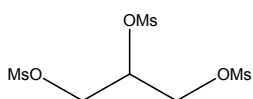


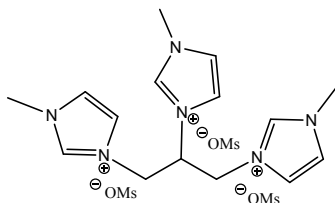
Supplementary information

1. NMR characterization of trimesylate precursors^a



¹H NMR (400 MHz, DMSO-*d*₆): δ 3.25 (s, 9H), 4.45 (d, 4H), 5.15 (m, 1H). FT-IR (500-4000cm⁻¹): 768cm⁻¹ (S-O), 1113, 1380 cm⁻¹ (S=O), 2866, 2985 cm⁻¹ (C-H). ¹³C NMR (125MHz): 14, 15, 45, 53. HR-MS m/z [M-OMs]⁺: 138.19. Calcd (%): C 22.08, H 4.32, O 44.12, S 29.47; Found: C 21.07, H 4.31, O 44.12, S 29.46.

2. NMR characterization of Glycerol-tri (3-methylimidazolium) trimesylate [GLY(mim)₃][OMs]₃



[GLY(mim)₃][OMs]₃, Thick liquid: ¹H NMR (400MHz, DMSO- *d*₆): δ 2.41 (m, 3 x 3H), 3.47 (s, 3 x 3H), 3.66 (m, 5H), 9.24 (s, 3 x 1H), 7.59-7.67 (m, 3 x 2H); FT-IR (500-4000cm⁻¹): 1198, 1210cm⁻¹ (S=O), 1398, 1465cm⁻¹ (C=C), 1623cm⁻¹ (C=N), 3095cm⁻¹ (Ar-H), 2912cm⁻¹, 2870cm⁻¹ (C-H). ¹³C NMR (125MHz): 33.26, 39.4, 45.44, 48.5, 118, 120.34, 125.96, 136.90. HR-MS m/z [M-OMs]⁺: 382.18. Analysis: C₂₁H₄₁N₆O₉S₃, Calcd (%): C 40.83, H 6.69, N 13.60, O 23.31, S 15.56; Found: C 40.80, H 6.66, N 13.61, O 22.98, S 15.6.

3. Synthesis of Glycerol-tri (3-methylimidazolium) bis(trifluoromethanesulfonyl)imide [GLY(mim)₃][NTf₂]₃

In round bottom flask, as aforementioned procedure the prepared glycerol-tri (3-methylimidazolium)trimesylate (0.17 mol) and bis(trifluoromethanesulfonyl)imide lithium salt (0.52 mol) was reacted in acetone at room temperature for 28h. Then, the reaction mixture was filtered and washed three times with acetone for complete removal of salts formed during reaction. The [GLY(mim)₃][NTf₂]₃ was afforded by evaporating the acetone under vacuum. (Yield 91.96%)

[GLY(mim)₃][NTf₂]₃, Thick liquid: ¹H NMR (400 MHz, DMSO- *d*₆): δ 3.65 (s, 3 x 3H), 3.80 (m, 5H), 8.78 (s, 3 x 1H), 7.8 (m, 3 x 2H). FT-IR (500-4000cm⁻¹): 1055cm⁻¹ (C-F), 1198cm⁻¹, 1210cm⁻¹ (S=O), 1346cm⁻¹, 1441cm⁻¹ (C=C), 1623cm⁻¹ (C=N), 3095cm⁻¹ (Ar-H), 2912cm⁻¹, 2870cm⁻¹(C-H). ¹³C NMR (125 MHz): 33.86, 36.18, 46.88, 49.46, 117.92, 121.11 (C-N), 126.15, 137. HR-MS m/z [M-OMs]⁺: 567.11. Analysis: C₂₄H₃₂F₁₈N₉O₁₂S₆, Calcd (%): C 24.58, H 2.75, N 10.76, O 16.37, S 16.40 Found: C 24.50, H 2.78, N 10.76, O 16.30, S 16.38.

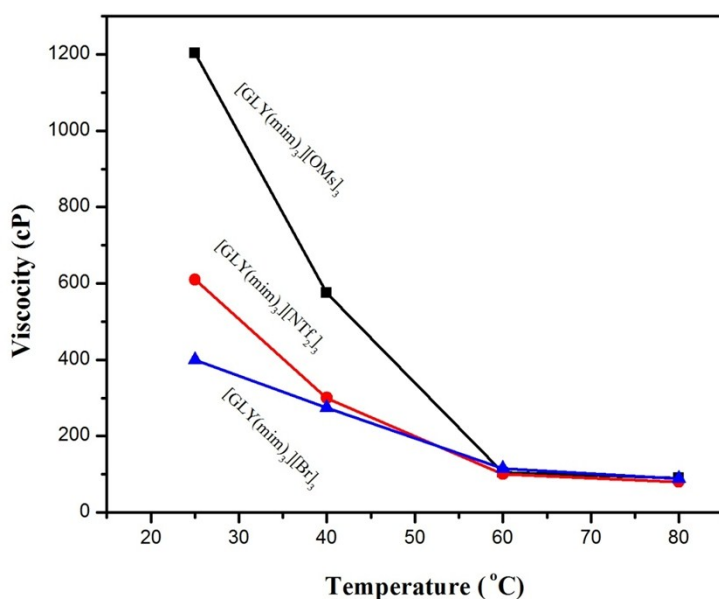
4. Glycerol-tri (3-methylimidazolium) bromide [GLY(mim)₃][Br]₃

Glycerol-tri(3-methylimidazolium) bromide IL was also synthesized by same strategy as was done in case of [GLY(mim)₃][NTf₂]₃ using glycerol-tri(3-methylimidazolium)trimesylate (0.17 mol) and potassium bromide (0.52 mol) to form GLY(mim)₃][Br]₃. The crude salts in reaction mixture were removed by filtration and [GLY(mim)₃][Br]₃ IL was obtained by evaporating acetone under reduced pressure. (Yield 92.50%)

[GLY (mim)₃][Br]₃, Thick liquid: ¹H NMR (400MHz, DMSO- *d*₆): δ 3.51 (s, 3 x 3H), 3.83 (m, 5H), 8.80 (s, 3 x 1H), 7.71-7.80 (m, 3 x 2H). FT-IR (500-4000cm⁻¹): 1198cm⁻¹, 1210cm⁻¹ (S=O),

1364 cm^{-1} , 1441 cm^{-1} (C=C), 1623 cm^{-1} (C=N), 3095 cm^{-1} (Ar-H), 2912 cm^{-1} , 2870 cm^{-1} (C-H). ^{13}C NMR (125 MHz): 33.96, 39.58, 46.12, 50.25, 120.79, 128.55, 137.16. HR-MS m/z [M-OMs] $^+$: 367.25. Analysis: $\text{C}_{18}\text{H}_{32}\text{Br}_3\text{N}_6$. Calcd (%): C 37.73, H 5.64, Br 41.89, N 14.69; Found: C37.70, H 5.61, Br 41.91, N14.65.

5. Viscosity determination of Tricationic RTIL



The viscosity of the ILs is of enormous importance for CO_2 adsorption, its use as a solvent and catalyst in chemical reactions. Viscosity of all tri-cationic ILs was observed in range of 400cP to 1207cP at ambient temperature. However, the viscosity obtained for $[\text{GLY}(\text{mim})_3][\text{NTf}_2]_3$ and $[\text{GLY}(\text{mim})_3][\text{Br}]_3$ IL were considerably lower than $[\text{GLY}(\text{mim})_3][\text{OMs}]_3$ IL that may attribute to hydrogen bonding interaction between cation and [OMs] anion. Further, we studied viscosity at 40, 60 and 80°C, predominantly decrease in viscosity was found in range 600-230cP, 70-150cP and 60-110cP respectively. Hence, viscosities decreased in the order; $[\text{OMs}] > [\text{NTf}_2] > [\text{Br}]$ was evident in the structural effect of the anion, where the viscosity lowest for large anion

[NTf₂] and higher to [OMs] containing planer symmetric anion. Therefore, the presence of symmetric tri-cationic and anion moieties mainly responsible for hydrogen bonding and van der Waal interaction, which produce positive effect on viscosity tri-cationic RTIL.

Kinetics

Table S1. Kinetic parameters at different temperature

T°C	Kinetic equation	R	K	1/T	lnk
110	$y = 0.424x - 2.635$	0.994	0.4248	0.00261	-0.86
120	$y = 0.609x - 2.635$	0.992	0.6094	0.00254	-0.49
130	$y = 0.800x - 2.635$	0.986	0.8000	0.00248	-0.22

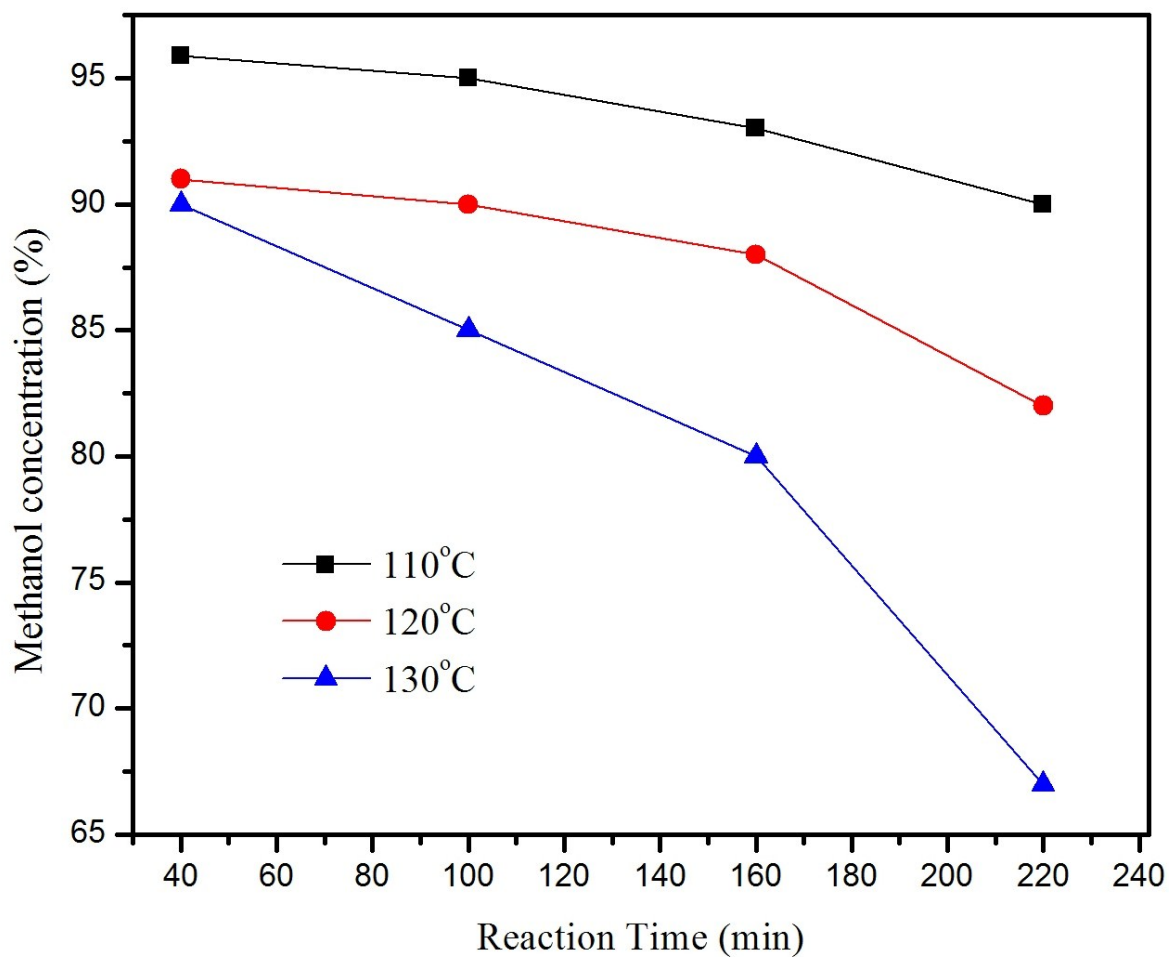


Figure S1. The remaining methanol concentration vs time profile at different temperature over $[\text{GLY}(\text{mim})_3][\text{NTF}_2]_3/\text{DBU}$ catalyst system. Reaction condition; MeOH 616mmol, IL/DBU ratio 1:3, $P(\text{CO}_2) = 7.5\text{MPa}$.