

# Ionic liquids-functionalized porphyrins as bifunctional catalysts for cycloaddition of carbon dioxide to epoxides



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## ABSTRACT

Six ionic liquids-functionalized metalloporphyrins have been designed, prepared and characterized by NMR, MS and elemental analysis. They were applied as efficient bifunctional catalysts to the cycloaddition of epoxides and carbon dioxide without additive and organic solvent yielding cyclic carbonates. 5,15-Di[4-(4-tributylammonio)butoxy]phenyl]porphyrin zinc(II) dibromide (**JB<sub>p</sub>**) and 5,15-di[3-(4-tributylammonio)butoxy]phenyl]porphyrin zinc(II) dibromide (**JB<sub>m</sub>**) have been demonstrated excellent activities under optimized conditions. It has been found that both the structure of porphyrin complex cations and the anion moieties would strongly affect their catalytic performance. The catalysts were versatile for the cycloaddition of CO<sub>2</sub> to various terminal epoxides in satisfying yields with excellent selectivities. Moreover, phenoxypropylene carbonate was able to be obtained under atmosphere pressure of CO<sub>2</sub> and in large-scale. Furthermore, a plausible mechanism involving Lewis acid-base synergistic catalysis has been proposed according to our experimental results.

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## 1. Introduction

Straightforward fixation of carbon dioxide that is widely considered as an abundant, cheap, renewable, non-flammable, non-toxic feedstock in chemistry has attracted considerable attention in decades [1–3]. Hence, transformation of CO<sub>2</sub> to useful chemicals is very fascinating in view of environment concerns. Some achievements have been disclosed including the syntheses of urea, methanol, carbon monoxide, salicylic acid and organic carbonates from CO<sub>2</sub> [4–12]. One of the most successful strategies is of cyclic carbonate synthesis from epoxides and CO<sub>2</sub> (Scheme 1) with 100% atom economy [13–16]. Cyclic carbonates have widely used as intermediates, aprotic polar solvents, raw materials and fuel additives [17–20]. Various catalyst systems have been successfully developed for this cycloaddition reaction embodying metal salts [21], metal oxides [22], organocatalysts [23], ionic liquids [24] and metal complexes [25–27]. Among them, metalloporphyrins comprising different metal centers (Zn, Mg, Al, Co, Cr, Ru, Fe, Sn, etc.) have received much interesting in light of their unique frameworks that were facile to be functionalized [28–32].

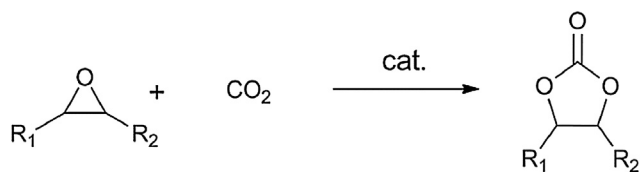
Some ammonium-functionalized porphyrin catalysts have been reported in recent years [33–35] and show higher catalytic activity than traditional binary catalytic systems. However, these bifunctional catalysts with higher symmetry present larger steric hindrance. The steric barriers at the periphery of the rigidly planar metalloporphyrin play an important role for the activity and selectivity [9].

Ionic liquids (ILs) have been utilized as effective catalysts in PO/CO<sub>2</sub> cycloaddition [24,36–41]. The first example was reported by Peng and Deng in 2001 [42]. Afterward, Girard's group reported a series of imidazolium-based ionic liquids catalysts for the cycloaddition of epoxides and CO<sub>2</sub> [43]. However, there are some drawbacks, such as high catalyst loading, relative lower turnover numbers (TON). ILs composed of cation/anion pairs are generally defined as molten salts with melting points lower than 100 °C. In 2011, our group reported a series of novel metal-containing crown ether complex cation ionic liquids that enlarged the family of ionic liquids, which were different from the classical ionic liquids with melting points lower than 200 °C [44]. So we expect to merge ammonium moieties into porphyrin rings to form new type of ILs with metalloporphyrin skeleton.

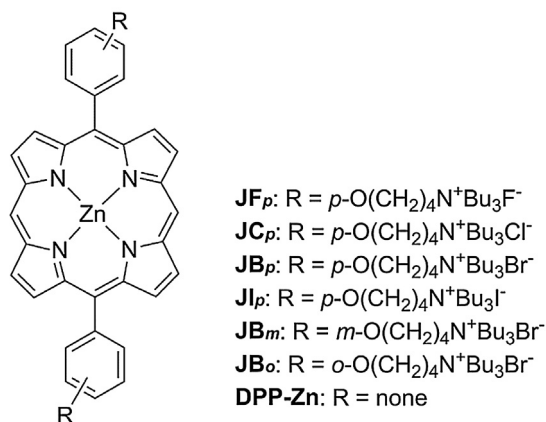
In this work, a series of ammonium-functionalized metalloporphyrin ionic liquids (MPILs) in different position (*para*, *meta* and *ortho*) of *meso*-benzene ring were fabricated (Fig. 1). These catalysts with lower symmetric demonstrate smaller steric

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**Scheme 1.** The cycloaddition of epoxides and CO<sub>2</sub>.



**Fig. 1.** Structures of MPILs catalysts.

**Table 1**  
The melting points of MPILs.

Entry	Cat.	M.p. [°C] <sup>a</sup>
1	<b>JF<sub>p</sub></b>	163
2	<b>JC<sub>p</sub></b>	170
3	<b>JB<sub>p</sub></b>	174
4	<b>JI<sub>p</sub></b>	156
5	<b>JB<sub>m</sub></b>	160
6	<b>JB<sub>o</sub></b>	155
7	<b>DPP-Zn</b>	>300

<sup>a</sup> All melting points were determined on a XT-4 melting point apparatus without calibration.

hindrance. Their melting points are lower than 200 °C (Table 1). All of them were employed as bifunctional homogeneous catalysts in the cycloaddition reaction of epoxides and CO<sub>2</sub> without solvent and co-catalyst.

## 2. Experimental section

### 2.1. Materials and facilities

Epoxides were obtained from Aldrich Company. Salicylaldehyde, 3-hydroxybenzaldehyde and 4-hydroxybenzaldehyde were purchased from Sinopharm Chemical Reagent Co. Ltd. PO was distilled from CaH<sub>2</sub>. Other chemicals and reagents were commercial products and used to the reaction without further purification.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AM-300/AM-400/AM-600 spectrometer using CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub> or CD<sub>3</sub>OD as solvent and trimethylsilane (TMS) as an internal standard. The MALDI-TOF mass spectra were acquired by a Bruker BIFLEX III spectrometer workstation. The ESI mass spectra were obtained from a Bruker ESQUIRE 6000 spectrometer.

### 2.2. Synthesis of catalysts

The synthetic route of catalysts is shown in Scheme 2.

#### 2.2.1. Synthesis of dipyrromethane (a)

Compound **a** was prepared by following the literature method [45].

#### 2.2.2. Synthesis of benzaldehydes derivatives (b)

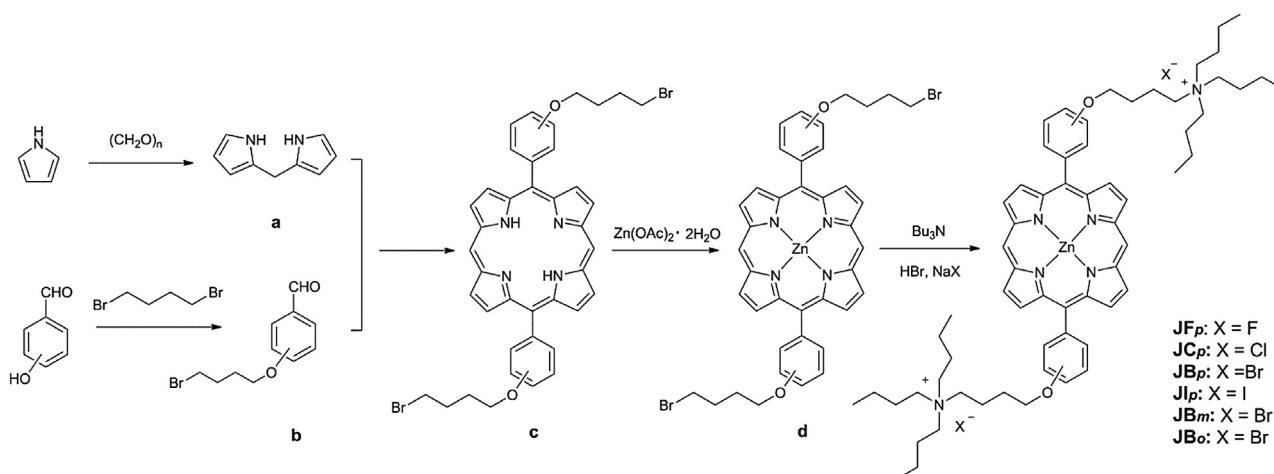
Following the procedure of literature [46].

#### 2.2.3. General procedure for synthesis of free porphyrins (c)

Compound **a** (392 mg, 2.68 mmol) and compound **b** (690 mg, 2.75 mmol) were dissolved in 500 mL of freshly distilled dichloromethane in a dried 1000 mL three-neck round-bottom flask equipped with a magnetic stir bar under dark. After bubbling the solution with Ar for 10 min, TFA (0.12 mL, 1.62 mmol) was introduced into the flask *via* syringe. The clear solution was stirred for 4 h at room temperature. After addition of DDQ (735 mg, 3.24 mmol), it was stirred for an additional hour. Then 4 mL of triethylamine (Et<sub>3</sub>N) was added to neutralize the mixture. When solvent was distilled off, residue was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/1, v/v) as an eluent. The porphyrin **c** was collected as purple crystal after evaporating solvents.

#### 2.2.4. General procedure for synthesis of porphyrin-zinc complexes (d)

To a dried 250 mL round-bottom flask equipped a magnetic stir bar, a solution of free base porphyrin **c** (459 mg, 0.60 mmol) in THF



**Scheme 2.** Synthetic route of catalysts.

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