View Article Online

Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: G. Wang, C. Xu, L. Wang and W. Liu, *Dalton Trans.*, 2018, DOI: 10.1039/C8DT02576B.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/dalton



ARTICLE

Highly Efficient 3d / 4d-4f Coordination Polymer Catalyst for **Carbon Dioxide Fixation into Cyclic Carbonates**

Received 00th January 20xx. Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Gang Wang, Cong Xu, Li Wang, Weisheng Liu* Two novel highly efficient 3d/4d-4f one-dimensional (1D) double-chain coordination polymer catalysts with unique structures were synthesized for the first time. The X-ray single crystal structure analysis revealed that the two compounds are isomorphous and have a 1D metal-organic network coordination polymer structure. Both compounds also showed significant thermal stability and their structure remained stable up to 325 °C. The reaction conditions, type of substrate, amount of catalyst and its catalytic mechanism were investigated. The catalysts ([Dy₂M₂L₄ (OAc)₂ (MeOH)₅ (H₂O)]) (M=Zn, Cd) exhibited excellent catalytic activity in the cycloaddition of CO₂ and styrene oxide (C₈H₈O, SO). High product yields, high selectivity, and the highest turnover frequency (TOF) reached 28,400h⁻¹. Additionally, the catalyst can significantly enhance

the application of the present types of 3d/4d-4f in catalysis for the transformations involving the fixation of CO2.

Introduction

Carbon dioxide is the main greenhouse gas, but it is also an important C1 resource that can be further used. 1-3. Due to its abundance, non-toxic and inert characteristics, more and more chemists are paying attention to it. In this regard, the coupling of CO_2 and epoxides to form cyclic carbonates is an environmentally-friendly atomic economic response that reduces CO₂ emissions and conserves energy ⁴⁻⁶. Organic carbonates, such as dimethyl carbonate and diphenyl carbonate, which are widely used in the fields of organic solvents, green reagents and engineering plastics, can be derived from cyclic carbonates to perform the cycloaddition of CO_2 and epoxides as a commonly used effective approach ⁷⁻⁹.

Not surprisingly, green chemistry is the frontier and hot field of international chemical science research, and CO2 catalysis is one of the key branches of green chemistry and methodology ¹⁰⁻¹². CO₂ is both thermodynamically and kinetically stable, and therefore high-energy reactants and catalysis are required to overcome these challenges. However, it can be expedited by transition metal and rare earth salts, and related coordination compounds¹³ that are common catalysts for the conversion of CO₂ into cyclic carbonates have been a very effective strategy in previous studies ¹⁴⁻¹⁶. Also, although all kind of catalyst systems have been used to catalyse these reactions, several limitations still exist, such as low catalyst conditions ¹⁷⁻¹⁹. Therefore, it is especially important to design and synthesize catalysts with high efficiency, high selectivity and high activity. Research shows that two or more metal centres near the active site can activate multiple reactants for superior efficiency and unmatched selectivity. There has been a great deal of interest in the synergistic effect for controlling the metal centres in polynuclear complexes to enhance the catalytic performance ²⁰⁻²³. For example, the heteronuclear bimetallic Schiff base Ln-M complex developed by Shibasaki has been used by other groups as a catalyst for various synthesis reactions ²⁴⁻ ²⁶. Their results indicate that the proximity of different metal centres will generate potential synergy, which mainly contributes to high catalytic reactivity and selectivity. Additionally, for another, precise control of the supramolecular structure will modulate the catalytic activity of the catalyst and expand the scope of the catalyst. The rational design of heterometallic multinuclear catalysts for further evaluation of its catalytic performance has great challenges and excellent prospects ²⁷⁻²⁹. Motivated by these results, we decided to study a catalyst that uses a rare earth metal and transition metal as the active catalyst sites for the catalytic conversion of CO₂ to cyclocarbonates.

reactivity, low selectivity, air sensitivity and use of additional

solvents, even at high temperature and high pressure (> 5MPa)

With the ultimate goal of obtaining highly efficient catalysis, we report here the design and synthesis of heterometallic highly efficient 3d / 4d - 4f coordination polymer catalysts featuring ([Dy₂M₂L₄ (OAc)₂ (MeOH)₅ (H₂O)]) (M=Zn, Cd). The catalyst has higher reaction activity, selectivity and better substrate universality in the catalytic CO₂ cycloaddition reaction.

Experimental section

^{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,

⁺ Electronic supplementary information (ESI) available: Supporting Fig. S1 - S23 and Tables S1 - S3 containing additional structural data, characterization details, and catalytic data. CCDC 1815465 - 1815466. For ESI and crystallographic data in CIF or other electronic format see DOI: xxx-xxx-xxxx

Journal Name

Materials and Characterizations



Scheme, 1, Synthetic routes of complex1 and complex 2.

Carbon dioxide (CO₂, 99%) was purchased from commercial sources and used without further purification. 3,5di-tert-butyl-2-hydroxybenzaldehyde, methyl 5-allyl-3methoxysalicylate were purchased from Adamas Reagent, Ltd. All the epoxides were bought from Sigma-Aldrich, Korea and the metal salts (>99%) were bought from TCI chemicals. 5-allyl-2-hydroxy-3-methoxy benzohydrazide was prepared according to the literature method ³⁰. The infrared spectra were recorded on a Burker VERTEX 70 FTIR spectrometer using KBr pellets in the 400-4000cm⁻¹ region. UV/Vis absorption spectra were determined on an Agilent Technologies Cary 5000 UV-Vis-NIR spectrophotometer. The C, H, and N microanalyses were measured by Vario EL Cube elemental analyser. The ¹H NMR and ¹³C NMR data were collected on a JNM-ECS 400M NMR spectrometer. X-ray powder diffraction data were collected on PANalytical X'Pert Pro Diffractometer operated at 40 kV and 40 mA with Cu K α radiation (λ =1.5406Å). Thermogravimetric analysis experiments were performed using a TGA/NETZSCH STA449C instrument heated from 25-800℃ (heating rate of 10 ℃ organic hydrogen atoms were generated geometrically. For /min, nitrogen atmosphere).

Preparation of [Dy₂Zn₂L₄(OAc)₂ (MeOH)₅(H₂O)] · (solvent)_n (1)

General synthetic procedure for complex (1): 10 µL of triethylamine was added to a 1 mL acetonitrile and 5 mL methanol solution of 0.1 mmol H₃L. Then, 0.05 mmol $Zn(NO_3)_2 \cdot 6H_2O$ was added and the mixture was stirred for 10 min to obtain a suspension. To this solution 0.05 mmol Dy(OAc)₃·4H₂O was added and a clear solution was obtained. The mixture was stirred 30 min and filtered for crystallisation at room temperature. After about two weeks, yellow single crystals (Fig. S5(a), ESI +) suitable for crystal analysis were obtained. The abundant complexes powder for catalytic reaction were collected with the same method used to obtain a white solid and after filtration, it was washed with acetonitrile, and dried in the air, to obtain a 45% yield. Further, the products were characterized by IR, PXRD, and TGA. C₁₁₇H₁₆₀Dy₂N₉O₂₈Zn₂: Elemental analysis (%) found (calculated): C 54.02 (54.13), H 6.13 (6.21), N 4.79 (4.86). IR (KBr, u, cm ⁻¹) : 3435 (s), 2960(s), 1623 (s), 1550(s), 1464(s), 1426(s), 1250 (s) , 1173 (m), 1135 (m), 1071 (w), 844 (w), 815 (w), 780 (m).

Preparation of [Dy₂Cd₂L₄(OAc)₂ (MeOH)₅(H₂O)] · (solvent)_n (2)

General synthetic procedure for complex (2): 10 µL triethylamine was added to a 1 mL acetonitrile and 4 mL methanol solution of 0.1 mmol H_3L . Then, vio 0.05_{icl} mmol Cd(NO₃)₂·4H₂O was added and the mixture was stirred for the min to obtain a suspension. To this solution 0.05 mmol Dy(OAc)₃·4H₂O was added and a clear solution was obtained. The mixture was stirred 30 min and filtered for crystallisation at room temperature. After about two weeks, yellow single crystals (Fig. S5(b), ESI +) suitable for crystal analysis were obtained. The abundant complexes powder for catalytic reaction were collected with the same method used to obtain a white solid and after filtration, it was washed with acetonitrile, and dried in the air, to obtain a 45% yield. Further, the products were characterized by IR, PXRD and TGA. C₁₁₃H₁₄₂Dy₂N₉O₂₅Cd₂: Elemental analysis (%) found (calculated): C 51.53 (52.68), H 5.43 (5.56), N 4. 75 (4.89). IR (KBr, u, cm⁻¹) : 3432 (s), 2960(s), 1623(s), 1550 (s), 1460(s), 1383(s), 1250 (s), 1249 (s), 1170 (s), 1168 (m), 1078 (m), 1027 (w), 844 (w), 815 (w), 743 (m).

X-ray crystallography

Crystal data of Complex 1-2 and H₃L were collected on SuperNova, Dual, Cu at zero, AtlasS2 system, diffractometer (Cu Kα radiation, λ = 1.54178 Å, complex 1, Mo Kα radiation, λ = 0.71073 Å, complex 2) at 100 K. Data reduction was accomplished by the CrysAlisPro. Multi-scan absorption corrections were applied by using the program SADABS. The structure of the compounds was solved by using the direct method of SHELXTL-2013 ³¹ and refined by full matrix leastsquares cycles on F² through the Olex2 program ³². The contribution of severely disordered solvent molecules was treated as a diffusion treatment by the SQUEEZE program of PLA-TON ³³ and was further refined using the data generated. All of the non-hydrogen atoms were refined anisotropically. The details, see cif data in Supporting Information. X-ray crystallographic data and experimental details for all complexes structural analyses are summarized in Table S1. The CCDC reference numbers 1815465 and 1815466 for complex 1 and complex 2.

Catalytic cycloaddition of CO₂ with epoxides

The following general procedure is for the cycloaddition reaction of CO₂ and epoxides. The reactions were conducted in a 50 mL autoclave reactor. The catalyst, co-catalyst tetrabutylammonium bromide (TBAB) and epoxide (10 mmol) were added to the reactor. The reactor was subjected to three cycles of pressurisation (with CO₂ at 1.5 MPa), and depressurisation and the final pressure was stabilized at 1 MPa. The vessel was set in a thermostatic heating jacket, and the solution was mechanically stirred at 800 rpm. Then, the temperature of the reactor was raised to 120 °C. After 1 h, the reaction was cooled to room temperature, and a small liquot of the reaction mixture was taken for analysis by ¹H NMR in order to calculate the yield of the reaction.

Results and discussion

Crystal structure

Published on 28 July 2018. Downloaded by Western Sydney University on 7/31/2018 12:54:31 PM

actions Accep

Published on 28 July 2018. Downloaded by Western Sydney University on 7/31/2018 12:54:31 PM

Journal Name



Fig. 1. Structural fragments of complex1. (a) The coordination environment of two adjacent Dy1, Dy2, and Zn1, Zn2 centres. (b) 1D double-chain structure. (c) Dy1, Dy2 and Zn1, Zn2 centres coordination polyhedra. (d) Packing diagram along the axis showing ten djacent 1D chains. (e) A single chain thermo-ellipsoid model diagram.

The X-ray single crystal structure analysis showed that the two compounds are isomorphous and crystallise in the monoclinic system, space group P $2_1/c$ (Table S1, ESI ⁺). The structure of the catalyst 1 as a representative example will be discussed in detailhere. As shown in Fig.1(a), the Dy1 centre is eight-coordinate and has a twisted dodecahedron [DyO6N2] environment, the Dy2 centre has the same coordination environment, which is filled with two μ_2 -L moieties and two terminal MeOH ligands. The Dy1 and Dy2 centres are connected to six oxygen groups deriving from two μ_2 -L and two MeOH ligand, also two nitrogen groups originating from two μ_2 -L (Fig. 1(a) and (b), respectively). The Zn1 center is attached to four oxygen groups originating from two $\mu_2\text{-}L\text{,}$ and the other two oxygen groups are from the MeOH ligand and μ -OA_C⁻ anion. The Zn2 centre is linked to four oxygen groups deriving from two μ_2 -L, and the other two oxygen groups are from the H₂O ligand and $\mu\text{-}OA_{C}\text{-}$ anion. (Fig. 1(a) and (b), respectively). The Dy1 atom is double-linked to oxygen and nitrogen groups deriving from two μ_2 -L moieties, to form dimer motifs with Zn1, with the shortest Dy ... Zn separation of 7.685 Å, and the Dy-Zn distances measured were 7.740 and 7.685 Å for Dy1-Zn1 Dy2-Zn2, respectively. (Fig. 1(b) and (c)). These patterns are then further held together through the remaining oxygen and nitrogen groups of μ_2 -L to generate an intricate 1D chain structure (Fig. 1 (d) and (e)).

Thermogravimetric analysis

The stability of complex 1and 2 was investigated by thermogravimetric analysis (TGA) under a nitrogen atmosphere



at a temperature range of 25-800 $^{\circ}$ C. Two compounds exhibit high thermal stability. The results obtained (Fig.2) reveal that both complexes display a similar thermal behaviour due to their isomorphous structures. Accordingly, only the thermal stability of complex 1 is discussed in detail here. The TGA results of compound 1 revealed that the weight loss in this 25-200 $^{\circ}$ C interval was 4.7%, mainly due to the loss of solvent molecules and crystallisation water. When the temperature was up to 325 $^{\circ}$ C, the second weight loss of 55.8% can be attributed to the decomposition of the metal-organic network. The third stage of weight loss occurred mainly from 500 $^{\circ}$ C and above, involved a small weight loss, due to decomposition of the framework formed Dy₂O₃, ZnO and carbon residue, which cannot continue to decompose. Thus, the results show that the metal-organic compounds have excellent thermal stability.

Catalytic activity for CO₂ fixation

The research on the conversion of CO₂ to cyclic carbonate has drawn considerable attention in recent years ^{1, 2}. In this 3d/4d-4f synergistic catalysis system, the two metal centres of Dy and M (Zn, Cd) are located in the proper scope to enable the intramolecular synergistic action, and the exposed polymetallic sites act as Lewis acid activators, implying that the catalytic system has potential catalytic applications. In our preliminary tests, we chose styrene oxide as an epoxide to react with CO2 and to determine the optimum conditions for this coupling reaction (Table 1). We utilised 0.005 mol% each of catalyst 1 and 2, in 0.75 mol% of TBAB as co-catalysts for the cycloaddition of styrene oxide and CO₂ to obtain cyclic carbonate in a solventfree reaction under 120 $^\circ$ C, at 1 MPa, for 1h. Both catalysts achieved excellent yields (60 % and 88 %, respectively) and showed high catalytic activity with TOF as high as 17,580 h⁻¹ and 13,984 h⁻¹ after only 1h reaction (Table 1 entries 1-2). Since the catalyst 1 showed better catalytic activity, we chose catalyst 1 as a representative catalyst to further investigate the reactions. Various co-catalysts were tested under the same conditions, with TBAB giving the best result (Table 1 entries 3-5, Fig. 3(a)). Neither catalyst 1 nor TBAB alone could catalyse the reaction with satisfactory yield (1 % and 25 %, respectively), but the yield was increased to 93 % when both, catalyst 1 and TBAB, were

ARTICLE

ARTICLE

Published on 28 July 2018. Downloaded by Western Sydney University on 7/31/2018 12:54:31 PM

Table 1. Synthesis of cyclic carbonate via insertion of CO_2 to styrene oxide catalysed by complex 1 and 2 under different conditions ^a

		+ (CO ₂ –	Cat.an T. P So	d Co-ca	at → ree [C	o v v
Entry	Cat.	Cat. (mol%)	Co-cat.	Co-cat. (mol%)	т (°С)	Time (h)	Yield (%) ^b	TOF (h ⁻¹) ^b
1	1	0.005	Bu₄NBr	0.75	120	1	88	17600
2	2	0.005	Bu₄NBr	0.75	120	1	60	12000
3	1	0.005	Bu₄NI	0.75	120	1	61	12200
4	1	0.005	Bu₄NCI	0.75	120	1	55	11000
5	1	0.005	PPN-Cl	0.75	120	1	69	13800
6	1	0.005	Bu₄NBr	-	120	1	1	200
7	1	0.005	Bu₄NBr	0.25	120	1	69	13800
8	1	0.005	Bu₄NBr	0.5	120	1	75	15000
9	1	0.005	Bu₄NBr	0.75	120	1	88	17600
10	1	0.005	Bu₄NBr	1	120	1	93	18600
11°	1	0.005	Bu₄NBr	0.75	120	1	85	17000
12	1	-	Bu₄NBr	0.75	120	1	25	33
13	1	0.0025	Bu₄NBr	0.75	120	1	71	28400
14	1	0.005	Bu₄NBr	0.75	120	1	88	17600
15	1	0.0075	Bu₄NBr	0.75	120	1	92	12267
16	1	0.01	Bu ₄ NBr	0.75	120	1	95	9500
17	1	0.0125	Bu₄NBr	0.75	120	1	99	7920
18	1	0.01	Bu₄NBr	0.75	140	1	99	9900
19	1	0.01	Bu₄NBr	0.75	120	1	95	9500
20	1	0.01	Bu₄NBr	0.75	100	1	72	7200
21	1	0.01	Bu₄NBr	0.75	80	1	42	4200
22	1	0.01	Bu₄NBr	0.75	60	1	19	1900
23	1	0.01	Bu₄NBr	0.75	120	20 min	52	15600
24	1	0.01	Bu₄NBr	0.75	120	40 min	78	11700
25	1	0.01	Bu₄NBr	0.75	120	60 min	95	9500
26	1	0.01	Bu₄NBr	0.75	120	80 min	98	7538
27	1	0.01	Bu₄NBr	0.75	120	100 min	99	5964
28	H₃L	0.01	Bu₄NBr	0.75	120	1	45	458

Reaction conditions: (a) styrene oxide (10 m mol), CO₂ 1 MPa, solvent-free. (b). Determined by ¹H NMR spectroscopy. TOF = Yield/n_{cat}/h. (c). Reaction condition: 10 mmol styrene oxide, 0.005 mol % catalyst, 0.75 mol %TBAB, CO₂ 0.6 MPa. Selectivity of cyclic carbonates were all >99%.

used as co-catalysts. The yield remains unchanged when the CO₂ pressure decreased from 1.0 to 0.6 MPa, (Table 1 entries 9 and 11). With different concentration of TBAB (0.25 mol %, 0.5 mol %, 0.75 mol % and 1 mol %, respectively) good yields were obtained with initial TOF as high as 13,800 h⁻¹, 15,000 h⁻¹, 17,600 h⁻¹ and 18,600 h⁻¹ (Table 1 entries 7-10, Fig. 3(b)), respectively.

The reaction at different catalyst concentrations (Table 1 entries 12-17, Fig. 3(c)) showed that the catalyst also had excellent catalytic activity when the amount of catalyst 1 was 0.0025 mol% and TBAB was 0.75 mol%, with the highest initial TOF of up to 28,400h⁻¹. When the amount of catalyst 1 is 0.01mol%, reactions at a different temperature (60 °C, 80 °C, 100 °C, 120 °C and 140 °C, respectively) (Table 1 entries 18-22, Fig. 3(d)) showed that the catalyst also has outstanding catalytic activity with relatively high TOF up to 1,900 h⁻¹, 4,200 h⁻¹, 7,200 h⁻¹, 9,500 h⁻¹, 12,267 h⁻¹, respectively. With other conditions unchanged, the reaction time from 20 min to 100 min (Table 1 entries 23-27, Fig. 3(e)), the conversion of the product was almost complete after 60min, reaching 95%, so the choice of the reaction time was 60 min for substrate expansion. In short, the



Fig. 3. The yield of epoxy styrene and carbon dioxide converted to cyclocarbonate under different reaction conditions. Reaction conditions: (a).10 mmol styrene oxide, 0.005 mol% catalyst, 0.75 mol% co-catalyst, 120°C, 1 h, CO₂ 1 MPa. (b).10 mmol styrene oxide, 0.005 mol% catalyst, co-catalyst (0-1mol%), 120°C, 1 h, CO₂ 1 MPa. (c).10 mmol styrene oxide, catalyst (0-0.0125mol%), 0.75 mol% TBAB as the co-catalyst, 120°C, 1 h, CO₂ 1 MPa. (d).10 mmol styrene oxide, 0.01 mol% catalyst, 0.75 mol% TBAB as the co-catalyst, temperature ($60-140^{\circ}$ C), 1 h, CO₂ 1 MPa. (e).10 mmol styrene oxide, 0.01 mol% catalyst, 0.75 mol% TBAB as the co-catalyst, 0.75 mol% Catalyst, 0.75 mol% TBAB as the co-catalyst, 0.75 mol% Catalyst, 0.75 mol% TBAB as the co-catalyst, 0.75 mol% TBAB as the co-catalyst, 0.75 mol% Catalyst, 0.75 mol% TBAB as the co-catalyst, 120°C, 1 mpa.

results from Table 1 and Fig. 3 revealed that the optimum conditions for the reaction of CO₂ with styrene oxide are as follows: the amount of the substrate is 10 mmol, with 0.01 mol% of catalyst and 0.75 mol% of co-catalyst, at 1 MPa and 120 $^\circ C$, for 1h to reach a yield of 95%.

In order to evaluate the high catalytic performance of this 3d-4f synergistic catalysis, we compared it with representative Zn catalysts and lanthanide complex catalysts under different conditions (Table S3). The results revealed that catalyst 1 has higher catalytic activity than most of the tested catalyst including some Zn catalysts and lanthanide catalysts, such as ZnBr₂, Zinc complexes ³⁴⁻³⁶ and lanthanide catalysts ^{2, 37, 38}, indicating that the high efficiency of this heterometallic catalyst system. Satisfyingly, when the amount of catalyst 1 and cocatalyst TBAB is 0.0025 mol% and 0.75 mol%, respectively, for the cycloaddition of styrene oxide under 120 °C, 1 MPa after only 1 h reaction, a medium yield of 71 % was obtained with an excellent TOF as high as 28,400 h⁻¹(Table 1 entry 13), which was a clear improvement compared with that of 25 % catalyzed with TBAB only. This efficiency can be compared with those of the most efficient metal catalysts, such as [EMIm]₂[Br₂Zn(Et₂PO₄)]₂ ³⁹, [L₁Zn₂]₄³⁶, Zn(OPO)₂³⁵, Ni(PPh₃)Cl₂/PPh₃/Zn ⁴⁰, ZnBr₂³⁴, Zn-CMP⁴¹, Mg-porphyrin⁴², Yb-DDPY³⁷, Ionic Rare Earth Metal², Yb-

Page 4 of 8

Journal Name



Table 2. Various carbonates from different epoxides catalysed by catalyst ${\bf 1}$ under same condition ${\bf a}_{\rm i}$

Entry	Substrte	Product	Yield (%) ^a	TOF(h ⁻¹)
1	<u>^</u>	, lo	99	9900
2	\checkmark		98	9800
3	\sim		94	9400
4	CI	CI	99	9900
5	Br	Br	98	9800
6	но	но	96	9600
7	γ°	Zor	90	9000
8		o th	95	9500
9		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	98	9800
10			95	9500
11	γ^{0}	You to	93	9300
12			99	9900
13	\diamondsuit	L ^e	35(93 ^b)	3500(1163)
14	\bigcirc	, Contraction of the second se	35(90 ^b)	3500(1125)
15	0 ^A O		3(50 ^b)	300(625)

Reaction conditions: (a) 10 mmol epoxide, 0.01 mol% catalyst, 0.75 mol% Bu₄NBr as the co-catalyst, 120°C, 1 h, CO₂ 1 MPa. (b) 10 mmol epoxide, 0.01 mol% catalyst, 0.75 mol% Bu₄NBr as the co-catalyst, 120 °C, 8 h, CO₂ 1 MPa. Yields were determined by ¹ H NMR. Selectivity of cyclic carbonates were all >99 %.

mesocate⁴³, helicate-1(Zn-Tb)³⁸, $[Yb(\mu-L)(\mu_3-L)(H_2O)]_nBr_n^{44}$ (Table S3).

To investigate the wide applicability of the novel 3d-4f catalyst system, a sequence of monosubstituted terminal epoxides and internal epoxide substrates were examined under the identical conditions. The results revealed that all the functionalized terminal epoxides could be obtained with excellent yields (the yield of most substrates was >90%) and high selectivity (99 %) at 120 °C and 1 MPa of CO₂ pressure, after only1 h reaction (Table 2 entries 1-12). The internal epoxides, such as cyclopentene oxide, cyclohexene oxide and stilbene oxide, exhibited lower activity compared with the terminal counterparts, but performed with for a relatively long time to afford the products in reasonably good yields (93%, 90%

and 50%, respectively) (Table 2 entries, 13, 14 and 15) which was ascribed to the steric effect. The results shown approach to the steric effect and the results shown approach to the activity and displayed broader substrate scopes.

Mechanism



Fig. 4. The proposed mechanism for the cycloaddition reactions catalysed by the catalyst

In order to determine whether the structure of the catalyst changes before and after the catalytic reaction, we characterized the structure of the catalyst by UV/Vis absorption spectroscopy and ¹H NMR (Fig. S9 and Fig. S10), the spectroscopic (UV/Vis and ¹H NMR) analyses of TBAB, free styrene, free carbonates, H₃L, before catalysis, and after catalysis were carried out. UV/Vis absorption spectroscopy indicates that the structure of the catalyst did not change significantly before and after catalyst did not change

significantly before and after the contrast reaction. In summary, the catalyst has good stability and a consistent structure before and after catalysis.

Based on the results of the multi-metal catalyst systems that have been studied and reported to date 37, 38, 44, the synergistic effect of polymetal systems may originate from different metal systems and a possible approach are proposed (Fig. 4). As shown in Fig. 4, both Zn and Dy ions may play an important role in activating the components of the reaction. The oxygen atom of the epoxy compound first activates the epoxy ring by binding to Lewis acidic Dy(III) and Zn(II) sites. Then, TBAB opened the epoxy ring with Br⁻ as a nucleophile to attack the less-hindered carbon atom of the epoxide. Subsequently, the open epoxy ring interacts with CO₂ to form an alkyl carbonate anion, which is converted to the corresponding cyclic carbonate by a final ring-closing step, and finally TBAB is recycled again. In addition, since the Lewis base sites (N atoms) may also promote the cycloaddition reaction 45-⁴⁸. H₃L was used as a catalyst with TBAB for the model reaction. The catalytic yield with H₃L of 45% was significantly improved compared to the 25% yield catalysed with TBAB only (Table 1, entries 12, 28). Therefore, we hypothesise that the catalysts may increase the

Published on 28 July 2018. Downloaded by Western Sydney University on 7/31/2018 12:54:31 PM

D

Ð

sactions Accep

Journal Name

ARTICLE

affinity for CO_2 by the incorporation of amide groups into the structure and binding to multiple Lewis acid sites, which may explain the high catalytic activity of the catalyst. The higher catalytic activity of the catalyst 1 and TBAB system results from the synergistic effect of combining the Zn ions with the Lewis acidic Dy(III) sites ⁴⁹.

Conclusions

In this study, we successfully synthesised two novel 3d/4d-4f 1D double-strand coordination polymer catalysts with unique structures for CO₂ fixation. The X-ray single crystal structure analysis revealed that the two compounds are isomorphous and have a 1D metal-organic network coordination polymer. The topological analysis of the underlying 1D chains allowed us to establish that all metal atoms of each chain are exposed to the outside and become potential catalytically active sites. Both compounds also showed significant thermal stability and their network remained stable up to 325 °C. Importantly, catalyst 1 showed high catalytic activity (> 95%) and CO₂ conversion selectivity (> 99%) to obtain cyclic carbonates with a wide substrate scopes under suitable conditions. The cycloaddition reaction between CO₂ and a styrene oxide resulted in TOF up to 28,400 h⁻¹. In addition, the application of the current types of 3d-4f catalysts in catalysis are highlighted and particularly, involve the conversion of fixed CO₂.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSFC, Grant 21431002).

Notes and references

- J. Zhu, T. Diao, W. Wang, X. Xu, X. Sun, S. A. C. Carabineiro and Z. Zhao, *Applied Catalysis B: Environmental*, 2017, **219**, 92-100.
- 2. Z. Zhao, J. Qin, C. Zhang, Y. Wang, D. Yuan and Y. Yao, *Inorg Chem*, 2017, **56**, 4569-4576.
- 3. J. Ai, X. Min, C. Y. Gao, H. R. Tian, S. Dang and Z. M. Sun, *Dalton Trans*, 2017, **46**, 6756-6761.
- 4. A. Decortes, A. M. Castilla and A. W. Kleij, *Angew Chem Int Ed Engl*, 2010, **49**, 9822-9837.
- C. Y. Gao, H. R. Tian, J. Ai, L. J. Li, S. Dang, Y. Q. Lan and Z. M. Sun, *Chem Commun (Camb)*, 2016, **52**, 11147-11150.
- W.-Z. Qiao, H. Xu, P. Cheng and B. Zhao, *Crystal Growth & Design*, 2017, 17, 3128-3133.
- a. W. W. Tao Wang, a Yuan Lyu,*a Xingkun Chen,ac Cunyao Li,ac Yan Zhang,ac Xiangen Songa and Yunjie Ding*ab, *RSC* Adv., 2017, 7, 2836-2841.
- 8. H. Yasuda, L.-N. He and T. Sakakura, *Journal of Catalysis*, 2002, **209**, 547-550.
- 9. M. Ramin, J. Grunwaldt and A. Baiker, *Journal of Catalysis*, 2005, **234**, 256-267.

- 10. S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger Coordination Chemistry Reviews, 2001;1255,3946@5147976B
- 11. H. Xu, B. Zhai, C. S. Cao and B. Zhao, *Inorg Chem*, 2016, **55**, 9671-9676.
- 12. D. Zhao, X.-H. Liu, C. Zhu, Y.-S. Kang, P. Wang, Z. Shi, Y. Lu and W.-Y. Sun, *Chemcatchem*, 2017, **9**, 4598-4606.
- 13. D. Zhao, X. H. Liu, J. H. Guo, H. J. Xu, Y. Zhao, Y. Lu and W. Y. Sun, *Inorg Chem*, 2018, **57**, 2695-2704.
- M. Aresta, A. Dibenedetto and A. Angelini, *Chem Rev*, 2014, 114, 1709-1742.
- 15. C. Maeda, Y. Miyazaki and T. Ema, *Catalysis Science & Technology*, 2014, **4**, 1482-1497.
- Q. Liu, L. Wu, R. Jackstell and M. Beller, *Nat Commun*, 2015, 6, 5933-6933.
- J. Sun, S.-i. Fujita, F. Zhao and M. Arai, *Green Chemistry*, 2004, 6, 613-616.
- 18. T. Ema, Y. Miyazaki, T. Taniguchi and J. Takada, *Green Chemistry*, 2013, **15**, 2485-2492.
- C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adan,
 E. Martin and A. W. Kleij, J Am Chem Soc, 2013, 135, 1228-1231.
- 20. M. Raynal, P. Ballester, A. Vidal-Ferran and P. W. van Leeuwen, *Chem Soc Rev*, 2014, **43**, 1734-1787.
- C. J. Brown, F. D. Toste, R. G. Bergman and K. N. Raymond, Chem Rev, 2015, 115, 3012-3035.
- 22. J. N. Rebilly, B. Colasson, O. Bistri, D. Over and O. Reinaud, *Chem Soc Rev*, 2015, **44**, 467-489.
- 23. I. Nath, J. Chakraborty and F. Verpoort, *Chem Soc Rev*, 2016, **45**, 4127-4170.
- 24. R. M. Haak, S. J. Wezenberg and A. W. Kleij, *Chem Commun* (*Camb*), 2010, **46**, 2713-2723.
- 25. J. Park and S. Hong, *Chem Soc Rev*, 2012, **41**, 6931-6943.
- 26. S. Matsunaga and M. Shibasaki, *Chem Commun (Camb)*, 2014, **50**, 1044-1057.
- C. Piguet, M. Borkovec, J. Hamacek and K. Zeckert, Coordination Chemistry Reviews, 2005, 249, 705-726.
- 28. D. E. Barry, D. F. Caffrey and T. Gunnlaugsson, *Chem Soc Rev*, 2016, **45**, 3244-3274.
- 29. D. Zhao, X. H. Liu, Z. Z. Shi, C. D. Zhu, Y. Zhao, P. Wang and W. Y. Sun, *Dalton Trans*, 2016, **45**, 14184-14190.
- K. Cheng, Q. Z. Zheng, Y. Qian, L. Shi, J. Zhao and H. L. Zhu, Bioorg Med Chem, 2009, 17, 7861-7871.
- G. M. Sheldrick, Acta Crystallogr C Struct Chem, 2015, 71, 3-8.
- O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Journal of Applied Crystallography*, 2009, 42, 339-341.
- A. L. S. P.vander Sluis, Acta Crystallogr. A, 1990, 46, 194-201.
- H. Xie, S. Li and S. Zhang, Journal of Molecular Catalysis A: Chemical, 2006, 250, 30-34.
- R. Ma, L.-N. He and Y.-B. Zhou, *Green Chemistry*, 2016, 18, 226-231.
- R. M. Haak, A. Decortes, E. C. Escudero-Adan, M. Martinez Belmonte, E. Martin, J. Benet-Buchholz and A. W. Kleij, *Inorg Chem*, 2011, 50, 7934-7936.
- 37. N. Wei, Y. Zhang, L. Liu, Z.-B. Han and D.-Q. Yuan, *Applied Catalysis B: Environmental*, 2017, **219**, 603-610.
- L. Wang, C. Xu, Q.-X. Han, X.-L. Tang, P. Zhou, R. Zhang, G. Gao, B. Xu, W. Qin and W.-S. Liu, Chemical Communications, 2018, 54, 2212-2215.

Published on 28 July 2018. Downloaded by Western Sydney University on 7/31/2018 12:54:31 PM

- J. K. Lee, Y. J. Kim, Y.-S. Choi, H. Lee, J. S. Lee, J. Hong, E.-K. Jeong, H. S. Kim and M. Cheong, Applied Catalysis B: Environmental, 2012, 111-112, 621-627.
- 40. F. Li, C. Xia, L. Xu, W. Sun and G. Chen, *Chemical Communications*, 2003, **0**, 2042-2043.
- 41. Y. Xie, T. T. Wang, R. X. Yang, N. Y. Huang, K. Zou and W. Q. Deng, *ChemSusChem*, 2014, **7**, 2110-2114.
- 42. T. Ema, Y. Miyazaki, J. Shimonishi, C. Maeda and J. Y. Hasegawa, *J Am Chem Soc*, 2014, **136**, 15270-15279.
- 43. Q. Han, L. Wang, Z. Shi, C. Xu, Z. Dong, Z. Mou and W. Liu, *Chem Asian J*, 2017, **12**, 1364-1373.
- 44. C. Xu, Y. Liu, L. Wang, J. Ma, L. Yang, F. X. Pan, A. M. Kirillov and W. Liu, *Dalton Trans*, 2017, **46**, 16426-16431.
- 45. M. Liu, L. Liang, X. Li, X. Gao and J. Sun, *Green Chemistry*, 2016, **18**, 2851-2863.
- 46. Y. Ren, O. Jiang, H. Zeng, Q. Mao and H. Jiang, *RSC Advances*, 2016, **6**, 3243-3249.
- 47. R. R. Kuruppathparambil, T. Jose, R. Babu, G.-Y. Hwang, A. C. Kathalikkattil, D.-W. Kim and D.-W. Park, *Applied Catalysis B: Environmental*, 2016, **182**, 562-569.
- 48. L. Liu, S. M. Wang, Z. B. Han, M. Ding, D. Q. Yuan and H. L. Jiang, *Inorg Chem*, 2016, **55**, 3558-3565.
- A. Barthel, Y. Saih, M. Gimenez, J. D. A. Pelletier, F. E. Kühn,
 V. D'Elia and J.-M. Basset, *Green Chemistry*, 2016, 18, 3116-3123.

View Article Online DOI: 10.1039/C8DT02576B

This journal is © The Royal Society of Chemistry 20xx

Dalton Transactions



Graphical abstract

33x13mm (300 x 300 DPI)