Surporting information

Paradigm for efficient synthesis of bio-based polycarbonate with deep eutectic solvents as catalysts by inhibiting the degradation of molecular chains

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Characterization of DESs

[EminOH]Cl

^{1}H NMR (600 MHz, DMSO) δ 9.29 (s, 1H), 7.79 (d, *J* = 1.7 Hz, 1H), 7.75 (d, *J* = 1.7 Hz, 1H), 5.49 (s, 1H), 4.26 – 4.22 (m, 2H), 3.87 (s, 3H), 3.70 (d, *J* = 5.0 Hz, 2H). FT-IR (KBr) ν:3439, 3145, 3057, 2955, 2871, 1649, 1568, 1444, 1347, 1169, 1067, 937, 1067, 862, 787, 746, 613 cm^{-1}.

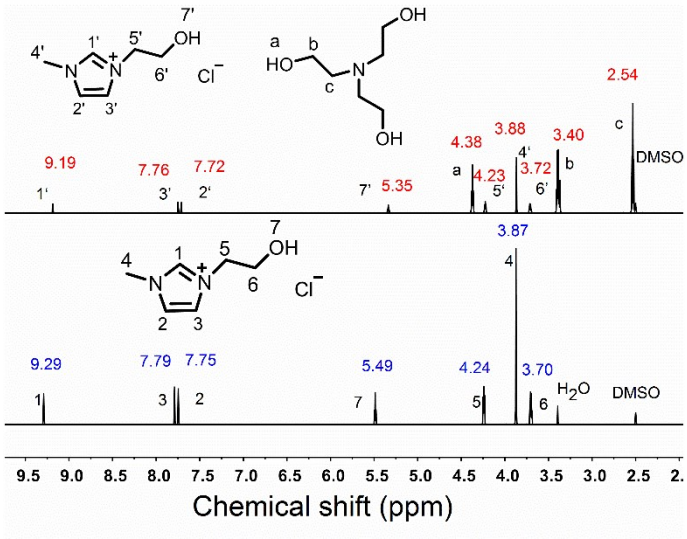

Figure S1. ^{1}H NMR spectra of [EminOH]Cl-2TEOA and [EminOH]Cl.

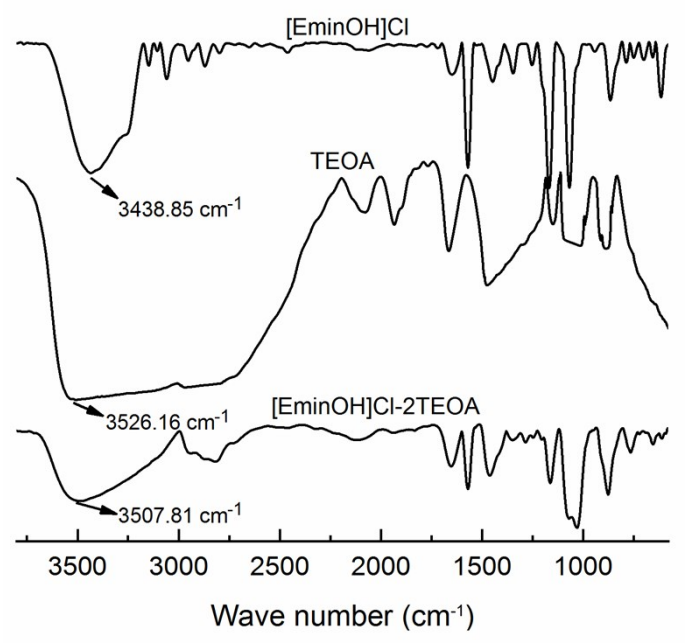

Figure S2. FT-IR spectra of [EminOH]Cl, TEOA and [EminOH]Cl-2TEOA.

[EminOH]Cl-2TEOA

^{1}H NMR (600 MHz, DMSO) δ 9.19 (s, 1H), 7.76 (t, *J* = 1.7 Hz, 1H), 7.72 (t, *J* = 1.7 Hz, 1H), 5.35 (s, 1H), 4.38 (t, *J* = 5.6 Hz, 6H), 4.25 – 4.21 (m, 2H), 3.88 (s, 3H), 3.72 (d, *J* = 5.0 Hz, 2H), 3.40 (q, *J* = 6.0 Hz, 12H), 2.54 (t, *J* = 6.2 Hz, 12H). FT-IR

(KBr) ν:3508, 2949, 3057, 2817, 2114, 1655, 1573, 1459, 1354, 1287, 1164, 1031, 870, 770, 650 cm^{-1}.

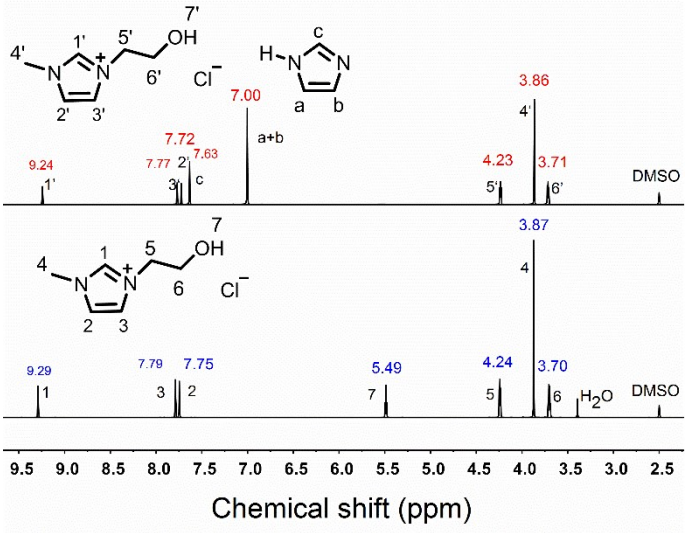

Figure S3. ^{1}H NMR spectra of [EminOH]Cl-2IM and [EminOH]Cl.

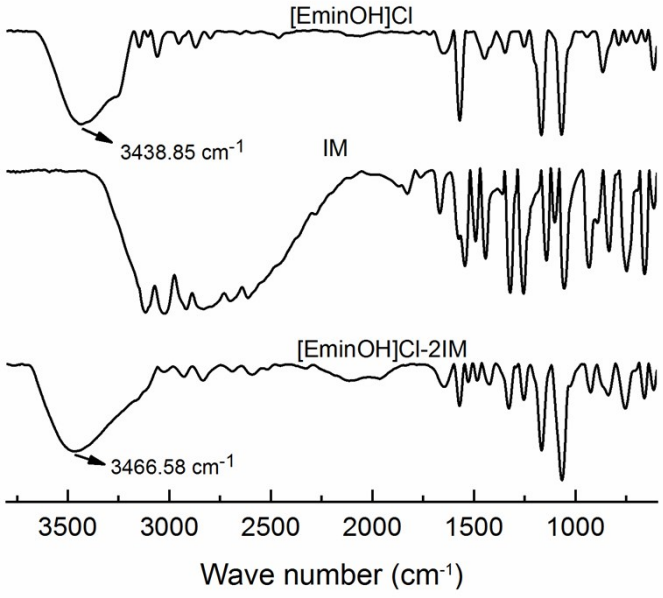

Figure S4. FT-IR spectra of [EminOH]Cl, IM and [EminOH]Cl-2IM.

[EminOH]Cl-2IM

^{1}H NMR (600 MHz, DMSO) δ 9.24 (s, 1H), 7.77 (t, *J* = 1.7 Hz, 1H), 7.72 (t, *J* = 1.7 Hz, 1H), 7.63 (s, 2H), 7.00 (d, *J* = 0.8 Hz, 4H), 4.23 (dd, *J* = 6.6, 3.5 Hz, 2H), 3.86 (s, 3H), 3.75 – 3.67 (m, 2H). FT-IR (KBr) ν:3467, 3021, 2932, 2833, 1647, 1572, 1522, 1481, 1429, 1325, 1254, 1164, 1062, 927, 846, 757, 663, 613 cm^{-1}.

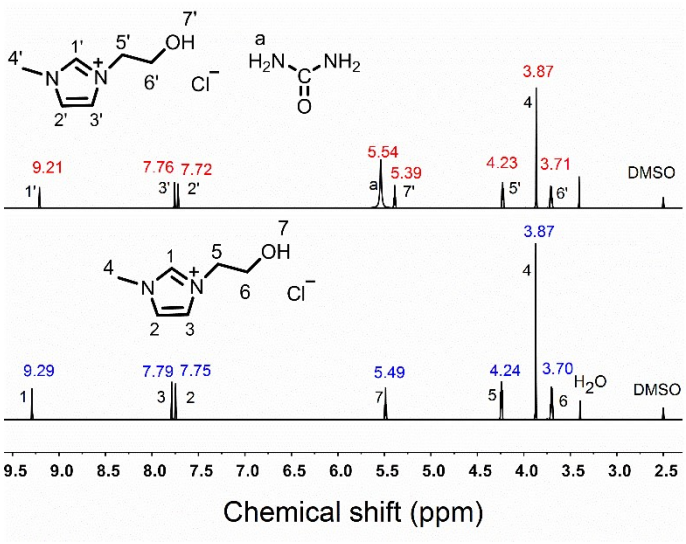

Figure S5. [1]H NMR spectra of [EminOH]Cl-2UREA and [EminOH]Cl.

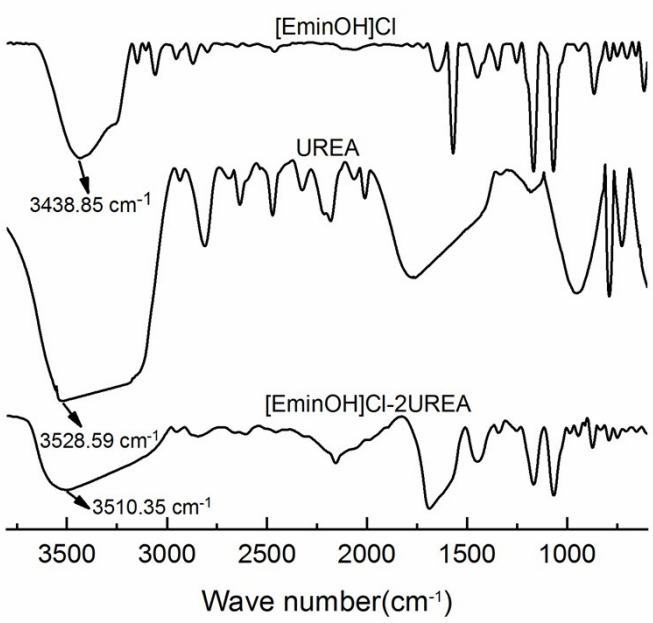

Figure S6. FT-IR spectra of [EminOH]Cl, UREA and [EminOH]Cl-2UREA.

[EminOH]Cl-2UREA

[1]H NMR (600 MHz, DMSO) δ 9.21 (s, 1H), 7.76 (t, *J* = 1.7 Hz, 1H), 7.72 (t, *J* = 1.7 Hz, 1H), 5.54 (s, 8H), 5.39 (t, *J* = 5.3 Hz, 1H), 4.25 – 4.18 (m, 2H), 3.87 (s, 3H), 3.71 (dd, *J* = 10.2, 5.2 Hz, 2H). FT-IR (KBr) ν:3510, 2957, 2849, 2154, 1686, 1449, 1339,1250, 1163, 1070, 871, 786, 745 cm^{-1}.

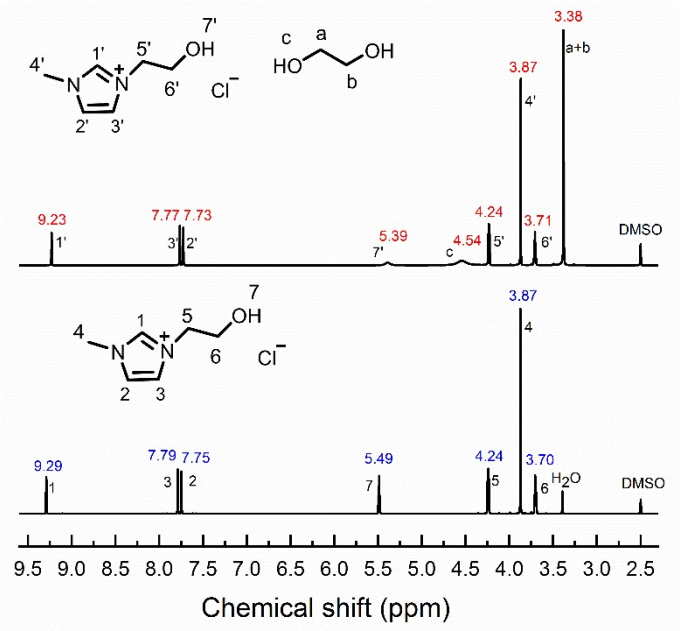

Figure S7. [1]H NMR spectra of [EminOH]Cl-2EG and [EminOH]Cl.

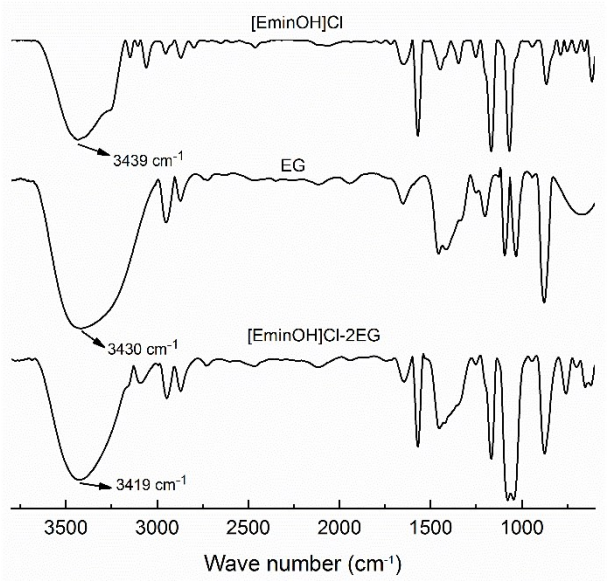

Figure S8. FT-IR spectra of [EminOH]Cl, EG and [EminOH]Cl-2EG.

[EminOH]Cl-2EG

[1]H NMR (600 MHz, DMSO) δ 9.23 (s, 1H), 7.77 (t, *J* = 1.7 Hz, 1H), 7.73 (t, *J* = 1.7 Hz, 1H), 5.39 (s, 1H), 4.54 (s, 4H), 4.23 (dd, *J* = 6.6, 3.5 Hz, 2H), 3.87 (s, 3H), 3.74 – 3.68 (m, 2H), 3.38 (s, 8H). FT-IR (KBr) ν: 3419, 3093, 2941, 2876, 1645, 1574, 1449, 1165, 1063, 871, 756, 653 cm^{-1}.

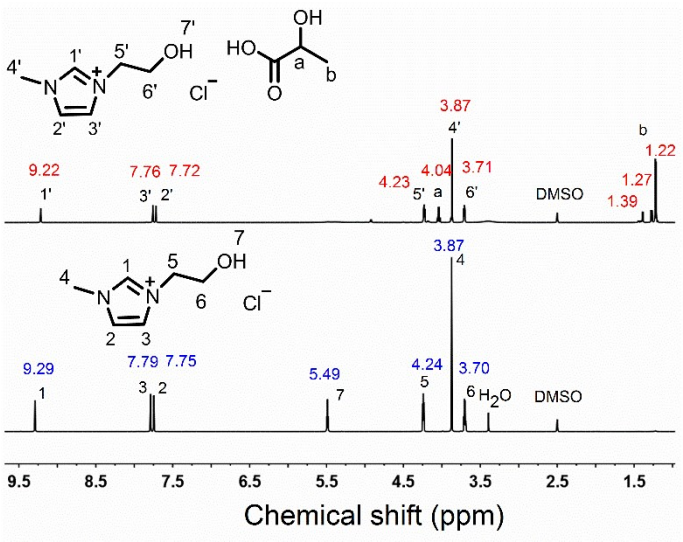

Figure S9. [1]H NMR spectra of [EminOH]Cl-2LA and [EminOH]Cl.

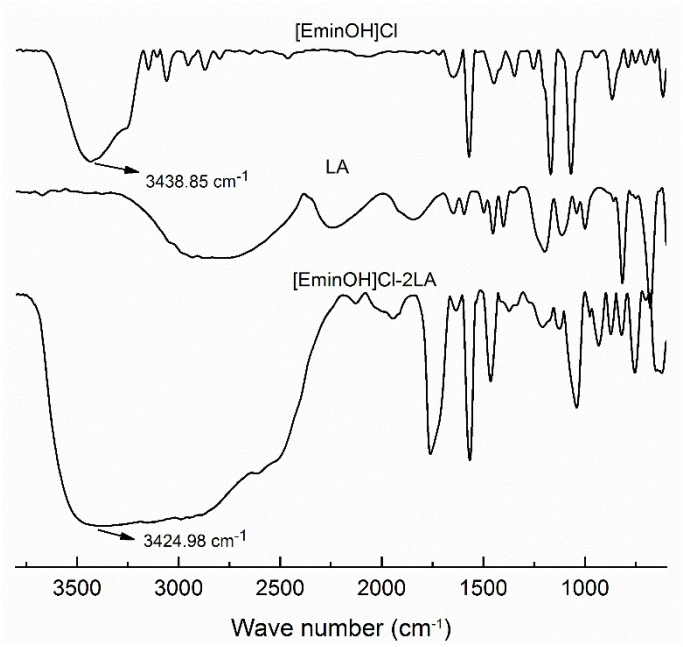

Figure S10. FT-IR spectra of [EminOH]Cl, LA and [EminOH]Cl-2LA.

[EminOH]Cl-2LA

[1]H NMR (600 MHz, DMSO) δ 9.22 (s, 1H), 7.76 (t, *J* = 1.7 Hz, 1H), 7.72 (t, *J* = 1.7 Hz, 1H), 4.23 (dd, *J* = 6.6, 3.5 Hz, 2H), 4.04 (q, *J* = 6.9 Hz, 2H), 3.87 (d, *J* = 8.3 Hz, 3H), 3.72 – 3.69 (m, 2H), 1.39 (d, *J* = 7.1 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 1H), 1.22 (d, *J* = 6.9 Hz, 4H). FT-IR (KBr) ν: 3425 2134 1946 1759 1566 1462 1373 1204 1129 1045 932 871 815 754 631 cm^{-1}.

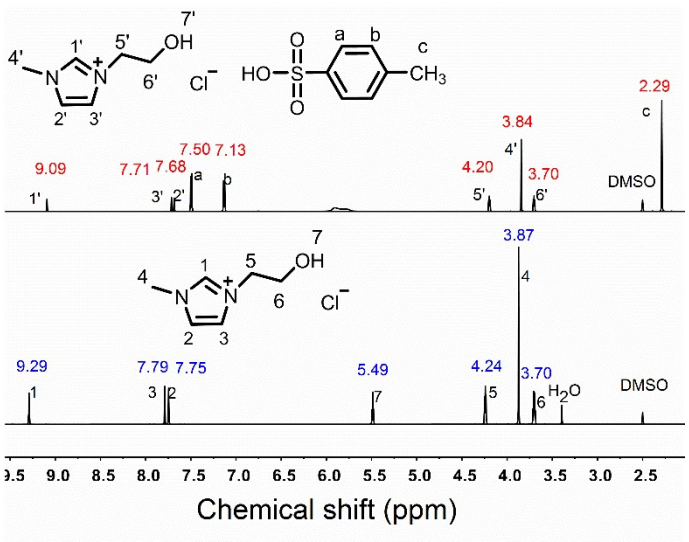

Figure S11. [1]H NMR spectra of [EminOH]Cl-2PTSA and [EminOH]Cl.

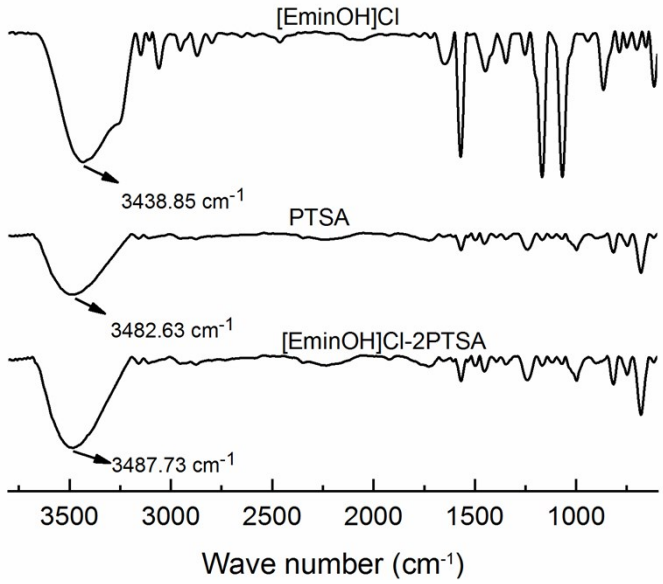

Figure S12. FT-IR spectra of [EminOH]Cl, PTSA and [EminOH]Cl-2PTSA.

[EminOH]Cl-2PTSA

[1]H NMR (600 MHz, DMSO) δ 9.09 (s, 1H), 7.71 (t, *J* = 1.6 Hz, 1H), 7.68 (t, *J* = 1.5 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 4H), 7.13 (d, *J* = 7.9 Hz, 4H), 4.22 – 4.18 (m, 2H), 3.84 (s, 3H), 3.71 – 3.69 (m, 2H), 2.29 (s, 6H). FT-IR (KBr) ν: 3419 3093 2941 2876 1645 1574 1449 1165 1063 871 756 653 cm^{-1}.

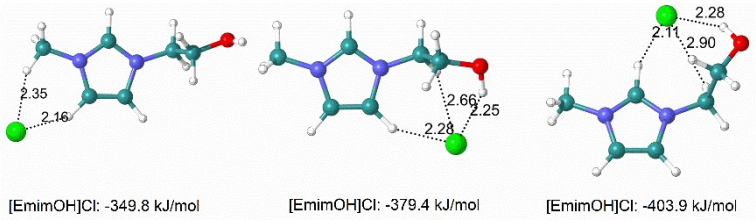

Figure S13. Possible hydrogen bonding network structure between the anion and the cation of [EminOH]Cl.

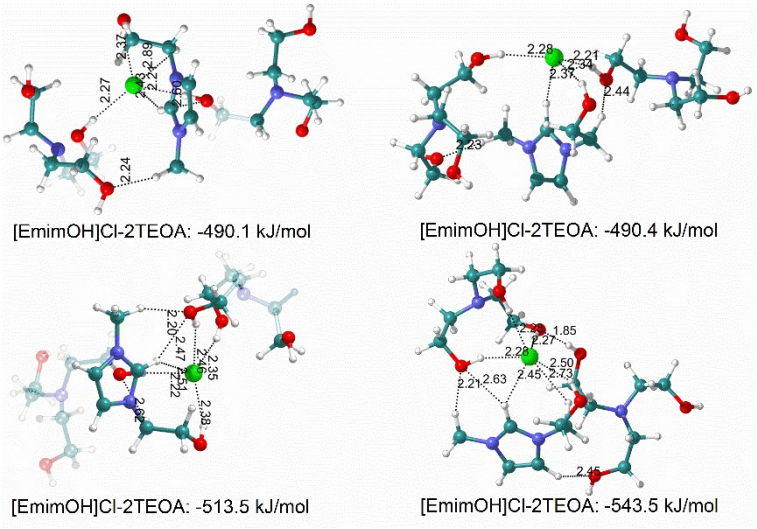

Figure S14. Possible hydrogen bonding network structure between [EminOH]Cl and TEOA.

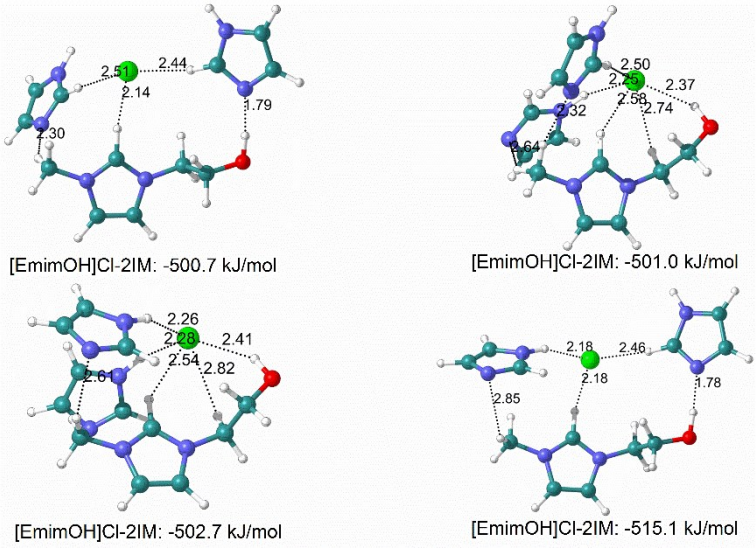

Figure S15. Possible hydrogen bonding network structure between [EminOH]Cl and IM.

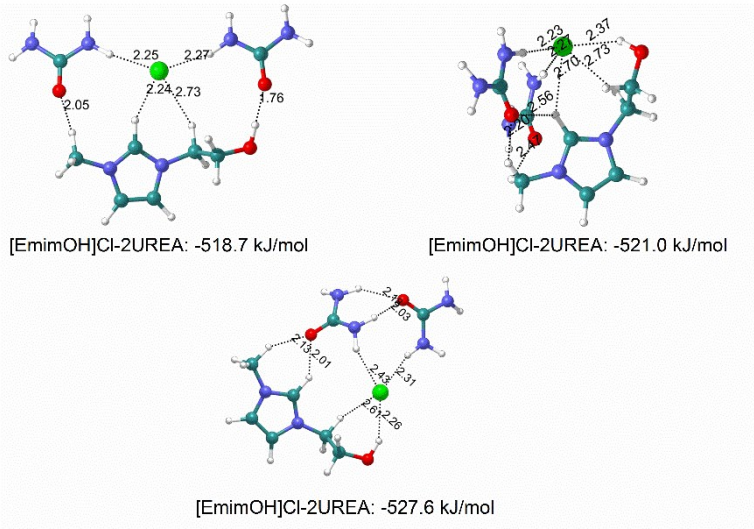

Figure S16. Possible hydrogen bonding network structure between [EminOH]Cl and UREA.

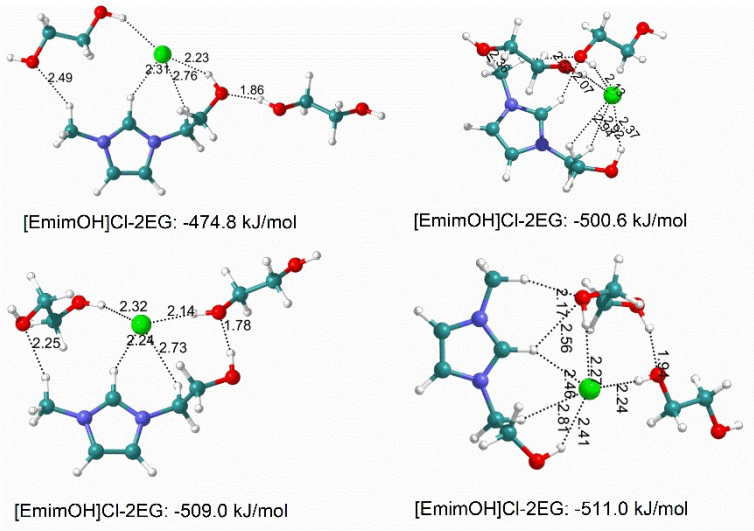

Figure S17. Possible hydrogen bonding network structure between [EminOH]Cl and EG.

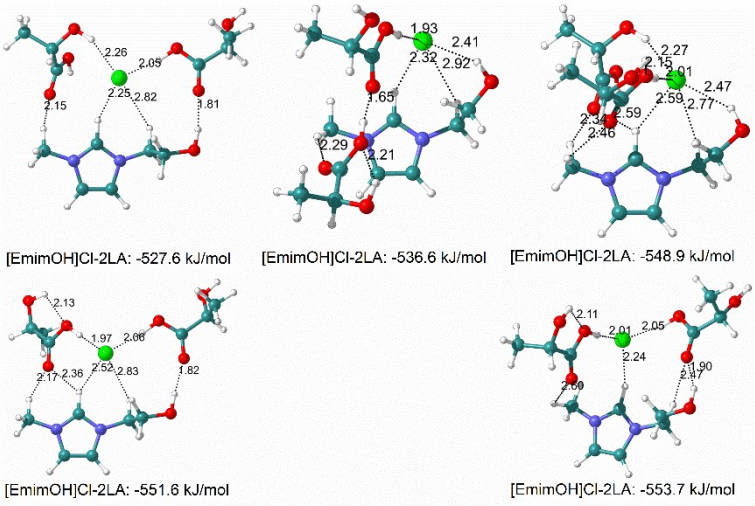

Figure S18. Possible hydrogen bonding network structure between [EminOH]Cl and LA.

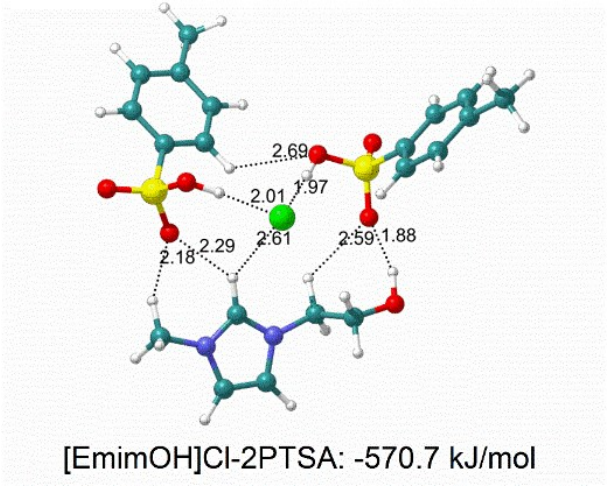

Figure S19. Possible hydrogen bonding network structure between [EminOH]Cl and PTSA.

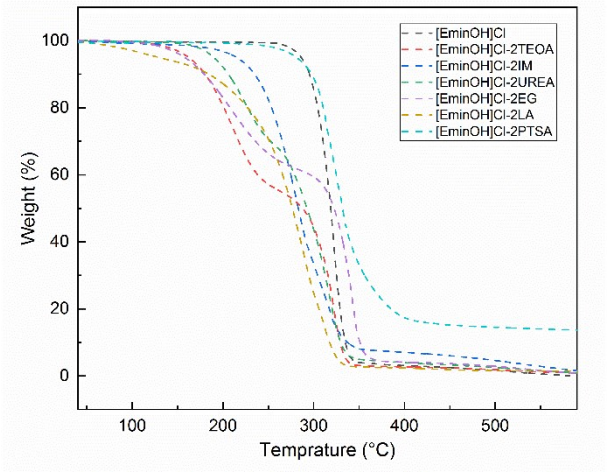

Figure S20. TGA curve of the catalysts.

Table S1 Thermal decomposition temperature of the catalysts

Entry	Catalyst	$T_{50\%}$ [a] (°C)
1	[EminOH]Cl	319
2	[EminOH]Cl-2TEOA	323
3	[EminOH]Cl-2IM	292
4	[EminOH]Cl-2UREA	283
5	[EminOH]Cl-2EG	288
6	[EminOH]Cl-2LA	282
7	[EminOH]Cl-2PTSA	332

[a] The temperature when the weight loss reached 50%.

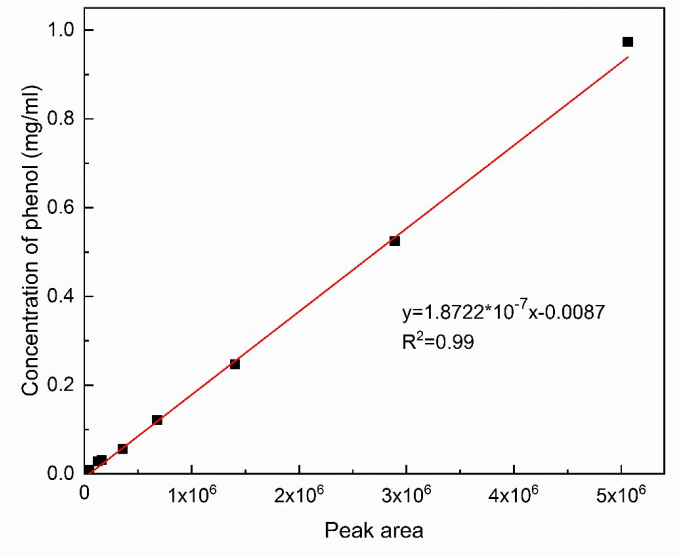

Figure S21. Standard curve equation between peak area and phenol concentration.

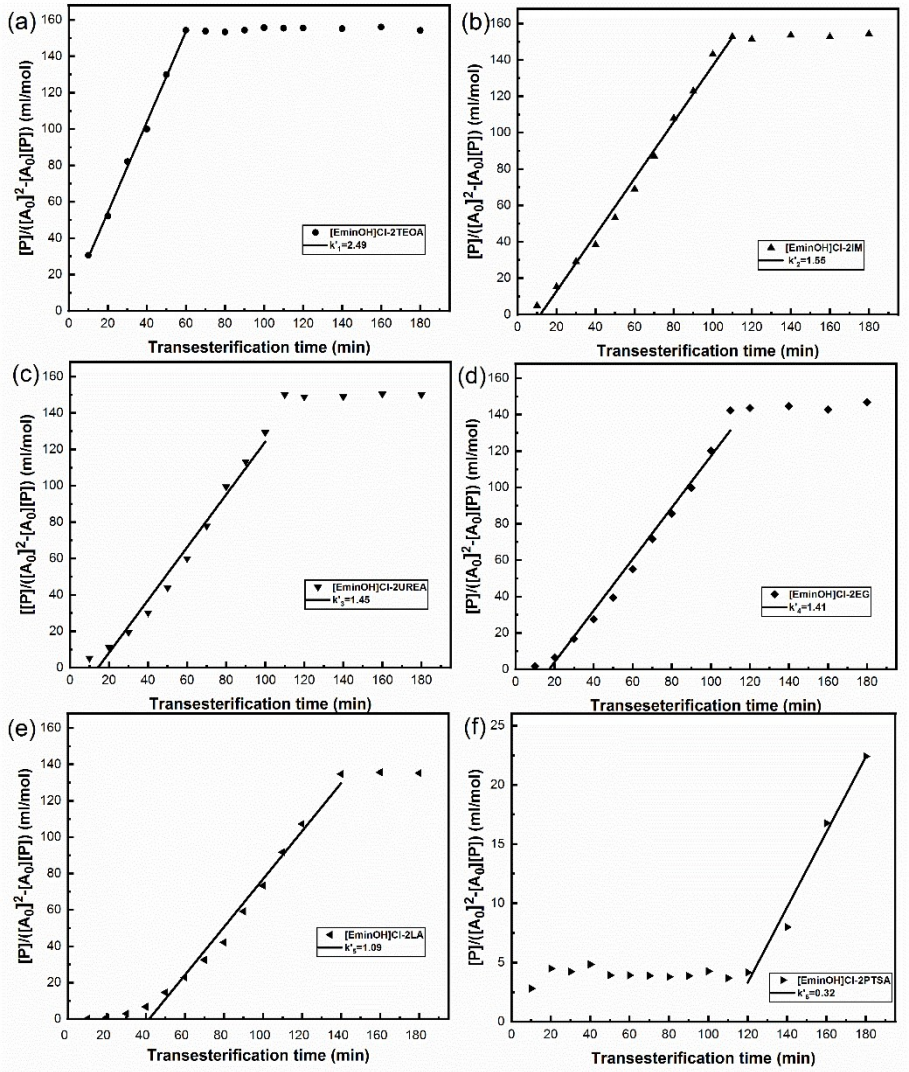

Figure S22. k' (slope) catalyzed by different DESs at 140 °C.

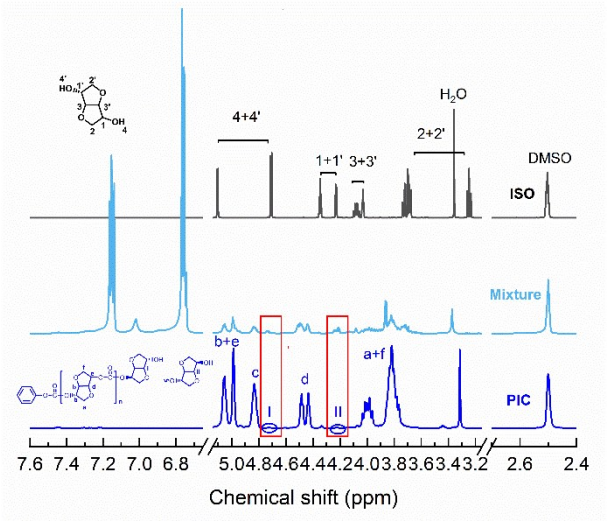

Figure S23. ^{1}H NMR spectra of ISO, pure PIC and degradation mixture with [EminOH]Cl-2IM.

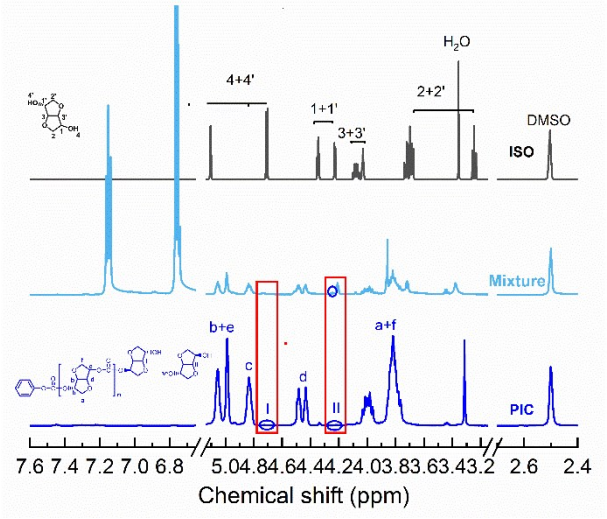

Figure S24. ^{1}H NMR spectra of ISO, pure PIC and degradation mixture with [EminOH]Cl-2UREA.

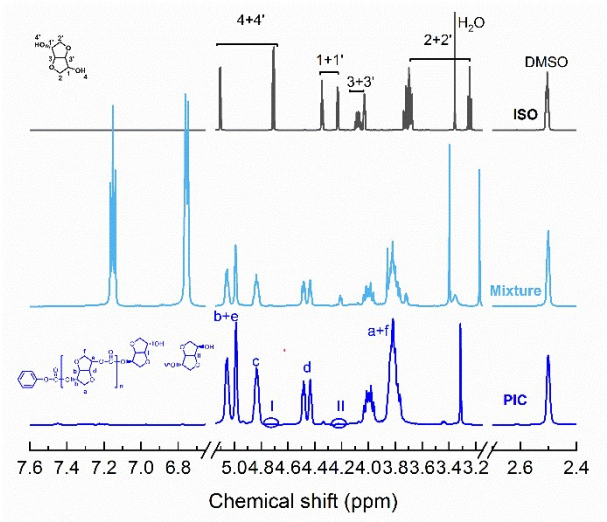

Figure S25. ^{1}H NMR spectra of ISO, pure PIC and degradation mixture with [EminOH]Cl-2EG.

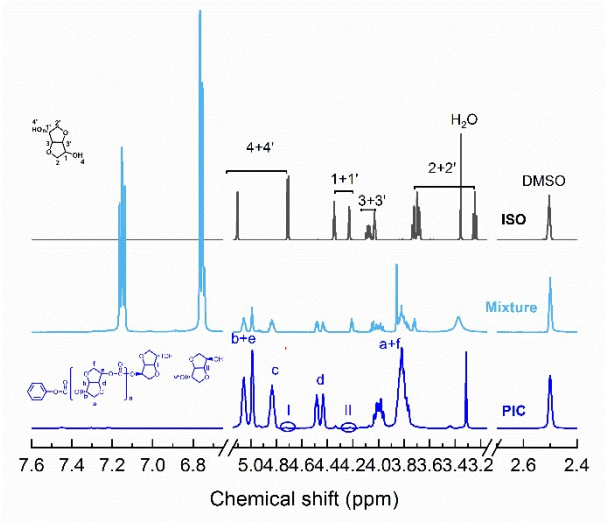

Figure S26. ^{1}H NMR spectra of ISO, pure PIC and degradation mixture with [EminOH]Cl-2LA.

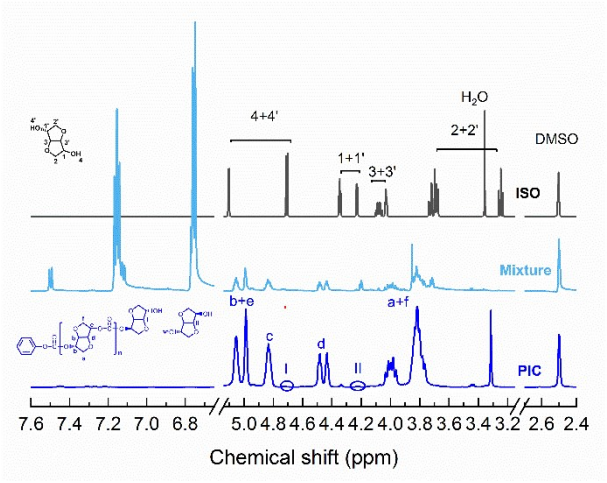

Figure S27. ^{1}H NMR spectra of ISO, pure PIC and degradation mixture with [EminOH]Cl-2PTSA.

Structural characterization of PIC

The detailed structure of the PIC prepared by [EminOH]Cl-2EG was determined by ^{1}H NMR and ^{13}C NMR using $CDCl_3$ as the deuterated reagent. As was shown in Figure S30 (a), the chemical shifts of the hydrogen atoms labeled 3 and 4 in the repeating unit were 4.98 and 4.54 ppm, respectively. The characteristic peaks appearing at 5.06-5.16 represented the hydrogen atoms at 2 and 5. The peaks of 4 hydrogen atoms appearing at 3.91-4.07 ppm belonged to the chemical shifts of 1 and 6. The characteristic peak appearing at 2.55 ppm belonged to the derivatives of 1,4-sorbitan, a major substance that caused yellowing of PIC.[1,2] Due to the existence of endo-hydroxyl groups and exo-hydroxyl groups in ISO, the carbon atoms on the carbonyl group of PIC had three shift peaks (Figure S18 (b)).[3-5] The peaks at 154, 153.5 and 153 ppm were

derived from the carbon atoms of a_1, a_2 and a_3, respectively. Other characteristic peaks were respectively assigned to the carbon atoms on ISO in the repeating unit.

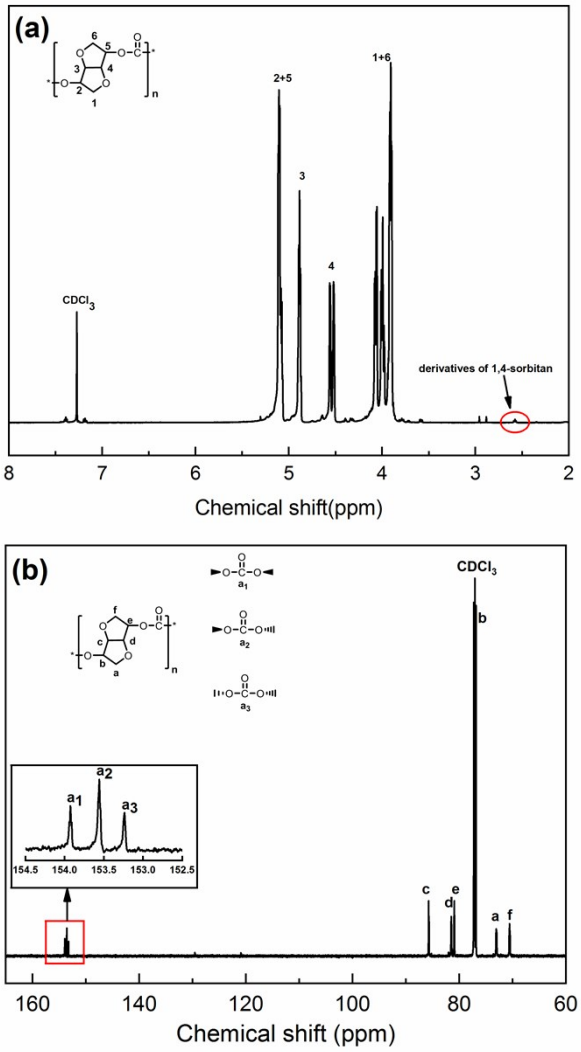

Figure S28. (a)[1]H NMR spectrum and (b) [13]C NMR spectrum of PIC.

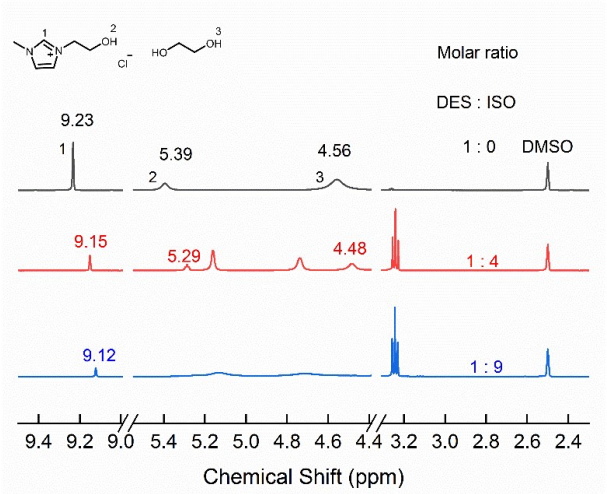

Figure S29. [1]H NMR spectra of ISO and [EminOH]Cl-2EG mixed in different molar ratios.

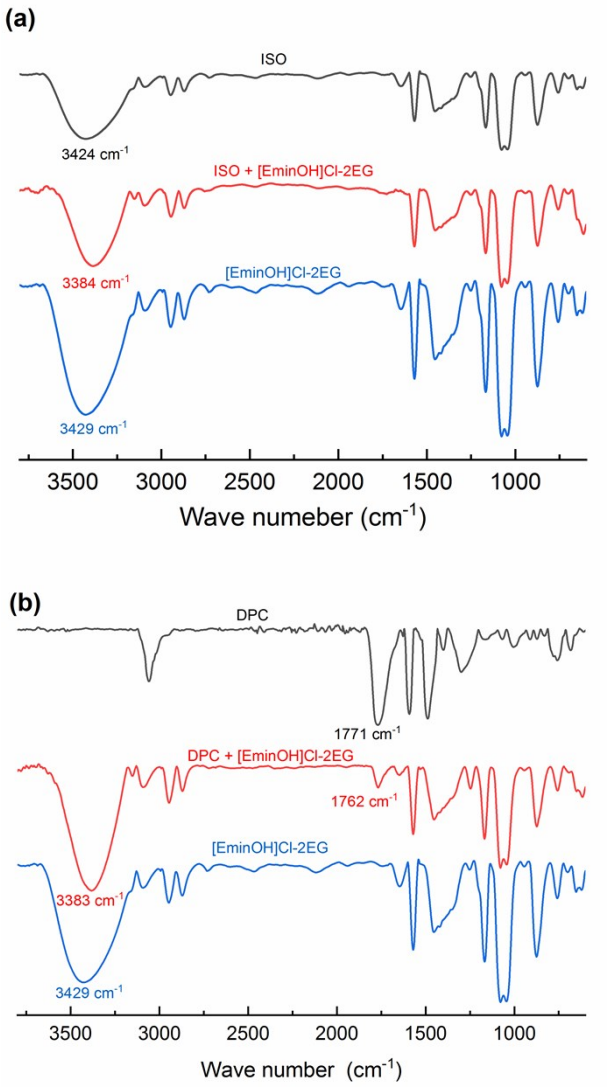

Figure S30. FT-IR spectra of (a) ISO with [EminOH]Cl-2EG and (b) DPC with [EminOH]Cl-2EG.

GPC data

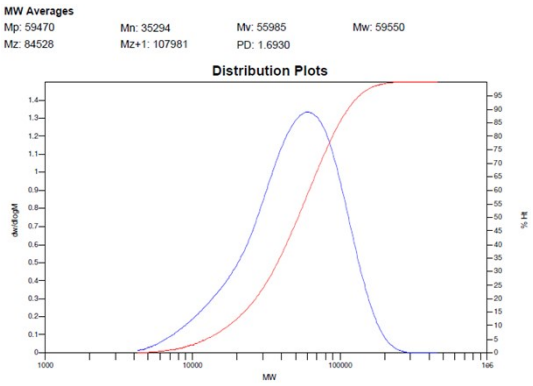

Figure S31. PIC synthesized by [EminOH]Cl.

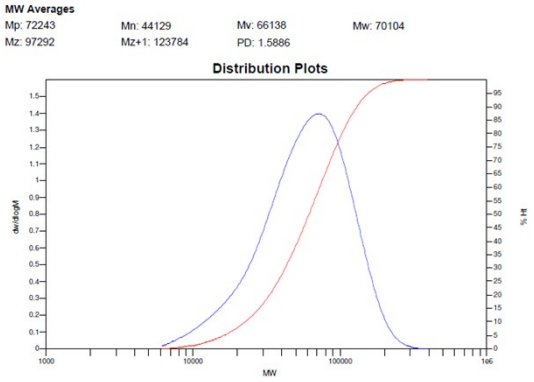

Figure S32. PIC synthesized by [EminOH]Cl-2TEOA.

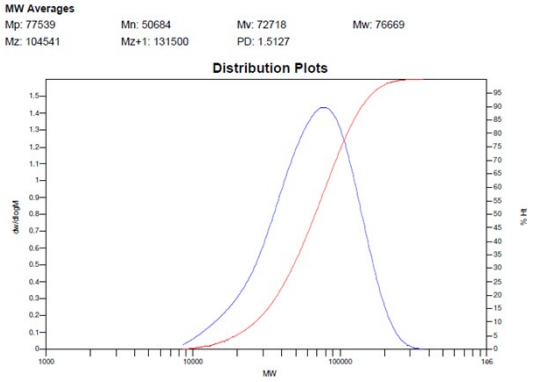

Figure S33. PIC synthesized by [EminOH]Cl-2IM.

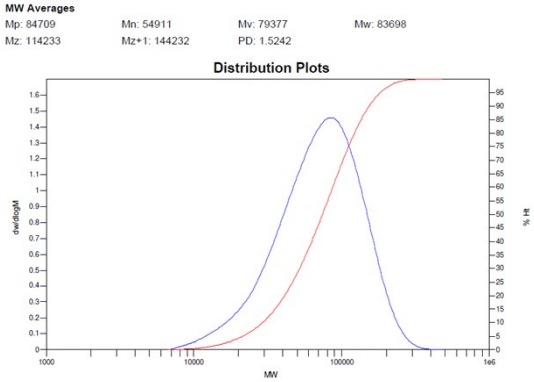

Figure S34. PIC synthesized by [EminOH]Cl-2UREA.

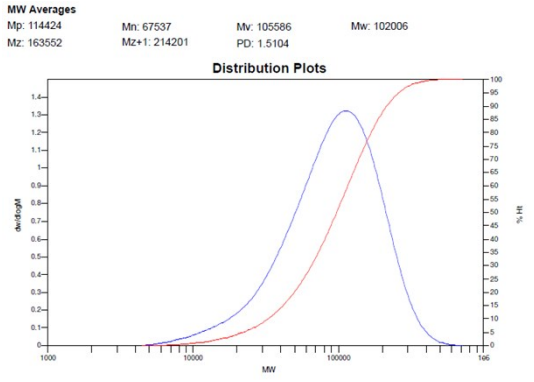

Figure S35. PIC synthesized by [EminOH]Cl-2EG.

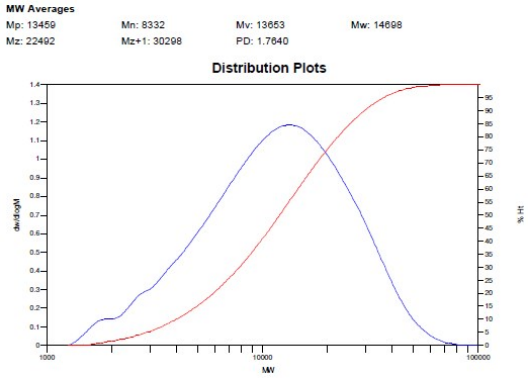

Figure S36. PIC synthesized by [EminOH]Cl-2LA.

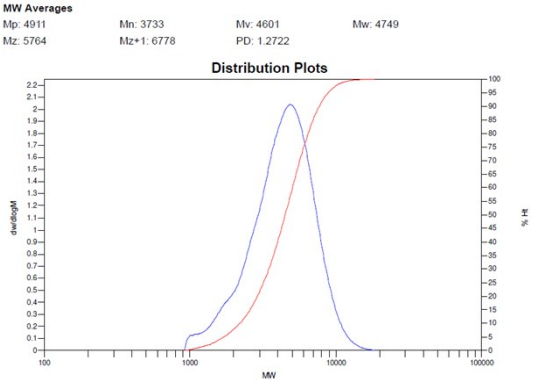

Figure S37. PIC synthesized by [EminOH]Cl-2PTSA.

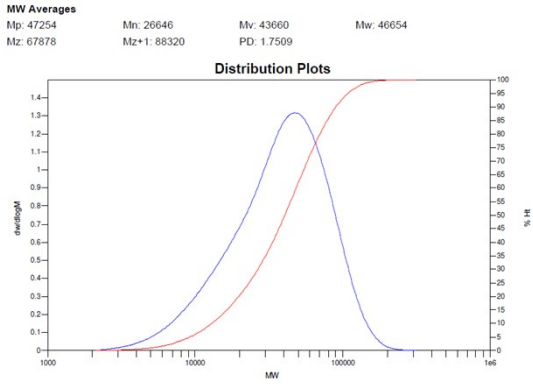

Figure S38. PIC synthesized by TEOA.

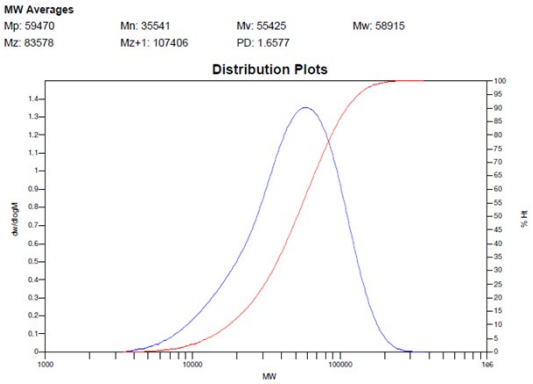

Figure S39. PIC synthesized by IM.

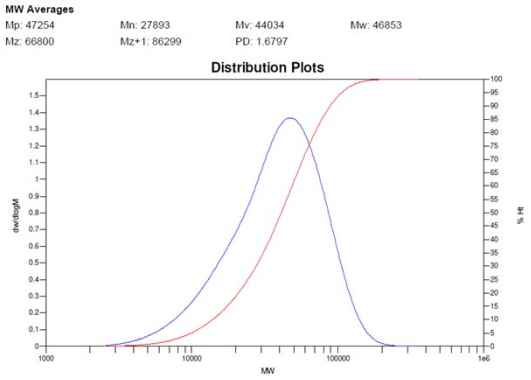

Figure S40. PIC synthesized by UREA.

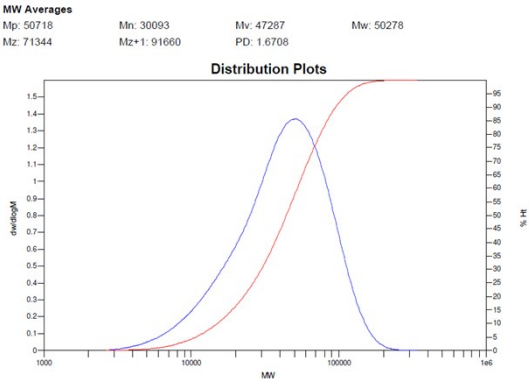

Figure S41. PIC synthesized by EG.

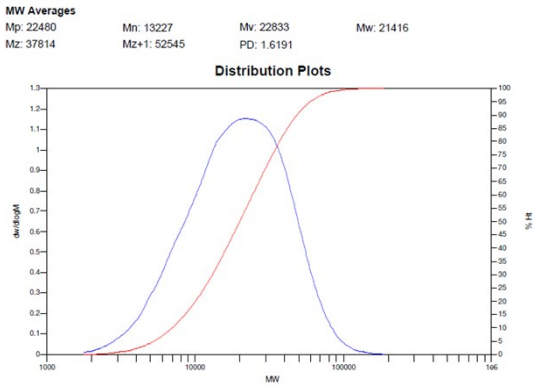

Figure S42. PIC synthesized by LA.

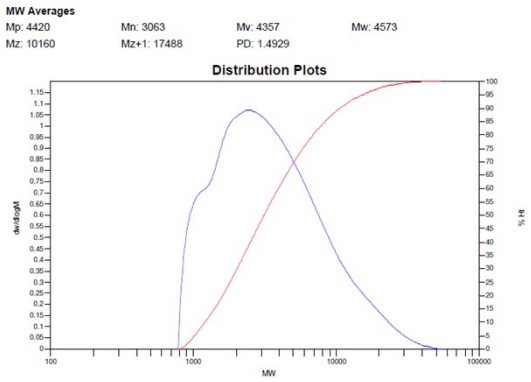

Figure S42. PIC synthesized by PTSA.

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