ARTICLE



Rare earth-porphyrin complex catalysts for transforming CO₂ into cyclic carbonate under mild conditions

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Revised: 9 February 2020

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Funding information

The National Natural Science Foundation of China, Grant/Award Number: 11847140; the Natural Science Basic Research Plan in Shaanxi Province of China, Grant/Award Number: 2019JQ-490; the Natural Science Foundation of Shannxi Province, Grant/Award Numbers: 2019JZ-44, 2017JQ2009; the Scientific Research Program Funds by Shannxi Provincial Education Department, Grant/ Award Number: Z18165

Abstract

A series of rare earth metal complexes RE(TPP)(acac) ($RE = Nd^{III}$, Yb^{III} , Eu^{III} , Er^{III} , Pr^{III} , and Lu^{III} ; TPP = 5,10,15,20-tetraphenylporphyrin) were synthesized and characterized via UV-vis, IR, and elemental analyses. Their catalytic activities on the synthesis of cyclic carbonates from carbon dioxide and epoxides under different reaction conditions (temperature, pressure, and reaction time) were investigated. Catalytic reaction tests showed that the complex Lu(TPP) (acac) could significantly enhance the catalytic reactivity under mild conditions without any co-solvent.

KEYWORDS

carbon dioxide, cyclic carbonates, rare earth metal-porphyrin complexes

INTRODUCTION 1

Though a major greenhouse gas that leads to global warming, CO_2 is recognized as an abundant, nontoxic, inexpensive, nonflamable, and renewable C1 resource. Therefore, the utilization of CO_2 is one of the important research directions of green chemistry.^[1-3] A lot of work has been done on CO₂ conversion, and significant progress has been made. At present, carbon dioxide can be converted into a variety of chemicals, such as urea,^[4] propylene carbonate (PC),^[5,6] polycarbonate,^[7] oxazolidinone,^[8] etc. In particular, PC can serve as an ideal solvent; its low toxicity and high boiling point make it widely used in the textile printing and dyeing industry and other fields. The synthesis of PC from CO_2 and propylene oxide has been commercialized by many industries. The atom economy of this reaction

can reach 100% in theory, which meets the requirements of green chemistry and sustainable development.^[9] This reaction has been widely used in industrial production. The advantage of currently available industrial catalysts is their stable catalytic performance; however, their low catalytic activity, harsh reaction conditions, high CO₂ pressure of 7-8 MPa or even higher, and many side effects prevent the reaction's progress. Therefore, designing catalysts with high catalytic activity and mild catalytic conditions has become the key to decreasing the industrial cost of this reaction.^[10]

Porphyrin is a large planar molecule composed of 18 atoms and 18 electrons and easily combines with metal atoms to form metal-porphyrin complexes. Up to now, metal-porphyrin complexes have shown catalytic activity for many organic reactions because of their

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conjugated electron system.^[11] Among these catalytic systems, the existing metal–porphyrin complex catalysts such as Mg(TPP),^[12] VoTPP,^[13] Al(TPP)(O₂CCH₃),^[14] and Cr(TPP)Cl^[15] exhibit good activity on the cycloaddition of carbon dioxide and epoxide. However, the reaction conditions of the existing catalysts are still harsh, so the development of a mild catalytic system remains an exciting topic. As far as we know, studies of rare earth metalloporphyrin complexes have not been reported in this context.

Rare earth metal ions with their high electron density can form coordination compounds with tetraphenylporphyrin (TPP). Here, we report the synthesis and characterization of a series of rare earth metal–TPP complexes of the type RE(TPP)(acac) (RE = $Pr^{III}(1)$, Nd^{III}(2), Eu^{III}(3), Er^{III}(4), Yb^{III}(5), and Lu^{III}(6)), as well as the investigation of the catalytic activity of the complexes for the synthesis of cyclic carbonates from carbon dioxide and propylene oxide.

2 | RESULTS AND DISCUSSION

2.1 | Catalytic activity for CO₂ fixation

The catalytic activity of rare earth metal complexes was examined at 80°C and 1.5 MPa in the cycloaddition reaction of CO₂ and propylene oxide to produce PC; the results are summarized in Table 1. Under optimum reaction conditions, TPP, RE(acac)₃, TBAB (tetrabutylammonium bromide), TPP/TBAB, RE (acac)₃·3H₂O/TBAB, **1–6** and **1–6**/ TBAB were tested for their catalytic performance. No product (entries 1–2, Table 1) was obtained when TPP or RE (acac)₃·3H₂O catalyst was used alone. The catalytic effect of the co-catalyst TBAB alone was unsatisfactory, with a yield of only 35% (entry 3, Table 1). Interestingly, the yield of the cycloaddition reaction product of carbon dioxide and propylene oxide could reach as high as 62% in the presence of TPP or RE (acac)₃·3H₂O and TBAB (entries 4–10, Table 1).

The maximum yield of **1–6** alone as the catalyst was only 33%, and the turnover frequency (TOF) of the catalytic reaction was 471 hr⁻¹ (entries 11–16, Table 1). In contrast, the catalytic activity and reaction yield of the system were significantly improved via the co-presence of 1–6 and TBAB (entries 17–22, Table 1). Obviously, the combination of **6** and TBAB showed the highest yield, up to 98%, and the highest activity, up to 1,374 hr⁻¹. The catalytic activity for the six different rare earth complexes is in the order **6** > **5** > **4** > **3** > **2** > **1**. It can be seen that the catalytic activity is closely related to the radius of the metal ions. The smaller the metal ion radius, the higher the charge density and the stronger the Lewis acidity.

TABLE 1	Synthesis of	propy	lene ca	arbonate	and	TOF	in
different cataly	yst systems ^a						

Entry	Catalyst	Yield ^b (%)	$TOF^{c}(h^{-1})$
1	TPP	0	—
2	RE (acac) ₃	0	_
3	TBAB	35	125
4	TPP/TBAB	44	422
5	Pr(acac) ₃ /TBAB	50	716
6	Nd(acac) ₃ /TBAB	52	736
7	Eu(acac) ₃ /TBAB	54	768
8	Er(acac) ₃ /TBAB	55	787
9	Yb(acac) ₃ /TBAB	59	844
10	Lu(acac) ₃ /TBAB	62	887
11	1	10	143
12	2	13	189
13	3	18	268
14	4	24	343
15	5	29	414
16	6	33	471
17	1/TBAB	60	859
18	2 /TBAB	68	974
19	3 /TBAB	75	1,073
20	4/TBAB	83	1,188
21	5 /TBAB	92	1,317
22	6 /TBAB	98	1,374

^aReaction condition: PO 0.21 mol, complex catalysts 0.15 mmol, TBAB 0.6 mmol, (1.5 MPa) at 80°C for 1 hr.

^bIsolated yield.

^cMoles of propylene carbonate produced per mole of catalyst per hour.

While the activation of carbon dioxide might be stronger, the catalytic activity was higher.^[16]

The synergistic effect of rare earth acetylacetone and TPP complexes with TBAB shows that both have certain catalytic activity, but the performance of the TPP complex is better. Compared with ErCl₃, Hdpza and TBAB catalyze the reactivity of carbon dioxide with epoxide, and the yield and conversion frequency of TPP and TBAB are higher.^[17]

The combination showing the highest PC yield is **6**/ TBAB with a maximum yield of 98% and the highest TOF of 1,374 hr⁻¹. In order to evaluate the high catalytic performance of this catalytic system, we compared it with representative catalysts under different conditions (Table 2). The results show that the catalytic activity of complex **6** is higher than those of most of the published rare earth catalysts such as Yb-Salen,^[18] La-bpzcp, 1-Gd,^[20] and so on.^[21,22]

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TABLE 2 Previously reported typical rare earth catalyst systems used for the synthesis of cyclic carbonates

Cat.	Co-cat.	Catalyst/epoxide (mole ratio)	P (MPa)	<i>T</i> (°C)	Time (h)	Conversion (%)	TOF (h^{-1})	References
Yb-Salen	PPNBr (0.1)	(cyclohexene oxide) 1:1000	2	100	18	75	41	[18]
La-bpzcp	TBAB (0.05)	(styrene oxide) (1:2000)	1	70	4	100	500	[19]
1-Gd	TBAB (2.5)	(styrene oxide) 1:3.33	0.1	80	12	99	2.7	[20]
Yb-complex	TBAB (0.75)	(styrene oxide) 1:1000	1	120	2.5	95	380	[21]
Tb-MOF	TBAB (2.5)	(Epichlorohydrin)	0.1	60	12	99	_	[22]
6	TBAB (0.29)	(propylene oxide) 1:1400	1.5	80	1	98	1,374	This work

TABLE 3 Synthesis of propylene carbonate catalyzed by 6/TBAB under	Entry	Co-cat.	Temp (°C)	Pressure (MPa)	Time (min)	PC yield (%)
different conditions ^a	1	TBAB	40	1.5	60	35
	2	TBAB	60	1.5	60	83
	3	TBAB	80	1.5	60	98
	4	TBAB	100	1.5	60	92
	5	TBAB	120	1.5	60	82
	6	PPNCl	80	1.5	60	87
	7	DMAP	80	1.5	60	36
	8	TBAB	80	0.5	60	62
	9	TBAB	80	0.7	60	76
	10	TBAB	80	0.9	60	79
	11	TBAB	80	1.2	60	85
	12	TBAB	80	1.5	30	42
	13	TBAB	80	1.5	40	60
	14	TBAB	80	1.5	50	86
	15	TBAB	80	1.5	70	98

^aReaction condition: PO 0.21 mol, complex catalyst 0.15 mmol, co-catalyst 0.60 mmol.

Therefore, the combination 6/TBAB was subjected to different conditions such as temperature, presence of a co-catalyst, pressure, and time. The cycloaddition reaction of carbon dioxide and propylene oxide was carried out at different reaction temperatures from 40 to 120°C with 6/TBAB (entries 1-5, Table 3). From the reaction results, it can be seen that the yield of PC increased sharply when the temperature increased from 40 to 80°C and then decreased from 80 to 120°C. When the reaction temperature reached 80°C, the yield of PC was the highest at 98%, which is possibly due to the ring addition reaction, which is an exothermic reaction; thus a low temperature is conducive to the conversion of propylene oxide and PC production. However, if the temperature is too low, the reactant activation is more difficult, so the combination of propylene oxide and the metal center is blocked, thereby reducing the reactivity.^[23] Therefore, 80°C was taken as the optimum temperature in this reaction.

Considering that co-catalysts such as ammonium salts are effective in improving the catalytic activity of complexes, different co-catalysts (TBAB, PPNCl, and DMAP) were tested, and TBAB was found to be the best performer (Table 3, entries 3, 6, and 7).

As shown in Table 3, the CO_2 pressure has a great influence on the yield of PC (entries 3, 8–11). The cycloaddition reaction of carbon dioxide and propylene oxide was tested at different pressures from 0.5 to 1.5 MPa at 80°C. When the reaction pressure was 0.5 MPa, the yield of the product was 62%. With the increase of the reaction pressure, the product yield increased, reaching a maximum at 1.5 MPa. It can be seen that the optimum CO_2 pressure was 1.5 MPa.

The dependence of PC yield on the reaction time was also investigated. The cycloaddition reaction of carbon dioxide and propylene oxide was carried out at different times from 30 to 70 min (entries 3, 12–15, Table 3). The yield of PC increased with increase of the reaction time.



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TABLE 4 Synthesis of propylene carbonate in different catalyst systems^a

^aReaction condition: PO 0.21 mol, complex catalysts 0.15 mmol, TBAB 0.6 mmol, (1.5 MPa) at 80°C for 1 hr.

^bIsolated yield.

^cMoles of propylene carbonate produced per mole of catalyst per hour.

When the reaction time was 30 min, the yield of PC was 42%. When the time was extended to 60 min, the yield of the product reached the maximum value of 98%. Further increase in the reaction time did not produce any effect. Increase in the yield of the product indicated that the degree of conversion of the reaction had reached a maximum. So the optimum reaction time was determined to be 60 min.

By adjusting the reaction substrate, the synthesized complexes were subjected to a comprehensive catalytic activity test. The additional reaction substrate was epichlorohydrin and styrene oxide. All test results are shown in Table 4. The result shows that the cycloaddition reaction of carbon dioxide and epoxide results in good yield and conversion frequency under the **6**/TBAB catalytic system. Among them, when propylene oxide was the reaction substrate, the catalyst worked best and gave the highest PC yield of 98% and conversion frequency of 1,317 hr⁻¹. As shown in Table 4, the regioselectivity depends on the structure and properties of reaction substrates.

2.2 | Mechanism for the cycloaddition reaction of epoxides and CO₂

From the steric hindrance effect, the small carbon and hydrogen atomic radii in the methyl group of propylene oxide lead to a small steric hindrance, so carbon dioxide can directly attack the position of the ternary ring with small steric hindrance and generate the target product. When styrene oxide is used as the reaction substrate, it has a large volume of epoxide relative to propylene oxide, and the reaction yield and the conversion frequency of the reaction are slightly lower than those of propylene oxide substrate, which may be due to the steric hindrance of styrene oxide over the open loop of propylene oxide and to the presence of the $P-\pi$ conjugation which enhances the π electron density of the system to make the structure of styrene oxide more stable.^[24,25] So the reaction may go through the first ring to form stable carbon positive ions (Scheme 1), which then combine with the process of carbon dioxide.^[26] In view of the electronic effect, under optimized reaction conditions, the electrondonating propylene oxide enhances the reactivity of the reaction substrate, while the electron-withdrawing epichlorohydrin and styrene oxide are less reactive than the electron-donating propylene oxide.

The frontier molecular orbitals including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of propylene oxide and epichlorohydrin are shown in Figures 1 and 2, respectively. The energy gap ($E_{\rm HOMO} - E_{\rm LUMO}$) of the HOMO and LUMO energies(in eV) are reported in Table 5. As can be seen from the table, the energy gap of the frontier molecular orbitals of epichlorohydrin is higher, so the barrier is more difficult to overcome, and the catalytic effect is better when propylene oxide is the substrate. In terms of the rigidity of the material, the structural stability of the styrene epoxide is strong,



SCHEME1 Plausible reaction mechanism



FIGURE 1 HOMO and LUMO frontier molecular orbitals of propylene oxide

whereas epichlorohydrin is nonrigid and easy to stretch and bend, so that epichlorohydrin yield and the conversion frequency are higher.

3 | EXPERIMENTAL

3.1 | Synthesis of propylene carbonate

PC was synthesized by the reference method.^[17] Complexes **1–6** (0.15 mmol) and TBAB (0.6 mmol), together with propylene oxide (15 ml, 0.214 mol), were added to a 100-ml autoclave, under continuous ventilation to maintain the CO₂ pressure of 1.50 MPa and 80°C for 1 hr. After completion of the reaction, the mixture was cooled to room temperature and the remaining reaction solution was subjected to vacuum distillation to obtain the product (PC) and weighed. The product was qualitatively analyzed by its IR spectrum. ¹H NMR and ¹³C NMR spectra were obtained by using a Varian INOVA 400-MHz spectrometer with TMS as internal standard.

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FIGURE 2 HOMO and LUMO frontier molecular orbitals of epichlorohydrin

TABLE 5	Calculated values of the HOMO, LUMO, and
energy gap	

Epoxide	E _{номо} (eV)	E _{LUMO} (eV)	Δ <i>E</i> (eV)
Propylene oxide	-0.29	0.02	0.31
3-Chloro-1,2-epoxypropane	-0.31	0.09	0.40

PC: ¹H-NMR (400 MHz, CDCl₃, TMS) δ : 1.493 (d, J = 6.4 Hz, 3H, CH₃), 4.043 (t, J = 7.6 Hz, 1H, CH), 4.576 (t, J = 8.0 Hz, 1H), 4.835–4.918 (m, 1H, CH); ¹³C-NMR (100 MHz, CDCl₃, TMS) δ : 13.740 (q, CH₃), 64.997 (t, CH₂), 67.900 (d, CH), 149.392 (s, C=O); IR (KBr, cm⁻¹): 2989 (w), 1793 (s), 1389 (m), 1187 (s), 1052 (s), 777 (m).

3.2 | Synthesis and characterization of TPP and complexes

3.2.1 | TPP, L1

TPP was synthesized according to the literature procedure.^[27]

p-Nitrobenzoic acid(0.1 mol) together with benzaldehyde(0.02 mol) and xylene(100 ml) were added to a 250-ml four-necked flask equipped with a thermometer, a magnetic stirrer, a water separator, and a constantpressure dropping funnel. Then the mixture was stirred and heated under reflux, and 0.02 mol of freshly distilled pyrrole (dissolved in 10 ml xylene) was slowly added dropwise with a constant-pressure dropping funnel. After refluxing for 4 hr, the reaction was stopped and cooled to room temperature. Then, 70 ml of absolute ethanol was added and the solution was allowed to stand overnight in a refrigerator. The resulting crude product was purified by a neutral alumina column to obtain blue-violet crystals: yield 48%. ¹H-NMR (400 MHz, CDCl₃, TMS) δ(ppm): 2.792 (s, 2H, N-H), 7.254-8.229 (m, 20H, Ar-H), 8.850 (s, 8H, CH_{pyrrole}). FT-IR (KBr, cm⁻¹): 3421 (w), 3316 (m), 3053 (w), 3018 (w), 1593 (m), 1472 (m), 1441 (m), 1348 (m), 1000 (w), 965 (s), 798 (s), 698 (s). UV–vis (CHCl₃) Soret band (nm, $10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$): 418 (4.9138); Q band (nm, $10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$): 515 (0.2307), 550 (0.1523), 590 (0.1492), 646 (0.1338). Aal. Calcd. for C₄₄H₃₀N₄ (614.98): C, 85.99; H, 4.89; N, 9.12. Found: C, 85.82; H, 4.92; N, 9.91.

3.2.2 | RE $(acac)_3 \cdot 3H_2O$ (RE = Nd, Yb, Eu, Er, Pr, Lu)

RE $(acac)_3 \cdot 3H_2O$ (Re = Nd, Yb, Eu, Er, Pr, Lu) were synthesized according to the reference method.^[28]

A typical synthesis of $Pr(acac)_3 \cdot 3H_2O$ is as follows: 7.11 g (0.02 mol) of the rare earth chloride PrCl₃.6H₂O was placed in a 100-ml three-necked flask and a small amount of distilled water was added to dissolve it. The pH was adjusted to about 4, and then acetylacetone (5.39 ml, 0.08 mol) and 25 ml of distilled water were added and stirred for 40 min on an electromagnetic stirrer. At the same time, ammonia solution was added to adjust the pH value to about 6. The solution was filtered and the obtained filter cake was washed with a large amount of distilled water until no more chlorine ions were detected by AgNO₃. Then the product was dried naturally in the air. The crude product of Pr(acac)₃·3H₂O was dissolved in a 60% ethanol aqueous solution and heated to reflux. The reaction mixture was cooled to room temperature to recrystallize, and dried in a vacuum drier to obtain pure green crystal $Pr(acac)_3$ ·3H₂O in 98% yield.

Compounds **1–6** were synthesized according to methods in the literature.^[29,31]

A typical synthesis of complex **5** is as follows: L1 (0.30 mol) and $Pr(acac)_3 \cdot 3H_2O$ (0.60 mol) were added to a 100-ml flask under nitrogen together with 40 ml of 1, 2, 4-trichlorobenzene and slowly heated to 210°C. After refluxing for 5 hr, the mixture was cooled to room temperature. The reaction solution was treated with neutral alumina and the unreacted TPP was separated from the complex in the reaction solution. Finally, the separated liquid was distilled under reduced pressure to give pure dark purple crystals of **1** in 42% yield. IR (KBr, cm⁻¹): 992 (s). UV-vis (CHCl₃) Soret band (nm, 10⁵ mol⁻¹ dm³ cm⁻¹): 548 (0.1705). Aal. Calcd. For **1–6** (855.33): C, 68.77; H 4.44; N, 6.55. Found: C, 68.54; H, 4.63; N, 6.76.

1: IR (KBr, cm⁻¹): 988 (s). UV-vis (CHCl₃) Soret band (nm, $10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$): 417 (4.9856); Q band (nm, $10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$): 549 (0.1723). Aal. Calcd. for: C₄₉H₃₈N₄O₂Nd (858.66): C, 68.47; H, 4.46; N, 6.52. Found: C, 68.21; H, 4.16; N, 6.48.

2: IR (KBr, cm⁻¹): 993 (s). UV–vis (CHCl₃) Soret band (nm, $10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$): 418 (5.3165); Q band (nm,

3: IR (KBr, cm⁻¹): 991 (s). UV–vis (CHCl₃) Soret band (nm, $10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$): 417 (5.0225); Q band (nm, $10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$): 550 (0.1705). Aal. Calcd. for: C₄₉H₃₈N₄O₂Eu (866.39): C, 67.87; H, 4.39; N, 6.46. Found: C, 67.54; H, 4.21; N, 6.52.

4: IR (KBr, cm⁻¹): 989 (s). UV-vis (CHCl₃) Soret band (nm, $10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$): 419 (4.8623); Q band (nm, $10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$): 551 (0.1609). Aal. Calcd. for: C₄₉H₃₈N₄O₂Er (881.68): C, 66.74; H, 4.31; N, 6.35. Found: C, 66.49; H, 4.49; N, 6.49.

6: IR (KBr, cm⁻¹): 993(s). UV-vis (CHCl₃) Soret band (nm, $10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$):418 (5.0214); Q band (nm, $10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$): 550 (0.1625). Aal. Calcd. for: C₄₉H₃₈N₄O₂Lu (889.39): C, 66.11; H, 4.27, N, 6.30. Found: C, 66.01; H, 4.23; N, 6.35.

It can be seen from the infrared data of the ligands and complexes that the N-H stretching vibration of the ligand porphyrin is at 3,316.2 cm^{-1} and is a strong absorption band. In the corresponding metal complex, since the hydrogen atom on the N-H bond in the porphyrin pore is replaced by a metal, the M-N bond is formed, so that the N-H bond band of the porphyrin disappears.^[32] From the UV data of the ligands and complexes, it can be seen that Soret absorption band of the complexes is not significantly displaced relative that to the of the ligand. However, when the metal is not inserted, the O band of the TPP has four absorption peaks, which are consistent with those reported in the literature.^[33,34] After the insertion of the metal, the number of Q bands was reduced to 1 as a result of the increase in the symmetry of the molecular structure.

4 | CONCLUSIONS

In summary, a series of rare earth metal complexes [RE (TPP)] (RE = Pr^{III} (1),Nd^{III} (2),Eu^{III} (3), Er^{III} (4), Yb^{III} (5), and Lu^{III} (6)) have been successfully synthesized and fully characterized. In the synthesis of propylene carbonate (PC) from propylene oxide and CO₂, complex **6** exhibited the best catalytic performance under mild conditions. After optimizing the reaction conditions such as temperature, pressure, and reaction time, the catalytic system achieved excellent conversion (98%) and showed high catalytic activity with an initial TOF of up to 1,374 hr⁻¹.

ACKNOWLEDGMENTS

This work was funded by the National Natural Science Foundation of China (No. 11847140), the Natural Science Foundation of Shannxi Province (No. 2019JZ-44; 2017JQ2009), the Natural Science Basic Research Plan in Shaanxi Province of China (No. 2019JQ-490), and the Scientific Research Program Funds by Shannxi Provincial Education Department (No. Z18165).

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How to cite this article: Wang W, Fan W, Jia X, Li L. Rare earth–porphyrin complex catalysts for transforming CO_2 into cyclic carbonate under mild conditions. *J Chin Chem Soc.* 2020;1–7. <u>https://doi.org/10.1002/jccs.201900560</u>