

Supporting Information

for

The role of interactions between cationic backbone and basic anions on green and ultra-selective catalytic synthesis of ethyl methyl carbonate in tunable ionized frameworks

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S1 Supplementary Figure

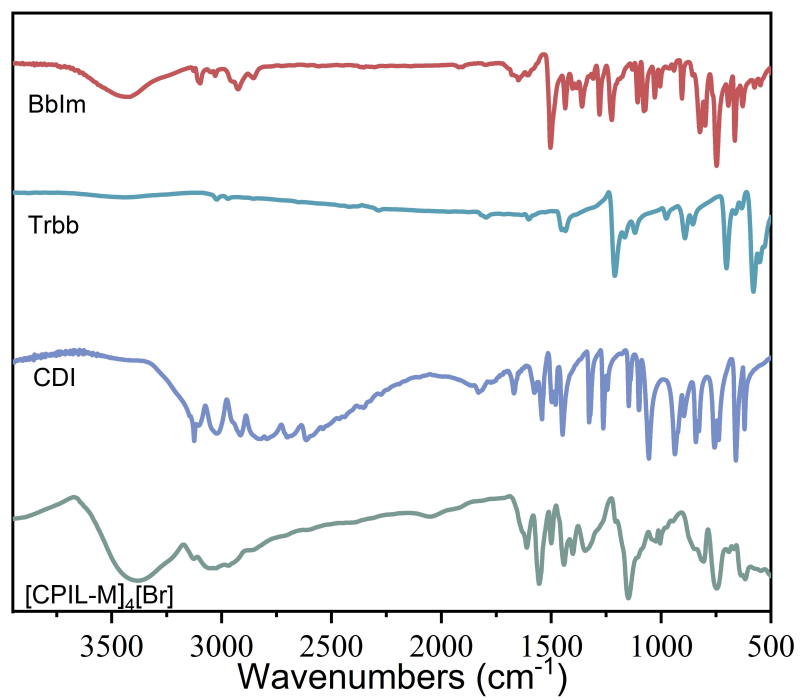


Fig. S1 FTIR spectra of Bblm, Trbb, CDI, and [CPIL-M]₄[Br].

S2 Supplementary Figures

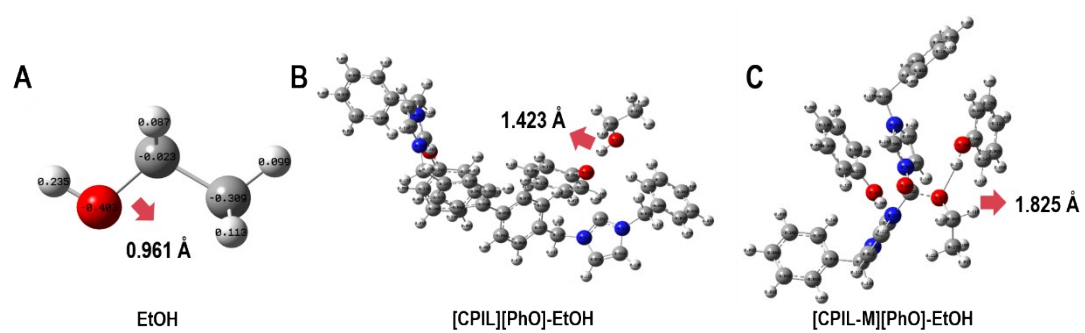


Fig. S2 Bond length of O-H on the hydroxyl of (A) pure ethanol, (B) ethanol interacted with [CPIL][PhO], and (C) ethanol interacted with [CPIL-M][PhO].

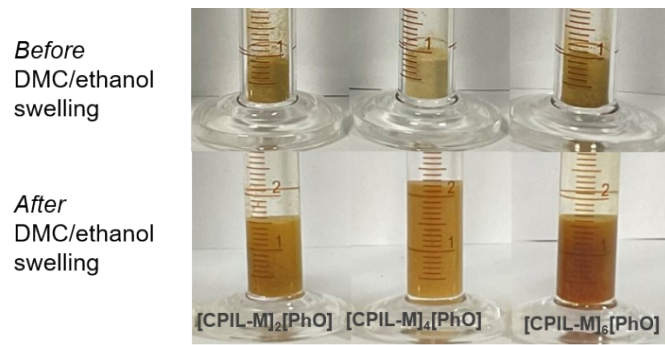


Fig. S3 Swelling properties of [CPIL-M]₂[PhO], [CPIL-M]₄[PhO] and [CPIL-M]₆[PhO] in the DMC/ethanol mixture.

S3 Supplementary Table

Table. S1 The basicity strength of [CPIL-M]₄[Br] and [CPIL-M]_n[PhO].

Catalyst	Basicity strength (mmol g ⁻¹)
[CPIL-M] ₄ [Br]	-1.333 ± 0.428 ^a
[CPIL-M] ₂ [PhO]	1.538 ± 0.064
[CPIL-M] ₃ [PhO]	1.959 ± 0.084
[CPIL-M] ₄ [PhO]	2.591 ± 0.101
[CPIL-M] ₅ [PhO]	1.221 ± 0.047
^a The [CPIL-M] ₄ [Br] could perform an ionic exchange with OH, thus showing an acidic feature with a minus basicity strength.	

The basicity strength of [CPIL-M]₄[Br] and [CPIL-M]₁₋₆[PhO] was assessed through acid-base titration. Specifically, 0.1 g of [CPIL-M]₄[Br] and [CPIL-M]₁₋₆[PhO] were each dissolved in 10 mL of 0.1 mol L⁻¹ HCl and allowed to react fully for 5 hours at 298 K. Subsequently, 3 mL of the supernatant liquid and 3 drops of phenolphthalein indicator were titrated with 0.01 mol L⁻¹ NaOH until the color of the solution turned pink. The basicity strength of these PILs were calculated by the following formula,

$$\text{Basicity strength} = [(10\text{mL}/3\text{mL}) * (3\text{ mL} * 0.1\text{ mol L}^{-1} - V_{\text{NaOH}}\text{ mL} * 0.01\text{ mol L}^{-1})] / 0.1\text{ g}$$

Table. S2 The PMI_{RRC}^1 of [CPIL-M]₁₋₆[PhO] under the reaction condition of reaction temperature of 80 °C, reaction temperature of 6 h, ethanol/DMC molar ratio of 1:1, catalyst dosage of 1.7%.

Catalyst	PMI_{RRC} (g g ⁻¹)
[CPIL-M] ₁ [PhO]	3.825
[CPIL-M] ₂ [PhO]	3.791
[CPIL-M] ₃ [PhO]	3.426
[CPIL-M] ₄ [PhO]	2.768
[CPIL-M] ₅ [PhO]	3.903
[CPIL-M] ₆ [PhO]	3.831

1. PMI_{RRC} : Process mass intensity: reactants, reagents, catalyst.