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Self-assembly of tetranuclear 3d-4f helicates as highly efficient catalysts for CO₂ cycloaddition reactions under mild conditions

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A series of novel asymmetry 3d-4f helicates Zn_3LnL_4 ($H_2L = N-(2-((3,5-di-tert-butyl-2-hydroxybenzylidene)amino)ethyl)-2$ hydroxybenzamide, <math>Ln = Dy(1), Gd(2), Er(3)) were successfully constructed *via* selective incorporation of groups with different coordination capabilities. These helicates with the well-defined conformation demonstrate high catalytic efficiency in converting CO_2 to cyclic carbonates under mild conditions. Particularly, Zn_3ErL_4 showed superior catalytic performance with high catalytic activity (TOF up to 38000 h⁻¹) and extraordinary selectivity (up to 99%) across the wide substrate scope. Meanwhile, these 3d-4f helicates showed stable catalytic performance without being influenced by the moisture and air. The results presented herein highlight an important consideration for constructing heterometallic and asymmetric complexes for catalyzing CO_2 conversion.

Introduction

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In recent years, the conversion of CO₂ into valuable chemicals has received a significant amount of attention in both industry and academia, largely on account of its economic and environmental impact.¹⁻¹⁰ Particularly, the cycloaddition of CO₂ with epoxides to cyclic carbonates, as one of the most effective and important routes for carbon capture and use (CCU), has been widely studied experimentally and theoretically owing in particular to their green chemistry for 100% atom efficiency.¹¹⁻¹⁶ Meanwhile, the cyclic carbonates are industrially very significant and have been extended to versatile applications from fabricating the polycarbonate materials to the pharmaceutical and fine chemical industries.¹⁷⁻²³ To date, several types of catalyst systems have been extensively studied for these cycloaddition reactions.²⁴⁻²⁸ One of the most common examples is symmetric metallosalen-complexes, which the metal ions such as Al, Zn, Cr, Co, Mn and Ru et al was coordinated within the N2O2 donor pocket structure provided by the salen ligand.²⁹⁻³⁶ In order to ensure the CO₂ sufficiently interaction with the catalyst, the selective incorporation of the catalytically Lewis base sites for CO₂ fixation and activation is paramount.^{13, 32, 37-41} Reducing the distance between amide group (Lewis basic center) and metal ions (Lewis acid center) can effectively enhance the contact between two reactants and further accelerate the reactions. Therefore, the precise control over the ligand structures provided an unheralded interest in increasing the catalytic activity and selectivity of these CO_2 cycloaddition reactions.

Helices, as the essential assemble formation in the majority of natural compounds and biology molecules, playing a critical role in endowing selective recognition and expressing behaviors that closely related to the central biology process. Similarly, the spatial coordination between the ligands and metal ions in complexes could also lead to the assembly of the highly organized helix architectures. Most recently, different types of the helical metal complexes (helicates) have been extensively investigated, from double-stranded to multiple stranded, linear to circular, two centers to multiple centers and singular metal ion to multi-ones.⁴²⁻⁵⁰ The versatile structures of the helical metal complexes provide an ideal platform for mimicking the biology behavior like enzyme catalyzing, gene and proteinexpressing.

In terms of catalyzing applications, the heterometallic helicates, bearing different metal ions (transition-metal ions or f-block elements) in one complex, is one of the most attractive one as the multiple metal centers offer divers metal-binding domains for the higher order of the complex construction and are able to provides various interactions with catalytic substrate in the single molecules.⁵¹⁻⁵⁴ Several 3d-4f heterometallic helicates with different assembly architectures were reported by our group, which showed the catalyzing ability in the CO₂ cycloaddition reactions under the ambient environment with wide scope of epoxides.⁵⁵⁻⁵⁸ However, the search for new hetero-multinuclear cooperative structures is still pivotal in this area, where structures with well-defined reactivity and enhanced catalysis profiles are needed.

Herein, a series of novel 3d-4f hetero-multinuclear cooperative structures Zn_3LnL_4 (Ln = Dy (1), Gd (2), Er (3)) were designed and synthesized in this work (Scheme 1). The

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⁺ Electronic Supplementary Information (ESI) available: Figure S1–S6 containing characterization details for ligand and complexes. Table S1–S4 containing additional structural data. CCDC 1942931-1942933. For ESI and crystallographic data in CIF see DOI: 10.1039/x0xx00000x

Scheme 1. Assembly strategy for the 3d-4f heterometallic helicates as the efficient catalysts for CO_2 conversion reactions.

bifunctional ligand, containing both C=N and C=O groups with different binding preferences for selectively coordinated with Zn^{2+} and Ln^{3+} ions, contributes to the construction of 3d-4f heterometallic helix structures.⁵⁹⁻⁶¹ The crystal structure further revealed the asymmetric conformation with the potential catalytically active sites for CO₂ cycloaddition reactions. The presence of lanthanide ions in these 3d-4f hetero-multinuclear structures leads to the additional Lewis-acid sites which enhanced catalytic reactivity. The catalytical properties of different complexes in CO₂ cycloaddition reactions have been systematically valued across the wide substrates scope while the stability of the acquired catalysts was compared in the presence of water and air. The mechanism of the catalyzing process in relation to the metal ions as well as the special conformation of the complexes was further discussed.

Results and discussion

Design and synthesis

A tetradentate ligand bearing C=N and C=O groups as metal binding sites was synthesized via two-step reactions (amidation and condensation) from the commercially available reactants.⁶²⁻⁶⁴ The formation of the ligand was confirmed by mass spectrometry, NMR, and FT-IR spectroscopy (Detailed in the experimental section and Figure S1-S5). As shown in Scheme 1, the ligand was designed with different binding groups for selectively coordination of Zn²⁺ and Ln³⁺ ions respectively. Meanwhile, the flexible and asymmetric backbone was formed, contributing to the spiral structure. As expected, three asymmetry and novel tetranuclear helicates Zn₃LnL₄ were assembled by adding the Zn(NO₃)₂·6H₂O and Ln(NO₃)₃·6H₂O to a mixed acetonitrile-methanol (4:1) solution of H_2L in presence of equivalent triethylamine. Single crystal X-ray structural analysis revealed that 1-3 are isostructural and crystallized in the monoclinic P-1 space group, which is only differed in the number of solvent molecules in the lattice. In parallel, FT-IR (Figure S5) and elemental analysis indicated that complexes 1-3 are isostructural. In order to estimate the stability of the complexes, thermal gravimetric analysis (TGA) was performed (Figure S6). The TGA demonstrated that the complexes 1-3 have high thermal stability and the thermal performances between the different catalysts are similar due to isomorphism. Taking complex 3 as an example, 3.6% of the weight loss in the range of 30 to 195°C, owing to the presence of solvent molecules in the crystal lattice. The weight decreased rapidly with the loss of 48.4% in 344 to 535 °C interval which is attributed to the

decomposition of the complex structures. The $\sqrt{LGA_{til}}$ excellent thermal stability without any obvious decomposition from room temperature up to 344 °C which further provided a steady platform for catalytic applications.

Structure Characterization

The crystals of the three complexes were prepared in a clear mixed solution of acetonitrile and methanol containing deprotonated ligand, $Ln(NO_3)_3$ ·6H₂O and $Zn(NO_3)_2$ ·H₂O by slow evaporation of the solvent. Due to the isomorphic crystal structures in complexes 1-3, complex 3 was taken as an example for further crystal structure discussions. The unit cell is formed by an equal amount of the M enantiomer and P enantiomer, thus the crystal system is achiral (Figure S7). The asymmetric helical structure consists of four deprotonated ligands, three Zn²⁺ ions, one Er³⁺ ion, one monodentate nitrate and two acetonitrile as one unit in the lattice. In the complex, four ligands and three Zn²⁺ are wrapped around the lanthanide Er³⁺ center. Among them, Zn3 and Er1 are entangled in a head-tohead manner by two deprotonated ligands forming a double helix. As a consequence of the large coordination number of Er³⁺, two ligands are insufficient to meet the coordinating requirements of lanthanide ions, and further coordination with the other two deprotonated ligands which the carbonyl group and phenolic hydroxyl are inevitable to meet the saturated eight-coordinated environment. The Schiff base imine group at



Figure 1. (a) Coordination model of the ligand. (b) Coordination model of the ligand. (c) Molecular structure of the tetranuclear helicate. (d) Coordination polyhedrons of the Er and Zn ions in complex **3.** For clarity, half of the structure is transparent. Hydrogen atoms and solvent molecules are omitted.

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the other end of the two ligands coordinated with Zn1 and Zn2 ions could further stabilize the lanthanide ions and zinc ions. In the complex, the Er³⁺ ion is eight-coordinated in the central position. The coordination polyhedron of Er³⁺ ion is a dodecahedron. Both Zn1 and Zn2 are bridged on two sides of the Er³⁺ ion *via* the phenolic hydroxyl from two ligands. Zn1 and Zn2 are all four-coordinated with one N atoms of the imine from the deprotonated ligands and three O atoms of the phenolic hydroxyl from three ligands. The coordination polyhedron shows a tetrahedral configuration. The Zn3 ion is coordinated with two N atoms of the imine and two O atoms of the phenolic hydroxyl from the deprotonated ligands and monodentate coordinated nitrate. The coordination polyhedron is a square pyramid configuration. In the crystal, the distance between Er1 and Zn1, Zn2, Zn3 is 3.307, 3.305 and 6.686 Å, respectively. These ions are centered on lanthanide ions, extend in different directions and are linearly arranged in a 3:1 pattern to form a unique 3d-4f asymmetric unsaturated double helix structure, which as the novel structure is reported for the first time.

Catalytic performance

 $\rm CO_2$ conversion reactions receive a significant amount of attention across a range of fields of science and energy area, largely on account of their low cost, environmentally friendly and easily accessible precursor. Previous research has shown that salen zinc-containing compounds have preferable performance in the catalytic reaction of the cycloaddition of $\rm CO_2$ to epoxides. A series of multiple nuclear 3d-4f complexes which contain the similar structure of classical salen complexes have been synthesized. In the structure, monodentate coordinated $\rm NO_3^-$ with $\rm Zn^{2+}$ can be displaced by suitable substrates, $\rm La^{3+}$ and $\rm Zn^{2+}$ ions act as Lewis acidic sites to enhance the catalytic activity, and amides coordinated with lanthanide can be considered as basic sites. The above inferred that complexes have great prospects in $\rm CO_2$ conversion reactions.

Styrene oxide (SO) was taken as a model substrate to investigate the cycloaddition reaction in which the CO₂ reacts with epoxides to form cyclic carbonates. Firstly, the effect of the lanthanide metal ions on the catalytic reaction was investigated. 0.01 mol% of helicates 1-3 as the catalyst and 0.8 mol% of tetrabutylammonium bromide (TBAB) as cocatalyst was used to catalyze the cycloaddition reaction under 120 °C, 1 MPa without solvent for 2 h. As shown in Table 1 (entry 1-3), catalysts 1-3 have obtained excellent yields (93%, 92% and 95%, respectively) with high TOF values (4650 h⁻¹, 4600 h⁻¹ and 4750 h⁻¹, respectively). The results indicated that different Ln³⁺ have little effect on the activity of the catalyst while the catalytic activity increased as the decrease of Ln³⁺ radius. We chose complex 3 as a model catalyst in the further optimization process regarding to its catalytic activity. Owning to the vital role of the co-catalysts in the epoxides ring-opening process and the reaction intermedia formation process, the effect of various cocatalysts on catalytic performance, such as TBAC, TBAB, TBAI, PPN-Cl, under the same conditions has been studied (Figure 2a). The results demonstrate that TBAB is the finest selection of cocatalyst in this system. Neither catalyst 3 (0.01 mol%, Table 1,

		+ co	2 <u>cat., co-c</u> T, P	cat.			
Entry	Cat.	т	Р	Time	Yield	TOF	
		(°C)	(bar)	(h)	(%) ^b	(h⁻¹)º	
1	1	120	10	2	93	4650	
2	2	120	10	2	92	4600	
3	3	120	10	2	95	4750	
4 ^d	3	120	10	2	1	50	
5	-	120	10	2	33	-	
6	H_2 L	120	10	2	47	2350	
7	3	120	10	0.5	69	13800	
8	3	120	10	3	99	3300	
9	3	80	10	2	34	1700	
10 ^e	3	120	10	2	76	38000	
11 ^f	3	120	10	2	93	4650	
12 ^g	3	120	10	2	96	4800	
13 ^h	3	120	10	2	97	4850	
14 ⁱ	-	120	10	2	34	-	

^a Reaction conditions: 10 mmol styrene oxide, 0.01mol% catalyst, 0.8 mol% co-catalyst TBAB, 10 bar. ^b Yield was determined by ¹H NMR analysis. Selectivity of cyclic carbonates were all > 99%. ^c TOF = conversion· n_{cat} ⁻¹·h⁻¹. ^d Without co-catalyst. ^e Catalyst reduced to 0.001 mol%. ^f Not excluding the air inside the reaction system. ^g 0.02mL of H₂O was added to the reaction system. ^h 0.2mL of H₂O was added to the reaction system. ⁱ Without catalyst, 0.02mL of H₂O was added to the reaction system.

entry 4) nor TBAB (0.8 mol%, Table 1, entry 5) alone could achieve satisfactory catalytic yield (1%, 33%, respectively) in the cycloaddition reaction, but the yield was increased to 95% in the binary catalytic system composed of complex **3** and TBAB. Besides, considering Lewis base site (N atom) may also contribute to the cycloaddition reaction in which H₂L combined with TBAB was utilized as a catalyst for the model reaction (Table 1, entry 6). The yield of the cycloaddition reaction was increased to 47% compared with the system only contained TBAB as the control, which further confirmed our assumption.

Because there are multiple factors that affect the cycloaddition reaction, variable control studies are performed to optimize the reaction conditions. The reaction yield remains above 90% when pressure was reduced from 10 bar to 2 bar, and the related TOF changed slightly which suggests the pressure had no obvious effect on this system (Figure 2b). The yield progressively increased with time and the growth rate gradually decreased (Figure 2c). The yield can reach 69% after half hour with a high TOF 13800 h⁻¹ (Table 1, entry 7), meanwhile, when the reaction time was extended to 3 h, the yield was more than 99% with a TOF of 3300 h⁻¹ (Table 1, entry 8). We further investigated the effect of the temperature on

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 Table 1. Synthesis of cyclic carbonate via insertion of cccQatific

 styrene oxide catalyzed by complexes 1-3^aOI: 10.1039/D0DT01743D

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Figure 2. The yields of cycloaddition reaction of epoxy styrene and carbon dioxide under different reaction conditions: (a) 10 mmol styrene oxide, 0.01 mol% catalyst, 0.8 mol% co-catalyst, 120 °C, CO₂ at 10 bar, 1 h. (b) 10 mmol styrene oxide, 0.01 mol% catalyst, co-catalyst (0.2–1 mol%), 120 °C, 2 h, CO₂ at 10 bar. (c) 10 mmol styrene oxide, catalyst (0–0.01mol%), 0.8 mol% TBAB as the co-catalyst, 120 °C, 2 h, CO₂ at 10 bar. (d) 10 mmol styrene oxide, 0.01 mol% catalyst, 0.8 mol% TBAB as the cocatalyst, temperature (40-120 °C), 2 h, CO₂ at 10 bar. (e) 10 mmol styrene oxide, 0.01 mol% catalyst, 0.8mol% TBAB as the co-catalyst, 120 °C, time (0.5-3 h), CO₂ at 10 bar. (f) 10 mmol styrene oxide, 0.01 mol% catalyst, 0.8 mol% TBAB as the co-catalyst, 120 °C, time (0.5-3 h), CO₂ at 10 bar. (f) 10 mmol styrene oxide, 0.01 mol% catalyst, 0.8 mol% TBAB as the cocatalyst, 120 °C, time 2 h, CO₂ at (2–10 bar).

the reaction. The conversion rate was increased slowly between 40 °C and 60 °C, while remarkable increase happened at temperature 80 °C, 100 °C, 120 °C with linear correlation (Figure 2d). It should be noted that when the temperature drops to 80 °C, the value of TOF can still reach 1700 h⁻¹ (Table 1, entry 9). With different loading of co-catalyst TBAB (0.4 mol%, 0.6 mol%, 0.8 mol%, 1.0 mol%, respectively), high yield was attained with considerable TOF as 4050 h⁻¹, 4650 h⁻¹, 4750 h⁻¹, 4850 h⁻¹, respectively (Figure 2e). TOF changed little when the amount of co-catalyst is more than 0.6 mol%. The concentration of the catalyst reduced from 0.01 mol% to 0.001 mol%, the corresponding yield was decreased by only 19% (Figure 2f). TOF of the catalyst was reached to the highest as 38000 h⁻¹ when catalyst 3 was 0.001mol% and co-catalyst TBAB was 0.8 mol% (Table 1, entry 10), indicating such catalyst achieve the excellent catalytic performance with a high TOF. Therefore, the optimal reaction conditions for the cycloaddition reaction were 0.005 mmol% of the catalyst with 0.6 mmol% of co-catalyst TBAB, at 120 °C under 8 bar for 2 hours. Water and air have large impact on the most catalytic system $R^{12}CO_{2}^{10$

Tabl	e 2. Vari	ious ca	irbonates	from	different	epoxides	catalyzed
by va	arious ca	talysts	under di	fferen	t conditio	ons.	

, Entry	Substrate	Product	Yield (%) ^a	TOF ^c	Yield (%) ^b	TOF ^c
1	0		93	9300	97	1213
2	°	o o t	95	9500	91	1138
3	0 Br	O O O Br	95	9500	99	1238
4	$\overset{\circ}{\smile}$		78	7800	83	1038
5			98	9800	99	1238
6			95	9500	99	1238
7			93	9300	98	1225
8	° ° °		86	8600	89	1113
9	0,00		97	9700	99	1238
10			97	9700	99	1238
11	°°		98	9800	99	1238
12			93	9300	98	1225
13	°		36	3600	33	413
14	°		67	6700	61	763

Reaction conditions: ^a 10 mmol epoxide, 0.005 mmol% catalyst, 0.6 mmol% TBAB, 120 °C, 2 h, 8 bar. ^b 10 mmol epoxide, 0.01 mmol% catalyst, 1 mmol% TBAB, 80 °C, 8 h, 8 bar. TOF = conversion n_{cat} -1·h⁻¹. ^c Yields were determined by ¹H NMR. Selectivity of cyclic carbonates were all > 99%.

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of water (volume ratio = 18%) was explored which the conversion rate is slightly improved (Table 1, entries 12-13). One possible reason is that the presence of water accelerates the co-catalyst hydrolyzing, makes the co-catalyst better participate in the catalytic reaction, and has excellent resistance to water. (Table 1, entry 14). To evaluate the catalytic performance of our catalytic system, we compared it with the Zn-containing complexes and lanthanide catalysts, such as $Zn(OPO)_{2}$, 25 Zn-CMP, 65 ZnBr₂, 66 Ni(PPh₃)Cl₂/PPh₃/Zn, 67 Yb-mesocate, 68 and Helicate-1(Zn-Tb). 69 The results show that our catalytic system.

To further explore our catalytic system into the universal scope, a series of epoxy compounds with different substituents were subjected to the cycloaddition reaction under different conditions. The reactions for terminal epoxides achieve impressive conversion rates (> 90%) and high selectivity (99%) under 8 bar and 120 °C for 2 hours (Table 2, entries 1-12), except for 2-decyloxirane (86%) and 2-(tert-butoxymethyl) oxirane (78%), due to the large steric hindrance. However, compared with terminal epoxides, the catalyst shows lower activity on internal epoxides such as cyclohexene oxide and cyclopentene oxide (Table 2, entries 13 and 14), being ascribed to the steric effect. At the same time, the substrates expansion experiment was carried out under the conditions of 80 °C and 8 bar for 8 hours. The results showed that under relatively mild conditions, the catalyst still exhibits high catalytic activity for epoxides with a wide substrate scope.

Catalytic mechanism

Based on the current experimental results and the reported studies of catalyst systems, ^{52, 54, 70-73} a tentative mechanism was proposed for the catalytic system in the conversion of CO_2 . In the catalyst system, two kinds of metals were involved, in which the eight-coordinated rare-earth ion is surrounded by four ligands, and three zinc ions are divided in contrast. Since Zn ions are relatively far from each other, it could act as independent catalytic centers to activate the epoxide (Figure 3). The reaction was initiated by the activation of epoxides. The coordination of oxygen atoms of the epoxide with the Lewis acid metal sites leads to electron transfer from oxygen to the metal center,



Figure 3. A possible mechanism for the cycloaddition reaction.

which weakens the C-O bond strength in epoxides. Then, the Brefrom TBAB attacked the less steric resistance carbon atom of the epoxide which was coordinated with metal center, meanwhile, the epoxide ring was opened due to the strong electronegativity and lower steric resistance of Br atoms. Subsequently, CO_2 is inserted into the Zn3-O bond and cyclization takes place by the internal attack of carbon dioxide on the C-Br bond while the co-catalyst recovered. In addition, the catalyst can synergistically functionalize by introducing amide groups to increase CO_2 affinity to multiple Lewis acid sites, which lead to higher catalyst efficacy.

Experimental

General information

Chemicals were purchased from commercial sources and used without further purification. The infrared spectra were recorded on a Bruker VERTEX 70 FT-IR spectrometer using KBr pellets in the 400-4000 cm⁻¹ region. ¹H and ¹³C NMR spectra were recorded using a JNM-ECS 400M spectrometer using CDCl₃ as a solvent and tetramethylsilane (TMS) as an internal standard. The C, H, and N microanalyses were performed by using a Vario EL cube elemental analyzer. TGA/NETZSCH STA449C instrument for thermogravimetric analysis experiments was carried out under nitrogen atmosphere, the test temperature is from 35 °C to 800 °C with the heating rate of 10 °C min⁻¹. Single-crystal X-ray diffraction data were collected on a Bruker FRAMBO diffractometer (Mo radiation, λ = 0.71073 Å) at 293 K. Data reduction was accomplished by the Bruker SAINT program. Empirical absorption corrections were carried out on the SADABS program. All the structures were solved by direct methods and refined by a full-matrix least-squares technique based on F² of the SHELXL 2018 through Olex2 program. All the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically.⁷⁴ The specific data of X-ray crystallography and experiment for the crystal are listed in Table S1-S4. For details, see the CIF date in the support part. The CCDC reference numbers of complexes 1-3 are 1942931, 1942932 and 1942933.

Synthetic procedures

Synthesis of ligand H₂L: N-(2-aminoethyl)-2-hydroxybenzamide was prepared according to the reported literature method.75 3,5-di-tert-butyl-2-hydroxybenzaldehyde (2.34 g, 10 mmol) was added to a solution of N-(2-aminoethyl)-2-hydroxybenzamide (1.8 g, 10 mmol) in 100 mL methanol. The reaction mixture was refluxed for 5 h and then cooled to the room temperature. The crude product was separated by filtration and further recrystallized in ethanol to afford H₂L as a yellow solid (3.56 g, Yield: 90%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 12.26 (s, 1H), 8.41 (s, 1H), 7.39 (m, 2H), 7.32 (dd, 1H), 7.09 (d, 1H), 6.99 (dd, 1H), 6.83 (m, 1H), 6.58 (s, 1H), 3.85 (s, 4H), 1.45 (s, 9H), 1.30 (s, 9H). ¹³C NMR (100 MHz, CDCl₃, ppm): 170.3, 168.2, 161.6, 158.0, 140.5, 140.1, 136.9, 136.7, 134.5, 127.5, 126.3, 117.7, 114.2, 100.0, 58.7, 40.5, 35.1, 35.1, 34.3, 34.2, 31.6, 31.5, 29.5, 29.5. IR (KBr, u, cm⁻¹): 3400 (s), 2962 (s), 1631 (s), 1591 (s), 1541 (s), 1467 (s), 1442 (s), 1361 (s), 1334 (s), 1296 (s), 1272 (s), 1253 (s), 1174 (s), 1147 (m), 1041 (m), 974 (w), 829 (w), 750 (s). Melting

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point 138-140 $^\circ\!\mathrm{C}.$ ESI-MS m/z [(M+H)^+]: 397.24.

The synthetic procedure of complex Zn₃LnL₄: In a 50 mL round bottom flask, 27 μ L (0.2 mmol) triethylamine was added to a solution of H₂L (0.1 mmol) in 15 mL acetonitrile. Then the Zn(NO₃)₂·H₂O (0.1 mmol) was added in the mixture solution and stirred for 15 min to obtain a suspension solution. To this solution, Ln(NO₃)₃·GH₂O (Ln = Dy, Gd, Er) (0.075 mmol) dissolved in 5 mL methanol was added and then stirred at room temperature for 1 hour. The product was filtered from the reaction mixture and further crystallized at room temperature. Zn₃DyL₄ (1): Elemental analysis (%) found (calculated): C 56.48 (57.71), H 5.98 (6.08), N 6.37 (6.87), Zn 9.46 (9.62). IR (KBr, v, cm⁻¹): 2958 (s), 2905 (s), 2866 (s), 1615 (s), 1591 (s), 1550(s), 1535 (s), 1478 (m), 1436 (s), 1410 (m), 1384 (s), 1359 (m), 1316 (m), 1258 (s), 1199 (w), 1164 (s), 1112 (w), 829 (m), 791 (w), 755 (m), 699(w), 588 (w), 540 (w).

Zn₃GdL₄ (2): Elemental analysis (%) found (calculated): C 57.04 (57.57), H 6.05 (6.06), N 6.33 (6.85), Zn 9.44 (9.64). IR (KBr, v, cm⁻¹): 2959 (s), 2908 (s), 2867 (s), 1614 (s), 1590 (s), 1550 (s), 1534 (s), 1477 (m), 1439 (s), 1413 (m), 1383 (s), 1362 (m), 1317 (m), 1257 (s), 1198 (w), 1166 (s), 1111 (w), 832 (m), 788 (w), 753 (m), 699 (w), 591 (w), 544 (w).

Zn₃ErL₄ (3): Elemental analysis (%) found (calculated): C 56.32 (57.86), H 5.93 (6.09), N 6.50 (6.88), Zn 9.35 (9.59). IR (KBr, *v*, cm⁻¹): 2958 (s), 2908 (s), 2868 (s), 1618 (s), 1592 (s), 1549 (s), 1536 (s), 1476 (m), 1439 (s), 1415 (m), 1382 (s), 1359 (m), 1319 (m), 1257 (s), 1199 (w), 1168 (s), 1112 (w), 836 (m), 788 (w), 755 (m), 699 (w), 588 (w), 542 (w).

General procedures for the cycloaddition of $\ensuremath{\text{CO}_2}$ to cyclic carbonates

The reactions were carried out in 50 mL autoclave reactors with catalyst, cocatalyst and epoxy substrates. Several cycles of gas exchanges were carried out to keep a high concentration of carbon dioxide in the reaction vessel until the pressure was stabilized to a specified number between 2 bar to 10 bar. Then, the autoclave was transferred into the oil bath at the corresponding temperature in the range of 40 °C to 120 °C and stirred at 800 rpm. After an appropriate time, the reaction was cooled to room temperature, and a small amount of reaction mixture was taken to be analyzed by ¹H NMR to calculate the conversions of the reaction.

Conclusions

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In summary, a series of novel asymmetry 3d-4f helicates were constructed for the first time based on a bifunctional ligand (H₂L) and Zn²⁺, Ln³⁺ ions, respectively. These amide-functionalized helicates have shown excellent catalytic activity on converting CO₂ to cyclic carbonate. In particular, **Zn₃ErL**₄ exhibited high catalytic activity and selectivity with a wide substrate scope under mild condition. These results provide new insights for designing novel 3d-4f helicates catalysts towards CO₂ conversions.

Conflicts of interest

There are no conflicts to declare.

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