Electronic Supplementary Material (ESI) for Green Chemistry.

Preparation of homogeneous lignin nanoparticles by efficient extraction of lignin and modification of its molecular structure using a functional deep eutectic solvent containing γ-valerolactone

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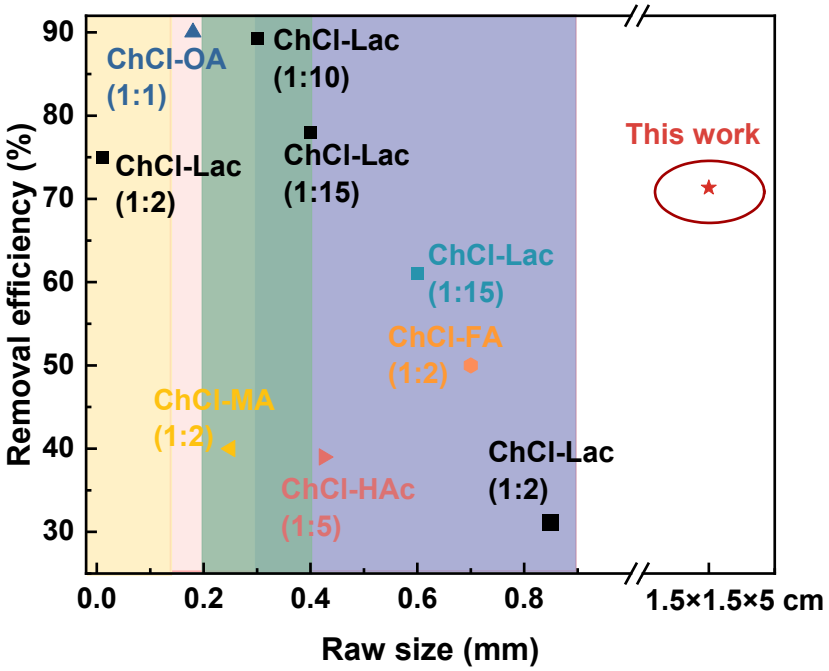

Fig. S1 Comparison of separation efficiency between this work (ChCl-5Saa/GVL) and previously reported green advance DES systems.

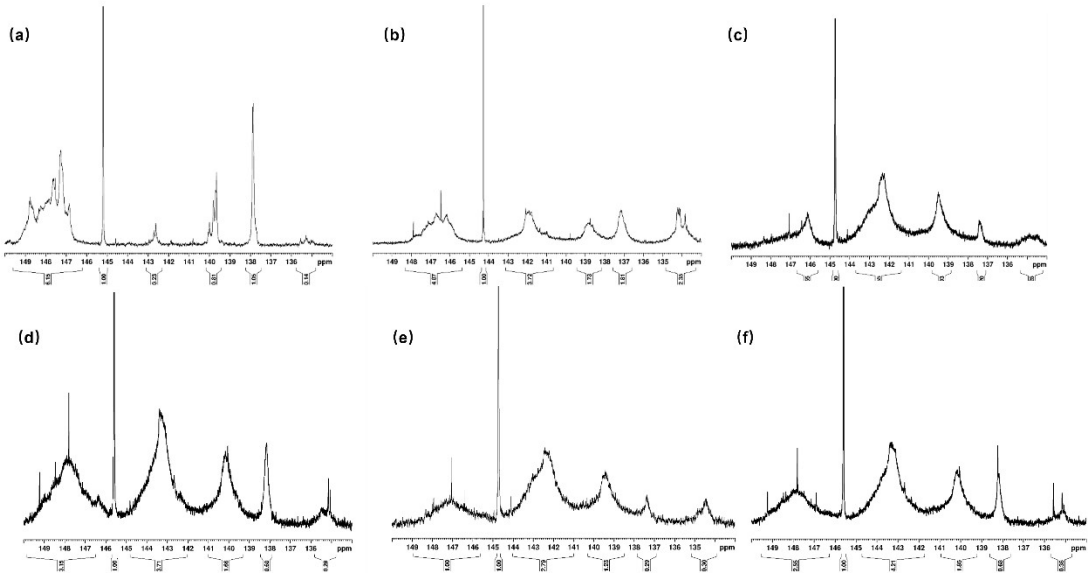

Fig. S2 ^{31}P NMR spectra and integrals (a, CEL; b, Alkali lignin; c, Regenerated lignin after ChCl-Lac treatment;d, Regenerated lignin after ChCl-5Saa/GVL treatment; e, residual lignin after ChCl-Lac treatment; f, residual lignin after ChCl-5Saa/GVL treatment).

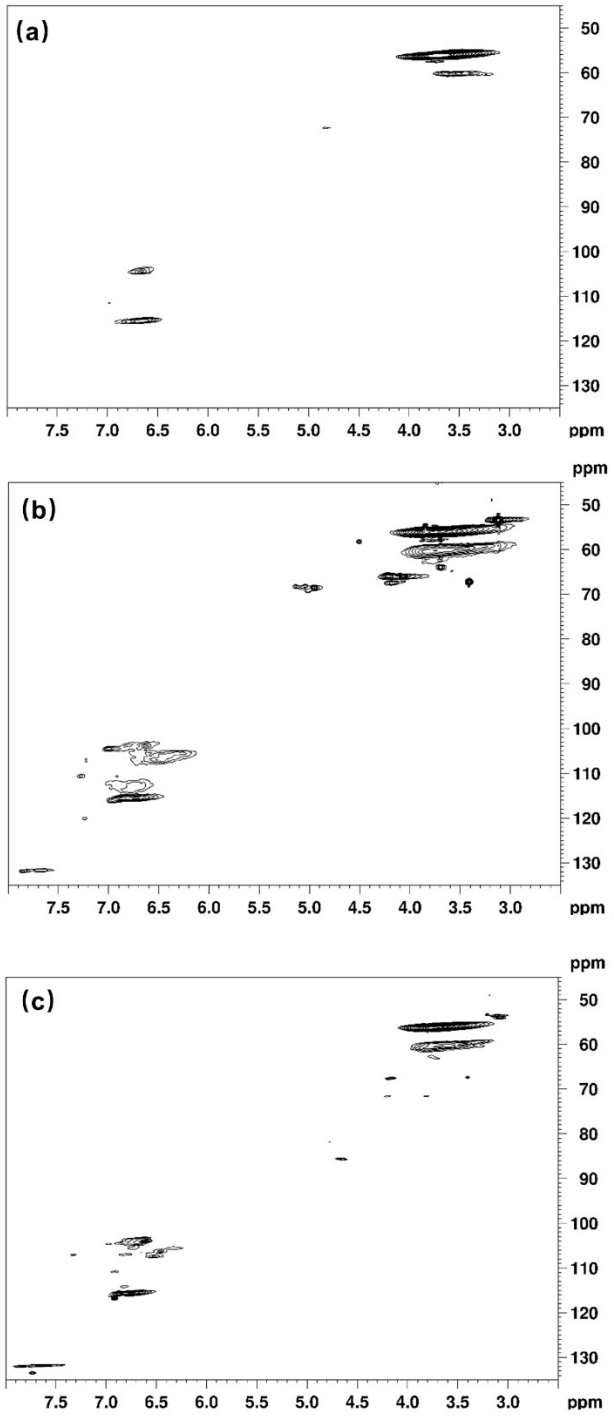

Fig. S3 Unaltered 2D-HSQC full-spectrum spectra of regenerated lignin treated with different DES systems (a, Alkali lignin; b, ChCl-Lac-Lignin; c, ChCl-5Saa/GVL-Lignin).

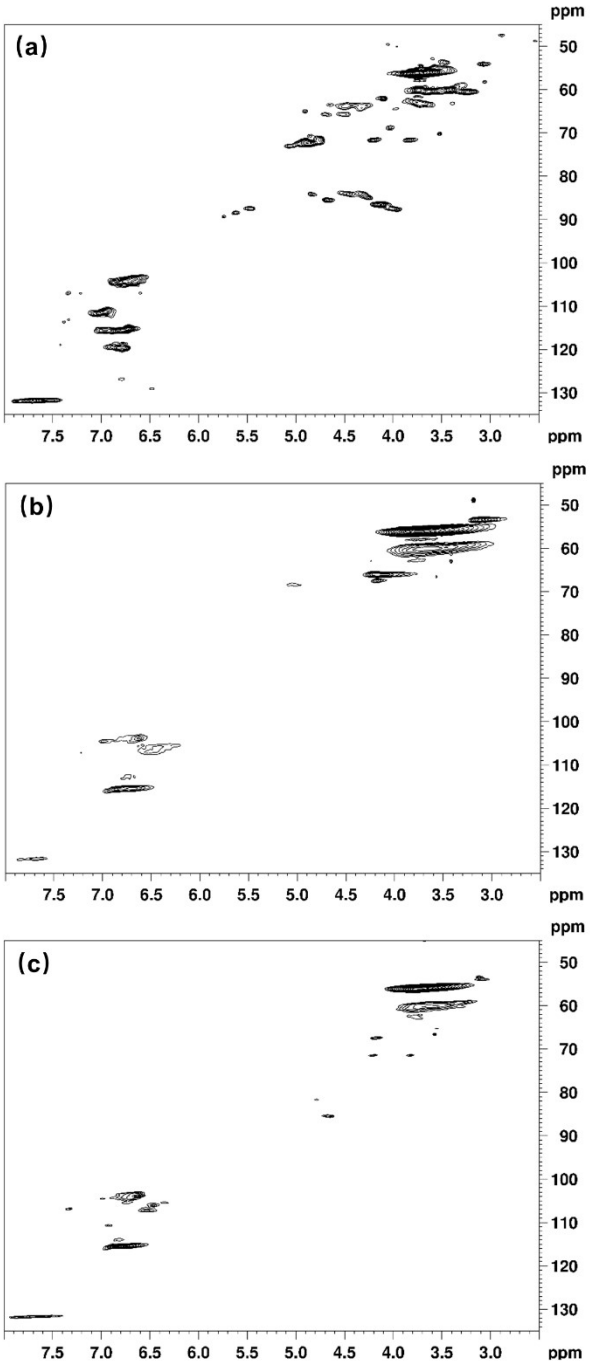

Fig. S4 Unaltered 2D-HSQC full-spectrum spectra of residual lignin in poplar before and after DES treatment (a, CEL; b, residual lignin after ChCl-Lac treatment; c, residual lignin after ChCl-5Saa/GVL treatment).

Table S1 Comparison of separation process conditions between this work (ChCl-5Saa/GVL) and previously reported green advance DES systems.

DESs (HBA:HBD)	Molar ratio	Feedstock	Condition	Lignin removal efficiency	References
ChCl-Lac	1:2	Poplar powder (ball mill 1 h)	110 °C, 9 h, 10%	75%	19
	1:2	Poplar powder (0.18 – 0.85 mm)	110 °C, 1.5 h, 10%	31.1%	37
	1:10	Poplar powder (0.18 – 0.85 mm)	130 °C, 1.5 h, 10%	89.3%	37
	1:15	Poplar powder (0.25 – 0.4mm)	145 °C, 6 h	78%	38
	1:15	oil palm empty fruit bunch (EFB) (0.250 – 0.707 mm)	120 °C, 8 h, 10%	61%	20
ChCl-OA	1:1	Poplar powder (0.18mm)	110 °C, 9 h, 5%	90%	39
ChCl-FA	1:2	EFB (0.250 –0.707 mm)	120 °C, 8 h, 10%	50%	40
ChCl-HAc	1:5	EFB (0.250 – 0.707 mm)	120 °C, 8 h, 10%	39%	20
ChCl-MA	1:2	EFB (0.250 – 0.707 mm)	120 °C, 8 h, 10%	40%	20
This work ChCl-5Saa/GVL	1:4:15	Poplar stick (1.5×1.5×5 cm)	120 °C， 3 h, 10%	71.35%	

ChCl-Lac: The choline chloride- lactic acid systems; ChCl-OA: The choline chloride-oxalic acid systems; ChCl-FA: The choline chloride- formic acid systems; ChCl-Hac: The choline chloride- acetic acid systems; ChCl-MA: The choline chloride- malic acid systems.

Table S2 Recycling performance of ChCl-5Saa/GVL treatment.

Cycles	Cellulose retention (%)	Lignin separation efficiency (%)	Hemicellulose separation efficiency (%)
0 (First pretreatment)	92.87	71.35	95.86
1	93.45	70.86	93.29
2	93.26	70.35	94.05
3	94.43	69.87	93.86
4	94.13	69.13	93.42
5	94.02	68.85	92.87

NMR of experimental methods:

1. ^{31}P NMR of quantification of OH groups

The OH groups of lignin were calculated by integrating the signal peaks by 31P NMR. Cyclohexanol was accurately formulated with pyridine and chloroform solvents, and chromium acetylpyruvate was used as a relaxation reagent. The signals of the internal standard cyclohexanol were used as a reference to calculate the content of various OH groups of lignin. Equation (1) was shown below:

$$\text{Content OH} = (\rho \times V \times 10^{-6}/M \times (A_2/A_1))/m \times 1000 \quad (1)$$

where A_1 is the integral area of the hydroxyl group in cyclohexanol. A_2 is the integral area of the hydroxyl group in the lignin structure. And m is the mass of the lignin sample (g). V is the volume of cyclohexanol added to the lignin (μL). M the molar mass of cyclohexanol ($g \cdot mol^{-1}$).

2. 2D HSQC of quantification of lignin inter-unit linkages

The NMR resolved lignin linkages and contents of lignin units were calculated based on the integrals of α-^{1}H/^{13}C correlation peaks verses the integrals of the aromatic-^{1}H/^{13}C correlation peaks in the 2D-HSQC spectra, equation (2)–(5) as follows:

$$C_9 = 1/2\ (I_{S2,6} + I_{S'2,6}) + G_2 \quad (2)$$

$$\text{Content } \beta\text{-O-4} = I_A/C_9 \times 100\% \quad (3)$$

$$\text{Content } \beta\text{-}\beta = I_B/C_9 \times 100\% \quad (4)$$

$$\text{Content } \beta\text{-5} = 0.5 \times I_C/C_9 \times 100\% \quad (5)$$