabutylammonium bromide ([Bu<sub>4</sub>N]Br, 24.2mg, 0.075mmol) were added into the reactor, charged with 10bar CO<sub>2</sub>. After sealing, the reactor was put into a 120 °C oil bath, reacted at 3 h. After the reaction finished, the reactor was put out of oil, cool to room temperature and the CO<sub>2</sub> was released slowly. The product was moved to a 2ml centrifugal tube and separates the catalyst solids via centrifugation.

The cycloaddition reactions under mild conditions were conducted in 5ml round bottle with a small magnetic stirrer. Propylene oxide derivatives (10mmol), Compound **1-6** (0.0025mmol) and  $[Bu_4N]Br$  (96.8mg, 0.3mmol) were then added into the bottle. We use a rubber plug to seal the bottle and plunge a needle which is connected with a CO<sub>2</sub> ballon. After each 3h, the ballon should be recharged with CO<sub>2</sub>. The reaction was put into oil bath at desired temperature and

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reacted for a certain time. After finished, the round bottle was put out of the oil, separate the catalyst solids via centrifugation. The yield of product was calculated by using  ${}^{1}H$  NMR analysis.



Figure 1. Structural fragments of 1. a) Coordination environment of two adjacent Eu1 centers. b) 1D double chain structure. c)  $Er_2$  unit and coordination polyhedra around Er centers. d) Packing diagram along the*a* axis showing three adjacent 1D double chains. e) Topological representation of an underlying 1D chain showing a topologically unique binodal 3,5-connected net; rotated view along the *b* axis; Er nodes (bink balls). centroids of u-L and u-L moieties (grav).

#### Catalyst recycling tests.

In recycling experiments, catalyst **6** was used in a five-fold amount (X mol%) in comparison with standard tests, along with 50 mmol epichlorohydrin substrate and 3 mol% of [Bu<sub>4</sub>N]Br co-catalyst. The reaction was performed at 70 °C using 1 atm CO<sub>2</sub> and 12 h reaction time. After the reaction, reaction mixture was analyzed by <sup>1</sup>H NMR and a solid catalyst was separated by centrifugation, washed with CH<sub>2</sub>Cl<sub>2</sub> for 3 times and dried at 70°C for 6 h. A subsequent reaction was then continued with the precise mass of rest catalyst and same quantity of epichlorohydrin which could keep the same ratio of catalyst and substrate.

#### **RESULTS AND DISCUSSION**

#### **Structural Features**

The X-ray single crystal analysis reveals that all compounds **1-6** are isomorphous and crystalize in a triclinic system, space

group *P*-1 (**Table S3**, ESI). Herein, the structure of **1** will be discussed in detail as a representative example.

As shown in **Figure 1**, the Er1 centers are seven-coordinate and have a distorted pentagonal bipyramid [ErO<sub>7</sub>] environment, which is filled by two distinct  $\mu$ -L and  $\mu_3$ -L moieties, as well as one terminal H<sub>2</sub>O ligand. There are also two unbound chloride



Figure 2. Two typical coordination modes of the ligand L observed in compounds 1.

anions per each cationic  $[Er_2(\mu-L)_2(\mu_3-L)_2(H_2O)_2]^{\dagger}$  unit. Each Er1 center is connected to five carboxylate groups coming from three  $\mu_3$ -L and two  $\mu$ -L blocks (Figure 2, mode B and A, respectively). The adjacent Er1 atoms are doubly interconnected by two carboxylate groups from two  $\mu_3$ -L moieties, forming a dimeric Er<sub>2</sub> motifs with a shortest Er...Er separation of 5.204 Å (Figure 1b,c). These motifs are then further held together via remaining carboxylate groups of  $\mu_3$ -L and µ-L to generate an intricate 1D double chain (Figure 1). From a topological perspective (Figure 1e), an underlying metal-organic chain is composed of the 5-connected Er1 nodes, 3-connected  $\mu_3$ -L nodes, and 2-connected  $\mu$ -L linkers. This chain can be classified as a binodal 3,5-connected net with the unique topology, which is defined by the point symbol of  $(3.4^2)(3^2.4^2.5^3.6^2.7)$ . Herein, the  $(3.4^2)$  and  $(3^2.4^2.5^3.6^2.7)$ notations correspond to the  $\mu_3$ -L and Er1 nodes, respectively. The topology of 1D double chains in 1 well contrasts with the kgd topological 2D layers identified in related coordination polymers derived from  $[H_2L]^{+.47}$  In **1**, the chloride anions are located in the pores of the structure (Figure 1d) and could be divided into two parts, the connector Cl<sup>-</sup> (Cl1) and the inner Cl<sup>-</sup> (Cl2). There are some weak interactions between Cl1 and an imidazolate H10 atom, as well as Cl2 and an imidazolate H27 atom (Figure S1, ESI).

#### **Thermogravimetric Analysis**

The stability of compounds **1–6** was examined by thermogravimetric analysis (TGA) in air atmosphere in the temperature range of 20–800 °C. The obtained results (**Figure S2**, ESI) indicate that all compounds show a similar thermal behavior owing to their isomorphous structures. Thus, only the thermal stability of **1** is discussed in detail. TGA of **1** displays a loss of one coordination and one crystallization water

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molecules on heating up to 140 °C with the observed weight loss of 4.2% (calculated weight loss is 4.3%). After removal of water, a dehydrated sample apparently remains stable up to 450 °C. Above this temperature, the decomposition of metal-organic network occurs. These data indicate that the metal-organic compounds derived from an imidazolium-based aromatic carboxylate  $[H_2L]^+$  blocks have an excellent thermal stability.



Figure 3. a) Recycling of catalyst 6 in the coupling reaction of epichlorohydrin and CO<sub>2</sub> under optimized reaction conditions: catalyst (0.025 mol%), CO<sub>2</sub> (1 atm), 70  $^{\circ}$ C, [Bu<sub>4</sub>N]Br (3 mol%) 12h. b) PXRD pattern of 6 before and after being recycled for 8 times.

#### Luminescent Studies

The transient and steady-state photoluminescence spectra of compound 1-6 were collected on the crystalline samples at room temperature. As the result, 3 and 4 shows no obvious peak which could be owing to Tm complex, so only 1,2 and 5,6 can be disscused above. The solid state emission spectra of Er compounds 1 and 2 were measured under the excitation wavelength 310nm where the Yb compounds 5 and 6 were 332nm. As is shown in ESI Figure S3, both Er and Yb compounds show broad bands NIR emission. During 1400-1600nm, the band could be owing to the  ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transitions and the band in the range of 900-1100nm due to  ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$  transitions. According to **Figure S3**, the unfortunately, because of the relatively low efficient sensitization effect of ligand to Er<sup>3+</sup> and Yb<sup>3+</sup> ion, we failed to get stable lifetime and quantum yield value.

## Catalytic Activity for CO<sub>2</sub> Fixation

In our initial tests, we selected epichlorohydrin as an epoxide to react with CO<sub>2</sub> and to explore optimum conditions for this coupling reaction (Table 1). Initially, a mixture of catalyst (0.1 mol%; Compouns 1-6) and co-catalyst (0.75 mol%; tetrabutylammonium bromide, [Bu<sub>4</sub>N]Br) was tested in the presence of 10 bars of CO2 at 120 °C and under solvent free conditions, resulting in the formation of the corresponding cyclic carbonate in 92-98% yields (entry 1-7). These results reveal that such a series of CPs can efficiently catalyse the CO<sub>2</sub> fixation, whereas a blank test performed in the absence of the CP catalyst but in the presence of [Bu<sub>4</sub>N]Br co-catalyst showed only 21% product yield (entry 8). Further optimization of the reaction conditions was performed, allowing to achieve high product yields (up to 98%) at a milder reaction temperature (70 °C), atmospheric CO<sub>2</sub> pressure (1 bar), although at slightly prolonged reaction time (12 h) and higher catalyst loading. Under similar reaction conditions, all compounds 1-6 are quite active with the product yields ranging from 76% for **1** (the least active, entry 9) to 98% for **6** (the most active entry 14). According to **table 1**, we can see that the activity of chlorine compound **1**,**3** and **5** are not higher than bromine compound **2**,**4** and **6**. This may be because of the bromine anions could the increases rigidity of the structure and the channel of **2**,**4** and **6** may be easier to attract halogenated groups.<sup>48, 49</sup> Furthermore, several typical epoxide substrates (epibromohydrin, allyl glycidyl ether, epoxy styrene, phenyl glycidyl ether, propylene

Table 1. Synthesis of cyclic carbonates catalysed by Ln CPs 1-6 at different conditions.							
	Å	0.025mol% Cat.					0-4
CI		1atm CO <sub>2</sub> ,Solvent free				Cl	Ŭ,
Entry	Cat.	т	$P_{CO_2}$	Time	Co-cat.	Yield. <sup>b,c</sup>	TOF
		(°C)	(bar)	(h)	(mol%)	(%)	(h <sup></sup> ) <sup>u</sup>
1 <sup>e</sup>	1	120	10	3	0.75	92	307
2 <sup>e</sup>	2	120	10	3	0.75	97	323
3 <sup>e</sup>	3	120	10	3	0.75	93	310
4 <sup>e</sup>	4	120	10	3	0.75	98	327
5 <sup>e</sup>	5	120	10	3	0.75	93	310
6 <sup>e</sup>	6	120	10	3	0.75	98	327
7 <sup>e</sup>	6	120	10	3			
8		120	10	3	0.75	21	70
9	1	70	1	12	3	76	253
10	2	70	1	12	3	88	293
11	3	70	1	12	3	78	260
12	4	70	1	12	3	92	307
13	5	70	1	12	3	85	283
14	6	70	1	12	3	98	327
15	6	30	1	12	3	40	133
16	6	50	1	12	3	75	250
17	6	70	1	3	3	46	613
18	6	70	1	6	3	67	447
19	6	70	1	9	3	80	356
20 <sup>f</sup>	6	70	1	12	3	74	247
21 <sup>g</sup>	6	70	1	12	3	66	220
22	6	70	1	12	0.1	45	150
23	6	70	1	12	0.5	60	200
24	6	70	1	12	1	74	247
25	6	70	1	12	2	83	277
26 <sup>h</sup>	6	70	1	12	3	58	193
27	6	70	1	12			
28		70	1	12	3	15	50

<sup>a</sup>Reaction conditions: epichlorohydrin (10 mmol), catalyst (0.025 mol%), [Bu<sub>4</sub>N]Br as the co-catalyst, CO<sub>2</sub> balloon (1 bar). <sup>b</sup>Determined by <sup>1</sup>H NMR. <sup>c</sup>TOF = Yield/n<sub>cat</sub>/h. <sup>d</sup>Selectivity for cyclic carbonate was always above 99%. <sup>e</sup>Catalyst (0.1mol%). <sup>f</sup>Co-catalyst [Bu<sub>4</sub>N]I. <sup>g</sup>Co-catalyst [Bu<sub>4</sub>N]Cl. <sup>h</sup>Catalyst (0.0125 mol%).

oxide, epoxy cyclohexane, ethylene glycol diglycidyl ether, 1,2epoxyisobutane, 1,2-epoxybutane) were examined for this cycloaddition reaction catalysed by **6**. Under the optimized reaction conditions, the epichlorohydrin, allyl glycidyl ether, and epibromohydrin are highly reactive, while other substrates (epoxy styrene, phenyl glycidyl ether, propylene oxide, epoxy cyclohexane, ethylene glycol diglycidyl ether, 1,2epoxyisobutane, 1,2-epoxybutane) lead to inferior yields of

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cyclic carbonates that are in the range of 15%-58% (Table S2, ESI).

Given a heterogeneous nature of the present catalytic systems, we attempted to recycle the compound 6 and apply it in consecutive catalytic runs (Figure 3). The PXRD results show that after eight cycles, the framework of 6 is essentially retained, also maintaining its catalytic activity. A slight difference in the obtained product yields can be explained by an accuracy of the product analysis by NMR spectroscopy. Furthermore, a comparison of the catalytic performance of 6 with other CPs or MOFs applied for the present type of catalytic transformations<sup>38,45,53-55,</sup> (Table S2) reveals a number of advantages, namely higher TON or TOF values, milder reaction conditions, and the use of the solvent-free system. A possible mechanism for the cycloaddition reaction between CO2 and an epoxide can be suggested; it comprises several stages. (1) Terminal water ligand in CP leaves a Ln<sup>3+</sup> coordination sphere. (2) Lewis acidic  $Ln^{3+}$  site can coordinate an oxygen atom of an epoxide. (3) The nucleophilic Br attacks the less-hindered carbon atom to open an epoxy ring. (4)  $CO_2$ then interacts with an oxygen anion of the opened epoxy ring, forming an alkyl carbonate salt. (5) Finally, a cyclic carbonate product is obtained through an intramolecular ring closure. As the consequence, we can get an excellent yield of the corresponding cyclic carbonate when using an elevated temperature and pressure (Figure 3). Under mild conditions, a possible pathway could be described as a chain cracking pathway. First, the chain by chain structure separates partly and the open halogen anion site evolves. Then, the halogen atom of halogenated propylene oxide is easily attracted by the  $\delta^+$ - $\pi$  system and the oxide atom are coordinated with a waterfree Ln<sup>3+</sup> centre. The nucleophilic Br<sup>-</sup> from the [Bu<sub>4</sub>N]Br attacks the less-hindered carbon atom to open the epoxy ring. At last, CO<sub>2</sub> inserts and an intramolecular ring closure occur. Under mild conditions, the halogenated propylene oxide can react via both mechanistic pathways. Other epoxy substrates cannot reach an ideal yield because of lower temperature and CO<sub>2</sub> pressure so that it cannot get the energy barrier of the reaction.

# CONCLUSIONS

In the present study, we have obtained a novel series of lanthanide 1D double chain coordination polymers with a general formula  $[Ln(\mu-L)(\mu_3-L)(H_2O)]_n X_n [Ln/X = Er/Cl (1), Er/Br$ (2), Tm/Cl (3), Tm/Br (4), Yb/Cl (5), and Yb/Br (6)]. Singlecrystal X-ray structural analysis revealed that all compounds are isomorphous and feature a cationic 1D metal-organic network with encapsulated halide anions. Topological analysis of the underlying 1D chains was performed, allowing to identify a novel type of binodal 3,5-connected net. All compounds 1-6 also exhibit a remarkable thermal stability, with their dehydrated networks remaining stable up to 450 °C. Hence, the present work widens a family of thermally stable coordination polymers derived from an imidazolium-based aromatic carboxylate  $[H_2L]^+$  blocks.

Interestingly, under mild conditions, the obtained compounds 1-6 act as highly efficient heterogeneous catalysts for the cycloaddition reaction between CO<sub>2</sub> and a halogenated propylene oxide, resulting in TONs up to 3920 and TOFs up to 326. The reaction conditions were optimized and the substrate scope was investigated. The most active catalyst 6 can also be recycled for at least 8 times without any notable loss of activity, thus highlighting the application of the present type of lanthanide coordination polymers in heterogeneous catalysis and, in particular, for the transformations involving the fixation of carbon dioxide. Future research aiming at widening the scope and optimizing further the catalytic reaction parameters will be pursued.

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## Notes and references

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# **Graphic Abstract**

A series of Ln-CPs shows highly heterogeneous catalytic activity for cycloaddition reactions with TON = 3920 and  $TOF = 326h^{-1}$ .