

## Supporting Information

### Zn-based ionic liquids as highly efficient catalysts for chemical fixation of carbon dioxide to epoxides

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## 1. Synthesis of Zn-based task-specific ionic liquids

**Synthesis of 1-butylimidazole.** The synthesis procedure was carried out according to the literature.<sup>1</sup> NaH (17.6 mmol, 60 wt% in mineral oil) suspended in anhydrous THF (~20 mL) was added to 100 mL round bottom flask. Upon addition of imidazole (16.2 mmol) hydrogen gas was evolved. The reaction mixture was stirred at 40 °C until the gas evolution ceased. Then *n*-butyl bromide (16.2 mmol) was added and the reaction mixture was heated under reflux (70 °C) overnight. After cooling to room temperature, the solid precipitate was filtered off and washed with THF. The filtrate was reduced in volume under reduced pressure. MeOH was added and then washed three times with hexane. Finally the solvent in the MeOH phase was removed via rotary evaporation. The product was dried under vacuum overnight to give yellow-brownish oil. Yield: 89%.

**Synthesis of ionic liquid [(CH<sub>2</sub>CH<sub>2</sub>OH)Bim]Br.** The synthesis procedure was carried out according to the literatures.<sup>2,3</sup> A mixture of 1-butylimidazole (24.2 mmol), 2-bromidethanol (26.6 mmol) and toluene (25 mL) was charged into 100 mL round bottom flask and stirred at 70 °C for 24 h. Then the mixture was cooled down to room temperature, and the solvent toluene was dumped. The resultant crude solid was washed repeatedly with ethyl acetate (3×30 mL) and dried at 60 °C for 12 h under vacuum. Yield: 93%. The synthetic procedures for ionic liquids [(CH<sub>2</sub>CH<sub>2</sub>OH)Mim]Br, [(CH<sub>2</sub>COOH)Mim]Br and [(CH<sub>2</sub>COOH)Bim]Br were similar to that of [(CH<sub>2</sub>CH<sub>2</sub>OH)Bim]Br. The main differences were the corresponding 1-methylimidazole was used to replace 1-butylimidazole, bromoacetic in synthesis of

carboxyl-containing ILs was used to replace 2-bromidethanol which was used for synthesis of hydroxyl-containing ILs.

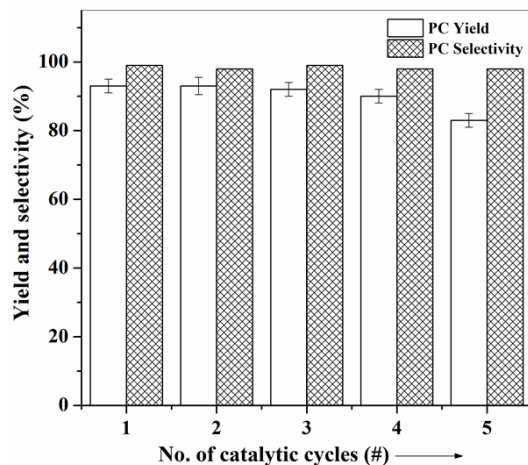
**Synthesis of ionic liquid [(CH<sub>2</sub>CH<sub>2</sub>OH)Bim]ZnBr<sub>3</sub>.** In a typical experiment, ionic liquid [(CH<sub>2</sub>CH<sub>2</sub>OH)Bim]Br (10.1 mmol) was dissolved in 25 mL acetonitrile, anhydrous ZnBr<sub>2</sub> (10.1 mmol) was added in batches and stirred at 70 °C for 4 h. Then the mixture was cooled down to room temperature, and the solvent acetonitrile was removed via rotary evaporation. The product was dried under vacuum overnight to afford a transparent viscous liquid. Yield: 95%.

The synthetic procedures for ionic liquids [(CH<sub>2</sub>CH<sub>2</sub>OH)Mim]ZnBr<sub>3</sub>, [(CH<sub>2</sub>COOH)Mim]ZnBr<sub>3</sub> and [(CH<sub>2</sub>COOH)Bim]ZnBr<sub>3</sub> were similar to that of [(CH<sub>2</sub>CH<sub>2</sub>OH)Bim]ZnBr<sub>3</sub>. The main differences were the corresponding [(CH<sub>2</sub>CH<sub>2</sub>OH)Mim]Br, [(CH<sub>2</sub>COOH)Mim]Br and [(CH<sub>2</sub>COOH)Bim]Br were used to replace [(CH<sub>2</sub>CH<sub>2</sub>OH)Bim]Br, respectively.

## 2. Results and discussion

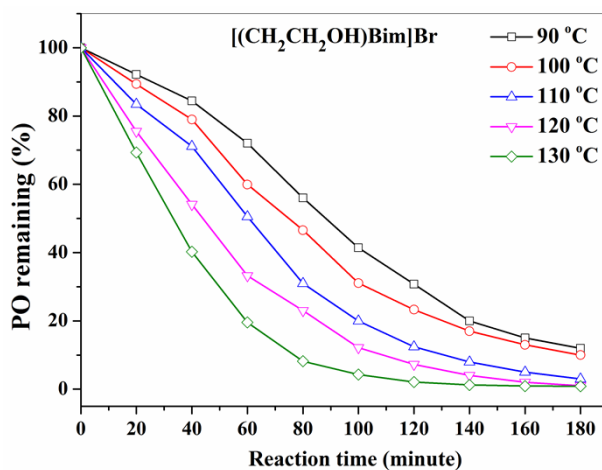
### 2.1. Reusability of [(CH<sub>2</sub>CH<sub>2</sub>OH)Bim]ZnBr<sub>3</sub> catalyst

The recyclability of catalyst plays an important role in practical applications. In order to examine the reusability of [(CH<sub>2</sub>CH<sub>2</sub>OH)Bim]ZnBr<sub>3</sub>, the coupling reaction of CO<sub>2</sub> with propylene oxide was repeated under 120 °C, 2.5 MPa, 1.0 h, as shown in Fig. S1.

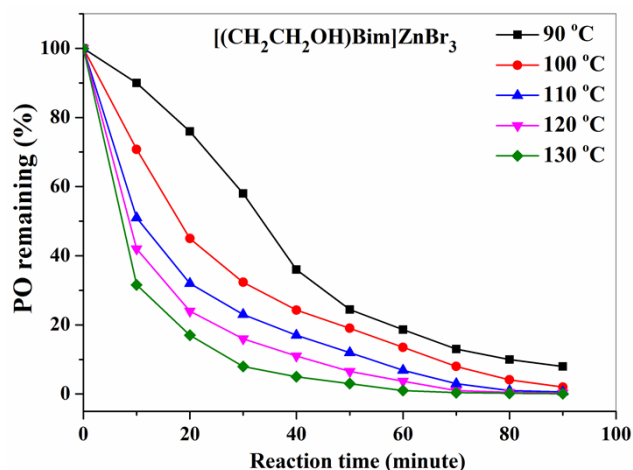


**Fig. S1** Recyclability of the [(CH<sub>2</sub>CH<sub>2</sub>OH)Bim]ZnBr<sub>3</sub> catalyst. Reaction conditions: PO 34.5 mmol, Cat. 0.04 mmol,  $T = 120\text{ }^{\circ}\text{C}$ ,  $P(\text{CO}_2) = 2.5\text{ MPa}$ ,  $t = 1.0\text{ h}$ . In the fifth run,  $t = 1.5\text{ h}$ .

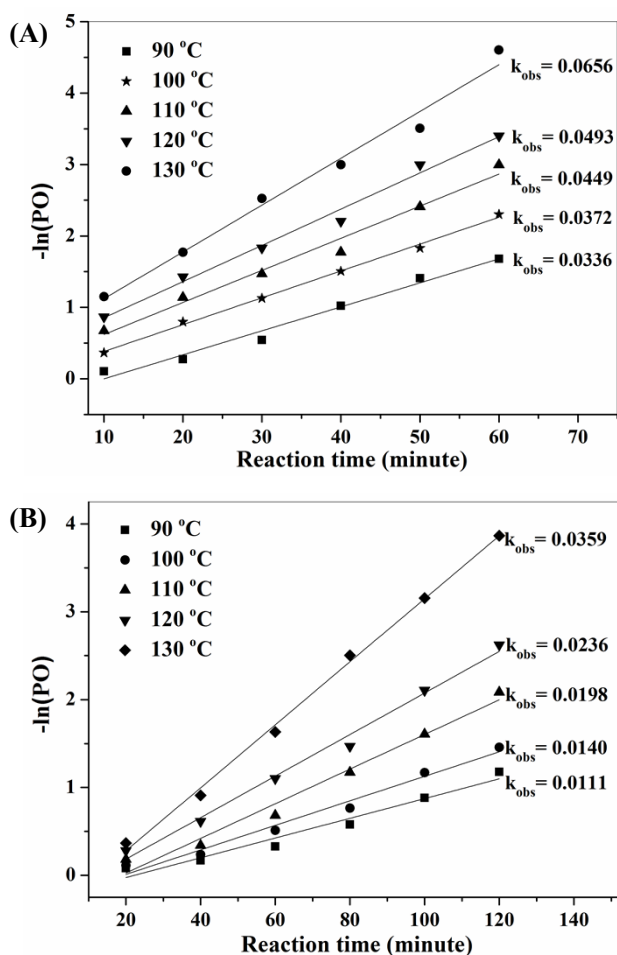
## 2.2. The activation energy and kinetic equation for PC synthesis<sup>4-6</sup>



**Fig. S2** Propylene oxide remaining as a function of reaction time over [(CH<sub>2</sub>CH<sub>2</sub>OH)Bim]Br catalyst. Reaction conditions: PO 34.5 mmol, Cat. 0.25 mol%,  $P(\text{CO}_2) = 2.5\text{ MPa}$ .



**Fig. S3** Propylene oxide remaining as a function of reaction time at different temperature over  $[(\text{CH}_2\text{CH}_2\text{OH})\text{Bim}]\text{ZnBr}_3$  catalyst. Reaction conditions: PO 34.5 mmol, Cat. 0.25 mol%,  $P(\text{CO}_2) = 2.5$  MPa.



**Fig. S4** Relationship of  $-\ln[\text{PO}]$  with reaction time at different temperature over (A)  $[(\text{CH}_2\text{CH}_2\text{OH})\text{Bim}]\text{ZnBr}_3$  and (B)  $[(\text{CH}_2\text{CH}_2\text{OH})\text{Bim}]\text{Br}$  catalysts. Reaction conditions: PO 34.5 mmol, Cat. 0.25 mol%,  $P(\text{CO}_2) = 2.5$  MPa.

As can be seen in Table S1, the fitted values of correlation coefficient R square were all approximately equal to 1, which indicated that the rate constant had a linear relationship with PO concentration and the reaction was first order here.

**Table S1** Kinetic equations and kinetic parameters at different temperature<sup>a</sup>

	T (°C)	Kinetic equation	R <sup>2</sup>	k (min <sup>-1</sup> )	1/T (K <sup>-1</sup> )
[(CH <sub>2</sub> CH <sub>2</sub> OH)Bim]ZnBr <sub>3</sub>	90	$y = 0.0336x - 0.3365$	0.9779	0.0336	0.00276
	100	$y = 0.0372x + 0.0063$	0.9966	0.0372	0.00268
	110	$y = 0.0449x + 0.1710$	0.9773	0.0449	0.00261
	120	$y = 0.0493x + 0.3472$	0.9871	0.0493	0.00255
	130	$y = 0.0656x + 0.4653$	0.9809	0.0656	0.00248
[(CH <sub>2</sub> CH <sub>2</sub> OH)Bim]Br	90	$y = 0.0111x - 0.2508$	0.9554	0.0111	0.00276
	100	$y = 0.0140x - 0.2690$	0.9750	0.0140	0.00268
	110	$y = 0.0198x - 0.3697$	0.9745	0.0198	0.00261
	120	$y = 0.0236x - 0.2892$	0.9886	0.0236	0.00255
	130	$y = 0.0359x - 0.4387$	0.9963	0.0359	0.00248

<sup>a</sup> Reaction conditions: PO 34.5 mmol, Cat. 0.25 mol%,  $P(\text{CO}_2) = 2.5$  MPa.

### 3. References

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