Supporting information

Synthesis of novel sustainable optical poly(isosorbide thioethers) with high refractive index and good biocompatibility by functional ionic liquid catalysts

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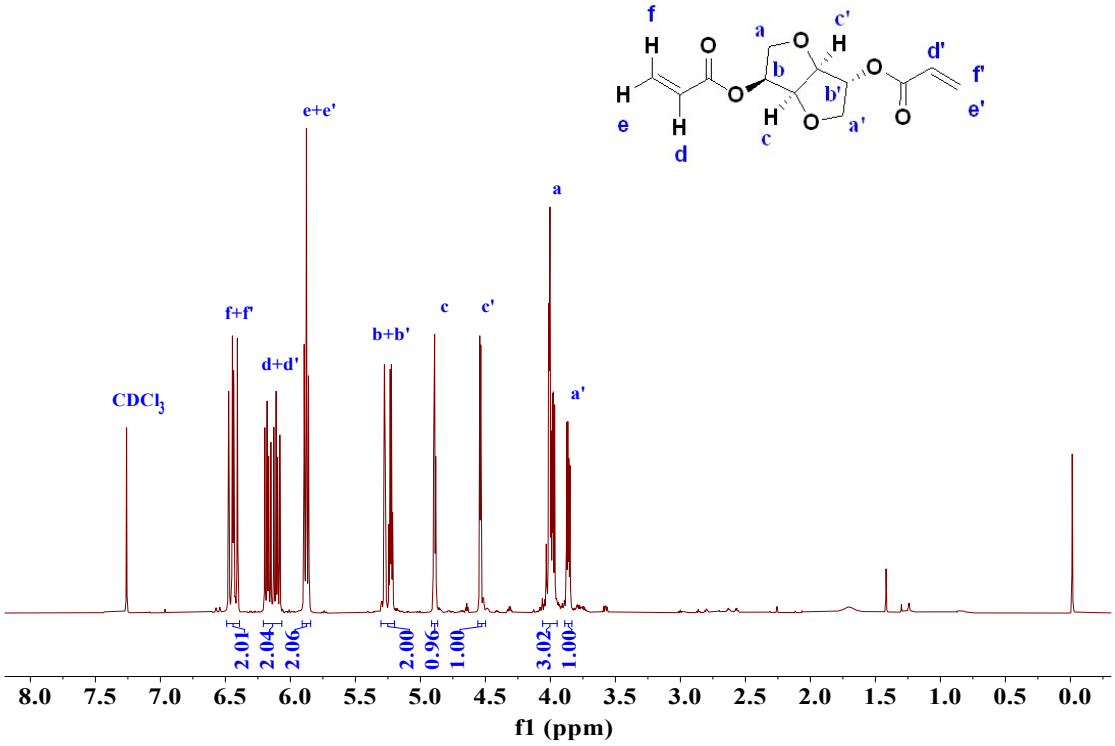

Figure S1. ^{1}H NMR spectrum of ISDA ($CDCl_3$, 600 MHz).

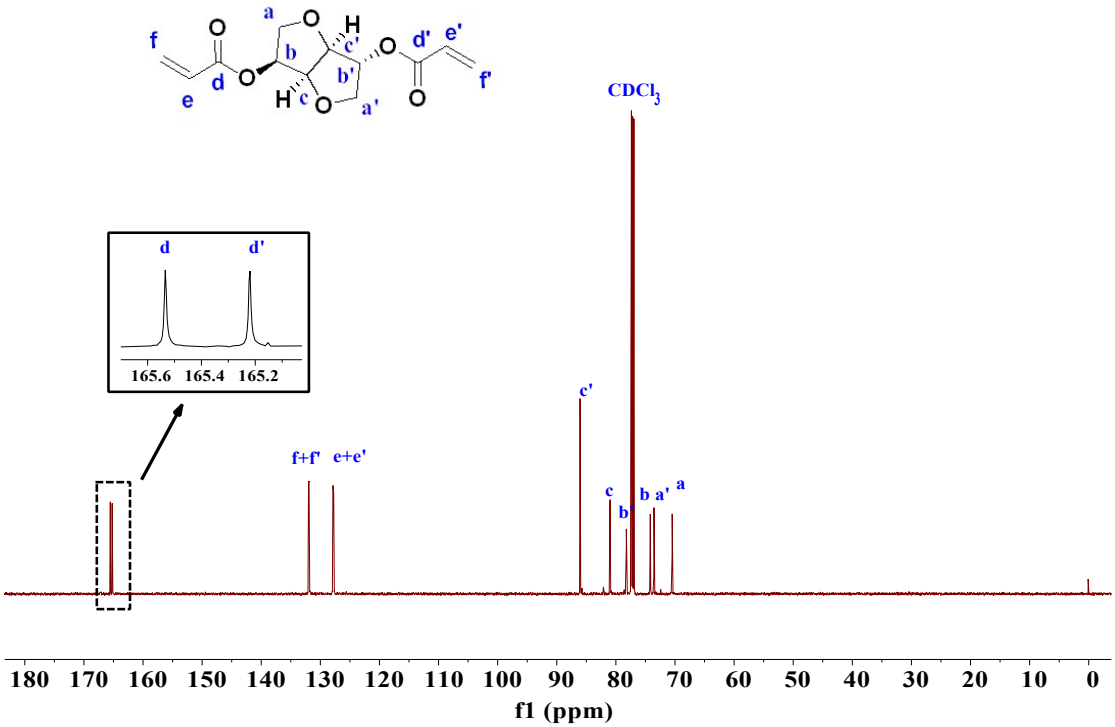

Figure S2. ^{13}C NMR spectrum of ISDA ($CDCl_3$, 150 MHz).

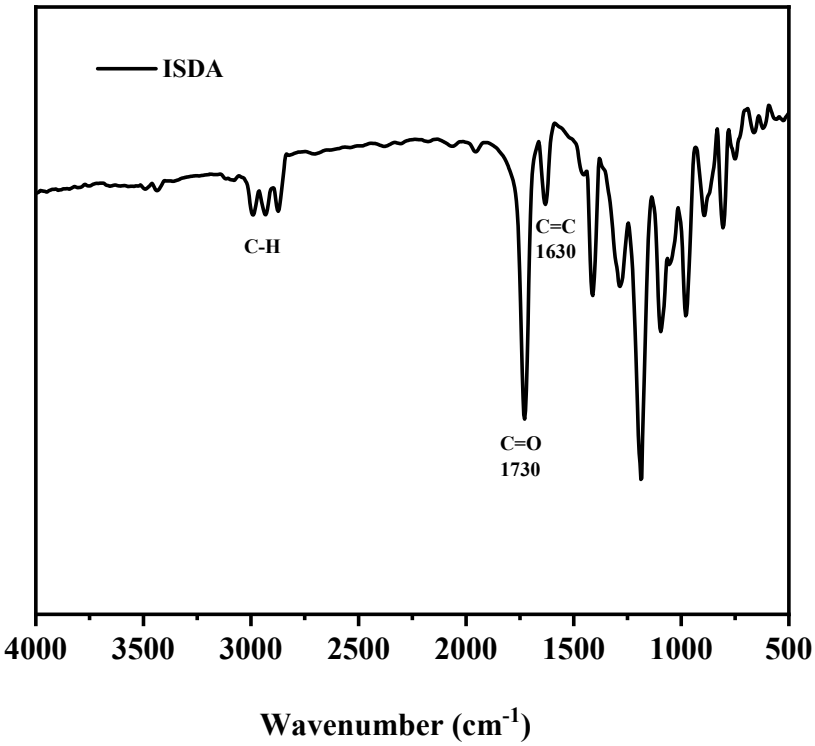

Figure S3. FT-IR spectrum of ISDA (KBr).

ISDA: ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 6.44 (d, 2H), 6.14 (d, 2H), 5.88 (d, 2H), 5.24 (m, 2H), 4.89 (t, 1H), 4.54 (d, 1H), 4.00 (m, 3H), 3.86 (d, 1H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 165.53, 132.00, 127.75, 86.06, 80.98, 78.23, 74.18, 73.58, 70.50. FT-IR (KBr, cm^{-1}): 2993, 2935, 2873, 1730, 1630, 1415, 1292, 1184, 1095, 976, 890, 806, 748.

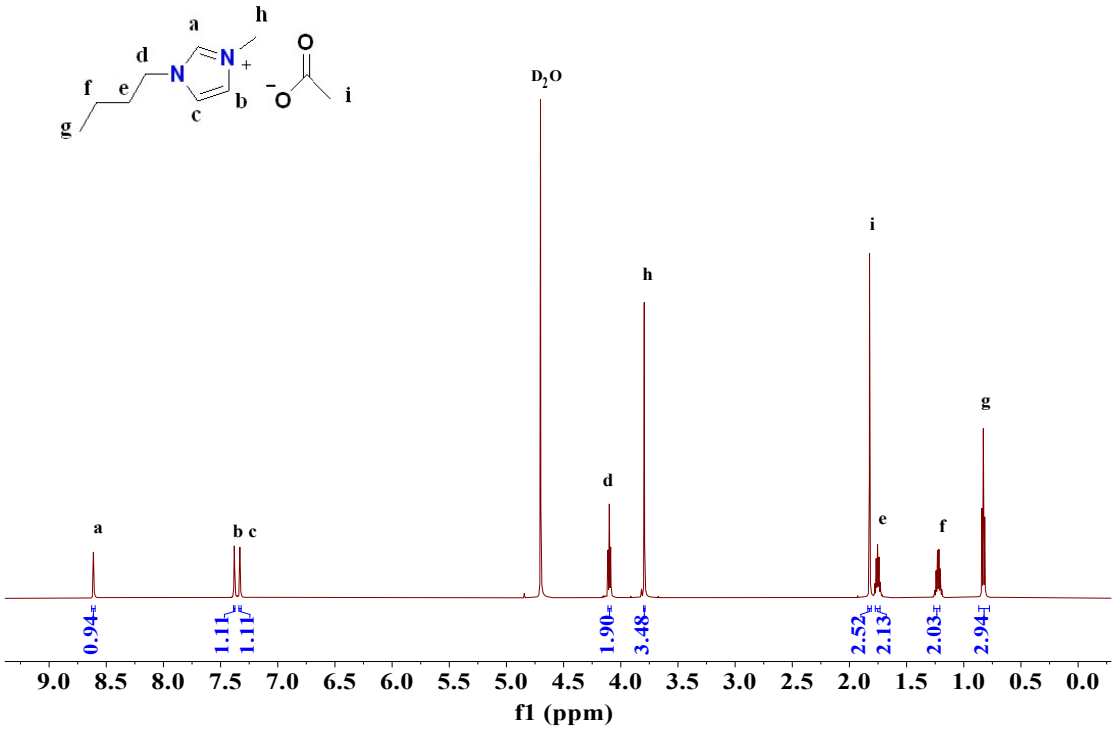

Figure S4. ^{1}H NMR spectrum of [Bmim][Ac] (D_2O, 600 MHz).

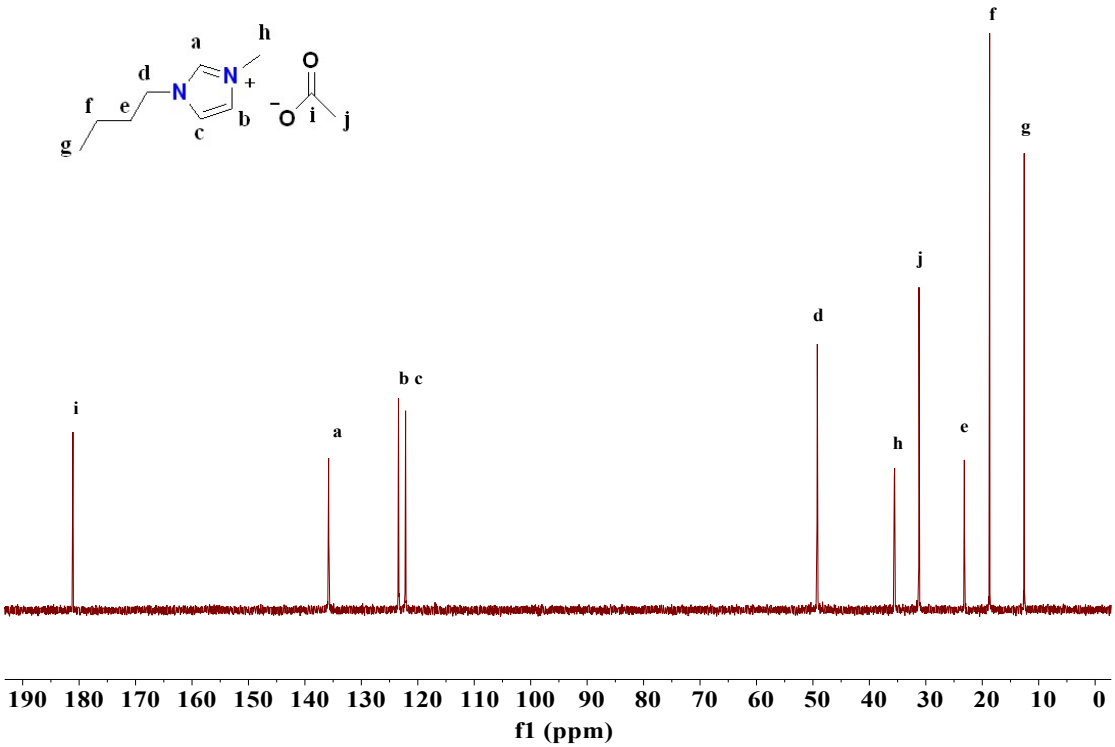

Figure S5. ^{13}C NMR spectrum of [Bmim][Ac] (D_2O, 150 MHz).

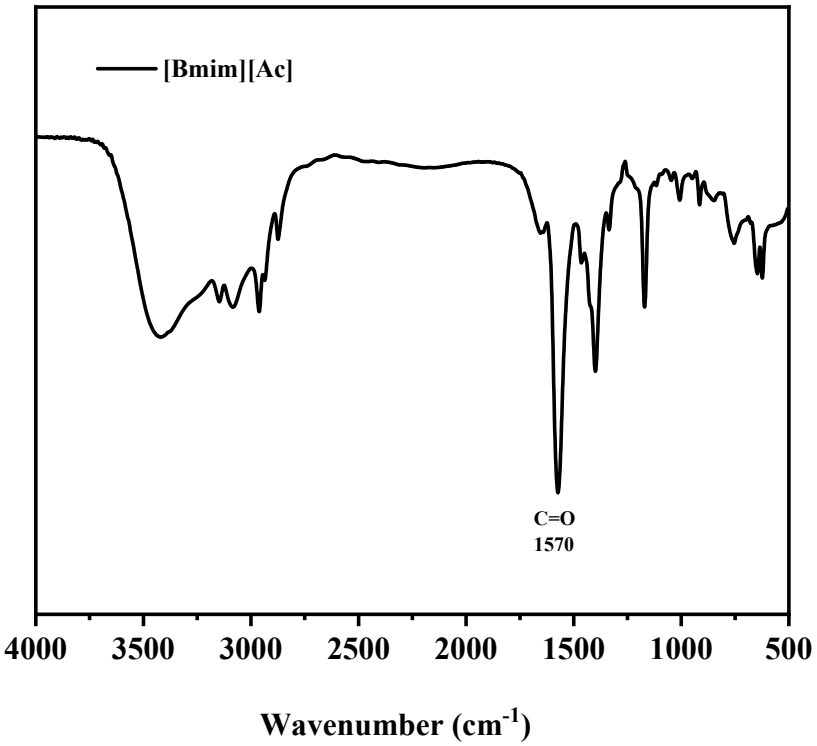

Figure S6. FT-IR spectrum of [Bmim][Ac] (KBr).

[Bmim][Ac]: ^{1}H NMR (600 MHz, D_2O, ppm) δ 8.61 (s, 1H), 7.38 (d, 1H), 7.33 (d, 1H), 4.09 (d, 2H), 3.79 (s, 3H), 1.82 (s, 3H), 1.75 (m, 2H), 1.24 (d, 2H), 0.83 (t, 3H). ^{13}C NMR (150 MHz, D_2O, ppm) δ 181.09, 135.80, 123.43, 122.16, 49.19, 35.55, 31.21, 23.16, 18.69, 12.57. FT-IR (KBr, cm^{-1}): 3428, 3150, 3095, 2964, 2870, 1570, 1395, 1170, 1010, 917, 754, 644, 622.

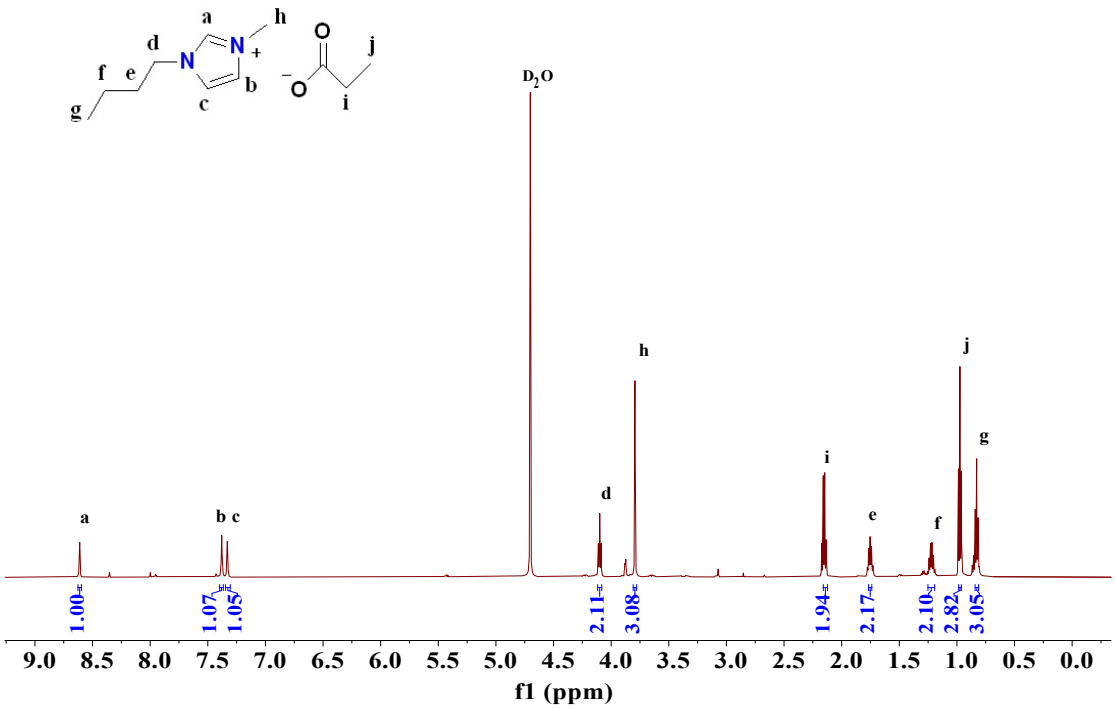

Figure S7. ^{1}H NMR spectrum of [Bmim][Pr] (D_2O, 600 MHz).

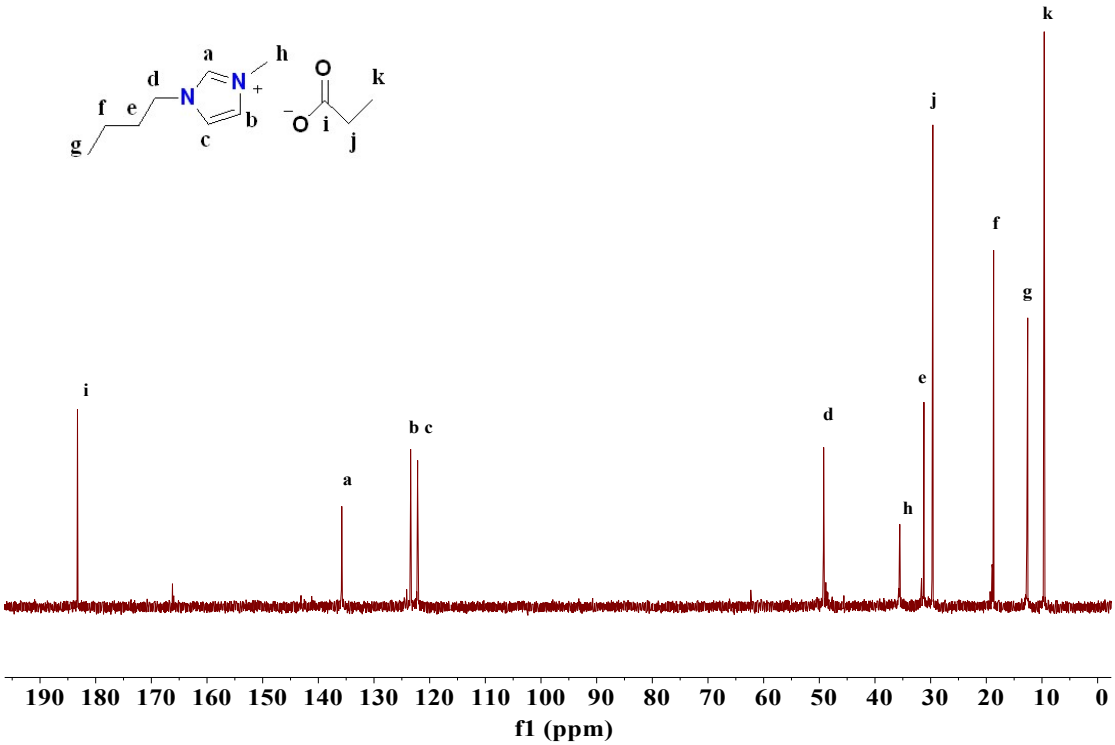

Figure S8. ^{13}C NMR spectrum of [Bmim][Pr] (D_2O, 150 MHz).

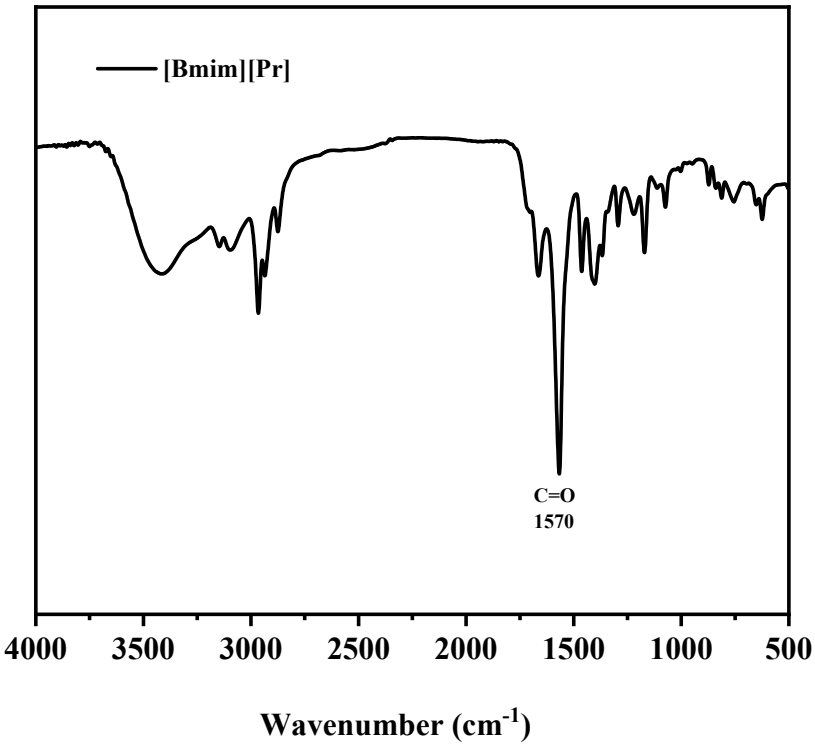

Figure S9. FT-IR spectrum of [Bmim][Pr] (KBr).

[Bmim][Pr]: ^{1}H NMR (600 MHz, D_2O, ppm) δ 8.61 (s, 1H), 7.38 (t, 1H), 7.33 (m, 1H), 4.10 (t, 2H), 3.79 (s, 3H), 2.15 (m, 2H), 1.75 (m, 2H), 1.22 (q, 2H), 0.98 (m, 3H), 0.83 (m, 3H). ^{13}C NMR (150 MHz, D_2O, ppm) δ 183.27, 135.79, 123.42, 122.16, 49.20, 35.54, 31.21, 29.61, 18.68, 12.77, 9.60. FT-IR (KBr, cm^{-1}): 3428, 3153, 3091, 2968, 2932, 2874, 1664, 1570, 1460, 1400, 1371, 1290, 1223, 1169, 1071, 874, 813, 756, 620.

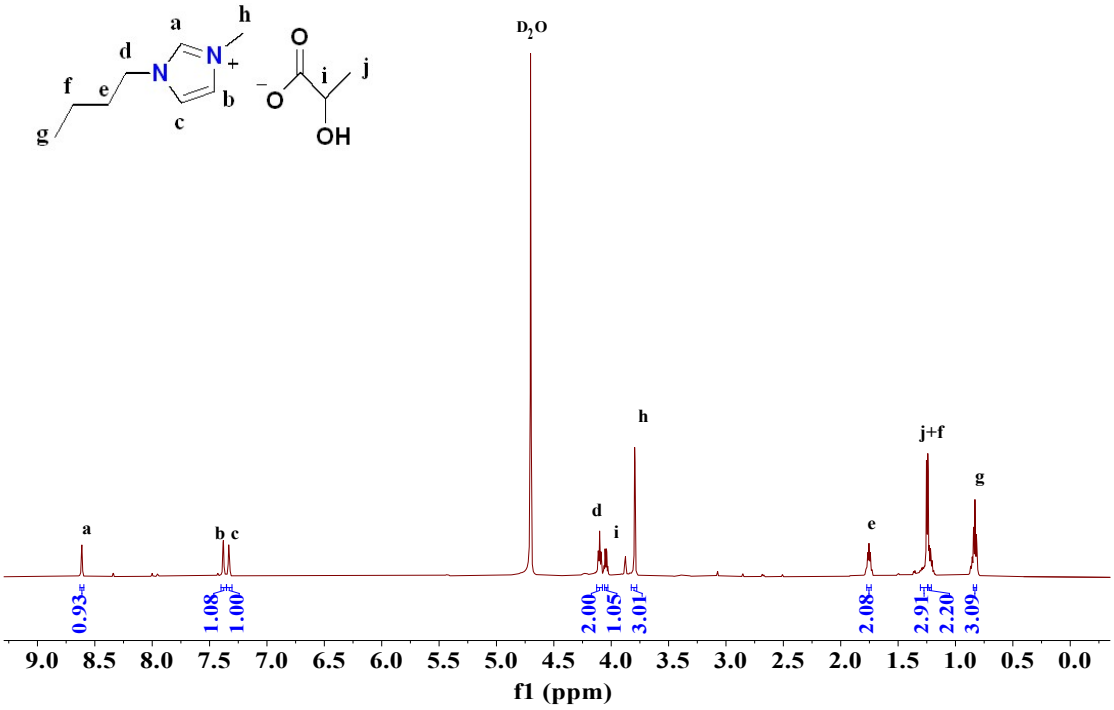

Figure S10. ^{1}H NMR spectrum of [Bmim][Lac] (D_2O, 600 MHz).

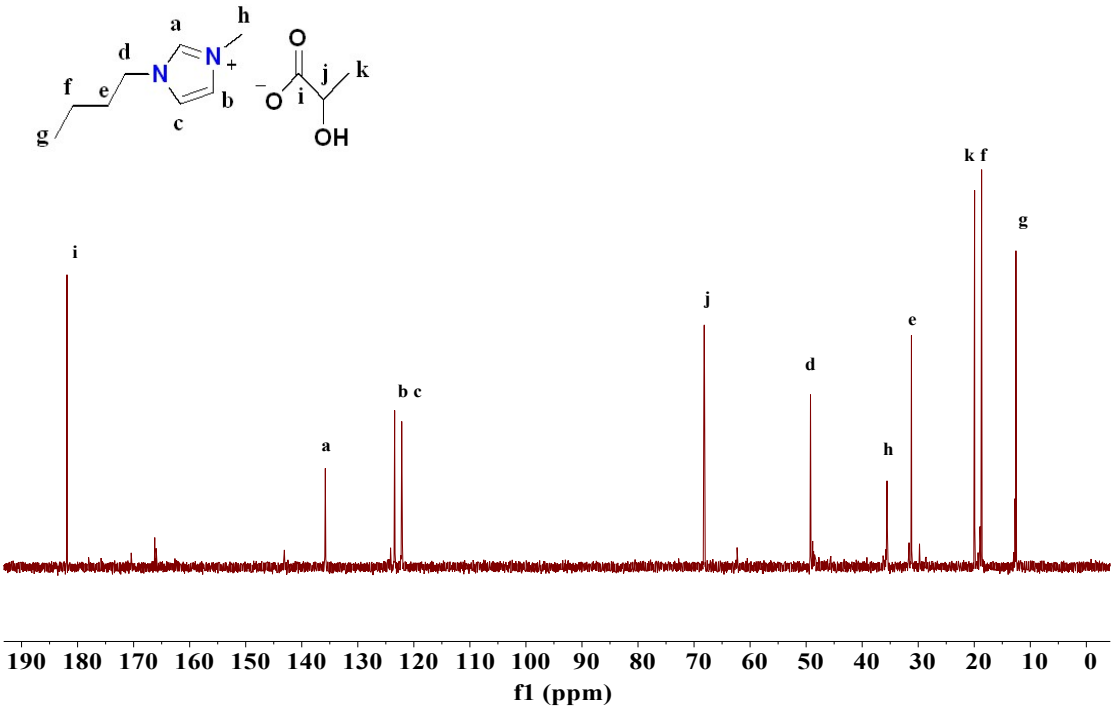

Figure S11. ^{13}C NMR spectrum of [Bmim][Lac] (D_2O, 150 MHz).

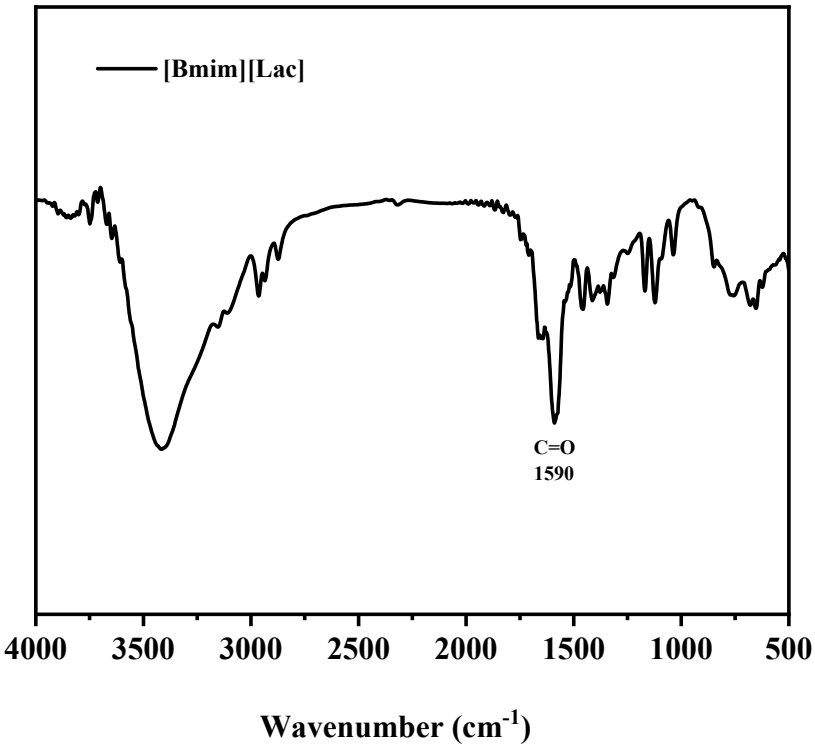

Figure S12. FT-IR spectrum of [Bmim][Lac] (KBr).

[Bmim][Lac]: ^{1}H NMR (600 MHz, D_2O, ppm) δ 8.61 (d, 1H), 7.38 (q, 1H), 7.33 (q, 1H), 4.10 (td, 2H), 4.04 (m, 1H), 3.79 (d, 3H), 1.75 (td, 2H), 1.25 (d, 3H), 1.22 (m, 2H), 0.83 (m, 3H). ^{13}C NMR (150 MHz, D_2O, ppm) δ 181.89, 135.80, 123.43, 122.10, 68.19, 49.20, 35.55, 31.22, 19.94, 18.69, 12.78. FT-IR (KBr, cm^{-1}): 3405, 3153, 3101, 2964, 2931, 2873, 1643, 1590, 1456, 1410, 1344, 1165, 1122, 1035, 852, 760, 684, 652.

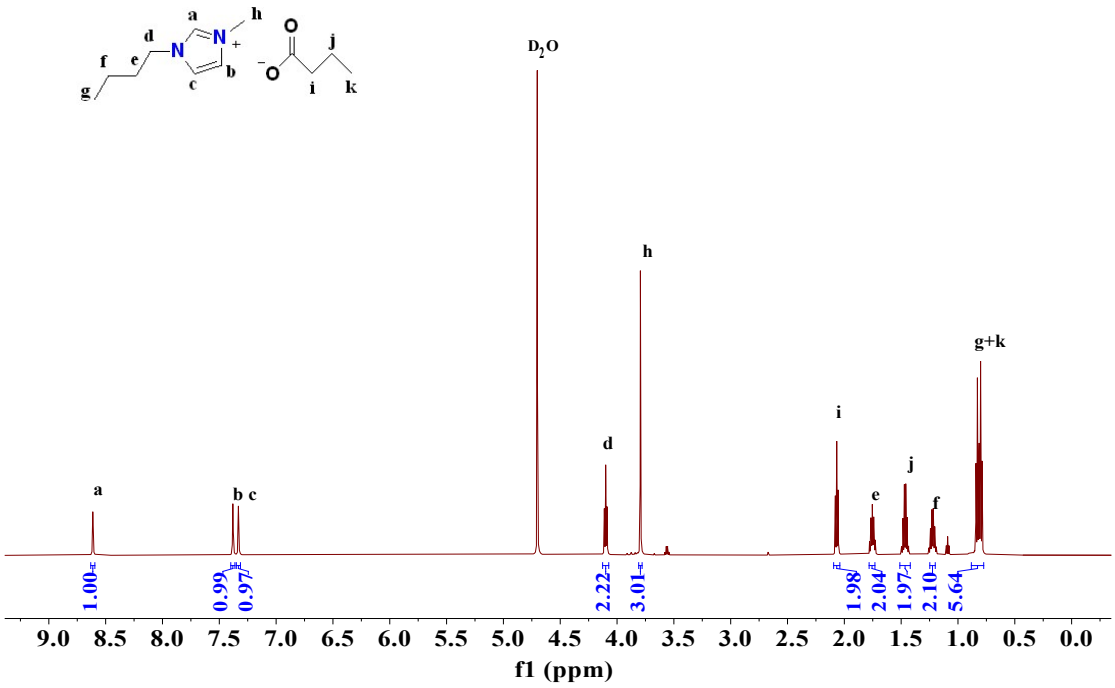

Figure S13. ^{1}H NMR spectrum of [Bmim][BA] (D_2O, 600 MHz).

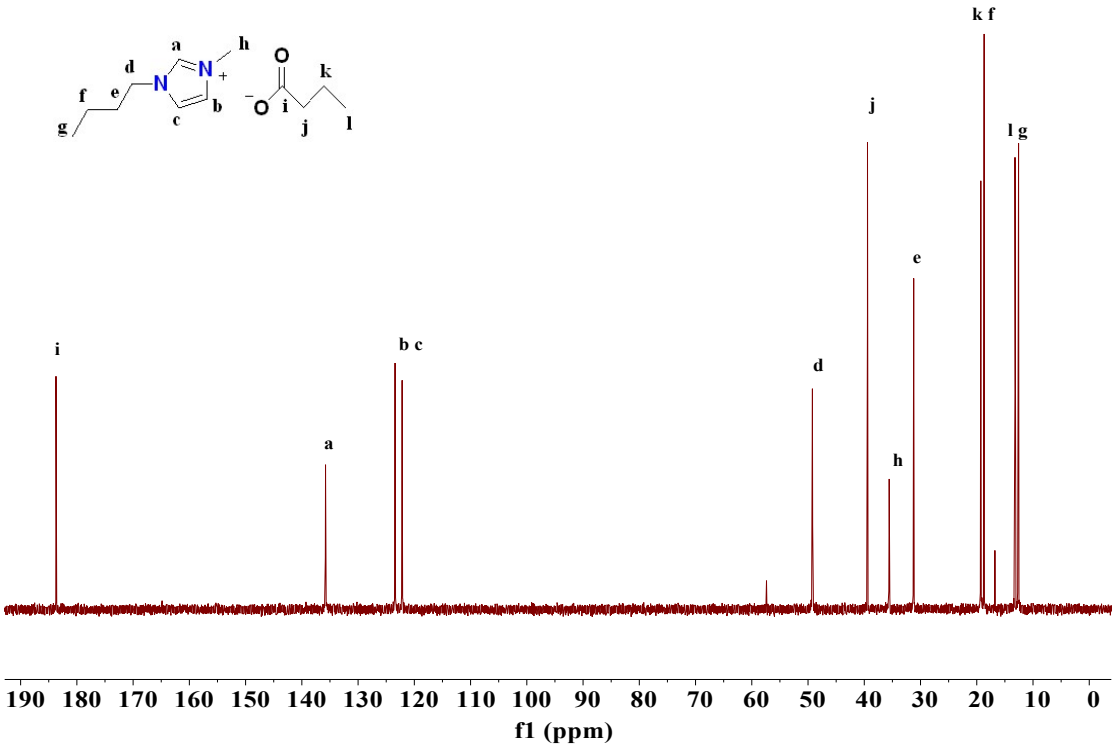

Figure S14. ^{13}C NMR spectrum of [Bmim][BA] (D_2O, 150 MHz).

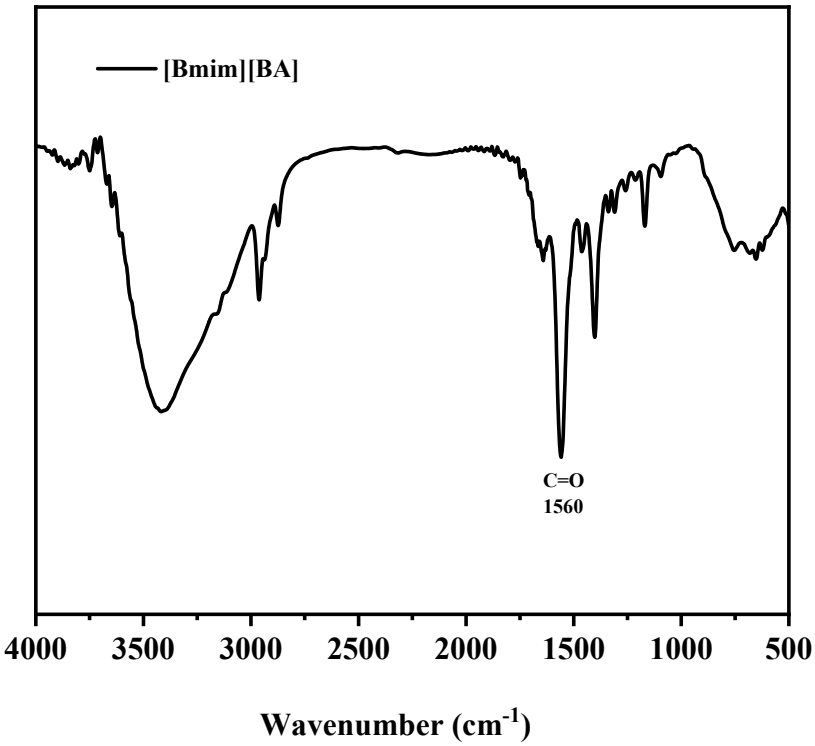

Figure S15. FT-IR spectrum of [Bmim][BA] (KBr).

[Bmim][BA]: ^{1}H NMR (600 MHz, D_2O, ppm) δ 8.61 (d, 1H), 7.38 (t, 1H), 7.33 (t, 1H), 4.10 (t, 2H), 3.79 (s, 3H), 2.07 (t, 2H), 1.76 (m, 2H), 1.47 (h, 2H), 1.22 (m, 2H), 0.82 (dt, 6H). ^{13}C NMR (150 MHz, D_2O, ppm) δ 183.71, 135.79, 123.43, 122.17, 49.20, 39.43, 35.55, 31.21, 19.28, 18.69, 13.20, 12.57. FT-IR (KBr, cm^{-1}): 3407, 2958, 2873, 1641, 1560, 1458, 1400, 1338, 1309, 1257, 1170, 1089, 760, 659, 619.

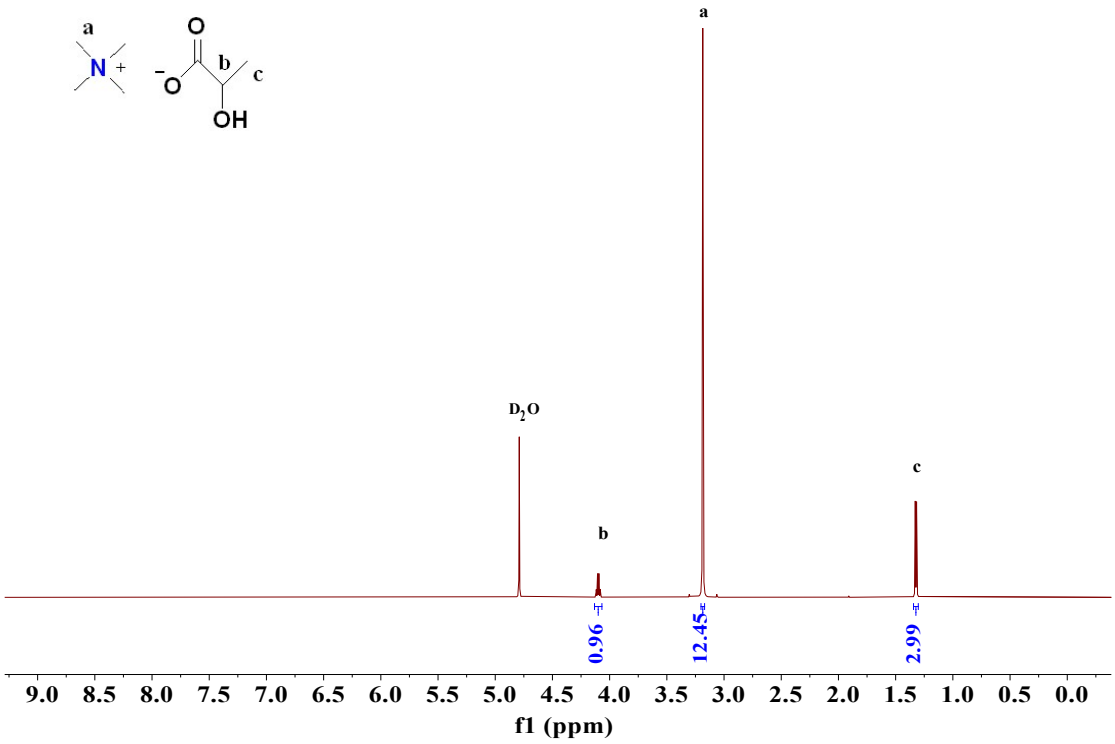

Figure S16. ^{1}H NMR spectrum of [TMA][Lac] (D_2O, 600 MHz).

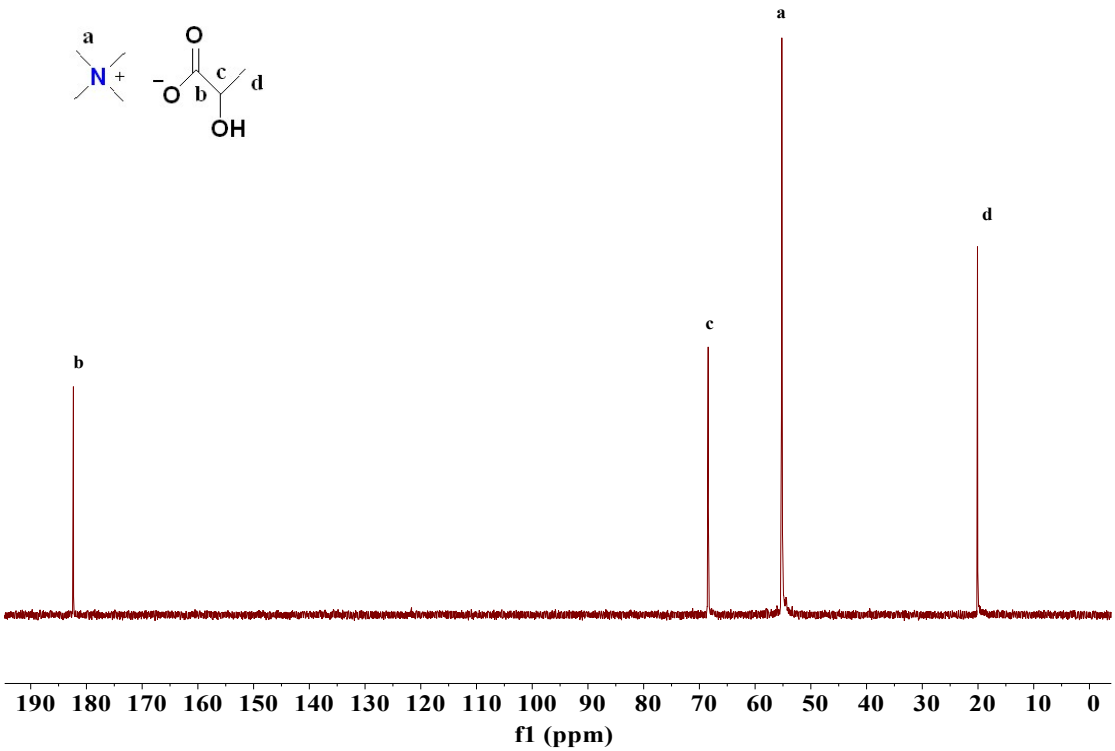

Figure S17. ^{13}C NMR spectrum of [TMA][Lac] (D_2O, 150 MHz).

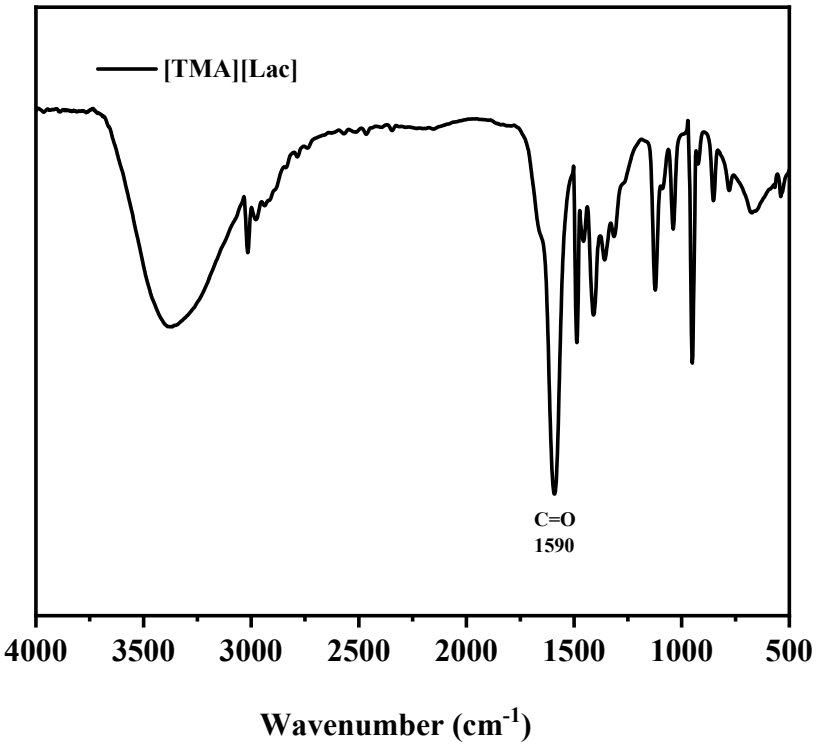

Figure S18. FT-IR spectrum of [TMA][Lac] (KBr).

[TMA][Lac]: ^{1}H NMR (600 MHz, D_2O, ppm) δ 4.10 (q, 1H), 3.19 (m, 12H), 1.32 (d, 3H). ^{13}C NMR (150 MHz, D_2O, ppm) δ 182.33, 68.46, 55.19, 20.08. FT-IR (KBr, cm^{-1}): 3401, 3012, 2970, 2933, 1590, 1489, 1452, 1400, 1355, 1313, 1122, 1039, 950, 850, 779, 667, 540.

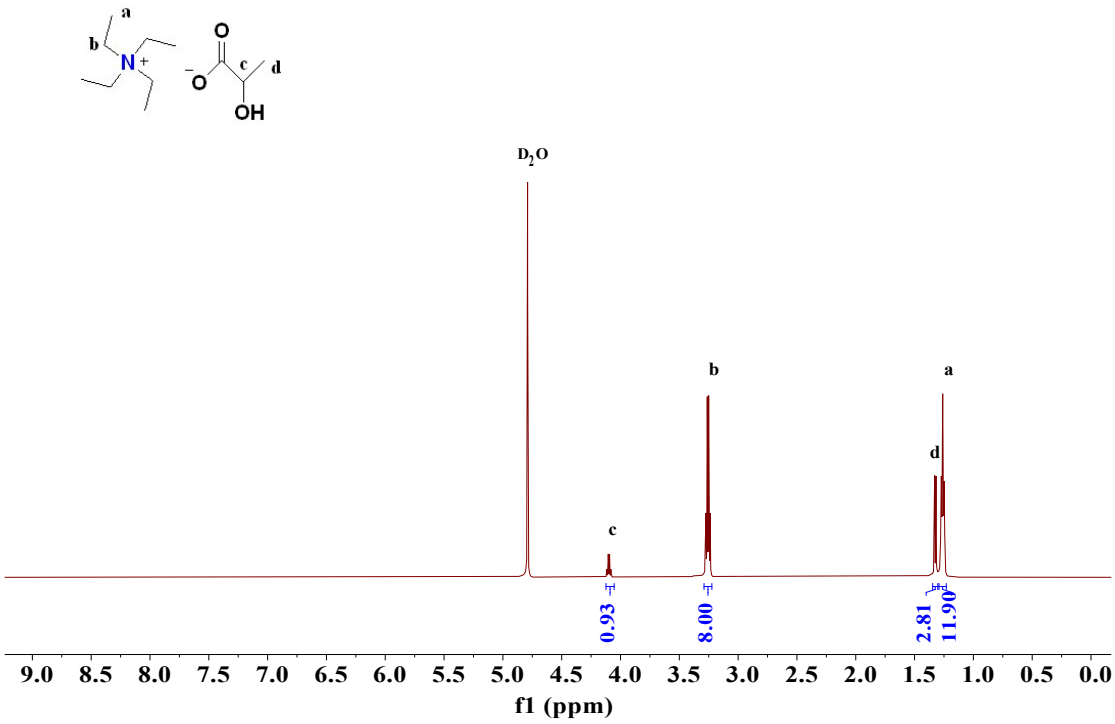

Figure S19. ^{1}H NMR spectrum of [TEA][Lac] (D_2O, 600 MHz).

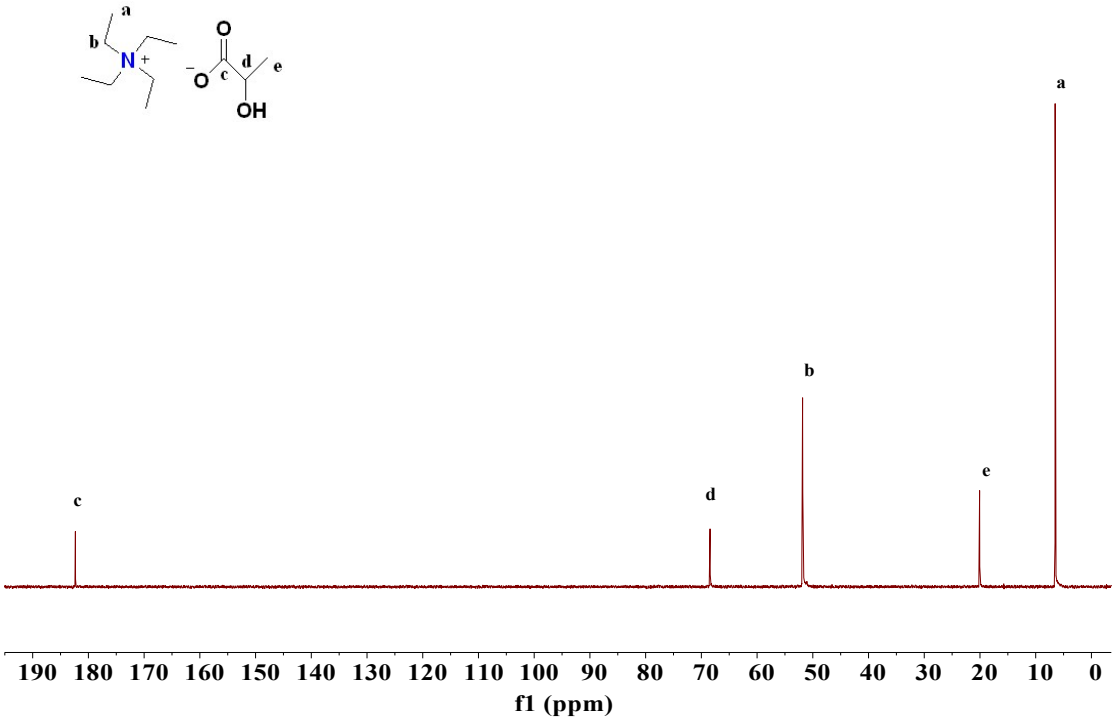

Figure S20. ^{13}C NMR spectrum of [TEA][Lac] (D_2O, 150 MHz).

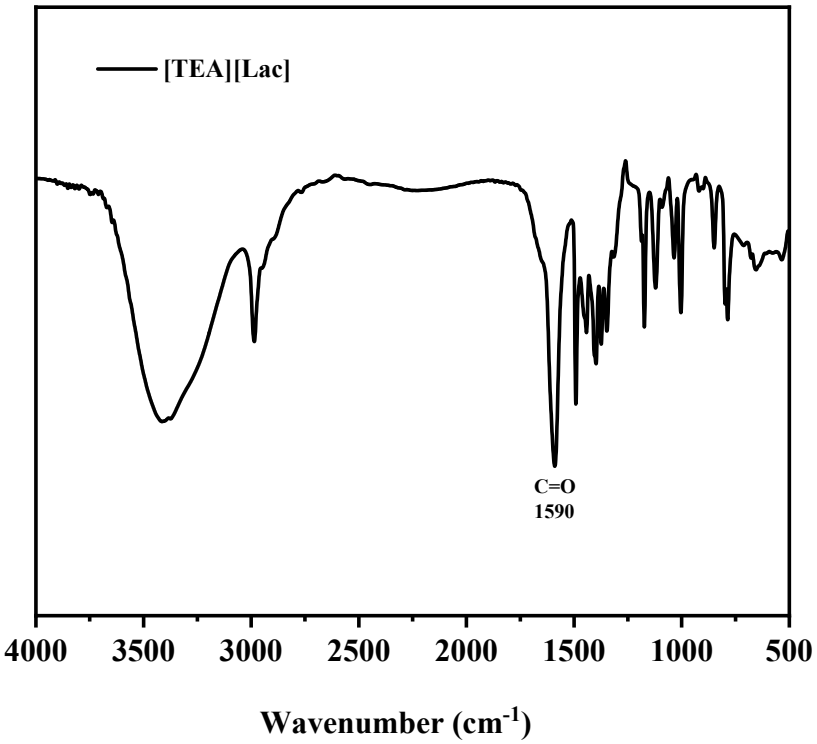

Figure S21. FT-IR spectrum of [TEA][Lac] (KBr).

[TEA][Lac]: ^{1}H NMR (600 MHz, D_2O, ppm) δ 4.10 (qd, 1H), 3.26 (q, 8H), 1.32 (dd, 3H), 1.26 (tdd, 12H). ^{13}C NMR (150 MHz, D_2O, ppm) δ 182.33, 68.46, 51.85, 20.07, 6.51. FT-IR (KBr, cm^{-1}): 3401, 2988, 1590, 1490, 1441, 1403, 1372, 1345, 1172, 1118, 1037, 1005, 922, 846, 789, 659.

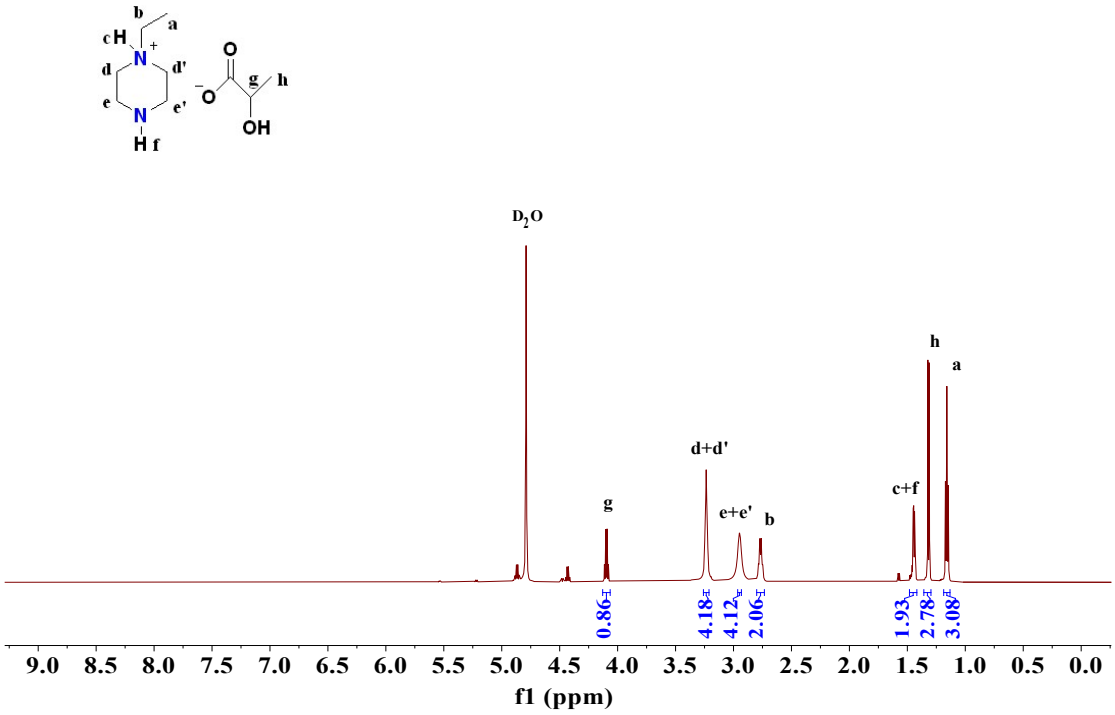

Figure S22. ^{1}H NMR spectrum of [Epe][Lac] (D_2O, 600 MHz).

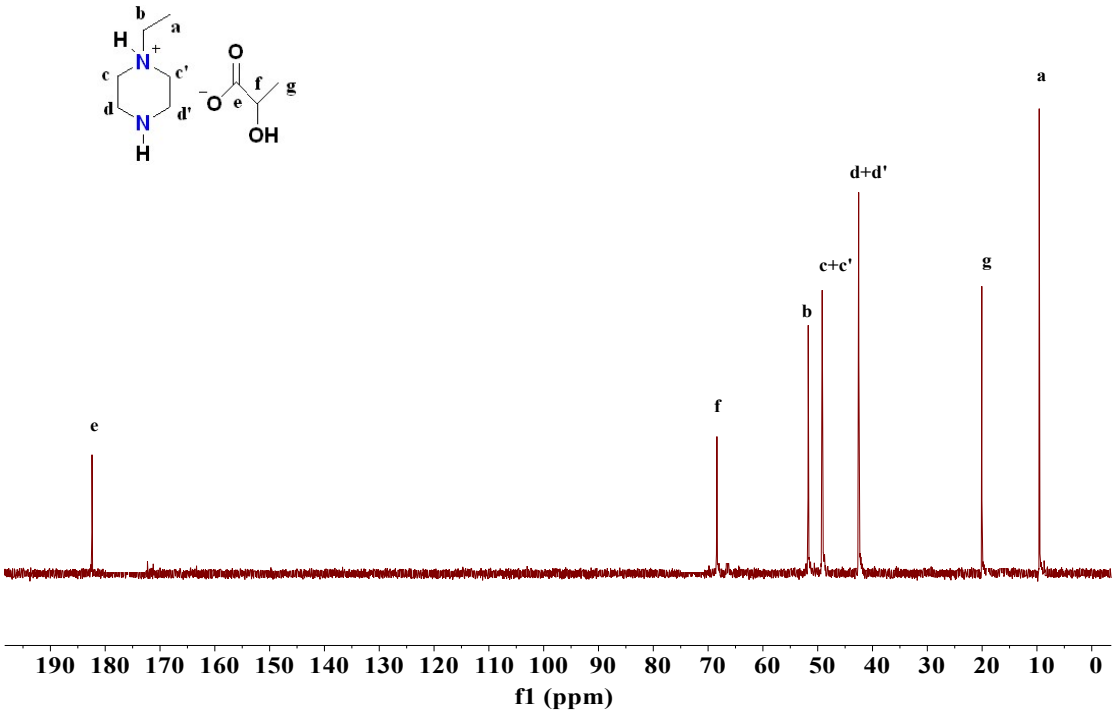

Figure S23. ^{13}C NMR spectrum of [Epe][Lac] (D_2O, 150 MHz).

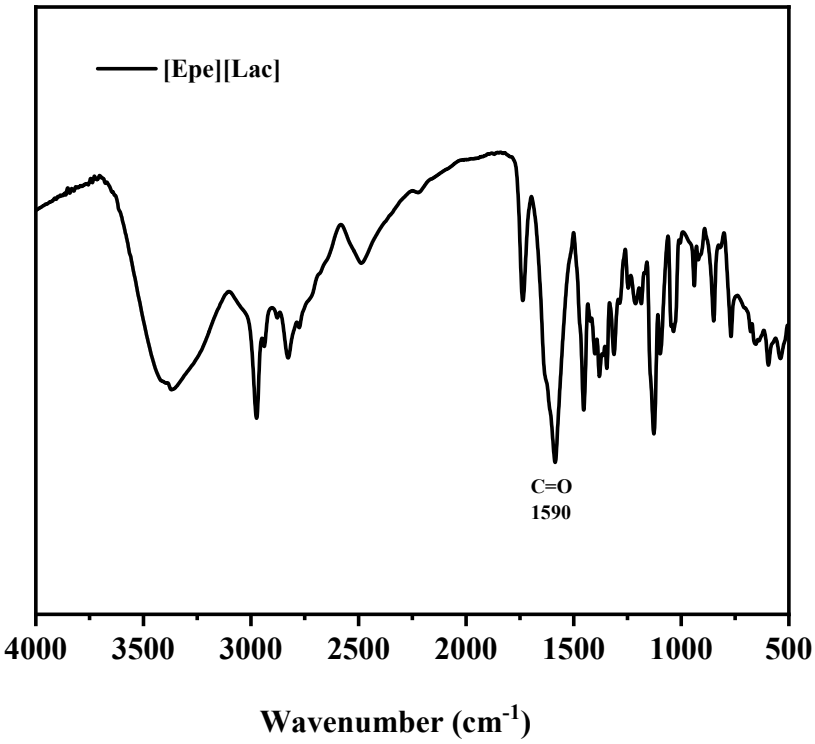

Figure S24. FT-IR spectrum of [Epe][Lac] (KBr).

[Epe][Lac]: ^{1}H NMR (600 MHz, D_2O, ppm) δ 4.10 (q, 1H), 3.24 (m, 4H), 2.95 (m, 4H), 2.77 (q, 2H), 1.44 (m, 2H), 1.32 (d, 3H), 1.16 (t, 3H). ^{13}C NMR (150 MHz, D_2O, ppm) δ 182.41, 178.41, 175.81, 72.76, 68.42, 66.59, 51.72, 49.18, 42.51, 20.06, 19.01, 16.67, 9.58. FT-IR (KBr, cm^{-1}): 3401, 2977, 2941, 2828, 2772, 2491, 1739, 1590, 1450, 1400, 1380, 1346, 1311, 1208, 1131, 1093, 1031, 937, 851, 766, 662, 599, 538.

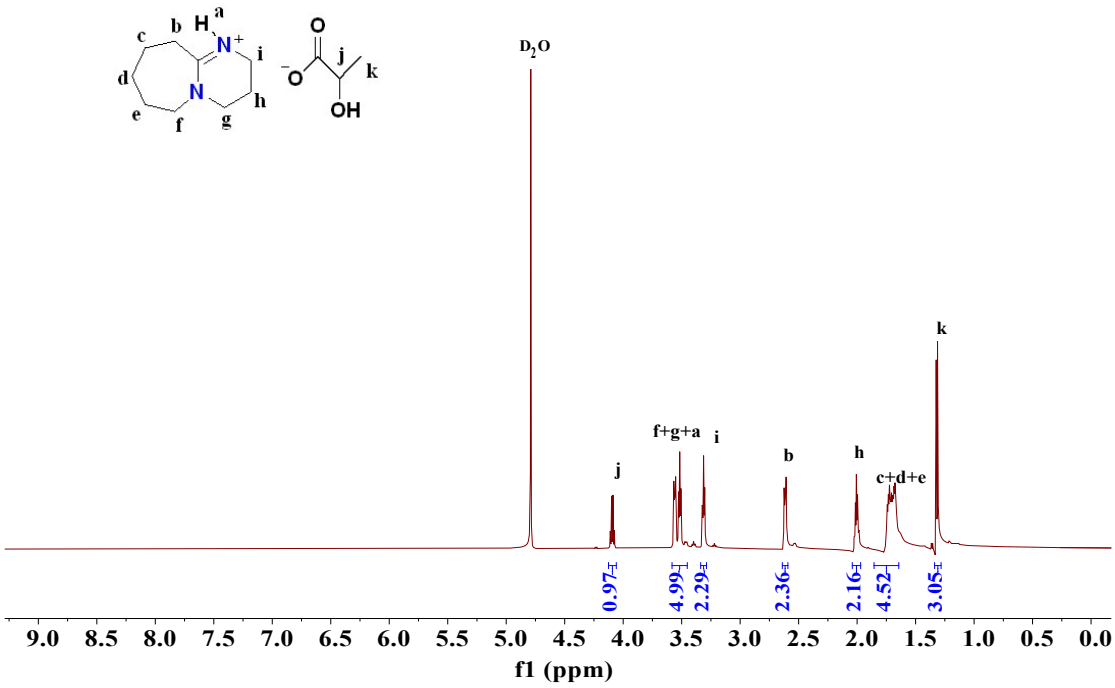

Figure S25. ^{1}H NMR spectrum of [DBU][Lac] (D_2O, 600 MHz).

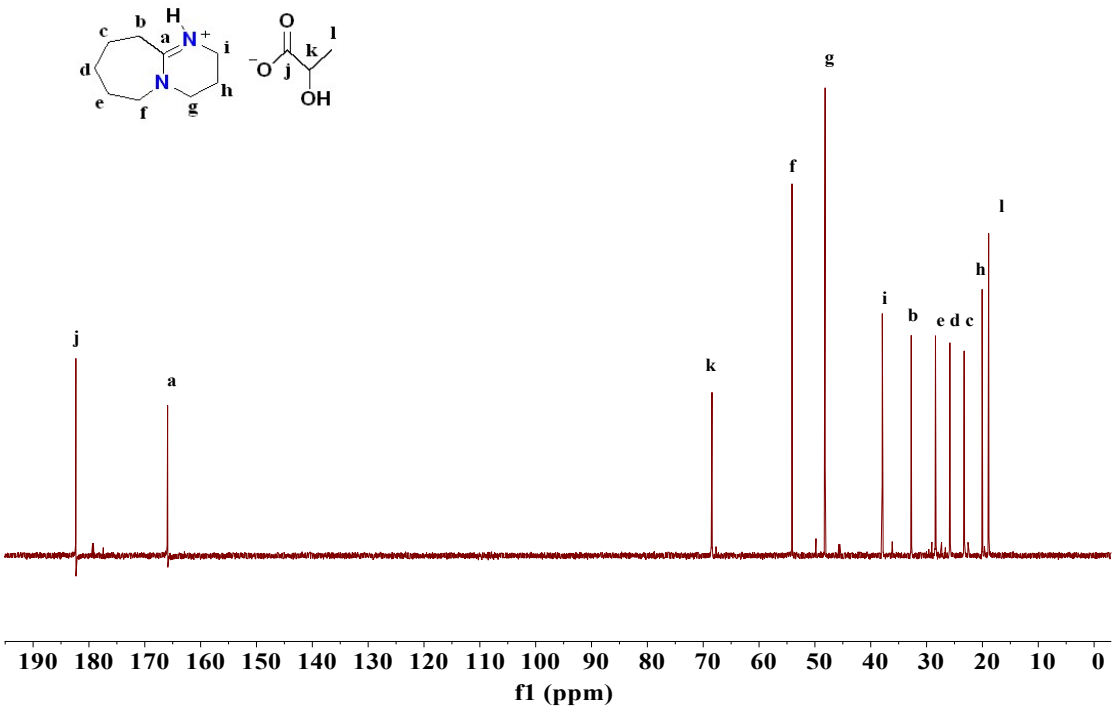

Figure S26. ^{13}C NMR spectrum of [DBU][Lac] (D_2O, 150 MHz).

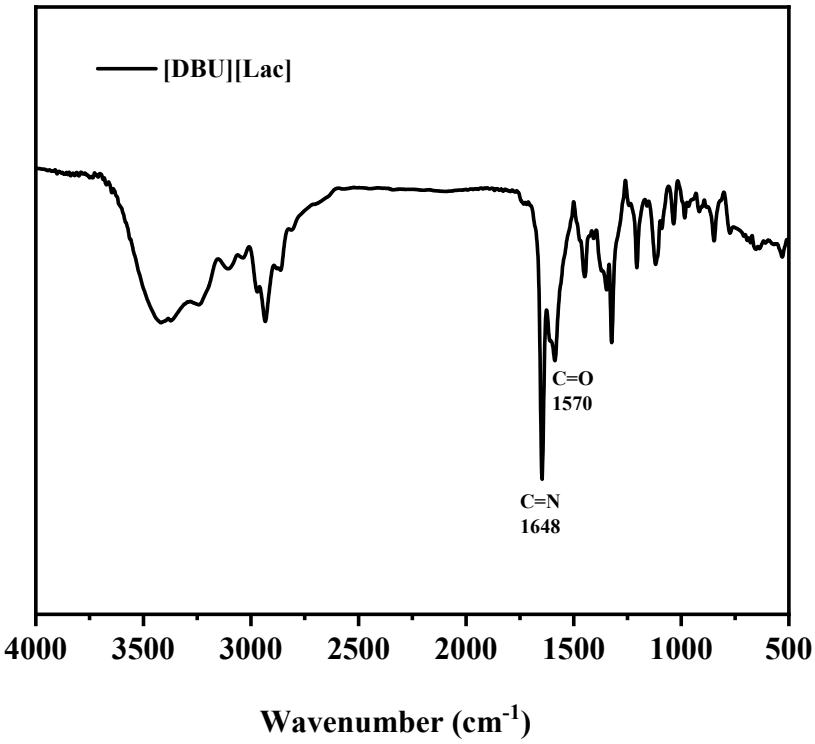

Figure S27. FT-IR spectrum of [DBU][Lac] (KBr).

[DBU][Lac]: ^{1}H NMR (600 MHz, D_2O, ppm) δ 4.09 (qd, 1H), 3.54 (dt, 5H), 3.31 (t, 2H), 2.62 (m, 2H), 2.01 (pd, 2H), 1.71 (m, 5H), 1.32 (dd, 3H). ^{13}C NMR (150 MHz, D_2O, ppm) δ 182.34, 165.91, 68.45, 54.10, 48.17, 37.92, 32.75, 28.41, 25.83, 23.27, 20.06, 18.87. FT-IR (KBr, cm^{-1}): 3401, 3238, 3099, 3036, 2966, 2932, 2858, 2805, 1648, 1570, 1453, 1350, 1324, 1209, 1116, 1032, 983, 914, 844, 771, 641, 540.

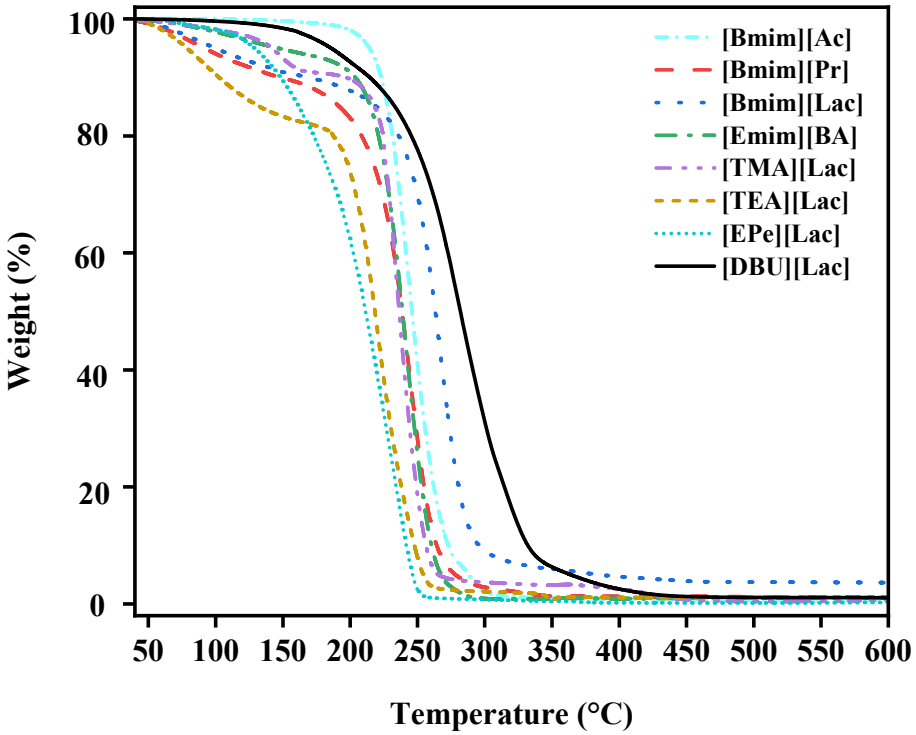

Figure S28. TGA curves of different catalysts.

Table S1. Thermal decomposition temperature of catalysts. [a]

Entry	Catalyst	$T_{d\text{-}5\%}$ [b] (°C)	$T_{d\text{-}max}$ [c] (°C)
1	[Bmim][Ac]	214	253
2	[Bmim][Pr]	91	246
3	[Bmim][Lac]	100	270
4	[Bmim][BA]	146	243
5	[TMA]Lac]	142	237
6	[TEA][Lac]	79	222
7	[EPe][Lac]	129	233
8	[DBU][Lac]	186	285

[a] Measured by TGA at nitrogen atmosphere.

[b] Temperature at 5% weight loss ($T_{d\text{-}5\%}$).

[c] Temperature at maximum weight loss rate.

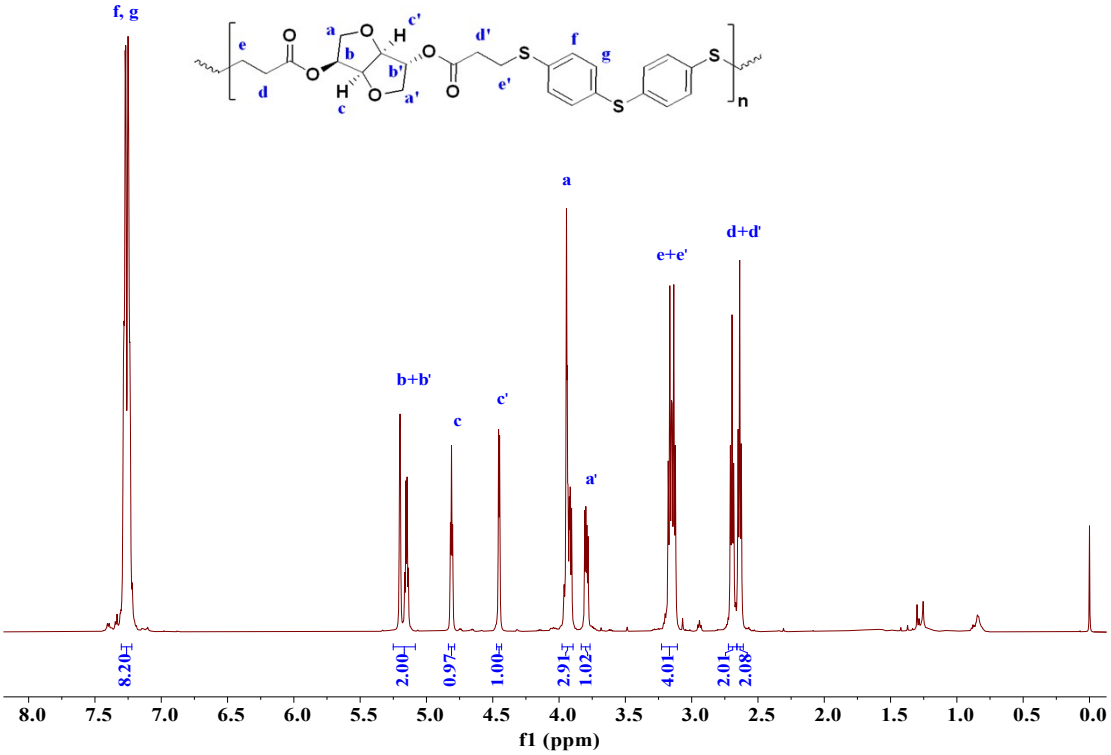

Figure S29. ^{1}H NMR spectrum of $PIT_{100}E_0$ synthesized by [DBU][Lac] ($CDCl_3$, 600 MHz).

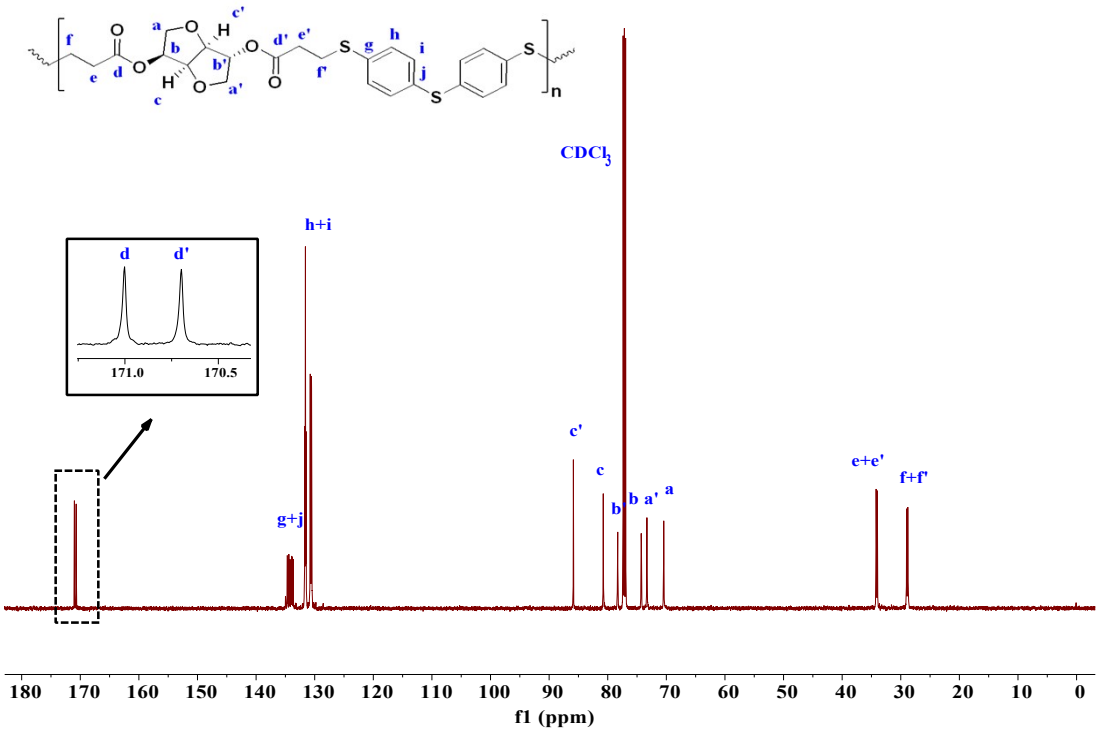

Figure S30. ^{13}C NMR spectrum of $PIT_{100}E_0$ synthesized by [DBU][Lac] ($CDCl_3$, 150 MHz).

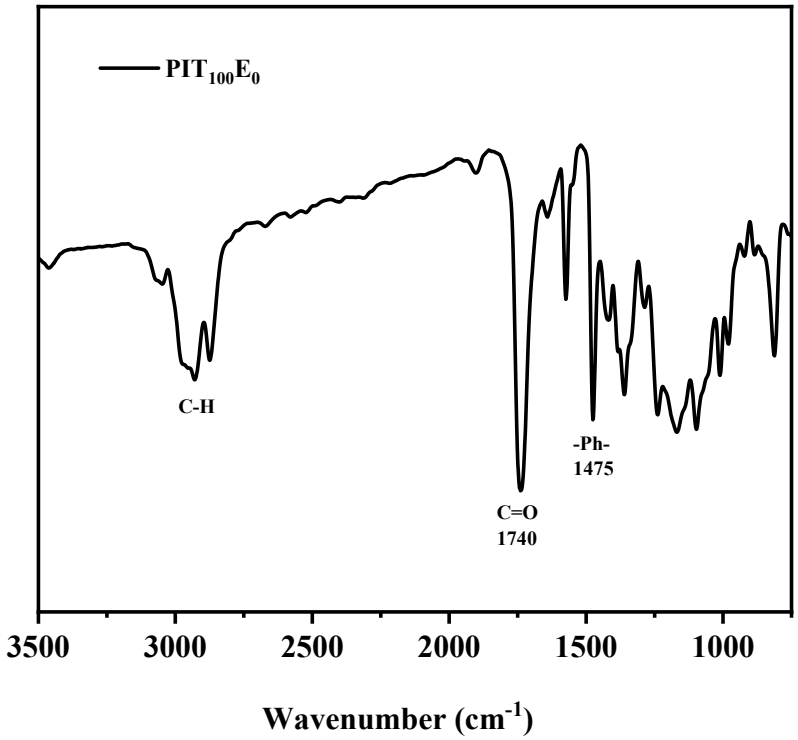

Figure S31. FT-IR spectrum of $PIT_{100}E_0$ synthesized by [DBU][Lac] (KBr).

$PIT_{100}E_0$: ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.26 (d, 8H), 5.17 (m, 2H), 4.81 (t, 1H), 4.45 (d, 1H), 3.93 (m, 3H), 3.79 (d, 1H), 3.15 (dt, 4H), 2.70 (t, 2H), 2.64 (t, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 170.70, 134.37, 133.68, 131.58, 130.65, 85.86, 80.76, 78.31, 74.27, 73.34, 70.46, 34.01, 28.89. FT-IR (KBr, cm^{-1}): 2975, 2930, 2871, 1740, 1638, 1571, 1480, 1423, 1357, 1290, 1238, 1168, 1095, 1008, 975, 809.

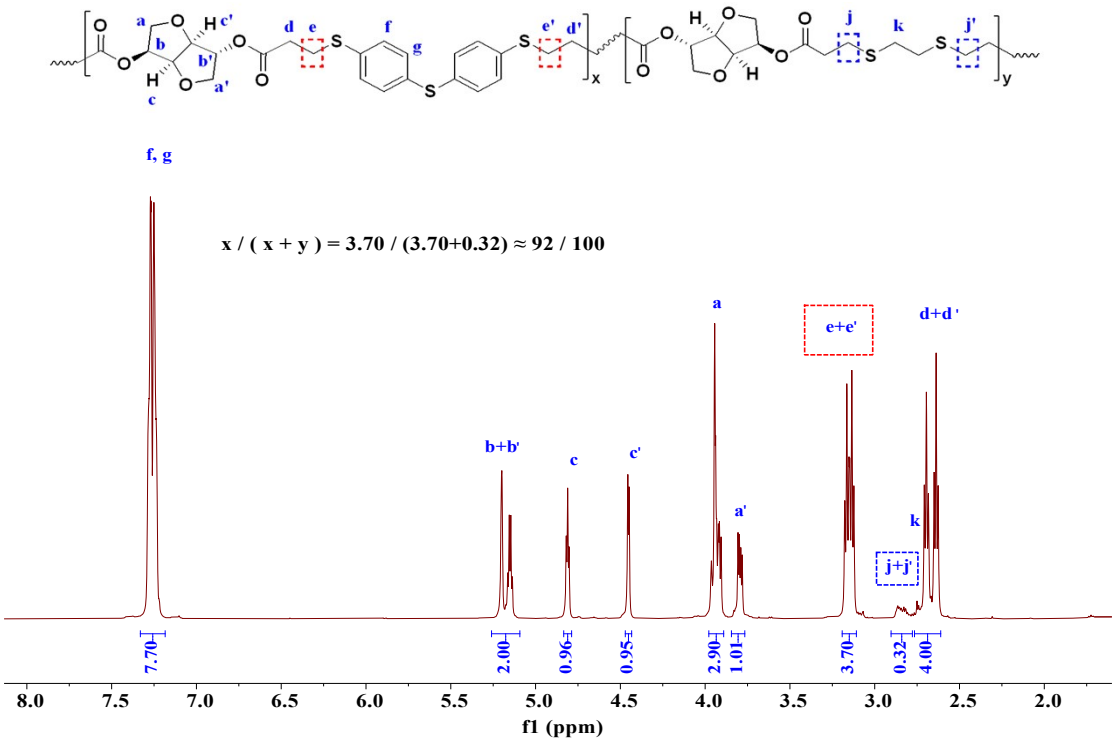

Figure S32. ^{1}H NMR spectrum of $PIT_{90}E_{10}$ synthesized by [DBU][Lac] ($CDCl_3$, 600 MHz).

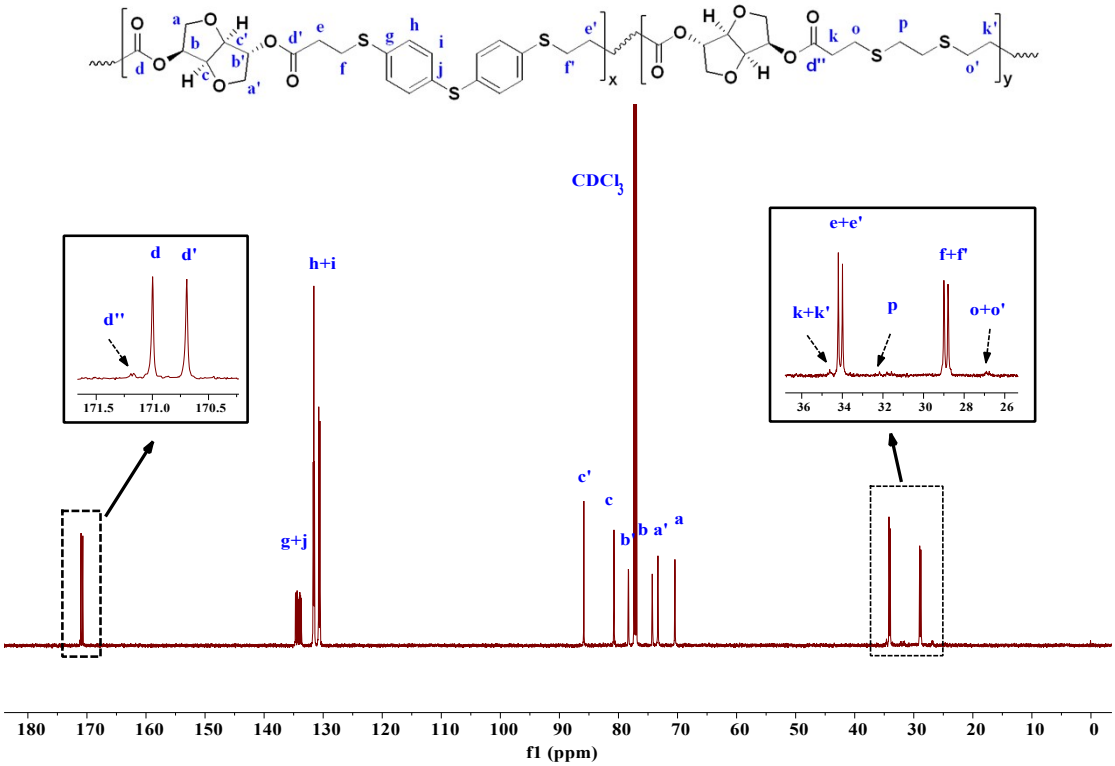

Figure S33. ^{13}C NMR spectrum of $PIT_{90}E_{10}$ synthesized by [DBU][Lac] ($CDCl_3$, 150 MHz).

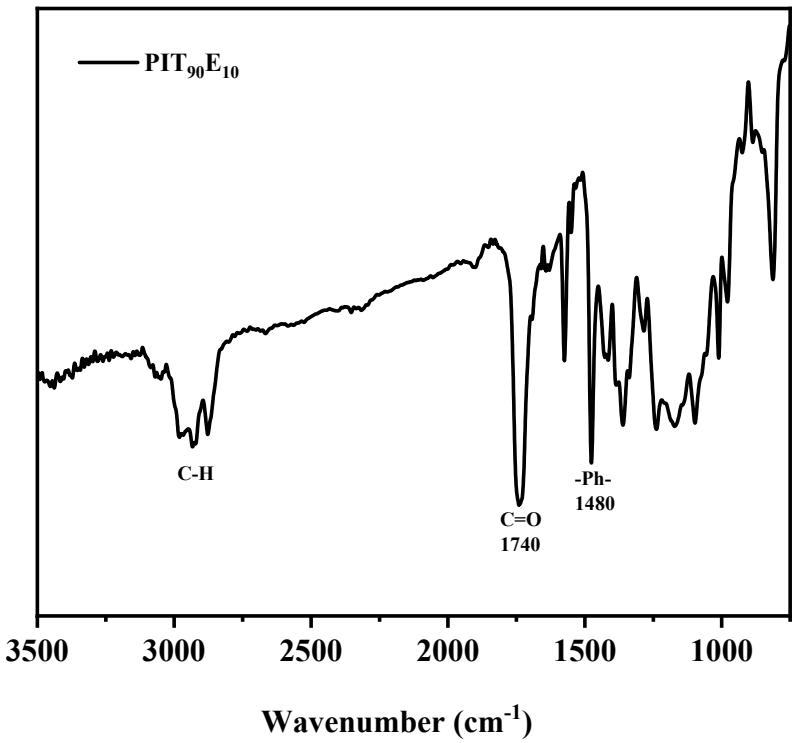

Figure S34. FT-IR spectrum of $PIT_{90}E_{10}$ synthesized by [DBU][Lac] (KBr).

$PIT_{90}E_{10}$: ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.26 (d, 8H), 5.17 (m, 2H), 4.81 (t, 1H), 4.45 (d, 1H), 3.93 (m, 3H), 3.79 (d, 1H), 3.15 (dt, 4H), 2.84 (m, 0H), 2.67 (dt, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 170.69, 134.37, 133.96, 131.58, 130.65, 85.86, 80.76, 78.31, 74.27, 73.29, 70.44, 34.01, 28.79. FT-IR (KBr, cm^{-1}): 2980, 2932, 2876, 1740, 1638, 1575, 1480, 1425, 1355, 1283, 1238, 1168, 1095, 1012, 982, 811.

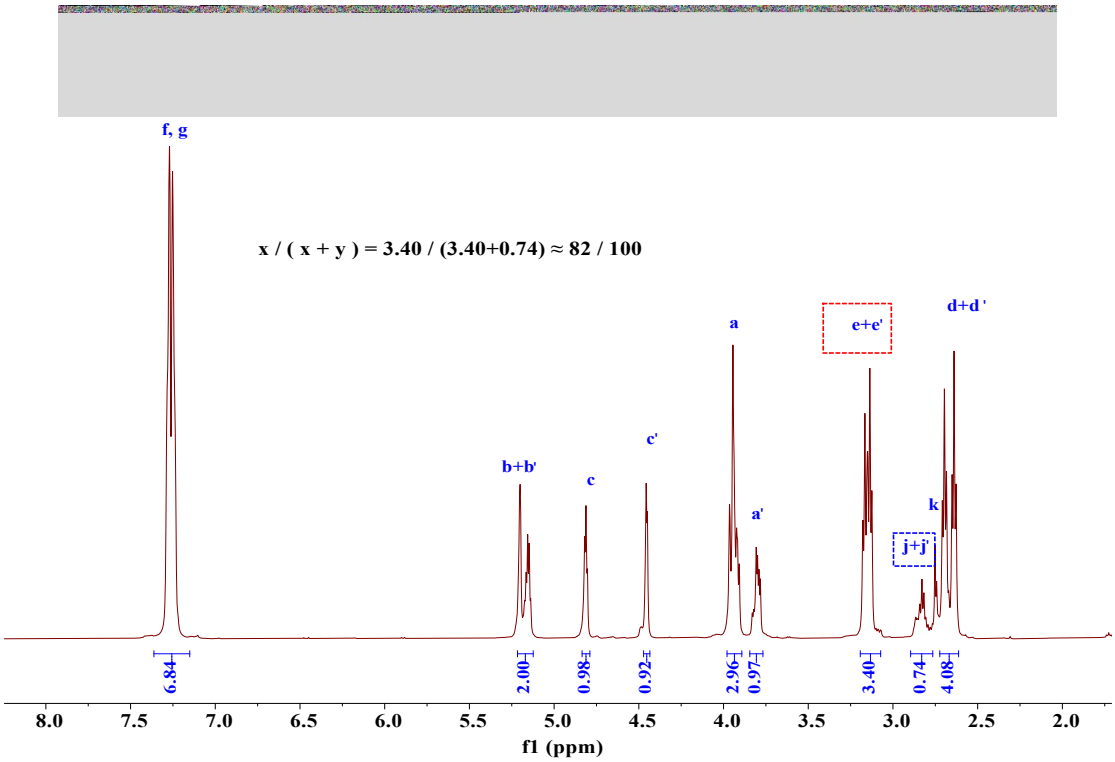

Figure S35. ^{1}H NMR spectrum of $PIT_{80}E_{20}$ synthesized by [DBU][Lac] ($CDCl_3$, 600 MHz).

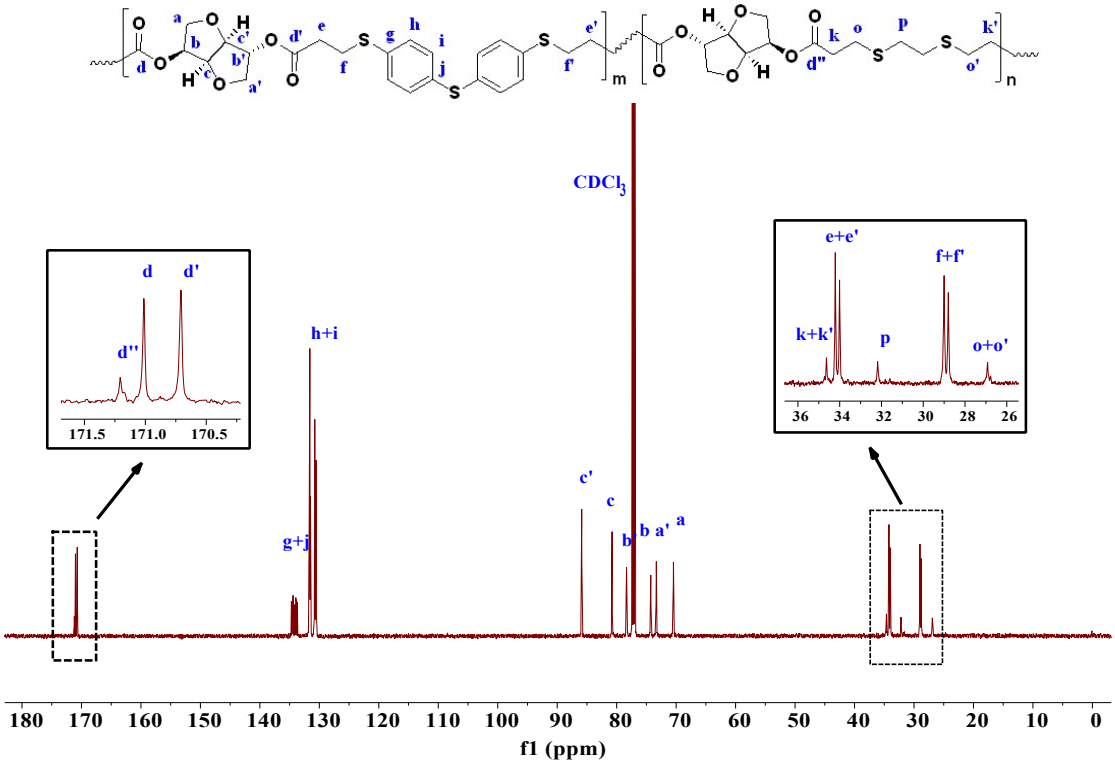

Figure S36. ^{13}C NMR spectrum of $PIT_{80}E_{20}$ synthesized by [DBU][Lac] ($CDCl_3$, 150 MHz).

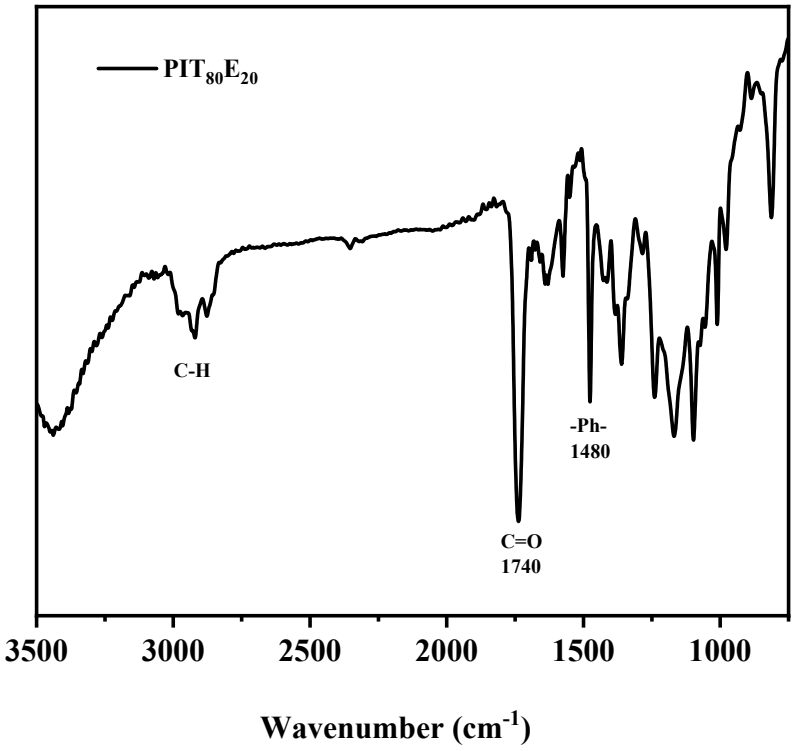

Figure S37. FT-IR spectrum of $PIT_{80}E_{20}$ synthesized by [DBU][Lac] (KBr).

$PIT_{80}E_{20}$: ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.26 (d, 7H), 5.17 (m, 2H), 4.82 (q, 1H), 4.45 (d, 1H), 3.94 (m, 3H), 3.81 (d, 1H), 3.15 (dt, 3H), 2.83 (td, 1H), 2.67 (dt, 4H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 170.86, 134.52, 133.90, 131.59, 130.67, 85.88, 80.78, 78.32, 74.28, 73.34, 70.47, 34.63, 34.01, 32.18, 28.91, 26.92. FT-IR (KBr, cm^{-1}): 2984, 2923, 2877, 1740, 1642, 1575, 1480, 1423, 1363, 1290, 1241, 1164, 1096, 1009, 975, 812.

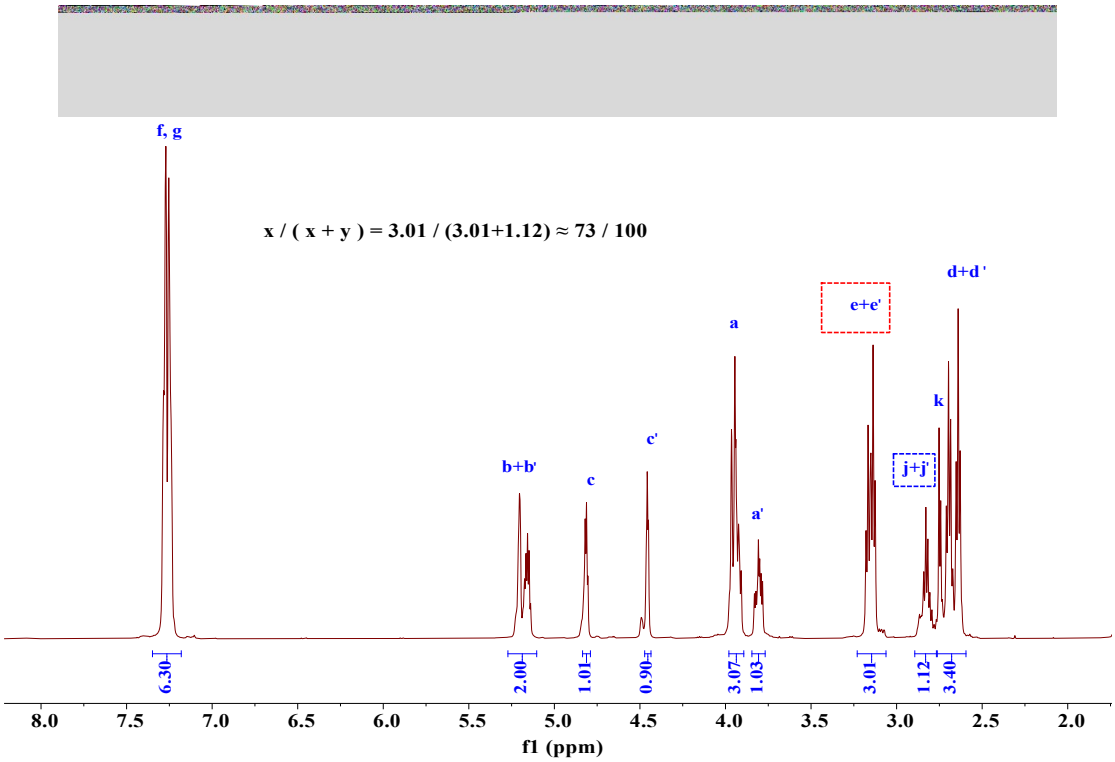

Figure S38. ^{1}H NMR spectrum of $PIT_{70}E_{30}$ synthesized by [DBU][Lac] ($CDCl_3$, 600 MHz).

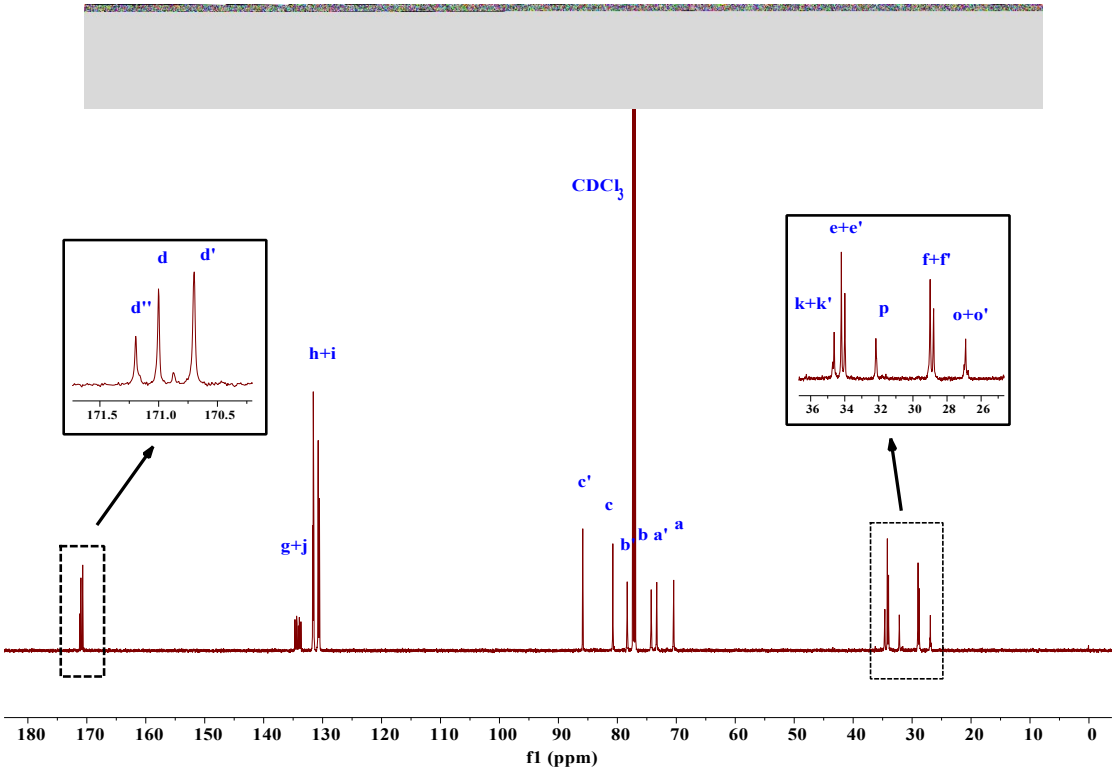

Figure S39. ^{13}C NMR spectrum of $PIT_{70}E_{30}$ synthesized by [DBU][Lac] ($CDCl_3$, 150 MHz).

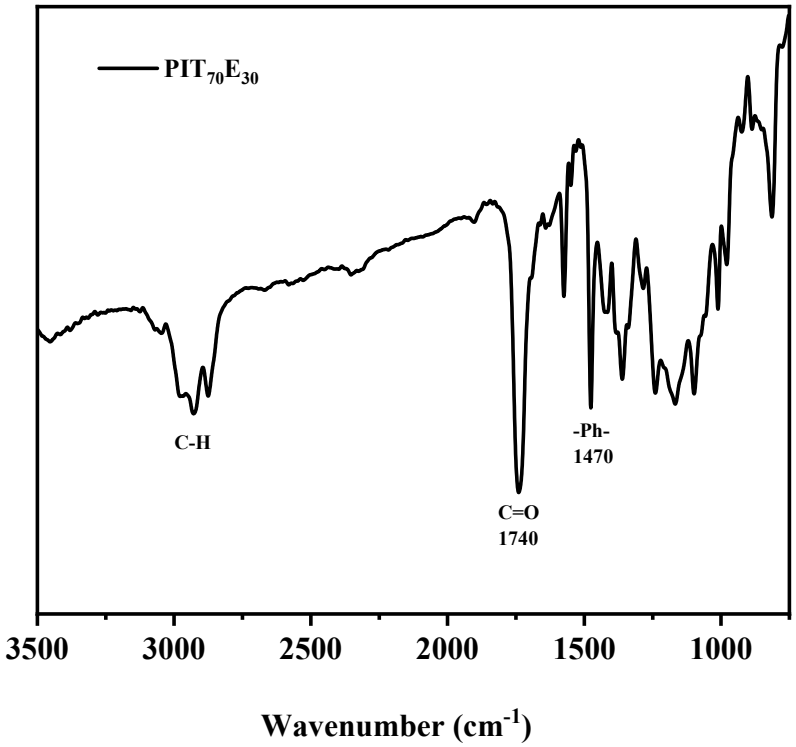

Figure S40. FT-IR spectrum of $PIT_{70}E_{30}$ synthesized by [DBU][Lac] (KBr).

$PIT_{70}E_{30}$: ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.26 (d, 6H), 5.18 (d, 2H), 4.82 (q, 1H), 4.46 (t, 1H), 3.94 (m, 3H), 3.81 (d, 1H), 3.15 (dt, 3H), 2.82 (dt, 1H), 2.68 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 170.96, 134.49, 133.93, 131.58, 130.62, 85.87, 80.77, 78.33, 74.27, 73.32, 70.46, 34.67, 34.10, 32.17, 28.86, 26.91. FT-IR (KBr, cm^{-1}): 2980, 2930, 2876, 1740, 1639, 1575, 1480, 1423, 1357, 1290, 1238, 1168, 1095, 1013, 976, 817.

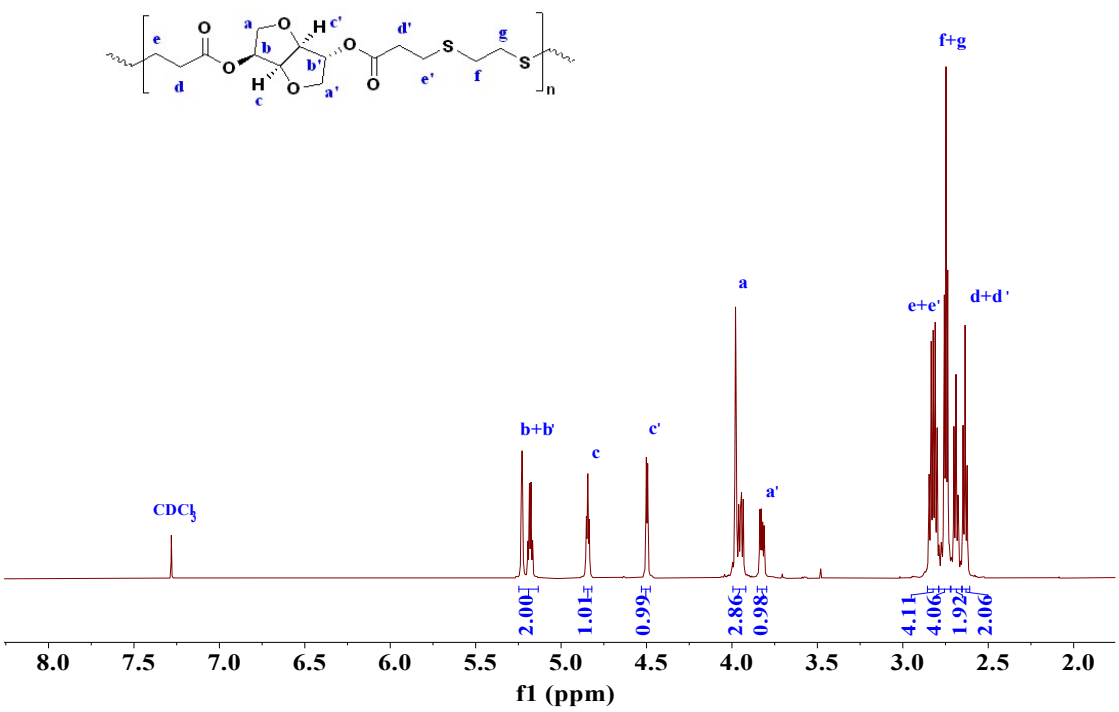

Figure S41. ^{1}H NMR spectrum of PIT_0E_{100} synthesized by [DBU][Lac] ($CDCl_3$, 600 MHz).

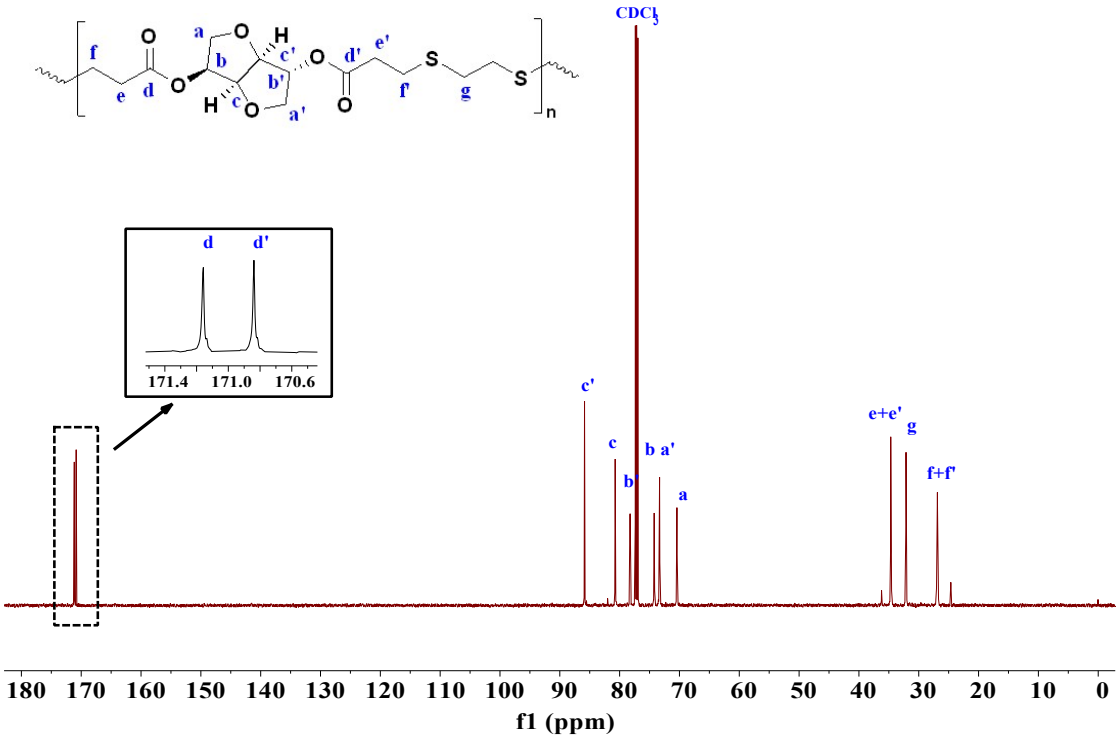

Figure S42. ^{13}C NMR spectrum of PIT_0E_{100} synthesized by [DBU][Lac] ($CDCl_3$, 150 MHz).

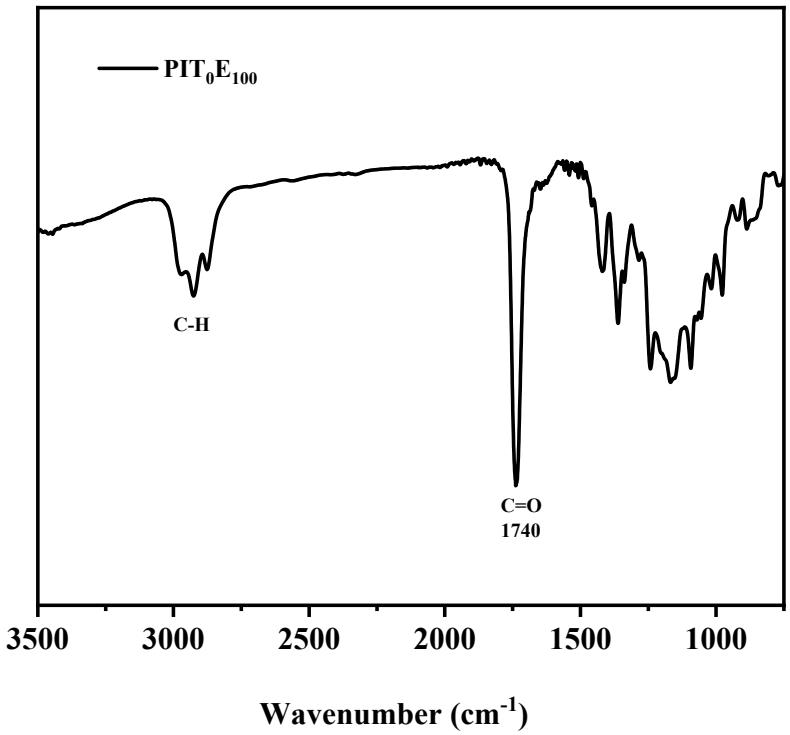

Figure S43. FT-IR spectrum of PIT_0E_{100} synthesized by [DBU][Lac] (KBr).

PIT_0E_{100}: ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 5.20 (m, 2H), 4.84 (t, 1H), 4.50 (d, 1H), 3.96 (m, 3H), 3.82 (d, 1H), 2.82 (dt, 4H), 2.75 (m, 4H), 2.69 (t, 2H), 2.64 (t, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm) δ 170.84, 85.87, 80.74, 78.25, 74.21, 73.30, 70.44, 34.65, 32.12, 26.91. FT-IR (KBr, cm^{-1}): 2975, 2930, 2871, 1740, 1421, 1359, 1290, 1244, 1163, 1093, 1018, 977, 914, 882.

Tensile test

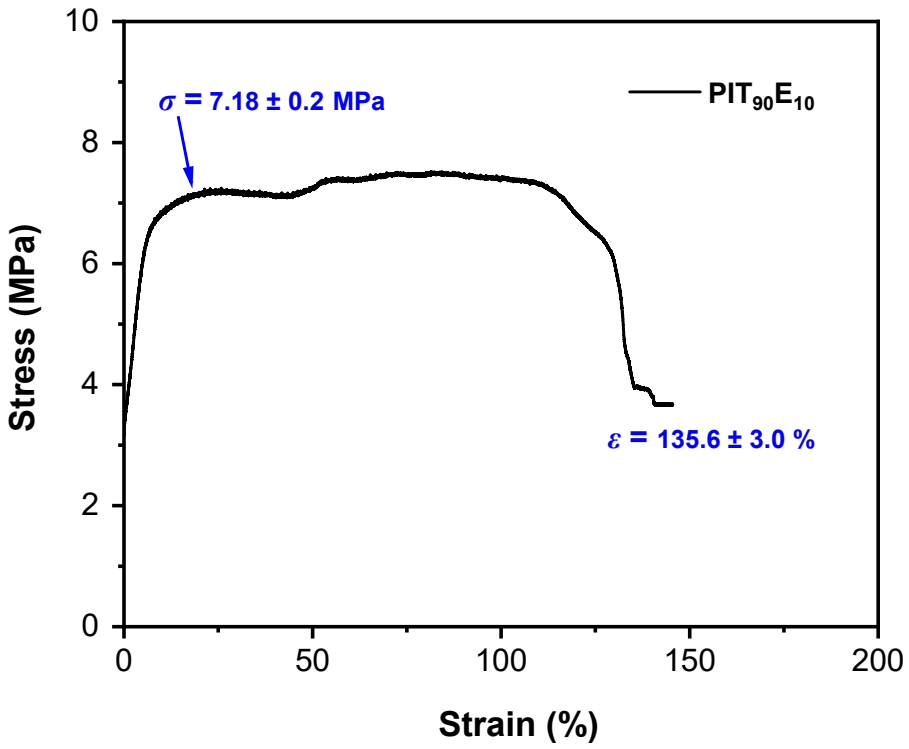

Figure S44. Mechanical behavior of representative $PIT_{90}E_{10}$ sample.

Swelling test

For polymer swelling capability testing, phosphate buffered saline (PBS) was chosen as the aqueous solution approaching the physiological environment of human body.[1] Firstly, the specimen of $PIT_{90}E_{10}$ were weighed at dry state and the dry weight (W_d) was obtained. Then it was immersed in PBS at a constant temperature of 37°C for fixed time interval and wet weight (W_w) were assessed after the removal of extra water with the help of tissue paper. The mass swelling ratio (SR) is calculated using following equation.

$$SR = (W_w - W_d) / W_d \times 100\%$$

where W_w - mass of the swollen wet hydrogel sample, W_d - mass of the dried sample.

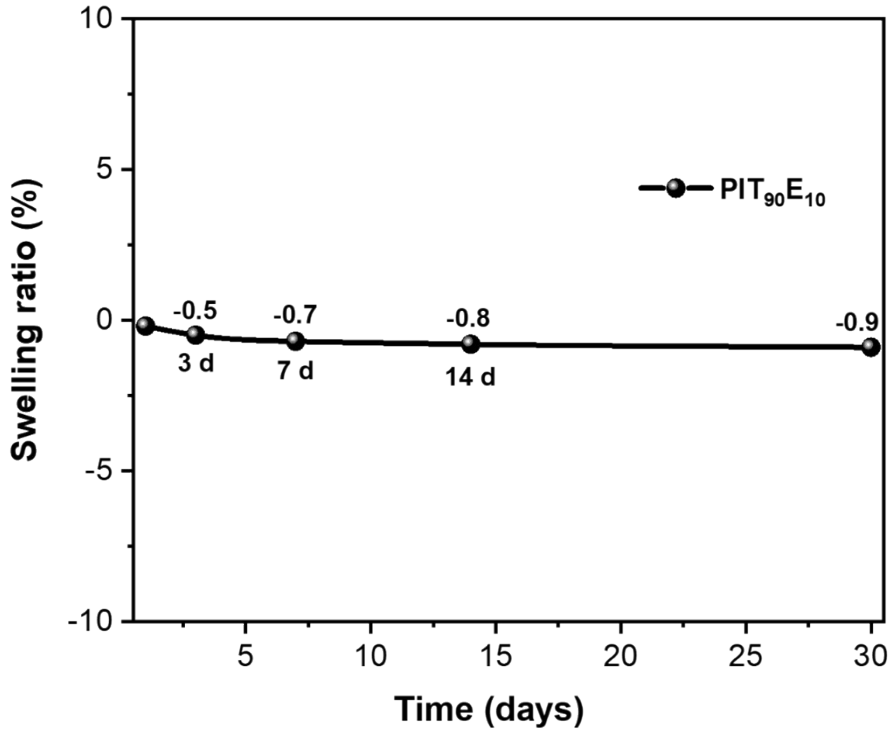

Figure S45. Swelling test of optical polymers in PBS buffer (pH = 7.4, 37 °C).

1. V. Hidalgo-Alvarez, N. D. Falcon, J. Eldred, M. Wormstone and A. Saeed, *Curr. Eye. Res.*, 2024, 1-10.