# Supporting Information

# Cellulose-dissolving protic ionic liquids as low-cost catalysts for direct transesterification reactions of cellulose

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The 5% weight loss temperature ($T_{d\text{-}5\%}$) was measured using thermogravimetry (TG-DTA7200, Hitachi High-Technologies). The samples were heated from room temperature to 500 °C at a scan rate of 20 °C $min^{-1}$ and nitrogen gas flow rates of 200 mL $min^{-1}$.

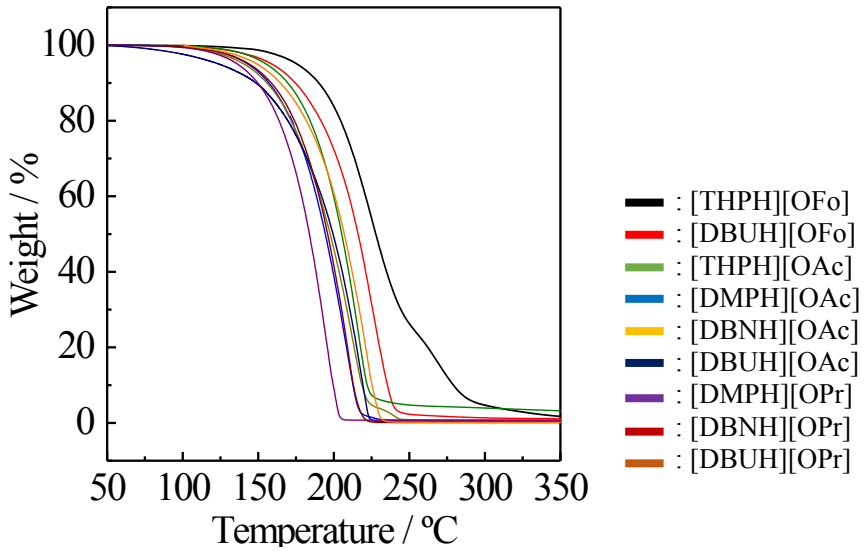


Figure S1 TG curves of PILs.

The melting temperature ($T_m$) was measured using DSC (DSC7020, Hitachi High-Technologies) in the range of -100 and 100 °C at the heating and cooling rates of 10°C $min^{-1}$, and nitrogen gas flow rates of 40 mL $min^{-1}$. The samples were tightly sealed in Al pans under Ar atmosphere in a dry glove box.

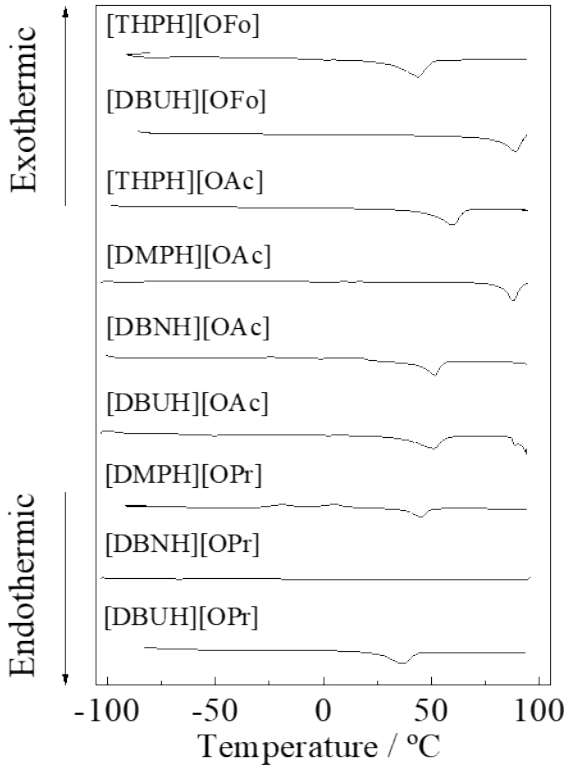


Figure S2 DSC curves of PILs.

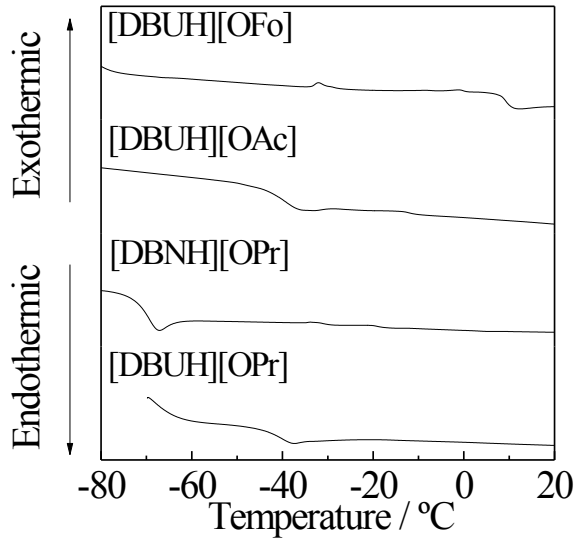


Figure S3 Expanded DSC curves of [DBUH][OFo], [DBUH][OAc], [DBNH][OPr], and [DBUH][OPr] (from -80 to 20 ℃).

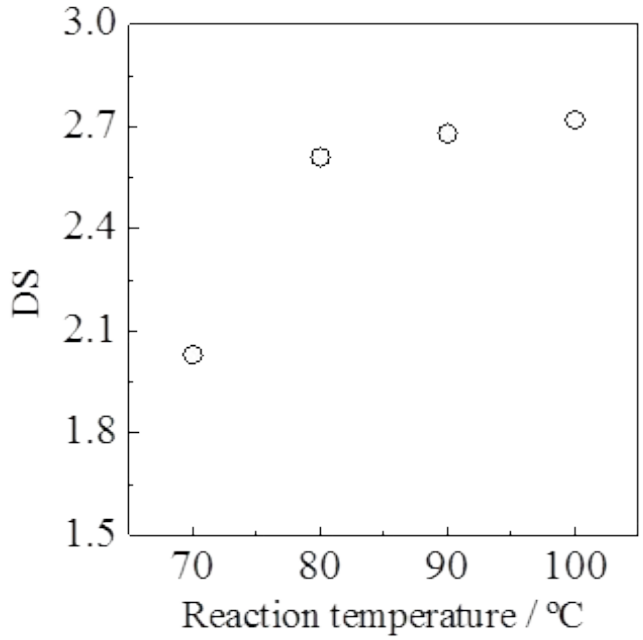


Figure S4 Effect of acetylation temperature on DS values in [DBUH][OAc] (acetylation time: 24 h, cellulose: 5 wt%, $Ac_2O$: 3 equivalent to AGU).

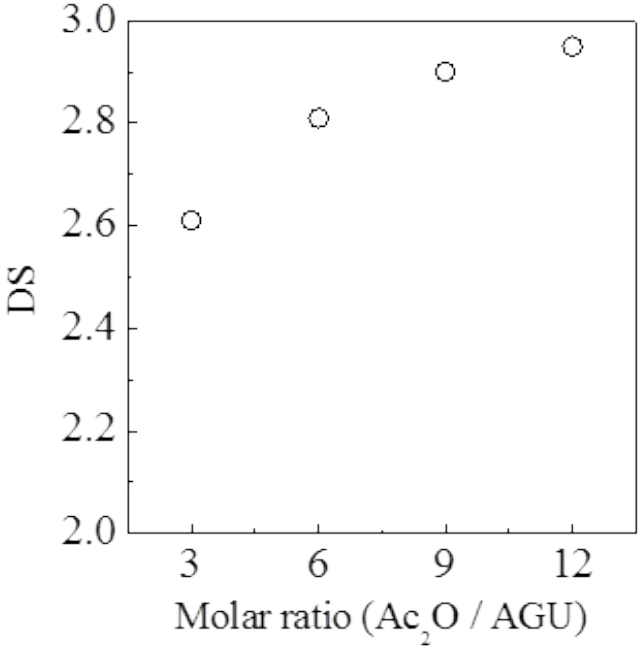


Figure S5 Effect of $Ac_2O$-to-AGU molar ratio on DS values in [DBUH][OAc] (acetylation temperature: 80 °C, acetylation time: 24 h, cellulose: 5 wt%).

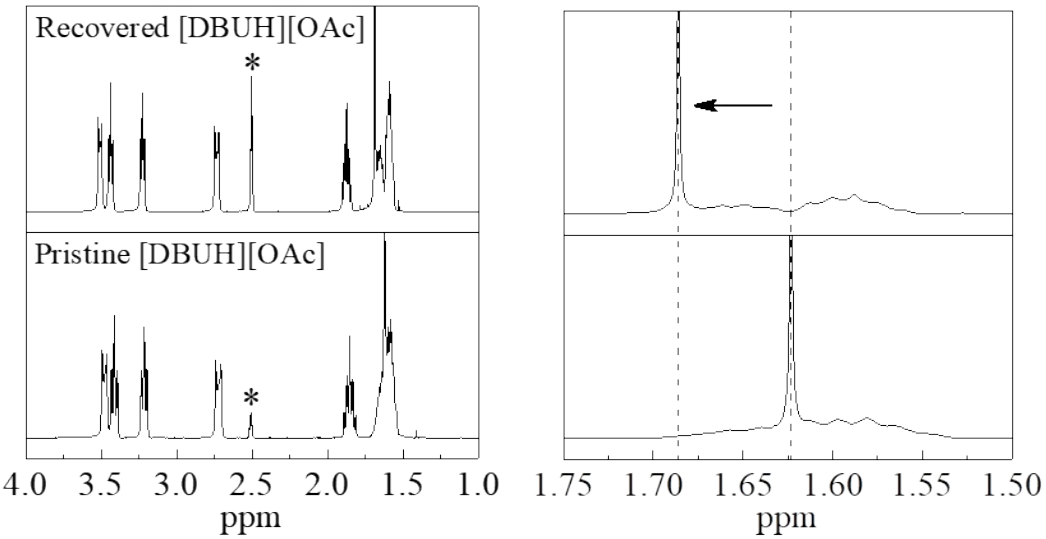

Figure S6 (a) $^1$H NMR spectra of recovered [DBUH][OAc] by the distillation under reduced pressure at 190 °C and the pristine one in DMSO-$d_6$ (*solvent) and (b) enlarged $^1$H NMR spectra in the range of 1.50 and 1.75 ppm.

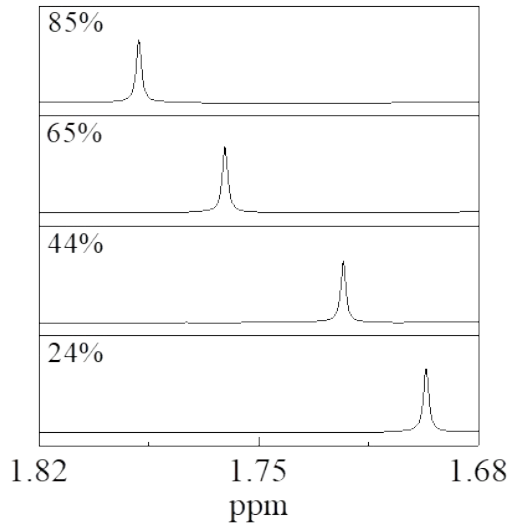


Figure S7 $^1$H NMR spectra of [DBUH][OAc] with excess amounts of AcOH (the excess molar number of AcOH to [DBUH][OAc] is expressed in percentage) in DMSO-$d_6$.

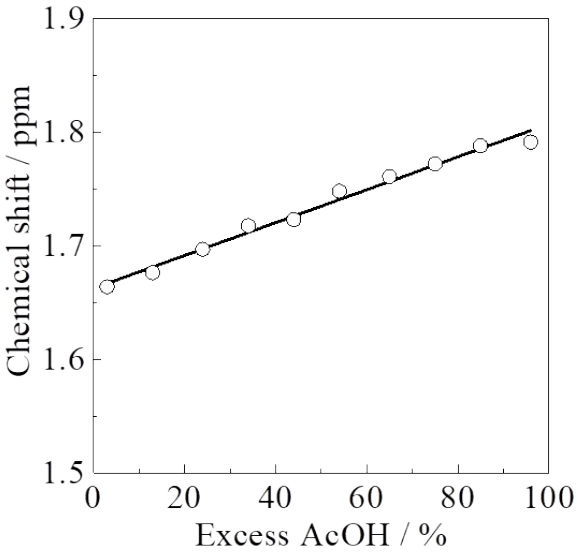


Figure S8 Relation between the chemical shift of methyl group of AcOH in [DBUH][OAc] and the excess amount of AcOH.

**Table S1** Collection rate of [DBUH][OAc] by distillation.

| Distillation condition | | Collection rate / % |
|---|---|---|
| Temperature / °C | Pressure / kPa | |
| 170 | 0.4 | 67 |
| 190 | 0.5 | 80 |
| 210 | 0.5 | 82 |

**Table S2** DS values of CA obtained in the recovered [DBUH][OAc].

| Recycled time | Excess AcOH [a] / % | DS values of CA [b] |
|---|---|---|
| 0 (pristine) | 0 | 2.73 |
| 1 | 17 | 2.17 |
| | 0 | 2.56 |
| 2 | 35 | 2.07 |
| | 0 | 2.31 |
| 3 | 40 | 1.99 |
| | 0 | 2.22 |

[a] Determined by the calibration curve. [b] Determined by $^{1}$H NMR.