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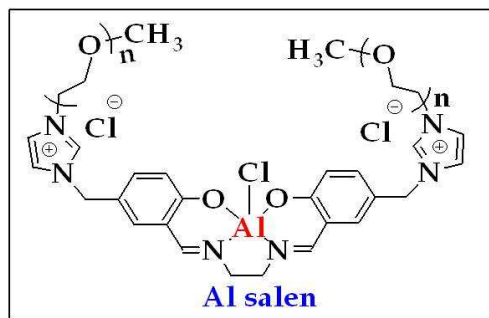
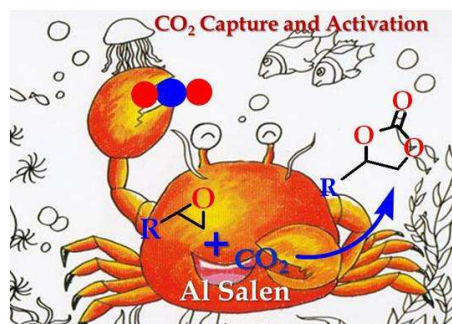
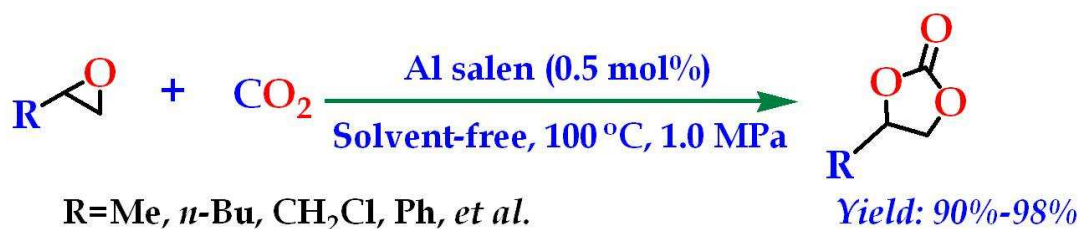
Graphical Abstract

An efficient fixation of CO₂ to cyclic carbonates catalyzed by salen aluminum complexes with built-in “CO₂ capture and activation” capability under mild conditions

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Polyether-based imidazolium ionic liquid functionalized salen Al complex displays high efficiency and reusability as a homogeneous, single-component and multi-functional catalyst for the cycloaddition of CO₂ to epoxides under mild conditions.



Highly efficient synthesis of cyclic carbonates from epoxides catalyzed by salen aluminum complexes with built-in “CO₂ capture” capability under mild conditions

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A series of monometallic salen aluminum complexes were prepared by covalent linkage of the imidazolium-based ionic liquid moieties containing various polyether chains with salen ligand at two sides of 5,5'-position. The salen aluminum complexes were proved to be efficient and recyclable homogeneous catalysts towards the organic solvent-free synthesis of cyclic carbonates from epoxides and CO₂ in the absence of co-catalyst. The catalysts presented excellent “CO₂ capture” capability due to the molecules containing the polyether chains and the metal aluminum center, in which over >90 % yield of cyclic carbonate could be obtained under mild conditions. The catalysts can be easily recovered and six times reused without significant loss of activity and selectivity. Moreover, based on experimental and previous works, the “CO₂ capture and activation” cycloaddition reaction mechanisms by monometallic or bimetallic salen aluminum complexes were both proposed.

Introduction

Carbon dioxide is one of the greenhouse effect gases but it has been attracted much attention as an inexpensive, nontoxic, nonflammable, bio-renewable and highly abundant single carbon atom (C1 resource) building block for organic synthesis in recent years.¹ Many procedures were developed towards the easy and economical chemical fixation of CO₂.² Among these, the synthesis of five-membered cyclic carbonates via the 100% atom-economical cycloaddition of epoxides with CO₂ is one of the most promising ways because cyclic carbonate products are widely used as aprotic high-boiling polar solvents, electrolytes for lithium-ion batteries, precursors of polymeric materials, and fine chemical intermediates.³ Therefore, various catalytic systems, including alkali metal halides,⁴ quaternary ammonium⁵ or quaternary phosphonium salts,⁶ ionic liquids,⁷ metalloporphyrins⁸ or metallosalen complexes,⁹ have been developed to promote this transformation so far.

Based on our previous works towards the biomimetic dioxygen activation¹⁰ and CO₂ fixation^{8a} over metalloporphyrins catalysts, metal salen complexes as another kind of enzyme-like catalyst have drawn our attentions due to the unique natures, such as easily synthesis procedures, modulating the steric and electronic properties conveniently by changing metal centers.^{9b} Many different binary salen catalysts for the coupling reaction of CO₂ and epoxides have been reported, in which co-catalyst is required for the ring opening of the epoxide. With respect to the binary salen catalyst systems, multi-functional metallosalen complexes presented higher catalytic activity and selectivity due to the two or three catalytic sites in one catalyst molecule. It is not only unnecessary to use co-catalyst, but also making easy to explore mechanism and reuse catalyst.¹¹ In

general, on the basis of the motive towards activating epoxide and CO₂, a Lewis acid (metal center) and an anion X⁻ (nucleophile) are required to build this kind of catalyst. Figure 1 shows a catalytic motif for the double activation of an epoxide with this type of compound.

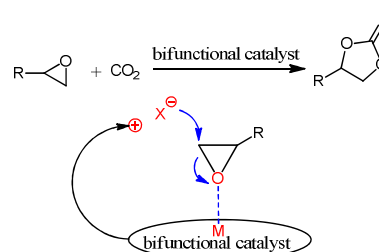


Figure 1 Cooperative activation of epoxide with bi-functional catalyst

Aluminum, as a nontoxic, readily available, environmental benign and earth-abundant metal, is a better choice, because the stronger Lewis acidity is important for the ring-opening of the epoxide.¹² Most recent, a series of mononuclear bi-functional salen aluminum complexes containing quaternary ammonium salts¹³ or quaternary phosphonium salts¹⁴ tethered into the frame of the salen ligand in the context of organic cyclic carbonate formation under the mild conditions had been reported. Even the μ -oxo-bimetallic salen aluminium complexes and its bi-functionalized compounds had been reported by North and co-workers, which provided a highly-active system under room temperature and atmospheric pressure

conditions.^{9d-g} However, in this case the introduction of high polar ionic groups to these complexes often leads to the decreased solubility of catalyst in epoxide substrate, in turn, the relatively low catalytic activity were obtained compared to the binary catalyst system. Meanwhile, distillation was necessary to recover the catalyst in each reaction cycle. Therefore, towards the fixation of CO₂ cyclic carbonates under mild conditions, the efficient and easy-recycling multifunctional salen catalyst is still desired.¹⁵

Polyethylene glycol (PEG) or polyethylene glycol monomethyl ether (*m*PEG), as an inexpensive, non-volatile and environmentally benign reagent, could be regarded as a CO₂-philic material through interaction of CO₂ with the oxygen atoms of the ether linkages of PEG or *m*PEG. More importantly, “CO₂-expansion” effect could lead to changes in the physical properties of the liquid phase mixture including lowered viscosity and increased gas/liquid diffusion rates.¹⁶ Addition of PEG or *m*PEG into the IL could enhance the rates of absorption of CO₂ significantly by decreasing the viscosity of the absorption system.¹⁷ PEG-functionalized basic ionic liquids (ILs) have been proved to be highly efficient and stable catalysts for the cycloaddition reaction of CO₂ to epoxides.¹⁸⁻¹⁹

In view of the “CO₂-expansion” effect of PEG or *m*PEG and the excellent reusability of the IL-functionalized salen complex,²⁰ encourage us to prepare imidazolium IL containing polyethylene oxide (PEO) chain grafted salen aluminum complexes and catalyze the cycloaddition reaction of CO₂ with epoxide.²¹ We envisage that the cooperative action of an anion X⁻ (nucleophile) and a metal center M (Lewis acid) of a catalyst promotes the ring-opening of the epoxide, and polyether-based imidazolium IL units possess built-in “CO₂ capture” capability.²² The introduction of polyether chains can effectively solve the CO₂ gas mass transfer in the liquid phase reaction system. Furthermore, the solubility properties of the PEG or *m*PEG with low molecular weight, that is, it is soluble in epoxide or product, but can be precipitated with ether, potentially endow the novel complexes with the feature of solvent-regulated separation.

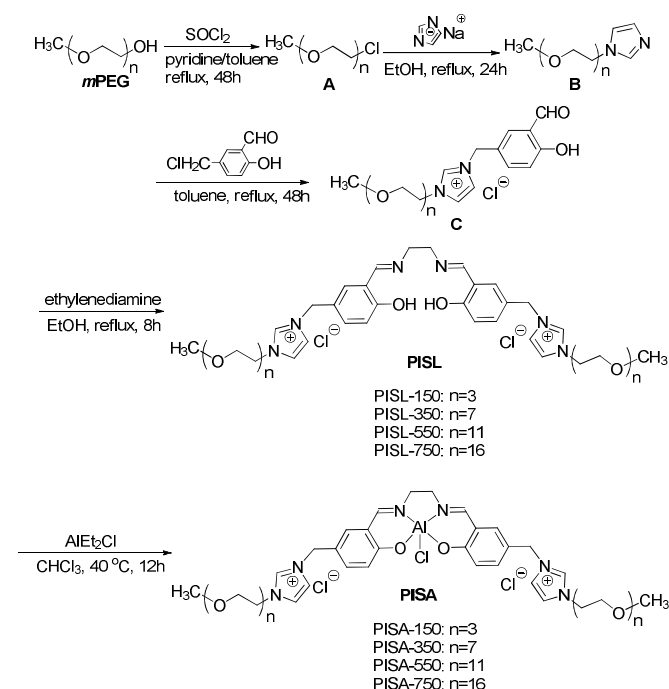
Herein, the novel mononuclear salen aluminum complexes (denoted as PISA) was synthesized by covalent linkage of the imidazolium-IL moieties containing various PEO chains with salen ligand at two sides of 5,5'-position. It has been proved that these catalysts could embody inherent “CO₂ capture” capability in the coupling reaction of CO₂ to epoxide under solvent-free and additive-free conditions. Thus, the enhanced solubility of the catalysts and the problem of gas-liquid phase mass transfer, even the separation of the catalysts can be well resolved. Notably, these catalysts are easily recycled and can be conveniently reused, which is an important aspect in the development of practical coupling processes. In addition, it was found that the total length of polyether chain in the range of low molecular weight have a certain influence on the catalytic performances of the novel complexes.

Results and discussion

Recently, the chiral salen manganese complex functionalized by polyether chain-modified imidazolium IL were first reported and acted as the inherent phase-transfer catalysts in the enantioselective epoxidation of unfunctionalized olefins with aqueous NaOCl as an oxidant.²³ However, the long polyether chain prepared by auto-polymerization of explosive ethylene oxide possesses broad molecular weight distribution and the hydroxyl at the end of chain increased the uncertainty of catalyst spatial structure. Therefore, the polyether-based IL functionalized salen aluminum complexes were synthesized by a similar method using commercialized *m*PEG with known molecular weight as the raw material. Meanwhile, the salen ligand was produced as the cheaper and readily-available salicylaldehyde and ethylenediamine, which is beneficial for industrial production.

Preparation of PISA

The synthesis route for the PISA was outlined in Scheme 1. At first, *N*-(polyoxyethylene methyl ether) imidazole **B** with different numbers of polymerized ethylene oxide unit (*n*=7, 11, 16), which was provided by combination between sodium imidazole and chlorine-substituted *m*PEG **A**, directly reacted with salicylaldehyde to afford *m*PEG-based IL-substituted salicylaldehyde **C**. The successive condensation between the aldehyde (-CHO) group of the compound **C** and the amino (-NH₂) groups of ethylenediamine was used to form the salen ligand **PISL**. Treatment of the **PISL** with diethyl aluminum chloride (0.9 M solution in toluene) under nitrogen gave the dianionic complex **PISA**. The newly-synthesized catalysts are light yellow solid powders at room temperature. Moreover, it is found that the PISA is miscible in some organic solvents, e.g., ethanol, water and DMF, but can be precipitated with other organic solvents, e.g., *n*-hexane, ether and ester. It is suggested that PISA should be an easily recoverable catalyst for the cycloaddition reaction by simple phase separation techniques via changing solvents.



Scheme 1 Synthesis of the catalysts of PISA.

Catalytic performances

Firstly, the activity of various homogeneous monometallic catalysts such as PISA-350 in the cycloaddition reaction of epoxides with CO₂ was explored using allyl glycidyl ether (AGE) as the model substrate under mild conditions in a semi-batch operation (CO₂ was continuously supplied to the reactor) and the results were shown in Table 1. To investigate the built-in stronger “CO₂ capture” capability originated the PEO moiety, the traditional IL (1-benzyl-3-methylimidazoliumchloride, denoted as **IL**), the neat complex ([*N,N'*-bis(salicylidene)ethylene diaminato] aluminum chloride, denoted as **SA**) and the simple IL-functionalized salen aluminum complex (denoted as **ISA1-4**) was also prepared for comparison (Chart 1).

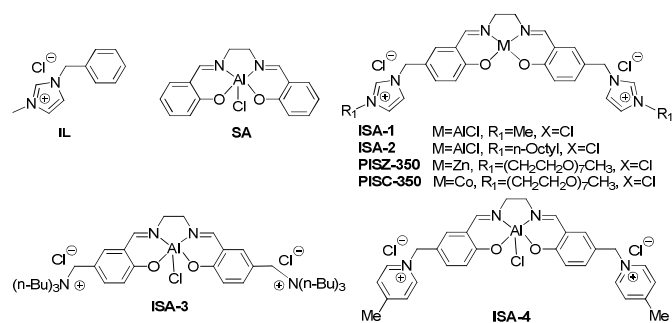


Chart 1 The structures of IL, SA, ISA1–4, PISA–350 and PISC–350.

Obviously, no reaction was occurred when SA was used as the catalyst even for 24 h (Table 1, entry 1).²⁴ In addition, 0.5 mol% of the conventional IL could catalyze the cycloaddition reaction, but the yield of allyl glycidyl carbonate (AGC) was very low (Table 1, entry 2) under 1.0 MPa CO₂ pressure at 100 °C for 2.5 h under solvent-free conditions.²⁵ However, together with equivalent mole ratio represent an efficient binary catalyst system for production of AGC (Table 1, entry 3). This observation encouraged us to evaluate the activity of various single component bi-functional catalysts in detail. As expected, catalyst ISA–1 presented the moderate yield in the absence of co-catalyst in the coupling reaction of CO₂ to AGE (Table 1, entry 5). But it was less active than catalyst PISA–350 with 96% yield of AGC under the above conditions (Table 1, entry 9). It is worth noting that both of the catalysts presented excellent selectivity (>98%) towards cyclic carbonates. There is no other product such as polycarbonate confirmed by FT-IR, ¹H NMR, ¹³C NMR and GC-MS. The remarkable enhancement of reaction rates using catalyst PISA–350 under mild conditions could be attributed to the “CO₂-expansion” effect of PEO chains.^{19, 26} Since CO₂ is an electron acceptor and oxyethylene (EO) group is an electron donor, the Lewis acid–base interaction between CO₂ and EO enhances the dissolution of CO₂ in the epoxide substrates (see Figure 2). The weak interaction between electron-donating functional groups and CO₂ was detected by in-situ FT-IR technique reported by Kazarian and co-workers.²⁷ Moreover, the remarkable difference between ISA–1 and PISA–350 under 1 atm CO₂ pressure could be also observed. More 92 % yield of AGC with PISA–350 as catalyst was obtained at 100 °C after 12 h (Table 1, entry 17), whereas the catalyst ISA–1 resulted in an extremely low yield (Table 1, entry 16).

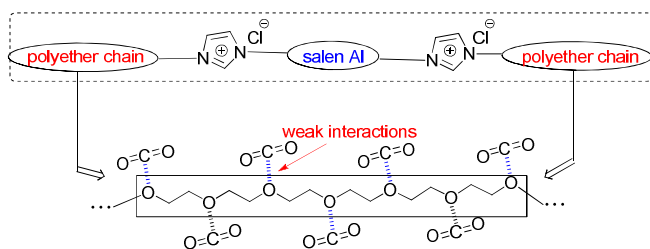


Figure 2 Possible forms of “CO₂ capture”

In order to better understand the stronger “CO₂ capture” capability originated from polyether chains, we firstly investigated the catalytic activity of simple IL-functionalized catalyst ISA–2 with longer alkyl side chains without oxygen atom on the imidazolium ring for comparison, when the length of the alkyl chain in increased from methyl to n-octyl group, the AGE conversion increased since the solubility of catalyst in epoxide AGE increased with the increasing hydrophobic alkyl chain length (see Figure 3). However, ISA–2 exhibited lower activity with respect to PISA–150 bearing three EO

units with the similar hydrophobic alkyl chain length. This result suggests that the presence of the oxygen atoms within the PEO chains was crucial to the “CO₂ capture” capability of catalyst, which attributed the weak interaction between CO₂ molecular and PEO chain. Moreover, bulky ILs, having longer distance between cation and anion, may be considered to have higher anion activation ability. Therefore, they are more effective in nucleophilic attack of the anion (X[−]) to the epoxide ring of AGE due to the weak electrostatic interaction. It follows that the total length of polyether chain in the range of low molecular weight directly affects the catalytic activity of catalysts in the coupling reactions.

Figure 3 also shows the effect of reaction time on the catalytic performance of 0.5 mol% of the catalyst PISA with different lengths of polyether chain in the cycloaddition reaction of AGE with CO₂ at 1.0 MPa CO₂ pressure and 100 °C within 2.5 h. It clearly suggests that the differences of reaction rates among various catalysts were observed. At relatively low pressure, the difference in solubility of CO₂ in PEG with different low molecular weight is negligible. Thus, when the numbers of ethylene oxide unit of the polyether chain increased from 3 to 11, the appropriate increased yield of AGC were obtained, which indicated the catalyst of the length of polyether chain has a certain effect on the coupling reaction. The PISA–550 with eleven EO units presented the highest catalytic activity. However, when the EO numbers further increased to 16, the slightly decreased yield of AGC was observed. The subtle drop probably derives from the increased mass-transport limitation.^{18a}

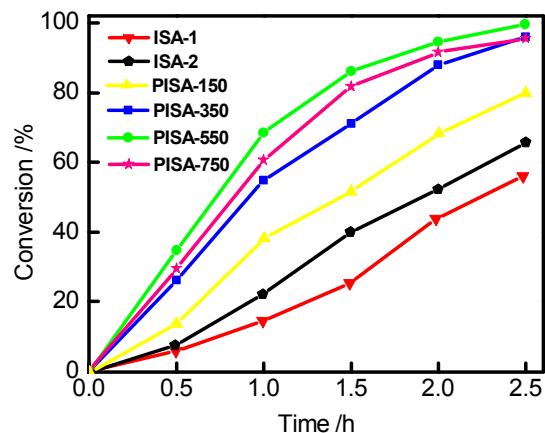
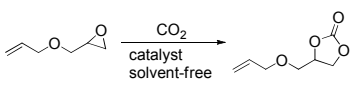


Figure 3 Effect of reaction time on the catalytic performance of various catalysts. Reaction conditions: 10 mL stainless-steel clave, AGE (6 mmol), catalyst (0.03 mmol), CO₂ pressure (1.0 MPa), reaction temperature (100 °C).

In consideration of a catalytic motif for the double activation of an epoxide in the coupling reaction system, it found that metal center, imidazolium cation and halogen ions (X[−]) were all important to obtain the high activity, those were indispensable. For instance, when directly using IL-functionalized ligand PISA–350 as catalyst, it shows moderate activity (Table 1, entry 4) due to the lack of metal center. Hence, the catalytic activity of catalyst is closely related with the metal center, these substantial literatures reported that the catalysts containing zinc ion or cobalt ion were the most attractive for CO₂ coupling with epoxide owing their high activity. However, the catalyst PISA–350 bearing zinc cation, has very low activity in cycloaddition reaction (Table 1, entry 10), which could be due that Zn²⁺ owns the weaker Lewis acidity than Al³⁺.^{8b} Additionally, using cobalt instead of aluminium as metal center, the catalyst PISC–350 exhibited higher activity with respect to catalyst PISA–350 under the identical conditions (Table 1, entry 11). Finally,

it was noteworthy that the activities of **ISA-3** with quaternary ammonium-based ILs and **ISA-4** with pyridinium-based ILs were both obviously inferior to that of **ISA-1** (see Figure 3), which shows the incorporation of the imidazolium group within salen ligand is beneficial to catalytic performance. It shows that both the metal center and imidazolium cation are critical for the rate-determined step in the coupling reaction, which could activate and ring-open epoxides.

Table 1 Results of the cycloaddition reaction of AGE with CO₂ catalyzed by various catalysts.^a



Entry	Catalyst	T /°C	p(CO ₂) /Mpa	time /h	Conv. ^b /%	Yield ^b /%	TOF ^c /h ⁻¹
1	SA	100	1	24	n.d.	n.d.	-
2	IL	100	1	2.5	16	15	12
3	SA/IL (1:1)	100	1	2.5	84	82	65.6
4	PISL-350	100	1	2.5	41	40	32
5	ISA-1	100	1	2.5	57	56	44.8
6	ISA-2	100	1	2.5	75	74	59.2
7	ISA-3	100	1	2.5	11	11	8.8
8	ISA-4	100	1	2.5	<3	2	1.6
9	PISA-350	100	1	2.5	96	95	76
10	PISZ-350	100	1	2.5	12	10	8
11	PISC-350	100	1	2.5	78	76	60.8
12	PISA-350	80	1	4	41	40	20
13	PISA-350	60	1	4	10	9	4.5
14	PISA-350	100	0.5	2.5	76	75	60
15	PISA-350	100	0.1	2.5	43	42	33.6
16	ISA-1	100	0.1	12	30	28	4.7
17	PISA-350	100	0.1	12	94	92	15.7
18	PISA-350	30	0.1	72	5	<3	<0.1

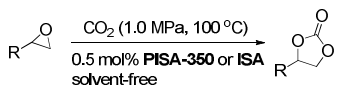
^a Reaction conditions: 10 mL stainless-steel clave, AGE (6 mmol), catalyst (0.03mmol). ^b Determined by GC using biphenyl as the internal standard. ^c Turnover frequency (TOF): mole of synthesized AGC per mole of catalyst per hour.

Furthermore, Table 1 also shows the effect of CO₂ pressure on the reactivity of the **PISA-350** at 100 °C after 2.5 h. The conversion of AGE decreased as CO₂ pressure decreased from 1 to 0.5 MPa, further drop to 0.1 MPa (Table 1, entry 14-15 vs entry 9). Lower CO₂ pressure could reduce the absorption of CO₂ in the solution of AGE, in turn, the turnover frequency (TOF) was decreased. In general, the cycloaddition reaction was more sensitive to temperature for the other similar catalytic system. While the reaction temperature was drop to 80 °C, further drop to 60 °C, the yield of AGC also decreased obviously (Table 1, entry 12-13 vs entry 9). Unfortunately, the coupling reaction could basically not occur under the room temperature and atmospheric pressure even for 72 h (Table 1, entry 18).

To evaluate the application range of the catalytic system, various epoxides, such as propylene oxide (PO), 1,2-epoxybutane, 1,2-epoxyoctane, 1,2-epoxydodecane, epichlorohydrin (ECH), styrene

oxide (SO) and cyclohexene oxide (CHO), were used as substrate for the reaction system using **PISA-350** as a catalyst. As shown in Table 2, most substrates could be smoothly converted to corresponding cyclic carbonates with high conversion and excellent selectivity (Table 2, entry 1-8). Both steric and electronic effects play an important role. The electron-withdrawing nature of the chloromethyl group of epichlorohydrin tends to drive the cycloaddition reaction for only 0.75 h under the similar conditions (Table 2, entry 5).¹⁵ Unfortunately, the internal epoxide, cyclohexene oxide, exhibited lower activity even after prolonging the reaction time to 24 h (Table 2, entry 8), presumably due to the high steric hindrance.²⁹ This steric effect was more likely to hinder the nucleophilic attack of the epoxide rather than its coordination to the Lewis acid metal center.³⁰ Especially, for 1,2-epoxyoctane and 1,2-epoxydodecane with a linear long alkyl chain (Table 2, entry 3-4), the excellent yields were obtained under quite mild condition as a consequence of higher solubility of the catalyst **PISA-350** in epoxide substrate, while no activity was observed using the catalyst **ISA-1** under the same pressure and temperature due to the characteristics of insolubility. Therefore, catalysts **PISA** with PEO chains not only enhanced the activity but also improved the dissolution of the catalyst under solvent-free condition.

Table 3 Results of the coupling reaction of CO₂ to various epoxide substrates over the **PISA-350** and **ISA-1**.^a



Entry	Epoxide	Product ^b	Time /h	Conv. ^c /%	Yield ^c /%	TOF ^d /h ⁻¹
1	1a	2a	2	99 (50)	98 (49)	98 (49)
2	1b	2b	4	99 (37)	98 (36)	49 (18)
3	1c	2c	6	97 (0)	95 (0)	31.7 (0)
4	1d	2d	9	98 (0)	97 (0)	21.6 (0)
5	1e	2e	0.75	97 (74)	90 (68)	240 (181)
6	1f	2f	2.5	96 (57)	95 (56)	76 (44.8)
7	1g	2g	4	94 (33)	90 (31)	45 (15.5)
8	1h	2h	24	50 (24)	45 (22)	3.8 (1.8)

^a Reaction conditions: 10 mL stainless-steel clave, epoxide (6 mmol), catalyst (0.03mmol), CO₂ pressure (1.0 MPa), reaction temperature (100 °C), value in parentheses refers to catalyst **ISA-1**. ^b Product identification via FT-IR, ¹H NMR, ¹³C NMR and GC-MS. ^c Same as in Table 1. ^d Same as in Table 1.

Recycling experiments

Based on the concept of “one-phase catalysis and two-phase separation”²⁰ and the special solubility of the **PISA**, the catalyst

bearing PEO chains could be precipitated from the reaction solution by the addition of ether (Et_2O). The upper organic phase was obtained by simple decantation and the lower catalyst solid can be reused by adding fresh reaction substrates.

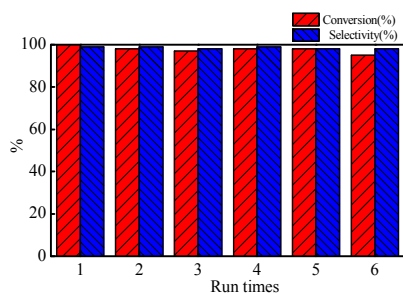


Figure 4 Recyclability and reusability of catalyst **PISA-350** in the coupling reaction of AEG with CO_2 . Reaction conditions: 10 mL stainless-steel clave, AGE (6 mmol), catalyst (0.03 mmol), CO_2 pressure (1.0 MPa), reaction temperature (100 °C), reaction time: 3 h.

Experiments were also conducted to examine the recyclability and reusability of the **PISA-350** catalyst using AGE as the substrate under the optimal reaction conditions. The results indicate that the **PISA-350** catalyst could be reused for six successive runs without any significant loss in its catalytic activity, and the selectivity still remained at 98 % (see Figure 4), reflecting high stability of the catalyst. The comparative FT-IR analysis of the fresh catalyst **PISA-350**, **ISA-1**, **SA** and the recovered **PISA-350** after the 6th reuse in the cycloaddition reaction was performed, and the results were shown in Figure 5. All the FT-IR spectra show characteristic vibration bands at around 1640 cm^{-1} and 1550 cm^{-1} , which are associated with the stretching vibration modes of $\text{C}=\text{N}$ and $\text{C}-\text{O}$, respectively (Figure 5a-d).²³ In addition, the stretching vibration $\nu(\text{C}-\text{N})$ of $\text{C}-\text{N}$ bond in the IL units at around 1491 cm^{-1} and the stretching vibration of $\text{C}-\text{O}-\text{C}$ groups in the PEO chain at 1098 cm^{-1} suggests the intact polyether-based imidazolium IL moiety on the salen ligand (Figure 5b vs. 5a, 5c).²³

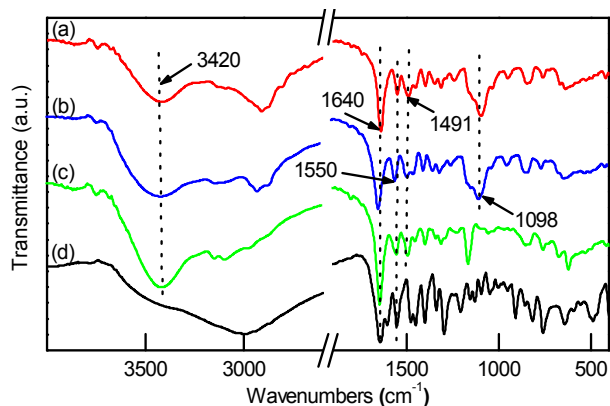


Figure 5 FT-IR spectra of **PISA-350** (a), the recovered **PISA-350** after the 6th reuse in the cycloaddition reaction (b), **ISA-1** (c) and **SA** (d).

Moreover, ^{27}Al NMR spectra of complexes **SA**, **PISA-350** and the recovered catalyst **PISA-350** have all found to display broad strong resonances around 70 ppm (Figure 6a-c), which are usually attributed to five-coordinate aluminum species.¹³ The results suggest that the recovered catalyst **PISA-350** presented here does not change the structure of catalytic active sites.

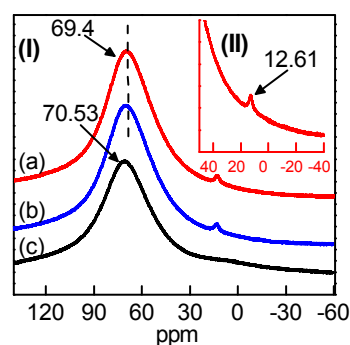


Figure 6 (I) ^{27}Al NMR spectra of **PISA-350** (a), the recovered **PISA-350** (b) and **SA** (c); (II) ^{27}Al NMR spectra of **PISA-350** (partial amplification figure).

In addition, thermogravimetric analysis (TGA) result (see Figure 7) proved that the **PISA-350** catalyst could endure about 238 °C with little loss of its weight. The decomposition of ionic liquid started from about 465 °C, showing the high thermal stability.²⁰

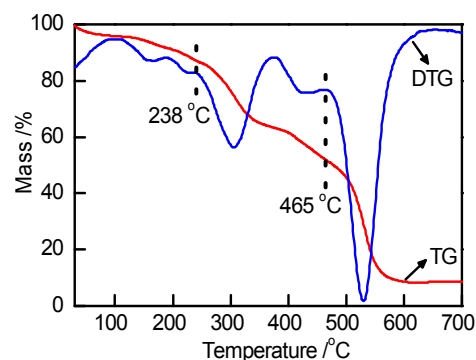
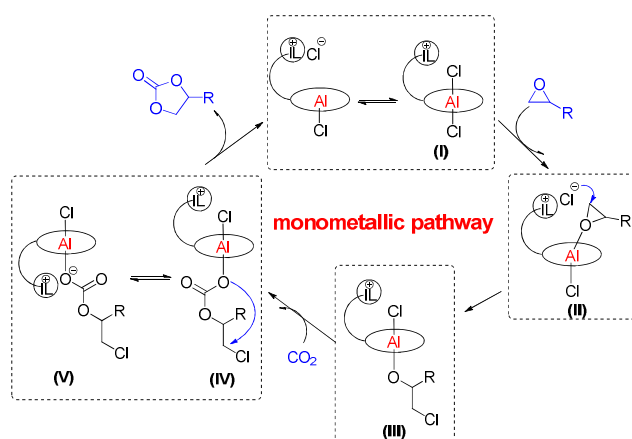


Figure 6 Thermogravimetric (TG) and differential thermogravimetric (DTG) results of the catalyst **PISA-350**.

Reaction mechanism

Based on the molecular structure of the complex **PISA** and the cycloaddition reaction results, a possible mechanism¹⁵ of monometallic pathway involving two nucleophiles for cyclic carbonate synthesis was proposed, which is shown in Scheme 2.



Scheme 2 The plausible mechanism for coupling reaction of epoxide with CO_2 catalyzed by **PISA** or **ISA-1**.

At first, the anion of ionic liquid units in catalyst PISA (Cl⁻) coordinates to the metal in the remaining trans axial position, thus generating a six-coordinated intermediate (**I**).¹³ As shown in Figure 6, ²⁷Al NMR spectra of the complex PISA-350 was found to display broad strong resonances at 69.4 ppm and a new weak signal around 12.61 ppm (see Figure 6a), while the neat complex SA which lacks the attached imidazolium-based ionic liquid units on the salen ligand exhibits a single resonance at 70.53 ppm (see Figure 6c). ²⁷Al resonance in complexes PISA or ISA-1 is assigned to the five-coordinate aluminum species and the weaker and narrow up-field signal to a six-coordinate species. These observations were also reported by Liu and Darensbourg.¹³⁻¹⁴ Subsequently, the coordination of the nucleophile (Cl⁻) serves to stabilize the other metal-chlorine bond, favoring coordination and nucleophilic attack of the epoxide (**II**) activated by metal center, followed by the ring opening. Meanwhile, the polyether-based ILs units capture and activate the CO₂ molecular. Next, the formed alkoxide species (**III**) acts in turn as a nucleophile that attacks CO₂ to form a metal carbonate species (**IV**). Certainly, the imidazolium cations could also stabilize the metal alkoxide bond (**V**) through charge interactions. The subsequent ring-closure forms relevant cyclic carbonate. In the meantime, the catalyst is regenerated. This mechanism insists that overall the role of the catalyst involve initial activation of the epoxide and stabilization of the ring-opened and carbonate intermediates formed during the reaction, which is important to reduce the reaction time and the pressure of reaction.

Experimental

Reagents and Methods

Polyethylene glycol monomethyl ether (*m*PEG, MW=350, 550, 750) was purchased from Alfa Aesar Chemical Reagent Co. Ltd. Propylene oxide (PO), epichlorohydrin (ECH), allyl glycidyl ether (AGE), styrene oxide (SO), cyclohexene oxide (CHO), sodium ethoxide (*ca.* 21% in ethanol), tri-*n*-butylamine, 4-methylpyridine and diethyl aluminum chloride (Et₂AlCl, 0.9 M solution in toluene) were obtained by J&K Scientific Ltd. 1,2-epoxybutane, 1,2-epoxyoctane and 1,2-epoxydodecane were used as received from TCI. Other commercially available chemicals were laboratory grade reagents from local suppliers. CO₂ was purified by passing through a column packed with 4A molecular sieves before use (99.99%). All of the solvents were purified by standard procedures.³¹ 5-chloromethylsalicylaldehyde was synthesized according to the published procedures.^{11a, 32}

FT-IR spectra were obtained as potassium bromide pellets with a resolution of 4 cm⁻¹ and 32 scans in the range 400-4000 cm⁻¹ using a Bruker spectrophotometer. ¹H NMR, ¹³C NMR and ²⁷Al NMR spectra were recorded on a Bruker Avance III 400 M spectrometer, which were using TMS, 1,4-dioxane and standard aqueous aluminum solution (1000 µg/mL certified atomic absorption standard solution) as a calibration reagent, respectively. The thermogravimetric and differential thermogravimetric (TG-DTG) curves were obtained on a NETZSCH STA 449C thermal analyzer. Samples were heated from room temperature up to 700 °C under flowing air using alumina sample holders. The sample weight was *ca.* 10 mg and the heating rate was 10 K/min. Thin layer chromatography (TLC) was conducted on glass plates coated with silica gel GF₂₅₄. The conversions and yields of cyclic carbonates products were measured by a GC2010 gas chromatograph (Shimadzu) equipped with the capillary column (Rtx-5, 30m×0.32mm×0.25µm) and the FID detector.

Preparation of polyether-based IL functionalized salen Al complex (PISA)

The preparation of PISA was outlined in Scheme 1.

Synthesis of Chlorine-substituted Poly(ethylene glycol) monomethyl ether (A)³³ To a 500 mL three-neck round bottom flask were added polyethylene glycol monomethyl ether (100 mmol, MW=350, 550, 750), pyridine (15.82 g, 200 mmol) and dry toluene (200 mL) under nitrogen atmosphere. The mixed solution was heated slowly to 80 °C and then thionyl chloride (23.79 g, 200 mmol) was added dropwise for 3 h. The mixture was stirred vigorously for an additional 48 h under reflux. After cooling to room temperature, a small amount of H₂O was added to quench the reaction, the lower red salts were extracted with toluene for three times, which merged into the upper organic phase. Afterwards, the pale-yellow organic phase concentrated and the residue was dissolved in CH₂Cl₂ (50 mL), washed with H₂O (3×50 mL), then dried over anhydrous Na₂SO₄. The solvent was evaporated, dried in vacuo to give a pale-yellow liquid A. Yield: 90 %. **A-350**: FT-IR (KBr), $\gamma_{\max}/\text{cm}^{-1}$: 2874, 1457, 1353, 1300, 1250, 1200, 1112, 947, 851, 745, 664, 534; ¹H NMR (CDCl₃/TMS, 400 MHz), δ_{H} ppm: 3.67-3.70(t, 2H, J=12 Hz, Cl-CH₂-CH₂), 3.55-3.60(m, 24H, (OC₂H₄)₆-O), 3.47-3.49(t, 2H, J=8 Hz, Cl-CH₂-CH₂), 3.31(s, 3H, O-CH₃).

Synthesis of N-(polyoxyethylene methyl ether) imidazole (B)³⁴ *Ca.* 21% sodium ethoxide ethanol solution (16.2 g, 50 mmol) was added dropwise into the anhydrous ethanol solution (100 mL) of imidazole (3.4 g, 50 mmol) under stirring. The obtained mixture was refluxed for 8 h. After the completion of the reaction, chlorine-substituted poly(ethylene glycol) monomethyl ether A (50 mmol) was dissolved in anhydrous ethanol (50 mL) and added dropwise into the above solution, the resulting mixture continued to be stirred under reflux for another 24 h before allowed to cool to room temperature. The residue was filtrated and the filtrate was evaporated in vacuo, and then washed with Et₂O (3×20 mL) to give an orange-red viscous liquid B, used without further purification. Yield: 82 %. **B-350**: FT-IR (KBr), $\gamma_{\max}/\text{cm}^{-1}$: 3114, 2873, 1457, 1351, 1325, 1298, 1251, 1200, 1109, 950, 847, 753, 666, 618, 537; ¹H NMR (CDCl₃/TMS, 400 MHz), δ_{H} ppm: 7.62 (s, 1H, ring CH=N=C), 7.48 (s, 1H, ring N-CH=CH), 7.01(s, 1H, ring N-CH=CH), 4.02-4.05(t, 2H, J=12 Hz, N-CH₂), 3.66-3.68(t, 2H, J=8 Hz, N-CH₂CH₂), 3.52-3.58(m, 24H, (OC₂H₄)₆-O), 3.31(s, 3H, O-CH₃). ¹³C NMR (CDCl₃/TMS, 100.4 MHz), δ_{C} ppm: 136.47, 128.00, 120.83, 70.89, 69.53, 69.47, 68.77, 65.60, 57.97, 46.06.

Synthesis of polyether-based IL modified salicylaldehyde (C) N-(polyoxyethylene methyl ether) imidazole B (30 mmol) in dry toluene (100 mL) was added dropwise into the stirring toluene solution of 5-chloromethylsalicylaldehyde (30 mmol, 5.1 g) under nitrogen atmosphere. The reaction was heated to reflux for 48 h. After cooling, the solvent was evaporated in vacuo and the lower viscous liquid was washed three times with dry benzene (3×20 mL) and ether (3×50 mL), respectively. The solvent was removed to obtain the compound C as the orange-red viscous liquids. Yield: 60 %. **C-350**: FT-IR (KBr), $\gamma_{\max}/\text{cm}^{-1}$: 3415, 3074, 2874, 1657, 1615, 1592, 1561, 1488, 1448, 1352, 1284, 1250, 1215, 1150, 1107, 931, 845, 770, 677, 632, 516, 458; ¹H NMR (D₂O, 400 MHz), δ_{H} ppm: 9.85(s, 1H, ring NCH), 9.75(s, 1H, CH=O), 8.65-8.89(s, 2H, ring NCH), 7.65(s, 1H, ring ArH), 6.87-6.98(s, 2H, ring ArH), 5.32(s, 2H, PhCH₂-N), 4.35-4.37(m, 2H, N-CH₂-CH₂), 3.83-3.85(m, 2H, N-CH₂-CH₂), 3.52-3.64(m, 24H, (OC₂H₄)₆-O), 3.31(s, 3H, O-CH₃). ¹³C NMR (D₂O, 100.4 MHz), δ_{C} ppm: 196.39, 160.29, 137.43, 133.43, 125.54, 122.71, 122.25, 121.14, 118.16, 70.98, 69.65, 69.56, 69.43, 68.28, 58.05, 52.02, 51.91, 49.31.

Synthesis of polyether-based IL functionalized salen ligand (PISL) The anhydrous ethanol solution (20 mL) of ethylenediamine (5 mmol, 0.3 g) was added dropwise into the solution of polyether-based ionic liquid modified salicylaldehyde C (10 mmol) in anhydrous ethanol (50 mL) in a 1:2 molar ratio at reflux. The

resulting mixture was refluxed for another 8 h, following, the solvent was evaporated to dryness and the polyether-based ionic liquid functionalized salen ligand **PISL** was obtained as the light yellow viscous liquids, used without further purification. Yield: 96 %. **PISL-350**: FT-IR (KBr), $\gamma_{\max}/\text{cm}^{-1}$: 3422, 2876, 1635, 1591, 1560, 1497, 1450, 1350, 1285, 1234, 1103, 943, 839, 759, 727, 667, 637, 518; ^1H NMR (D_2O , 400 MHz), δ_{H} ppm: 9.98(s, 2H, ring NCH), 8.41(s, 2H, CH=N), 7.89(s, 2H, ring NCH), 7.79(s, 2H, ring NCH), 7.00-7.20(m, 6H, ring ArH), 5.10(s, 4H, Ph- $\text{CH}_2\text{-N}_{\text{ring}}$), 4.18-4.20(t, 4H, J=8 Hz, N- $\text{CH}_2\text{-CH}_2$), 3.79-3.82(m, 4H, N- $\text{CH}_2\text{CH}_2\text{-N}$), 3.57-3.64(m, 48H, $(\text{OC}_2\text{H}_4)_6\text{-O}$), 3.32(s, 6H, O- CH_3).

Synthesis of PISA Under nitrogen protection and constant stirring at 40 °C, a 100 mL round-bottom flask containing the above-obtained salen ligand **D** (5 mmol), and anhydrous chloroform (50 mL) was added via hypodermic syringe to dissolve the ligand, then a little excess Et_2AlCl (0.9 M solution in toluene, 5.7 mL, 5.1 mmol) was added slowly. The reaction was highly exothermic and resulted in a yellow solution and pale yellow solid. The resulting yellow mixture was refluxed for an additional 12 h. After removal of the solvent in vacuum, the mixture was washed with ether for several times and then dried at 40 °C in vacuum to obtain the light yellow powders **PISA**. Yield: 90 %. For **PISA-350**: FT-IR (KBr), $\gamma_{\max}/\text{cm}^{-1}$: 3420, 3135, 2924, 1639, 1557, 1489, 1456, 1396, 1348, 1311, 1250, 1098, 949, 839, 761, 668, 641, 421; ^1H NMR ($\text{DMSO-}d_6$, 400 MHz), δ_{H} ppm: 9.41(s, 2H, ring NCH), 8.50(s, 2H, CH=N), 7.80-7.84(m, 4H, ring NCH), 7.42-7.59(m, 4H, ring ArH), 6.87-6.89(m, 2H, ring ArH), 5.37(s, 4H, Ph- $\text{CH}_2\text{-N}_{\text{ring}}$), 4.37-4.39(t, 4H, J=8 Hz, N- $\text{CH}_2\text{-CH}_2$), 3.86-3.88(m, 4H, N- $\text{CH}_2\text{CH}_2\text{-N}$), 3.78-3.80(t, 4H, J=8 Hz, N- $\text{CH}_2\text{-CH}_2$), 3.36-3.45(m, 48H, $(\text{OC}_2\text{H}_4)_6\text{-O}$), 3.32(s, 6H, O- CH_3); ^{13}C NMR ($\text{DMSO-}d_6$, 100.4 MHz), δ_{C} ppm: 168.50, 166.53, 138.85, 138.16, 135.16, 130.14, 124.99, 123.86, 123.33, 121.22, 73.11, 71.61, 69.92, 59.88, 54.93, 50.74, 38.41; ^{27}Al NMR ($\text{DMSO-}d_6$, 104.3 MHz), δ_{Al} ppm: 69.4, 12.61; For **PISA-550**: FT-IR (KBr), $\gamma_{\max}/\text{cm}^{-1}$: 3421, 2909, 1636, 1549, 1496, 1397, 1346, 1282, 1233, 1088, 1033, 952, 832, 757, 665, 630, 418; ^1H NMR ($\text{DMSO-}d_6$, 400 MHz), δ_{H} ppm: 9.42(s, 2H, ring NCH), 8.49(s, 2H, CH=N), 7.80-7.85(s, 4H, ring NCH), 7.42-7.59(m, 4H, ring ArH), 6.82-6.94(m, 2H, ring ArH), 5.38(s, 4H, Ph- $\text{CH}_2\text{-N}_{\text{ring}}$), 4.38-4.39(t, 4H, N- $\text{CH}_2\text{-CH}_2$), 3.85-3.89(m, 4H, N- $\text{CH}_2\text{CH}_2\text{-N}$), 3.78-3.80(t, 4H, J=8 Hz, N- $\text{CH}_2\text{-CH}_2$), 3.42-3.56(m, 80H, $(\text{OC}_2\text{H}_4)_6\text{-O}$), 3.23(s, 6H, O- CH_3); ^{13}C NMR ($\text{DMSO-}d_6$, 100.4 MHz), δ_{C} ppm: 168.65, 165.92, 138.92, 136.93, 136.65, 135.11, 130.46, 126.92, 123.33, 121.12, 73.12, 71.62, 71.42, 57.84, 54.88, 50.65, 39.23; ^{27}Al NMR ($\text{DMSO-}d_6$, 104.3 MHz), δ_{Al} ppm: 69.36, 12.50; For **PISA-750**: FT-IR (KBr), $\gamma_{\max}/\text{cm}^{-1}$: 3408, 2870, 1639, 1549, 1492, 1448, 1395, 1349, 1310, 1250, 1098, 949, 839, 761, 635, 526, 492, 420; ^1H NMR ($\text{DMSO-}d_6$, 400 MHz), δ_{H} ppm: 8.95(s, 2H, ring NCH), 8.52(s, 2H, CH=N), 7.91-7.93(s, 4H, ring NCH), 7.39-7.58(m, 4H, ring ArH), 6.86-6.92(m, 2H, ring ArH), 5.43(s, 4H, Ph- $\text{CH}_2\text{-N}_{\text{ring}}$), 4.37-4.41(t, 4H, N- $\text{CH}_2\text{-CH}_2$), 3.91-3.95(m, 4H, N- $\text{CH}_2\text{CH}_2\text{-N}$), 3.76-3.85(t, 4H, N- $\text{CH}_2\text{-CH}_2$), 3.42-3.51(m, 120H, $(\text{OC}_2\text{H}_4)_6\text{-O}$), 3.23(s, 6H, O- CH_3); ^{13}C NMR ($\text{DMSO-}d_6$, 100.4 MHz), δ_{C} ppm: 167.21, 165.20, 136.86, 136.47, 134.49, 128.91, 123.61, 123.03, 122.50, 119.90, 71.75, 70.25, 70.18, 68.57, 58.52, 53.55, 51.79, 36.87; ^{27}Al NMR ($\text{DMSO-}d_6$, 104.3 MHz), δ_{Al} ppm: 69.28, 12.42.

Synthesis of 1-benzyl-3-methylimidazoliumchloride A solution of benzyl chloride (0.1 mol, 12.68 g) in toluene (200 mL) was mixed with a solution of 4-methylpyridine (0.1 mmol, 9.3 g) and refluxed overnight. After cooling to room temperature, the yellow viscous liquids were collected in vacuum following washed with ether for several times. ^1H NMR (CDCl_3/TMS , 400 MHz), δ_{H} ppm: 10.49 (s, 1H, ring NCH), 7.72(s, 1H, ring NCH), 7.56(s, 2H, ring NCH), 7.49-7.51(s, 2H, ring ArH), 7.33-7.34(s, 3H, ring ArH), 5.58(s, 2H, CH_2), 4.04 (s, 3H, CH_3); ^{13}C NMR (CDCl_3/TMS , 400 MHz), δ_{C} ppm:

137.14, 133.30, 129.15, 129.13, 128.70, 123.82, 121.95, 57.24, 52.86, 36.36, 18.33.

Synthesis of the neat salen Al complex (SA) ^{24b} SA: FT-IR (KBr), $\gamma_{\max}/\text{cm}^{-1}$: 2987, 1641, 1605, 1550, 1474, 1453, 1400, 1340, 1297, 1242, 1206, 1153, 1129, 1094, 1052, 1033, 1004, 987, 957, 908, 858, 814, 759, 635, 592, 555, 486, 464; ^1H NMR ($\text{DMSO-}d_6$, 400 MHz), δ_{H} ppm: 8.53(s, 2H, CH=N), 7.35-7.41(s, 4H, ring ArH), 6.85-6.87(d, 2H, J=8 Hz, ring ArH), 6.71-6.75(t, 2H, J=16 Hz, ring ArH); ^{13}C NMR ($\text{DMSO-}d_6$, 100.4 MHz), δ_{C} ppm: 167.59, 164.96, 135.50, 134.60, 121.65, 120.05, 116.38, 53.53; ^{27}Al NMR ($\text{DMSO-}d_6$, 104.3 MHz), δ_{Al} ppm: 70.53.

Synthesis of simple IL-functionalized salen Al complex (ISA1-4)

Following a similar procedure of the above newly-synthesized complex (**PISA**), the simple IL-functionalized salen Al complexes (denoted as **ISA1-4**) were also prepared by using 1-methylimidazole, 1-octylimidazole, tri-*n*-butylamine and 4-methylpyridine, instead of **B** respectively. **ISA-1**: FT-IR (KBr), $\gamma_{\max}/\text{cm}^{-1}$: 3417, 3095, 1642, 1552, 1489, 1397, 1310, 1225, 1164, 1054, 853, 758, 671, 620; ^1H NMR ($\text{DMSO-}d_6$, 400 MHz), δ_{H} ppm: 9.40(s, 2H, ring NCH), 8.51(s, 2H, CH=N), 7.75-7.82(s, 4H, ring NCH), 7.47-7.53(s, 4H, ring ArH), 6.88-6.90(s, 2H, ring ArH), 5.36(s, 4H, Ph- $\text{CH}_2\text{-N}_{\text{ring}}$), 3.88(s, 6H, N- CH_3), 3.85-3.86 (m, 4H, N- $\text{CH}_2\text{CH}_2\text{-N}$); ^{13}C NMR ($\text{DMSO-}d_6$, 100.4 MHz), δ_{C} ppm: 167.19, 165.15, 137.07, 135.83, 128.67, 125.78, 124.38, 122.59, 119.72, 118.75, 53.55, 51.59, 36.33; ^{27}Al NMR ($\text{DMSO-}d_6$, 104.3 MHz), δ_{Al} ppm: 70.38, 12.61.

Cycloaddition procedure for the reaction of epoxides with CO₂

Epoxide (6 mmol), catalyst (0.03 mmol) and biphenyl (0.6 mmol, internal standard for GC analysis) were added into a 10 mL stainless-steel autoclave equipped with a magnetic stirrer, which had been previously dried at 100 °C for 2.5 h under vacuum. After the reaction mixture was then rapidly heated to the desired temperature (100 °C), the autoclave was pressurized with CO_2 from a reservoir tank to maintain a constant pressure (1.0 MPa). After stirring at ca. 200 rpm for the designated reaction time, the autoclave was cooled quickly to -5 °C and the remaining CO_2 was slowly released and absorbed in a small amount of ethyl acetate or ether. Subsequently, 20 mL ether was added into the reactor, the catalyst was separated as a solid by centrifugation, which was washed with Et_2O or EA three times and dried under vacuum for the recycling experiment without further purification. Each catalytic reaction was repeated for three times to secure reproducibility. The purity and structure of products were also confirmed by FT-IR, ^1H NMR, ^{13}C NMR spectra and GC-MS (Shimadzu GCMS-QP2010) analysis.

NMR characterizations of the typical cyclic carbonate products were as follows: 4-methyl-1,3-dioxolan-2-one: ^1H NMR (CDCl_3/TMS , 400 MHz), δ_{H} ppm: 4.77-4.86 (m, 1 H, ring CH- CH_3), 4.49-4.53 (t, 1 H, J=16 Hz, ring CH_2), 1.41-1.43 (d, 1 H, J=8 Hz, CH_3); ^{13}C NMR (CDCl_3 , 100.4 MHz), δ_{C} ppm: 155.15(C=O), 73.70 (ring CH- CH_3), 70.72 (ring CH_2), 19.31(CH_3); 4-hexyl-1,3-dioxolan-2-one: ^1H NMR (CDCl_3/TMS , 400 MHz), δ_{H} ppm: 4.68-4.75 (m, 1 H, ring CH), 4.51-4.55 (t, 1 H, J=16 Hz, ring CH_2), 4.05-4.09 (t, 1 H, J=16 Hz, ring CH_2), 1.77-1.84 (m, 1 H, $\text{CH}_2\text{CH}_2\text{CH}$), 1.64-1.72 (m, 1 H, $\text{CH}_2\text{CH}_2\text{CH}$), 1.30-1.49 (m, 8 H, $\text{CH}_3(\text{CH}_2)_4$), 0.88-0.91 (t, 3 H, J=12 Hz, CH_3); ^{13}C NMR (CDCl_3 , 100.4 MHz), δ_{C} ppm: 155.13(C=O), 77.10 (ring CH- CH_2), 69.43 (ring CH_2CH), 33.88 (CH_2CH_2), 31.51(CH_2CH_2), 28.80 (CH_2CH_2), 24.33 (CH_2CH_2), 22.46 (CH_2CH_2), 19.31(CH_3); 4-chloromethyl-1,3-dioxolan-2-one: ^1H NMR (CDCl_3/TMS , 400 MHz), δ_{H} ppm: 4.98-5.04 (m, 1 H, CH- CH_2), 4.59-4.63 (t, 1 H, ring CH_2), 4.40-4.44 (dd, 1 H, ring CH_2), 3.80-3.84 (dd, 1 H, $\text{CH}_2\text{-Cl}$), 3.72-3.76 (dd, 1 H, $\text{CH}_2\text{-Cl}$); ^{13}C NMR (CDCl_3 , 100.4 MHz), δ_{C} ppm: 154.35(C=O), 74.38 (ring CH), 67.00 (ring CH_2), 43.86 ($\text{CH}_2\text{-Cl}$); 4-allyl-1,3-dioxolan-2-one: ^1H NMR (CDCl_3/TMS , 400 MHz), δ_{H} ppm: 5.83-5.94 (1H, $\text{CH}_2=\text{CH}$), 5.19-5.31 (2H, $\text{CH}_2=\text{CH}$), 4.84-4.87(1H, ring $\text{CH}_2=\text{CH}$), 4.50-4.54 (1H,

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J=16 Hz, ring CH_2-CH), 4.38-4.42 (1H, J=16 Hz, ring CH_2-CH), 4.01-4.10 (2H, $CH_2-CH=$), 3.69-3.73 (1H, CH_2-CH), 3.60-3.64 (1H, CH_2-CH); ^{13}C NMR ($CDCl_3$, 100.4 MHz), δ_c ppm: 155.06(C=O), 133.71($CH_2=CH$), 117.79($CH_2=$), 75.17(CH_2-CH), 72.51(ring CH), 68.86 ($CH_2-CH=$), 66.27(ring CH_2); 4-phenyl-1,3-dioxolan-2-one: 1H NMR ($CDCl_3/TMS$, 400 MHz), δ_H ppm: 7.28-7.38(m, 4H, ring ArH), 5.58-5.62 (t, 1H, J=16 Hz, PhCHO), 4.71-4.75 (t, 1H, J=16 Hz, OCH_2), 4.26-4.30 (t, 1H, J=16 Hz, OCH_2); ^{13}C NMR ($CDCl_3$, 100.4 MHz), δ_c ppm: 153.75 (C=O), 134.78 (Ph), 128.72 (Ph), 128.23 (Ph), 124.83 (Ph), 76.95 (Ph), 70.13(CH_2).

Conclusions

Several salen Al complexes functionalized by polyether-based imidazolium IL have been first prepared and act as catalyst for the cycloaddition reaction of CO_2 and various epoxides to provide cyclic carbonate under quite mild conditions. Remarkable enhancement of the reaction rates was observed over the one-component trifunctional catalysts at low CO_2 pressure due to built-in “ CO_2 capture” capability originated from the polyether chains. Among them, the catalyst of PISA-550 showed the best catalytic activity, which afforded cyclic carbonate in good yield (90-98%) with high selectivity for various epoxides under mild conditions. Furthermore, the synthesis catalyst PISA could be facilely separated and recycled for six times with only a slight loss in its catalytic activity by control of the solvent.

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Notes and references

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