Supplementary information

Possible Means of Realizing a Sacrifice-free Three Component Separation of Lignocellulose from Wood Biomass Using an Amino Acid Ionic Liquid

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1. General procedures

Reagents and solvents were purchased from common commercial sources and were used as received or purified by distillation over appropriate drying agents. Reactions requiring anhydrous conditions were carried out under argon with dry, freshly distilled solvents and magnetic stirring. ^{1}H-NMR spectra and ^{13}C-NMR spectra were recorded on a JEOL JNM ECP500 spectrometer. Chemical shifts are expressed in ppm downfield from tetramethylsilane (TMS) in $CDCl_3$ as an internal reference. The water content of ILs was measured by Karl Fischer method using an 831 KF Coulometer (Metrohm, Ltd.).

2. Observation of dissolution of lignin in [P_{1ME}][Lys] and recovery of the IL

The dissolution process of lignin (lignin, alkali: Aldrich 471003-100G) in the ILs can be simply observed by the light loupe. Optical observation was carried out with a loupe fitted with a hot stage. To 1.0 g of [P_{1ME}][Lys] in a 5 ml glass vial tube was added cellulose microfibers (weighted) and put on the hot stage at 60°C, then at 100°C. The process of dissolution was monitored until lignin fibrils in the eye completely dissolved. We conducted dissolution experiments using ILs which included less than 800 ppm (0.08 wt%) water and we

confirmed that there was no difference in dissolution ability between [P_{1ME}][L-Lys] and [P_{1ME}][DL-Lys]. The recovery of ILs was accomplished by evaporating water from the precipitation liquid and dried under reduced pressure at 50°C for 5 h at 1.0 torr.

3. Preparation of regenerated lignin and solvent recovery

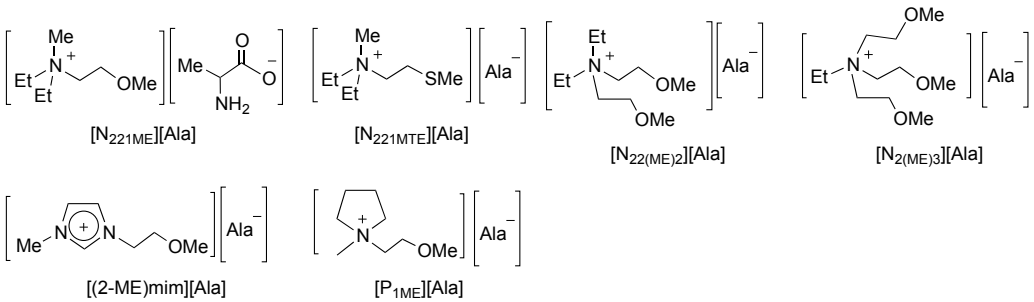
Lignin samples were dried at rt (25°C) for 2 h in a vacuum oven before use. A known weight of lignin sample was dispersed into 1.0 g of [P_{1ME}][Lys] in a 5 ml vial tube, and the mixture was heated and stirred until the sample was completely dissolved (less than 1 h). Finally, a transparent dark brownish lignin solution with about 40 wt% (vs. IL) concentration was obtained. After cooling to rt, the solution coagulated in the ethanol and to transparent regenerated lignin was obtained. The regenerated lignin was washed with running distilled water and dried at rt in a vacuum oven. The dry regenerated lignin films were frozen in liquid nitrogen, fractured, and vacuum-dried; the regenerated films were then cut into strips 10 mm long and 15 mm wide to measure the X-ray diffraction patterns. These patterns with Cu KR radiation ((*ì*) 1.5406 Å at 40 kV and 40 mA were then recorded in the range of 2*õ*) 5-40° by an X-ray diffraction diffractometer (Rigaku Ultima IV, Rigaku Denki, Japan).

4. Dissolution test of lignin

Table S-1. Results of dissolution test of lignin in various types of N-methyl-N-(2-methoxyethyl)pyrolidin-1-ium salts

Entry	IL	Solubility (wt % vs. solvent)		
		60°C	100°C	Total
1	[N_{221ME}][Ala]	5	15	20
2	[N_{221MTE}][Ala]	5	15	20
3	[$N_{22(ME)2}$][Ala]	5	15	20
4	[$N_{2(ME)3}$][Ala]	0	10	10
5	[(2-ME)mim][Ala]	0	13	13
6	[P_{1ME}][Ala]	20	15	35

[a] Since the resulting mixture was obtained as a black jelly-like sol, it was unsuccessful to observe further dissolution of lignin.



5. XRD and IR measurements of commercial lignin

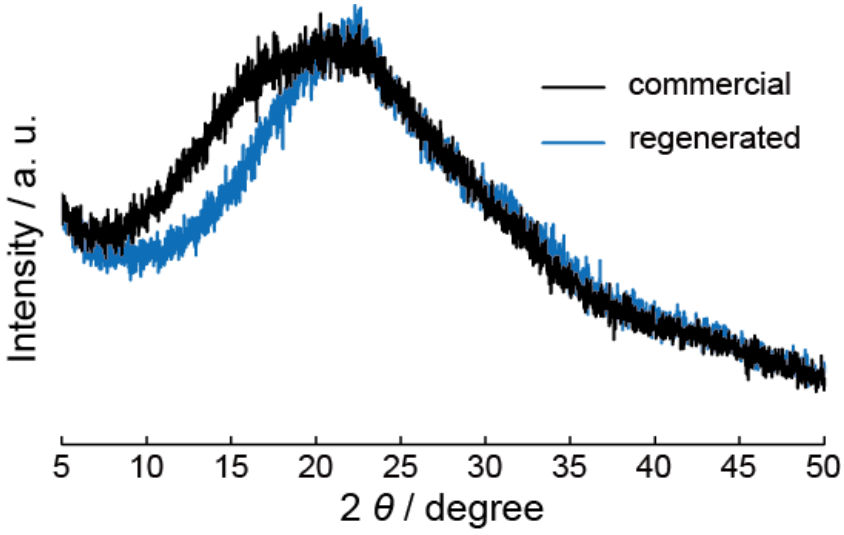


Figure S-1. XRD spectra of commercial available lignin (lignin, alkali: Aldrich 471003-100G) and the same lignin regenerated from the IL solution.

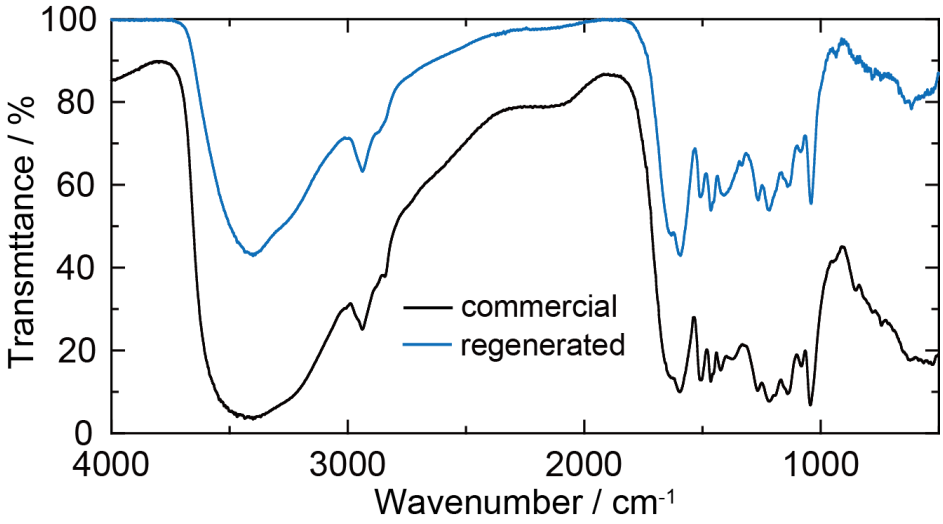


Figure S-2. IR spectra of commercial lignin (lignin, alkali: Aldrich 471003-100G) and the same lignin regenerated from the IL solution.

Elemental analysis of commercial lignin (Aldrich 471003-100G): Found: C, 49.91; H, 5.22; N, 0.00. (No nitrogen was detected).

6. XRD and IR measurements of lignin from Japanese cedar

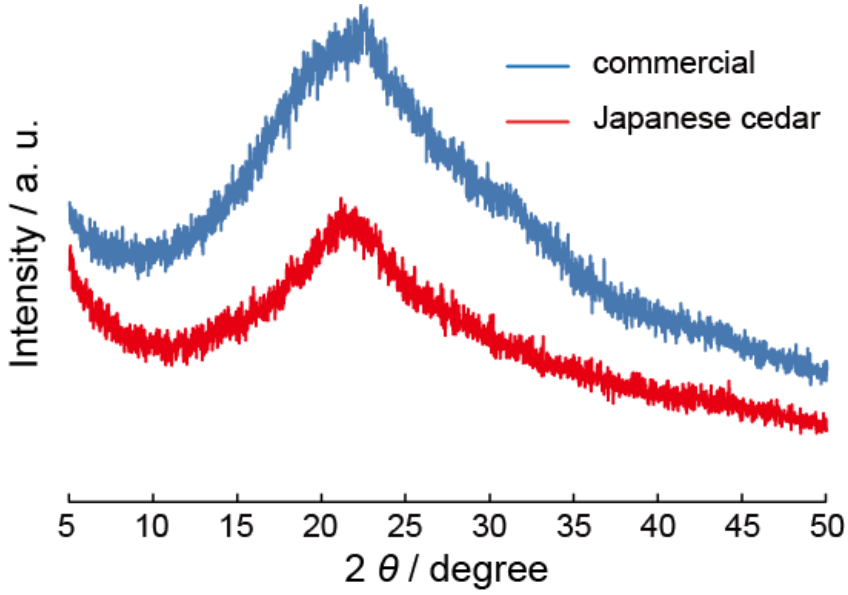


Figure S-3. XRD spectra of the lignin regenerated from the IL solution of commercial lignin (lignin, alkali: Aldrich 471003-100G) and Japanese cedar.

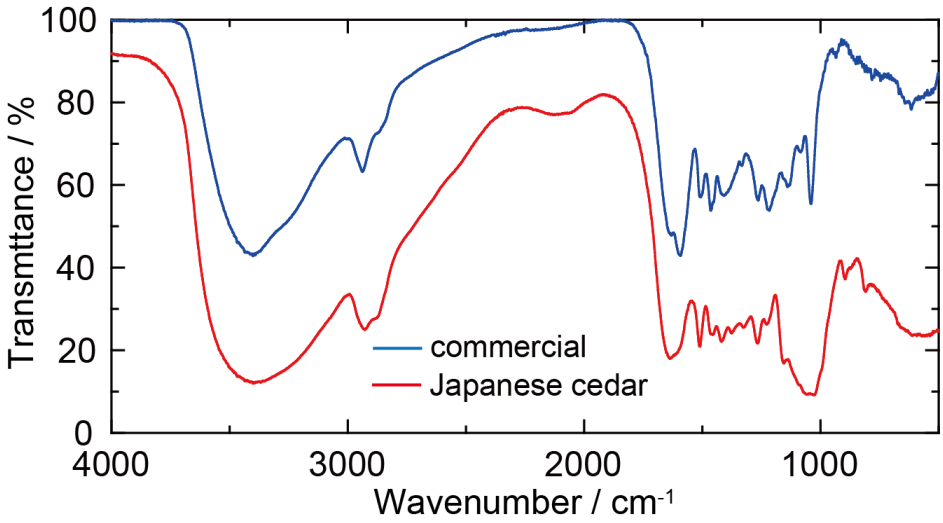


Figure S-4. IR spectra of lignins extracted from commercial lignin (lignin, alkali: Aldrich 471003-100G) and Japanese cedar.

Elemental analysis of lignin from Japanese cedar: Found: C, 49.10; H, 6.56; N, 0.53. Averaged results of three times measurements. A trace amount of nitrogen was detected, though it was a level closed to the calibration curve.

7. XRD and IR measurements of avicel and cellulose

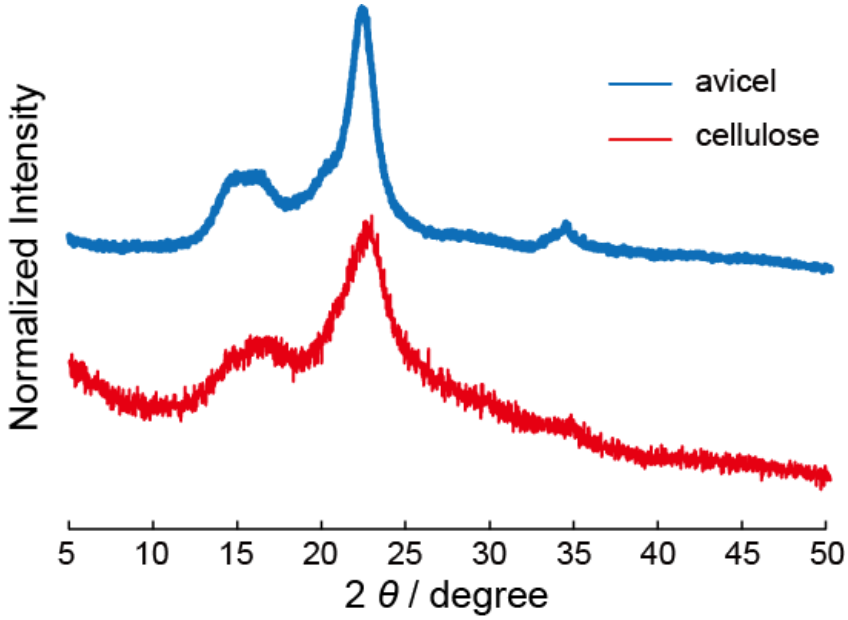


Figure S-5. XRD spectra of avicel (Avicel PH-101: Fluka 11365) and cellulose obtained from Japanese cedar.

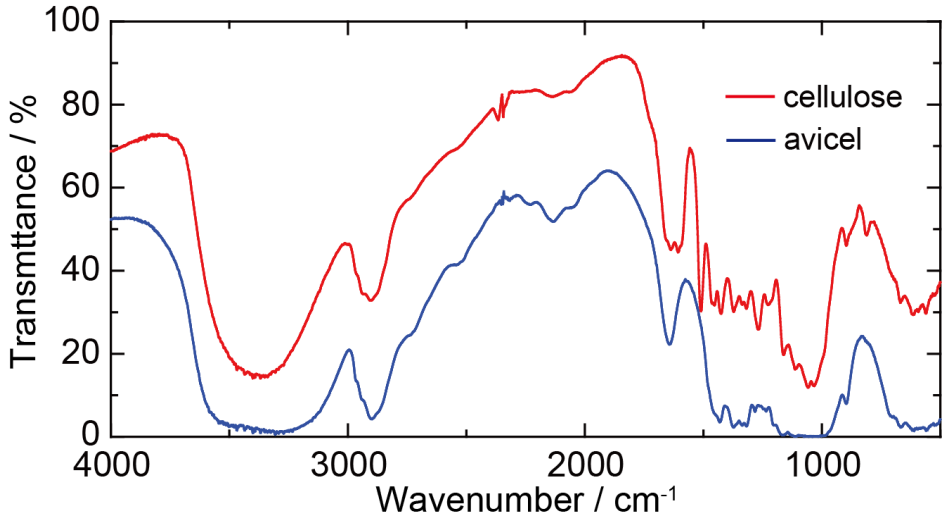


Figure S-6. IR spectra of avicel (Avicel PH-101: Fluka 11365) and cellulose obtained from Japanese cedar.

Elemental analysis of cellulose obtained from Japanese cedar: Calcd. for $C_6H_{10}O_5$: C 44.45; H, 6.22; N, 0.00. Found: C, 48.07; H, 6.40; N, 0.00. (No nitrogen was detected).

8. XRD and IR measurements of cellulose and hemicellulose

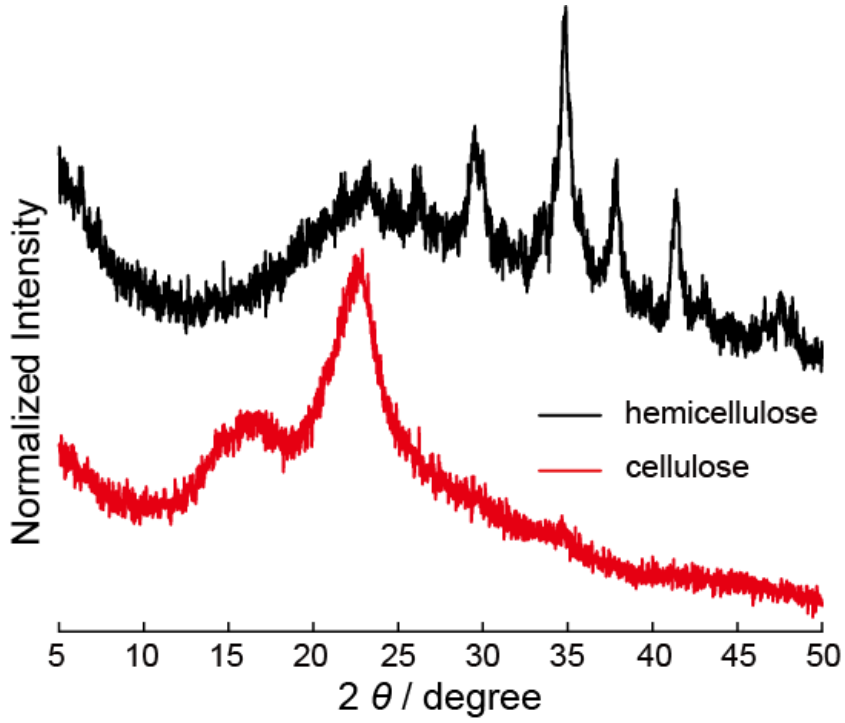


Figure S-7. XRD spectra of hemicellulose and cellulose extracted from Japanese cedar.

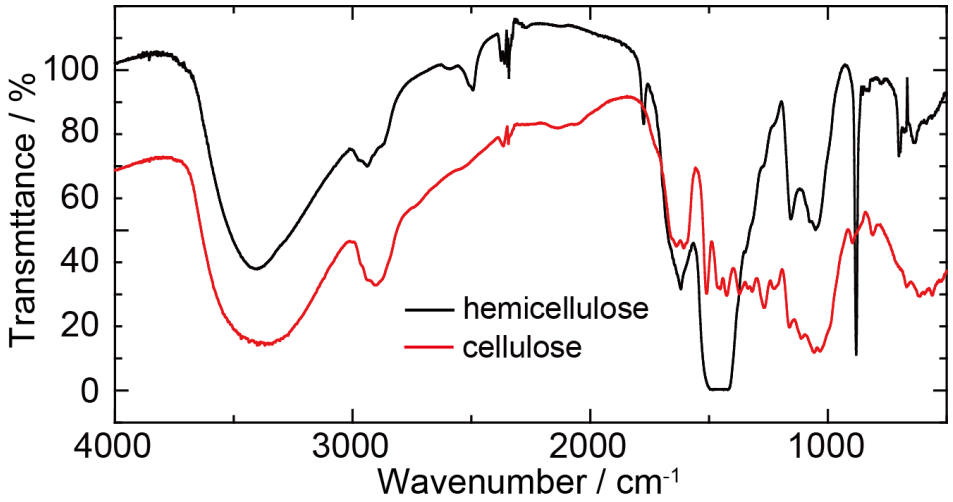


Figure S-8. IR spectra of hemicellulose and cellulose extracted from Japanese cedar.

Elemental analysis of hemicellulose extracted from Japanese cedar: Found: C, 47.04; H, 6.36; N, 0.00 (No nitrogen was detected).

9. Mass analysis of lignin

MALDI-QIT-TOF MS Spectrometry (MS/MS): Positive ion MALDI-TOF MS/MS spectra of the peptides were obtained by AXIMA-QIT (Shimadzu Corp., Kyoto, Japan) with a nitrogen laser operating at 337 nm. For collision-induced dissociation, argon was used as the collision gas. For MS/MS measurements, dried samples were dissolved in 10 μL of 75% acetonitrile and 0.1% trifluoroacetic acid. One-tenth (1 μL) of the solution was desalted by a C18 Zip-Tip and mixed on a stainless-steel target with 1 μL of the matrix solution (25 mg/mL DHB in 0.1% trifluoroacetic acid), and the mixture was dried under a gentle steam of air. In order to calibrate the mass spectra of peptides, angiotensin II (*m*/*z* 1046.54), adrenocorticotropic hormone (ACTH) fragment 18–39 (*m*/*z* 2465.20) were used. Mascot search was used for protein identification based on MALDI-QIT-TOF MS/MS spectra.

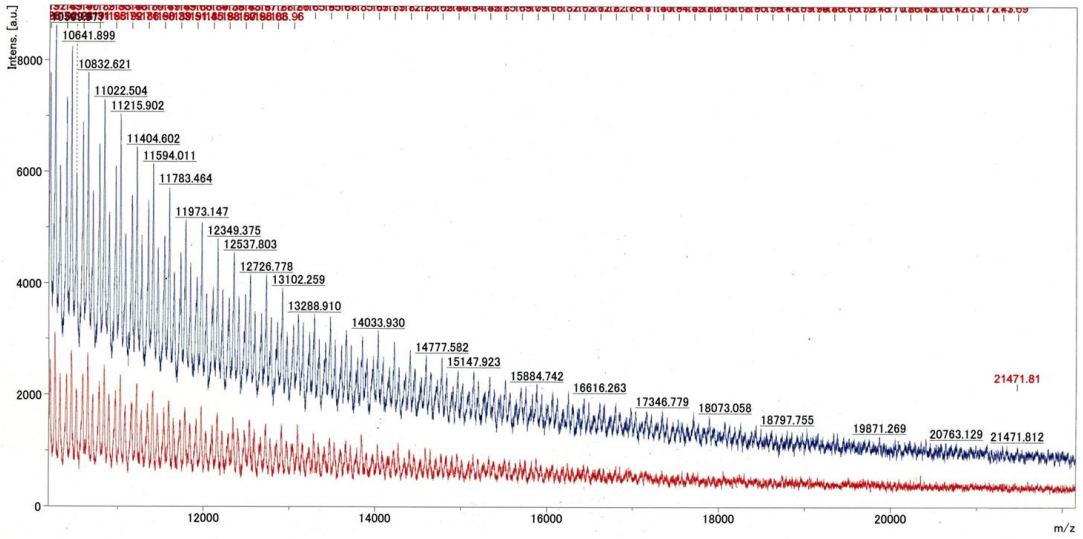


Figure S-9. MALDI-TOF-MS spectra of the lignin obtained from Japanese cedar.