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New bi-functional zinc catalysts based on robust and easy-to-handle
N-chelating ligands for the synthesis of cyclic carbonates from epoxides
and CO\(_2\) under mild conditions

Rongchang Luo, Xiantai Zhou, Wuying Zhang, Zhongxiu Liang, Jun Jiang and Hongbing Ji*

A series of novel zinc complexes were prepared by covalent linkage of various imidazolium-based
ionic liquid moieties with the 2,2'-bipyridine ligand at the two sides of the 4,4'-position. The
zinc(II) complexes containing the rigid N-chelating ligand proved to be stable, highly efficient
and easy-to-handle catalysts towards the synthesis of cyclic carbonate from epoxide and CO\(_2\)
without the use of any co-catalysts or organic solvent. The catalysts can be easily recovered and
reused without significant loss of activity and selectivity by control of solvent. The kinetic
study uncovered that the reaction was first-order with respect to epoxide. Moreover, a plausible
reaction mechanism was proposed, in which zinc center could promote ring-opening of the
epoxide for the synergetic effect with the anion X\(^-\) within ILs.

Introduction

It is well-known that CO\(_2\) is the major greenhouse gas suspected to
cause global warming. In terms of the so-called “sustainable society”
and “green chemistry” concepts, the effective utilization of carbon
dioxide as a safe, cheap, abundant renewable and environmentally
benign C\(_1\) building block in organic synthesis, has attracted much
attention both from industrial and academic viewpoints. In this
regard, the synthesis of five-membered cyclic carbonates via the 100
% atom-economical coupling reactions of CO\(_2\) and epoxides under
mild condition is one of a few industrial synthetic processes in this
area. On the other hand, cyclic carbonates are widely used as
electrolyte components for lithium batteries, polar aprotic solvents,
and intermediates in the production of pharmaceuticals and fine
chemicals. In the past few decades, numerous homogeneous catalytic systems
such as metal oxides, quaternary ammonium salt, alkali metal halides, ionic liquids (ILs),
transition metal complexes, N-heterocyclic carbenes (NHC), functional organic polymers
have been developed for promoting these transformations, which usually could
be operated under much milder conditions than heterogeneous
catalytic systems. Amongst such processes, transition metal-based
complexes in conjunction with Lewis base (such as onium salt) have
been employed as the high-efficiency binary catalysts under
relatively mild conditions (even room temperature and 1 atm
pressure). Meanwhile, various quaternary ammonium or
phosphonium groups were recently introduced into the frame of the
nitrogen-containing ligands (e.g. N\(_2\)O\(_2\)-ligand: salen\(^\text{12}\) or N\(_2\)-ligand: porphyrin\(^\text{13}\)), thus leading to a series of novel bi-functional metal
catalysts in one molecule. More interestingly, these
single-component analogues could be easily recovered and reused by
adding organic solvent (e.g. ether or ester). Consequently, the
efficient reusability of the catalyst makes the process more
economically and potentially viable for commercial application.\(^\text{12a}\)

For the cycloaddition of CO\(_2\) to epoxide, activation of epoxide and
subsequent epoxide ring opening are vital steps. Fig. 1 shows a
catalytic motif for the double activation of an epoxide with this type
of catalyst. In general, the cooperative action of an anion X\(^-\)
(nucleophilic) and a metal centre M (Lewis acid) promotes the
ring-opening of epoxide.\(^\text{13a}\) Hence, it seems to be currently the
most promising candidates with one particular trend as far as the
catalyst design is concerned: the grafting of ionic moieties on the
ligand backbone could perform as co-catalysts.\(^\text{15}\) Obviously,
bi-functionality has proven to be highly useful in various cases to
create more powerful catalyst mediators.\(^\text{12b}\) However, this category
of catalyst have being less developed as a probable result of the more
synthetically demanding characteristics of bi-functional catalyst
preparation.

Based on the above strategies, our group ever developed various
salen aluminium complexes functionalized by polyether-based
imidazolium ILs, which were used as high efficient, bi-functional
and homogeneous catalysts for the cycloaddition of CO\(_2\) to epoxides
under mild conditions (100 °C, 1.0 MPa) without the addition of
cocatalyst or organic solvent. Meanwhile, the catalysts presented
excellent “CO₂ capture” capability due to the weak interaction between the CO₂ molecule and the PEO chain. However, using zinc instead of aluminum as a metal center, it was disappointed that the similar Zn-containing catalyst presented lower activity with low TOF value under the identical conditions.

2,2'-Bipyridine ligands are currently attracting a great deal of interesting as the another nitrogen-containing ligand, which readily to interact with the metals via both σ-donating nitrogen atoms and π-accepting molecule orbitals. Metal complex containing the rigid 2,2'-bipyridine ligand was regard as efficient catalysts capable of carrying out various catalytic reactions under mild reaction conditions. Besides, the resulting complexes were very stable due to the formation of a five-membered chelate. However, to date, only few studies explored the type of metal complex in the formation of cyclic carbonates. Zinc as a kind of a strong Lewis acid and nontoxic metal, is a better choice for CO₂ coupling with epoxides. Therefore, 2,2'-bipyridine zinc(II) complexes can potentially facilitate for the cycloaddition reaction.

With this idea in mind, a new bi-functional 2,2'-bipyridine zinc(II) complexes bearing various IL moieties in one molecule were designed and synthesized. We initiated our study by examining the catalytic activity of the cycloaddition reaction of allyl glycidyl ether (AGE) with CO₂. It was found these Zn-containing catalysts were proved to be stable, efficient and easy-to-handle catalysts towards the synthesis of cyclic carbonate from epoxide and CO₂ under solvent-free condition in the absence of a co-catalyst. Meanwhile, we envisaged that the cooperative action between an anion X⁻ (nucleophile) within ILs and a metal center (Lewis acid). The large-scale synthesis of styrene cyclic carbonate (SC) catalyzed by 2,2'-bipyridine zinc(II) complexes was carried out and >90% yield could be obtained. Furthermore, the kinetics and mechanism of the reaction were investigated via the in situ IR spectroscopy.

Results and Discussion

Synthesis of catalysts

Because the catalytic performances of these Zn-containing catalysts are affected by the anion and/or ligand bonding to the zinc ion center, we choose zinc salts containing halide ions (e.g. Cl⁻, Br⁻, I⁻) as metal coordinating center due that halide anions were used as simple coordinating ligands to form a tetrahedral environment around the zinc ion. It is worth noting that an acidic metal center could coordinate with the epoxide in the coupling reaction, whereas a N-chelating ligand with suitable geometry and a leaving group may easily form a reactive metal–alkoxide bond.

The synthesis route for IL-functionalized 2,2'-bipyridine zinc(II) complexes (denoted as IL−BPZ) was shown in Scheme 1. In the first place, N-alkyl imidazole was added dropwise into the stirred suspension including 4,4'-dibromomethyl-2,2'-bipyridine in toluene (or acetone) solution at room temperature under nitrogen atmosphere. N-Alkyl-3-methyleneimidazolium bromine modified 2,2'-bipyridine ligand (denoted as IL−BP) was obtained immediately. Then, after metalation with ZnX₂ (X= Cl, Br, I) in ethanol, it resulted in the corresponding 2,2'-bipyridine zinc(II) complex IL−BPZ as white powder (Scheme 1).

Additionally, complex IL−BPZ was prepared by ion-exchange method in the NaBF₄ solution. Following the similar procedure, IL−BPZ was also obtained with a high yield using 4-methylpyridine instead of N-methylimidazole (Chart 1). It is particularly worth mentioning that these complexes were stable in air and soluble in water, DMF, but can be precipitated with other organic solvents, e.g., n-hexane, ether and ester. For comparison, the simple 2,2'-bipyridine zinc(II) complex BPZ and the traditional ionic liquid (1-benzyl-3-methylimidazoliumbromime, denoted as IL) were also prepared according the similar method in the literature (Chart 1).

Characterization of catalysts

Initially, the ¹H NMR of catalyst IL−BPZ and the corresponding ligand IL−BP1 were firstly recorded on Bruker AV 400M in DMSO-d₆ for the structure characterization. As show in Fig. 2, some peaks at 8.74-8.76, 8.40, 7.49-7.50 ppm originated from the proton of pyridine ring, and also at 9.41, 7.93, 7.83 ppm originated from the proton of imidazolium ring were observed in the ¹H NMR spectrum of IL−BP1. It is proposed that the new peak at 5.68 ppm due to methylene group resulted from the reaction between bromomethyl group (–CH₂Br) at the 4,4'-position of the 2,2'-bipyridine ligand and imidazolium ring. Compared with catalyst IL−BPZ1, normally, the coordination of nitrogen atoms of the pyridine groups to the metal zinc ion leads to a slightly shift. Thus, the direct proofs implied the successful synthesis of catalyst.

To further evaluate the detailed structure of catalyst, the new-synthesized complex IL−BPZ1, the corresponding ligand IL−BP1, as well as the simple (2,2'-bipyridine)ZnBr₃ (denoted as BPZ) for comparison, were characterized by FT-IR spectra (4000-400 cm⁻¹, see Fig. 3) and far-IR spectra (400-100 cm⁻¹, see...
Fig. 4). Firstly, the novel 2,2'-bipyridine ligand \(\text{IL–BP1}\), without characteristic vibration bands in the far infrared region, displayed major characteristic bands around 1597 cm\(^{-1}\), 1159 cm\(^{-1}\), 619 cm\(^{-1}\) (Fig. 3a). After metalation, the characteristic bands in the FT-IR spectra of the novel complex \(\text{IL–BPZ1}\) appear as apparent blue shift from 1597 cm\(^{-1}\), 1159 cm\(^{-1}\), 619 cm\(^{-1}\) to 1618 cm\(^{-1}\), 1167 cm\(^{-1}\) and 620 cm\(^{-1}\), respectively, compared with those of the corresponding ligand \(\text{IL–BP1}\) (Fig. 3a vs 3c).

Moreover, the far-IR spectra of the novel complex \(\text{IL–BP1}\) shows new characteristic vibration bands at around 262 cm\(^{-1}\) (Fig. 4c), which are associated with the stretching vibration modes of Zn–Br and Zn–N, respectively. These observations suggest that the 2,2'-bipyridine ligand could successfully coordinate with zinc ion through nitrogen atoms of the pyridine groups. Meanwhile, the IL-functionalized samples exhibited an additional feature at 1167 and 620 cm\(^{-1}\) assigned to the stretching vibration of characteristic peaks of imidazole fragment (Fig. 3c vs 3b). The new stretching vibration further suggests the grafting of imidazolium IL moiety on the 2,2'-bipyridine ligand. In addition, compared to the far IR spectra of the neat complex \(\text{BPZ}\) (\(\nu_{(Zn-Br)}=248\) cm\(^{-1}\), \(\nu_{(Zn-N)}=183\) cm\(^{-1}\)), see Fig. 4b), the blue-shift in the IR spectra of the novel complex \(\text{IL–BP1}\) (\(\nu_{(Zn-Br)}=262\) cm\(^{-1}\), \(\nu_{(Zn-N)}=206\) cm\(^{-1}\), see Fig. 4c) is mainly due to the electron-deficient substitutes of the imidazolium cations at the 4,4'-positions in the 2,2'-bipyridine ligands.  

Additionally, the UV–vis spectra of catalyst \(\text{IL–BPZ1}\) superimposed on that of the free ligand \(\text{IL–BP1}\) in water solution is reported in Fig. 5. The ligand \(\text{IL–BP1}\) and the corresponding zinc complex \(\text{IL–BPZ1}\) all typically shows two maximum absorption bands at 236 nm and 284 nm, attributed to \(\pi-\pi^*\) spin-allowed transitions involving the aromatic rings. Nevertheless, the UV–vis spectrum of a concentrated water solution of \(\text{IL–BPZ1}\) shows the presence of a broad band at around 490 nm that is missing in the absorption spectra of \(\text{IL–BPZ1}\) in dilute solution, which is due to the ligand-to-metal charge transfer transitions in the 2,2'-bipyridine Zn(II) complex. The observation implies that the active site (metal center) of the IL-functionalized 2,2'-bipyridine Zn(II) complex is maintained.

Thermal analysis was used to monitor the decomposition profiles of IL grafted complex of \(\text{IL–BPZ1}\), and the obtained results are depicted in Fig. 6. The first obvious large loss in weight centres is at 345 °C. The thermo-stability of catalyst \(\text{IL–BPZ1}\) was obviously superior to the corresponding ligand \(\text{IL–BP1}\) (or IL) that the large loss weight centres was at 295 °C (312 °C for \(\text{IL–BP1}\)), see Fig. 6a vs 6b, 6c). As mentioned, this weight loss is logically assigned to the successive cleavage of 2,2'-bipyridine ligand. Notably, the temperature of the successive cleavage of the 2,2'-bipyridine ligand moieties in the \(\text{IL–BPZ1}\) gets increased up to 520 °C, due to the mutual stabilization of the 2,2'-bipyridine ligand part and the ILs moieties. It is indirect proof for the successful grafting of ILs moiety on the 2,2'-bipyridine ligand. The third weight loss appeared 520°C and was followed by an additional weight loss at 600 °C which extended up to ca. 690 °C. The two steps were well distinguished in the

Fig. 2 The \(^1\)H NMR results of catalyst \(\text{IL–BPZ1}\) (red line) and the corresponding ligand \(\text{IL–BP1}\) (blue line).

Fig. 3 The FT–IR spectra of ligand \(\text{IL–BP1}\) (a), catalyst \(\text{BPZ}\) (b) and \(\text{IL–BPZ1}\) (c).

Fig. 4 The far-IR spectra of ligand \(\text{IL–BP1}\) (a), catalyst \(\text{BPZ}\) (b) and \(\text{IL–BPZ1}\) (c).

Fig. 5 (I) The UV–vis spectra of catalyst \(\text{IL–BPZ1}\) and the corresponding ligand \(\text{IL–BP1}\); (II) The UV–vis spectra of a concentrated water solution of catalyst \(\text{IL–BPZ1}\).
corresponding DTG curve (Fig. 6(B)). We tentatively assigned these steps to the complete decomposition of the ligand and ILs. The non-removable residue belonged to the formation of zinc oxide in air atmosphere at high temperature. It was indirect proof for the successful coordination to the 2,2′-bipyridine ligand using zinc salt with respect to the TG curve of ligand IL-BP or IL. According to TG-DTG data, the robust catalyst IL-BPZ1 remains stable up to 250 °C.

![Fig. 6 Thermogravimetric TG (A) and differential thermogravimetric DTG (B) results of catalyst IL-BPZ1 (a, blue line), ligand IL-BP1 (b, red line) and IL (c, green line).](image)

**Effect of catalysts**

The catalytic performances of the novel catalysts IL-BPZ were measured in the model cycloaddition reaction of allyl glycidyl ether (AGE) with CO₂, which was conducted in a semi-batch operation in the presence of the catalyst under mild conditions (0.5 mol%, 373 K, 1.0 MPa, 4 h, Table 1). In the absence of catalyst or the sole addition of ZnBr₂ even simple 2,2′-bipyridine ligand, the reaction does not proceed at all (Table 1, entry 1-3). While 1.0 mol% of the conventional ionic liquid IL (2 equiv.) could catalyse the cycloaddition reaction, the yield of allyl glycidyl carbonate (AGC) was very low (Table 1, entry 4) under solvent-free conditions. Note that simple 2,2′-bipyridine Zn(II) bromide complex (denoted as BPZ, see Chart 1), even IL-functionalized 2,2′-bipyridine ligand IL-BP without ZnBr₂ present poor catalytic performance under the given conditions (Table 1, entry 5-6). To our delight, 2,2′-bipyridine Zn(II) bromide complexes bearing various imidazolium-based IL units (IL-BPZ, Scheme 1), as a kind bi-functional complex, exhibit excellent catalytic performance. The catalytic performance with the employment of the catalyst IL-BPZ1 is similar to that upon the binary catalyst system for a simple physical mixture of complex BPZ with IL using the molar ratio of 1:2 (Table 1, entry 7-8 vs entry 9). This observation indicates IL-BPZ1 bearing intramolecular nucleophilic co-catalyst acts as single-component catalyst to complete the catalytic cycle based on the acid-base synergistic catalytic mechanism. Because the epoxide could be coordinated with the Lewis acidic site Zn to form the adduct of the metal-epoxide, then basic site Br⁻ anion of the IL makes a nucleophilic attack on the less hindered carbon atom of the coordinated epoxide followed by ring opening. Notably, the two-component catalytic system ZnBr₂/IL-BPZ1 with equivalent molar ratio has low catalytic performance in the cycloaddition reaction (Table 1, entry 10). It suspects that adding both separate components together may require a small induction period to form in situ the IL-BPZ1 system. When adding the substrate together with the separate components other complexes based on the zinc reagent may form because of the kinetic effect. Thus, when the molar ratio increased to 2:1, the similar results were obtained with respect to the complex IL-BPZ1 (Table 1, entry 11). Moreover, in the catalytic system, 92% yield of AGC could be obtained under even 1 atm CO₂ pressure for 12 h (Table 1, entry 12). Unfortunately, the coupling reaction could basically not occur under room temperature and atmospheric pressure even prolonged the reaction time to 72 h.

**Table 1 The results of the cycloaddition reaction of AGE with CO₂ catalyzed by various catalysts.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv. [%]</th>
<th>Yield [%]</th>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>ZnBr₂</td>
<td>n. r.</td>
<td>n. r.</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>2,2′-bipyridine</td>
<td>n. d.</td>
<td>n. d.</td>
<td>-</td>
</tr>
<tr>
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<td>IL</td>
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<td>20</td>
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<td>6</td>
<td>IL-BP1</td>
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<td>4.5</td>
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<tr>
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<td>84</td>
<td>42</td>
</tr>
<tr>
<td>8</td>
<td>IL-BPZ1</td>
<td>96</td>
<td>95</td>
<td>38</td>
</tr>
<tr>
<td>9</td>
<td>BPZ/IL (1:2)</td>
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<td>93</td>
<td>37.2</td>
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<tr>
<td>10</td>
<td>ZnBr₂/IL-BP1 (1:1)</td>
<td>49</td>
<td>47</td>
<td>23.5</td>
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<tr>
<td>11</td>
<td>ZnBr₂/IL-BP1 (2:1)</td>
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<td>12</td>
<td>IL-BPZ1</td>
<td>93</td>
<td>92</td>
<td>15.3</td>
</tr>
</tbody>
</table>

* Reaction conditions: 10 mL stainless-steel clave, AGE (6 mmol), catalyst (0.03mmol, 0.5 mol%), CO₂ pressure (1.0 MPa), reaction temperature (100 °C), reaction time (4 h).
* Determined by GC using biphenyl as the internal standard; Turnover frequency (TOF): mole of synthesized AGC per mole of catalyst per hour.
* Reaction proceeded for about 5 h under identical conditions.
* Reaction proceeded at 100 °C under 1 atm CO₂ pressure for about 12 h.

**Effect of reaction parameters**

The effect of temperature and pressure on the cycloaddition reaction is investigated. As expected, the reaction temperature had a positive effect on the catalytic reaction. From Fig. 7(I), it can be seen that the yield of the AGC achieved 96 % when the reaction temperature was 100 °C. However, no significant difference was observed when temperature was increased to 110 °C. When the reaction was carried out at low temperature (e.g. 80 °C), much lower conversion of AGE (less than 11 %) was obtained. Moreover, because the gas-liquid diffusion between epoxide and CO₂ may have an effect on the reaction kinetics in the mass transfer, there are optimal ranges of CO₂ pressure for the maximum conversion of AGE. The pressure has a great effect on the conversion of AGE upon varying the CO₂ pressure in the range 0.1-1.0 MPa, whereas the conversion changes
only slightly in the range 1.0-3.0 MPa (see Fig. 7(II)). It indicated that higher CO$_2$ pressure enhanced AGC yield due to the higher CO$_2$ concentration in the liquid phase of the reaction system under a low-pressure region.\textsuperscript{31} The results demonstrated that this catalytic system could be operated with high efficiency under mild conditions (100 °C, 1.0 MPa). Thus, the effect of the amount of catalyst on the cycloaddition was also examined (see Fig. 7(III)). The results indicated that the catalyst amount had significant impact on the reactions. The conversion of AGE significantly increased with enhancement of the amount of catalyst under the same reaction conditions (from 0.1 to 0.5 mol %). When the using amount of catalyst was further increased up to 0.75 mol%, the AGC conversion by only a small margin was obtained.\textsuperscript{76} In addition, the dependence of the AGE conversion on reaction time at the identical conditions was presented in Fig. 7(IV). It can be seen that the conversion of AGE increased rapidly with the reaction time and that nearly all the AGE could be converted within 6 h. It should be noted that the selectivity towards the desired AGC was essentially 99 %, since GC-MS analysis and $^1$H NMR showed that there were no other detectable products.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7.png}
\caption{Optimization of reaction conditions with catalyst IL-BPZ1; reaction conditions: 10 mL stainless-steel clave, AGE (6 mmol), (I) CO$_2$ pressure (1.0 MPa), 5 h, 0.5 mol% catalyst; (II) temperature (100 °C), 0.5 mol% catalyst, 5 h; (III) temperature (100 °C), CO$_2$ pressure (1.0 MPa), 5 h; (IV) temperature (100 °C), CO$_2$ pressure (1.0 MPa), 0.5 mol% catalyst.}
\end{figure}

\section*{Effect on the various structures of the catalysts}

Under the optimal conditions, we further evaluated the effect on the different structures of the catalyst on the coupling reaction of AGE to CO$_2$. Initially, the catalytic activity of catalysts IL-BPZ was affected by the chain length of the substituent in N-position of the imidazolium ring. As shown in Fig. 8, IL-BPZ series catalysts with longer alkyl side chains were proved the observed higher activity (IL-BPZ2 or IL-BPZ3 vs IL-BPZ1). The AGE conversion increased with the length of the alkyl chain increased from methyl to n-butyl, further to n-octyl. It can be assumed that the bulkiness of the alkyl imidazolium cation forces the bromide ion away from the cation, and this weaker electrostatic interaction would render the anion more nucleophilic. Therefore, they were more effective in nucleophilic attack of the anion to the oxirane ring of AGE.\textsuperscript{32} More importantly, IL-BPZ4 bearing three EO units exhibited the highest activity with respect to IL-BPZ3 owing the identical hydrophobic alkyl chain length, which was also shown by our group’s previous work.\textsuperscript{16} The phenomenon could be attributed to “CO$_2$-expansion” effect of PEO chains, which was originated from the weak interaction between the CO$_2$ molecule and the PEO chain.

Furthermore, the nature of halide groups bonded to the zinc center also significantly affected the catalytic activity (see Fig. 8(II)). When the Lewis acidity of the metal cation is stronger, the coordination of the epoxide is easier. In addition, a more nucleophilic anion is favourable for its interaction with the carbon atom of CO$_2$.\textsuperscript{29} Therefore, the conversion of the AGC increased with the increasing nucleophilicity and the leaving ability of halide ion (I$^\text{–}$>Br$^\text{–}$>Cl$^\text{–}$).\textsuperscript{33} On the basis of this result, it could be suggested that the leaving ability was beneficial to increasing catalytic activity. Additionally, the reactions also depend greatly on the kind of counter anions of imidazolium-based IL moieties in the catalysts (IL-BPZ1 vs IL-BPZ6). These results illuminate that the counter ions play an important role in the catalytic activity and the Br$^\text{–}$ is the most effective of these negative ions for the cycloaddition reaction of AGE with CO$_2$. The activity of Br$^\text{–}$ was higher than BF$_3$$^\text{–}$, which is consistent with the order of the nucleophilicity of the anions. Thus, these results indicate that non-nucleophilic nature of BF$_3$$^\text{–}$ anion is not favourable components for the coupling reaction, which leads to a lower conversion of the epoxide.\textsuperscript{34} The rate determining step of the epoxide-CO$_2$ reaction involves nucleophilic attack of the bromide anion to AGC. More nucleophilic anion will more easily attack the epoxide ring to form reaction intermediate. Additionally, the most common nitrogen containing organic cations within IL units are imidazolium and pyridinium derivatives. Fig. 8(IV) shows that the relationship between type of onium cation in IL units and the activity of the catalysts (IL-BPZ1 vs IL-BPZ8). The catalytic activity on the coupling reaction decreases in the order of imidazolium>pyridinium, which hints the incorporation of the imidazolium group within the 2,2’-bipyridine ligand is beneficial for catalytic performance.\textsuperscript{35}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig8.png}
\caption{The reactivity of various catalysts with different structures for the cycloaddition reaction of AGE with CO$_2$; reaction conditions: 10 mL stainless-steel clave, AGE (6 mmol), temperature (100 °C), CO$_2$ pressure (1.0 MPa), 0.5 mol% catalyst; (I) 2 h; (II) 4 h; (III-IV) 5 h.}
\end{figure}
Catalytic activity towards other epoxides

To survey the scope of substrates, we examined the cycloaddition reactions of other commercially available epoxides (such as propylene oxide (PO), 1,2-epoxybutane, epichlorohydrin (ECH), styrene oxide (SO) and its derivatives) with CO$_2$, by performing the reaction with 0.5 mol% catalyst IL−BPZ1 under the identical conditions (1.0 MPa, 100 °C, 5 h) as elaborated in Table 2. Obviously, most terminal epoxide substrates (1a−e) could be smoothly converted to corresponding cyclic carbonates with high conversion and excellent selectivity (Table 2, entries 1-5). The activity of epoxides decreased as the alkyl length increasing (entry 1 vs entry 2). Moreover, for bromo or chloro-substituted SO derivatives (such as 1g and 1h with electron-withdrawing substituents on the para-position of aromatic ring), the yields are generally lower than those with electron-donating substituents (e.g. methyl group 1e). It suggested that for SO and its derivatives the nucleophilic ring-opening occurs mainly at the α-carbon of the epoxide ring due to a consequence of the electron-withdrawing inductive effect of the phenyl group (Table 2, entry 6 vs entries 5, 7-8). Similarly, the electron-withdrawing nature of the chloromethyl group of ECH tends to drive the reaction towards the cyclic carbonate product (Table 2, entry 3). Unfortunately, the internal epoxide, cyclohexene oxide (CHO), exhibited lower activity (Table 2, entry 9) presumably due to the high steric hindrance. This steric effect was more likely to hinder the nucleophilic attack of the epoxide rather than its coordination to the Lewis acid metal center. Thus, both steric and electronic effects play an important role on the chemical coupling reaction of epoxide and CO$_2$.

<table>
<thead>
<tr>
<th>Entry</th>
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<td>1g</td>
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</table>

*Reaction conditions: 10 mL stainless-steel clave, epoxide (6 mmol), IL−BPZ1 (0.03 mmol), reaction temperature (100 °C), reaction time (5 h), CO$_2$ pressure (1.0 MPa), product identification via FT-IR, $^1$H NMR, $^{13}$C NMR and GC-MS; $^1$Same as Table 1.

Table 2 The results of the coupling reaction of CO$_2$ to various epoxide substrates over the IL−BPZ1.

Reusing of the Catalyst

A series of catalytic recycles were carried out to test the stability and reusability of the catalyst under the optimized conditions. In each cycle, the cyclic carbonate product was easily extracted with ethyl acetate or ether then the catalyst was precipitated after centrifugation. Subsequently, the solid precipitation was filtrated, washed with EtO and dried in vacuum and was reused in the subsequent reactions. The yields of the product obtained from the second (95%), third (92%), and fourth runs (90%) were similar to those obtained with the fresh catalyst under the identical conditions. Accordingly, the IL-catalyst could be reused at least four times with only a slight loss of catalytic activity, consistent with only a slight leaching of the active catalyst species. Therefore, the special solubility of the complexes endows them with the feature of solvent-regulated separation.

Large-scale synthesis of styrene cyclic carbonate

In view of the easy operation and analysis, we choose styrene oxide (SO, b.p.=191 °C) as a model substrate to apply the large-scale synthesis of SC using Mettler Toledo EasyMaxTM102 system equipped with a 100 mL stainless steel autoclave in a semi-batch operation (CO$_2$ was continuously supplied to the reactor). The course of reaction was also monitored by the in situ IR spectroscopy.

As shown Scheme 2, the >90 % yield of SC was obtained with IL−BPZ6 at 120 °C (keep Jacket temperature T$_j$ constant) without solvent, while the TOF value reach up to 240 h$^{-1}$. Meanwhile, from the results of in situ IR spectra, the intensity of the characteristic peak for SO at 876 cm$^{-1}$ and 815 cm$^{-1}$ (epoxy ring skeleton vibration) declined rapidly, whereas an increasing intensity of the signals at 1159 cm$^{-1}$, 1065 cm$^{-1}$ (asymmetrical C−O vibration) and the peak around 1810 cm$^{-1}$ (C=O stretching vibration) indicated the formation of SC as the sole product (see Fig. 10). The results suggest that the homogenous catalyst could maintain the high catalytic activity with excellent selectivity in large-scale production.
Firstly, it can be assumed that the concentrations of catalyst are constant during reaction and CO₂ is present in large excess due to the semi-batch operation so that b=c=0 (Eq. 2). Thus, in the event, the observed rate constant was determined from the slope of a linear plot of the natural logarithm of the changing sample concentration with time at different temperatures (Eq. 3-4). **Fig. 12-13** shows the determination of the observed rate constant for SO conversion by the catalyst IL-BPZ1 at 100 °C using propylene carbonate (PC) as solvent. It was repeated for the other reaction temperatures and catalyst compositions. All the kinetic experiments showed a good fit to first order kinetics, implies that the reactions are first order in SO (Eq. 5).

![fig10](image1)

**Fig. 10** (I) Three-dimensional stack plot of IR spectra collected every 1 min during the coupling reaction of SO and CO₂ with 0.25 mol% IL4BPZ6 at 120 °C (Tj) and 1.0 MPa CO₂ pressure without solvent; (II) Decreases of the epoxide ring vibrational modes with a concomitant increase of the SC peaks at different times.

Additionally, it was also noted that reactions carried out at the low concentration (0.25 mol% IL-BPZ1 or IL-BPZ6) had an induction period under solvent-free conditions. Meanwhile, we found that the induction period could be shortened following the increased reaction temperature (Fig. 11a vs Fig. 11b). Especially, catalyst IL-BPZ6 has shorter induction period due to the better solubility with respect to IL-BPZ1 (Fig. 11b vs Fig. 11c) in CO₂-epoxide mixture under identical conditions. Furthermore, if adding propylene carbonate as solvent, the induction period disappeared since catalyst IL-BPZ could be dissolved fully in the beginning stage (Fig. 12-13).

![fig11](image2)

**Fig. 11** Decrease in SO mole concentration with time with catalyst IL-BPZ1 or IL-BPZ6 (0.25 mol%) under solvent-free condition at 100 °C-120 °C (Tj) and 1.0 MPa CO₂ pressure (the green circle represents the reaction induction period). (A) IL-BPZ1, (B) IL-BPZ6, (C) IL-BPZ6 at 100 °C.

Kinetics studies and mechanistic considerations

To investigate the mechanism of cyclic carbonate synthesis, a study of the reaction kinetics was undertaken as depicted in Eq. 1-8 (the general form of rate equation). From the in situ IR spectra, the data were found to fit to the following rate equations: [SO], [CO₂] and [Cat] are the SO, CO₂ and catalyst concentrations respectively; a, b and c are the order of reaction; t is time and kobs is the observed pseudo-first-order rate constant for SO conversion (Eq. 1).

\[
\text{Rate}=k_{\text{obs}}[\text{SO}][\text{Cat}][\text{CO}_2]^a
\]

**Eq. 1**

\[
\text{Rate}=k_{\text{obs}}[\text{SO}]^b
\]

**Eq. 2**

\[
\text{Rate}=k_{\text{obs}}[\text{CAT}]^c
\]

**Eq. 3**

\[
\ln[\text{SO}]=k_{\text{obs}}t
\]

**Eq. 4**

\[
\text{Rate}=k_{\text{obs}}[\text{CAT}]^b
\]

**Eq. 5**

\[
\text{Rate}=\ln[k_{\text{obs}}]+b[\text{CAT}]
\]

**Eq. 6**

\[
\text{Rate}=k_{\text{obs}}[\text{CAT}]^c
\]

**Eq. 7**

\[
\text{Rate}=k_{\text{obs}}[\text{CAT}]^d
\]

**Eq. 8**

![fig12](image3)

**Fig. 12** Pseudo-first order kinetic plot of the natural logarithm of different SO concentration against time for the IL-BPZ1 (0.14 mol%) at 100 °C (Tj) and 1.0 MPa CO₂ pressure using PC as solvent.

Furthermore, assuming steady state conditions at the beginning of the reaction, and thus CO₂ and SO concentrations are more or less constant. The rate law for this process may be rewritten as Eq. 6, in which kobs represents the rate constant, b is the order of reaction and [Cat] is the concentration of IL-BPZ1. Then, by taking the natural logarithm of Eq. 6, Eq. 7 is obtained. The kinetic data was fitted by the natural logarithm of the observed pseudo-first order rate constant (ln[kobs]) against the natural logarithm of the catalyst concentrations (ln[Cat]) (Eq. 7). The logarithmic plot revealed that b is close to 2.0 suggesting the reaction is second order in the single-component catalyst IL-BPZ1 (Eq. 7, see Fig. 13).

![fig13](image4)

**Fig. 13** (I) Decrease in SO mole concentration ([SO]) with time with catalyst IL-BPZ1 (0.0043-0.0068 M) in PC (21 g) at 100 °C (Tj) and 1.0 MPa CO₂ pressure; (II) The fitting curve of the natural logarithm of the observed pseudo-first order rate constant (ln[kobs]) against the natural logarithm of the catalyst concentrations (ln[Cat]).

Based on the molecule structure of the complex IL-BPZ and the cycloaddition reaction results, a possible mechanism of the acid-base synergetic catalysis for cyclic carbonate synthesis is also proposed, which is similar to our previous work. The kinetic study hints bimetallic pathway involving two separated monometallic...
complexes has been inspired for the ring opening of epoxides (Scheme 3). This intermolecular mechanism is similar to the monometallic pathway, but there is the difference that the nucleophile X is coordinated to a metal centre, and it also attacks the epoxide activated by the second metal centre. This pathway is expected to occur when low catalyst/epoxide ratios are employed. Further experiments are in progress to elucidate the reaction mechanism.

Conclusions

Several 2,2'-bipyridine zinc(II) complexes functionalized by imidazolium based ILs were first prepared and used as catalysts for the cycloaddition reaction of CO₂ and various epoxides to provide cyclic carbonate under quite mild conditions. The catalyst of IL-BPZ4 with longer PEO chain showed the best catalytic activity, which afforded AGC in 98% yield and 99% selectivity within 2 h under 100 °C and 1.0 MPa CO₂ pressure conditions. The cooperative action mechanism for ring-opening of the epoxide between an anion X within ILs and a metal center was proposed. In addition, the reaction kinetic data via the in situ IR spectroscopy revealed that the reaction was first-order with respect to epoxide and second-order for catalyst at the low concentration range.

Experimental Section

Reagents and Methods: Propylene oxide (PO), propylene carbonate (PC), epichlorohydrin (ECH), allyl glycidyl ether (AGE), styrene oxide (SO), zinc bromide, 1-methylimidazol, sodium fluoroborate and 4-methylpyridine were obtained from J&K Scientific Ltd. 4-chlorostyrene oxide and 4-bromostyrene oxide was purchased from Alfa Aesar Chemical Reagent Co. Ltd. Zinc chloride was produced by Acros Organics. Sodium borohydride, zinc iodide, 4,4'-dimethyl-2,2'-dipyridyl and 2,2'-bipyridyl-4,4'-dicarboxylic acid were received from Energy Chemical. 1-butylimidazole and 1-octylimidazole were bought from TCI. Other commercially available chemicals were laboratory grade reagents from local suppliers. CO₂ was purified by passing through a column packed with 4Å molecular sieves before use (99.99%). All of the solvents were purified by standard procedures. 4-methylstyrone oxide was prepared using the Jacobsen’s catalyst.

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 aBruker spectrophotometer. The ultraviolet–visible light (UV-vis) spectra were recorded on a Shimadzu UV2450 spectrophotometer. The solution of samples in ultrapure water (ca. 1.0 mM) was poured into a 1 cm quartz cell for UV-vis adsorption with ultrapure water as the reference. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance III 400 M spectrometer. The thermogravimetric and differential thermogravimetric (TG–DTG) curves were obtained on a NETZSCHSTA 449C thermal analyser. 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⁻¹. 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. The course of reaction for kinetic study was also monitored by the in situ IR spectroscopy using a Mettler Toledo React IR ic10 reaction analysis system with DiComp ATR probe (Diamond, AgX 6mm×1.5m Fiber). In this manner, a single 256-scan background spectrum was collected. The infrared spectrometer was set to collect one spectrum every 1 min over 24 hour. Profiles of the absorbance at 815 cm⁻¹ with time were recorded and used to provide initial reaction rates for analysis. The cycloaddition reaction of epoxides with CO₂ was carried out according to the recently-published reference and NMR characterizations of the typical cyclic carbonate products (2a-4i) were also listed in the literature.

General Procedure for the Synthesis of various ionic liquid functionalized 2,2'-bipyridine zinc(II) complex

Synthesis of bis(1-methyl-3-methyleneimidazolium bromine) modified 2,2'-bipyridine: N-methylimidazol (0.821 g, 10 mmol) in dry toluene (100 mL) was added dropwise into the stirring toluene solution of 4,4'-dibromomethyl-2,2'-bipyridine (1.71 g, 5 mmol) under nitrogen atmosphere. The reaction was heated to reflux for 12 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 IL-BP as the viscous liquids. Yield: 92 %. Ligands IL-BP, IL-BP3 and IL-BP4 were also prepared using 1-butylimidazol, 1-ctoylimidazol and N-polyoxethylene methyl etherimidazol, instead of N-methyl imidazol, respectively. IL-BP1: FT-IR (KBr), γmax/cm⁻¹: 3405, 3079, 1597, 1566, 1459, 1387, 1338, 1279, 1206, 1160, 1108, 1080, 1024, 980, 825, 762, 729, 670, 620, 571, 501; ¹H NMR (400 MHz, D₂O) δmax=8.54-8.56 (d, J=8 Hz, 2H), 7.89 (s, 2H), 7.46-7.48 (d, J=8 Hz, 4H), 7.34-7.35 (d, J=4Hz, 2H), 5.52 (s, 4H), 3.87 (s, 6H); ¹³C NMR (100.4 MHz, D₂O) δmax=155.47, 149.92, 145.33, 136.85, 124.29, 116.66, 113.27, 127.71, 120.91, 51.42, 35.99.

Synthesis of bis(1-methyl-3-methyleneimidazolium bromine) modified 2,2'-bipyridine Zn(II) complex: Zinc bromine (2.5 mmol) dissolved in 100 mL anhydrous ethanol was added dropwise into the stirring absolute ethanol solution of above-obtained 2,2'-bipyridine ligand (1.26 g, 2.5 mmol) under nitrogen atmosphere. After white precipitate was emerged immediately, and then the reaction was heated to reflux for 12 h. After cooling, the white solid product was collected and washed thoroughly with ethanol (3×20 mL). Abundant white precipitate was obtained under nitrogen atmosphere. Yield: 92 %. Ligands IL-BPZ1, IL-BPZ3 and IL-BPZ4 were also prepared using 1-butilimidazol, 1-octylimidazol and N-polyoxethylene methyl etherimidazol, instead of N-methyl imidazol, respectively. IL-BPZ1: FT-IR (KBr), γmax/cm⁻¹: 3514, 3101, 1618, 1569, 1489, 1418, 1243, 1166, 1101, 1081, 1041, 1024, 980, 825, 762, 729, 670, 620, 571, 501; ¹H NMR (400 MHz, D₂O) δmax=9.33(s, 2H), 8.76-8.77(d, 2H), 8.44(s, 2H), 7.89(s, 2H), 7.80(s, 2H), 7.46-7.48 (d, J=8 Hz, 4H), 7.34-7.35 (d, J=4Hz, 2H), 5.52 (s, 4H), 3.87 (s, 6H); ¹³C NMR (100.4 MHz, D₂O) δmax=150.46, 137.75, 124.74, 124.03, 123.11, 120.28, 51.18, 35.99.
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Notes and references

School of Chemistry and Chemical Engineering, Key Laboratory of Low-Carbon Chemistry & Energy Conservation of Guangdong Province, Sun Yat-sen University, Guangzhou 510275, P.R. China. Email address: jihb@mail.sysu.edu.cn (H.B. Ji); Tel.: +86 20 84113658; Fax: +86 20 84113654.

References


Graphical Abstract

Highly active bi-functional zinc catalysts based on robust and easy-to-handle N-chelating ligands for the synthesis of cyclic carbonates from epoxides and CO$_2$ under mild conditions

Rongchang Luo, Xiantai Zhou, Wuying Zhang, Zhongxiu Liang, Jun Jiang and Hongbing Ji*

School of Chemistry and Chemical Engineering, Key Laboratory of Low-Carbon Chemistry & Energy Conservation of Guangdong Province, Sun Yat-Sen University, Guangzhou 510275, P.R. China

The zinc(II) complexes containing the rigid N-chelating ligand proved to be highly efficient and bi-functional catalysts towards the synthesis of cyclic carbonate from epoxide and CO$_2$ without the use of any co-catalysts or organic solvent.