Supplementary materials

A functional deep eutectic solvent for lignocellulose valorization via lignin stabilization and cellulose functionalization

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This document includes:

Fig. S1 The X-ray diffraction profiles of cellulose residues after pretreatment with different DES solutions (a) and pretreatment conditions (b).
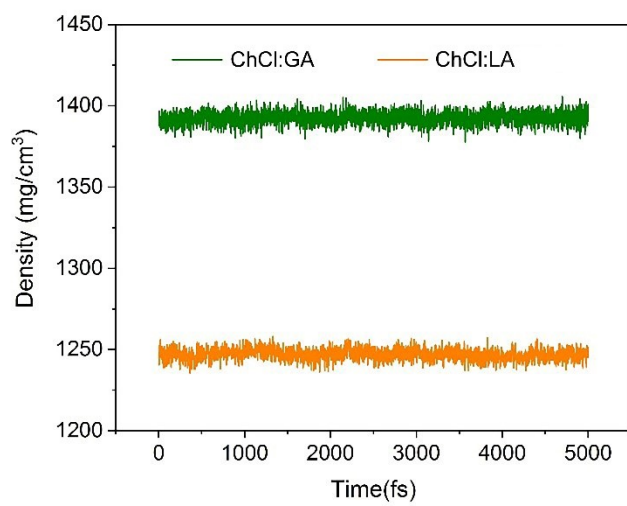
Fig. S2 The density of different DES solution.
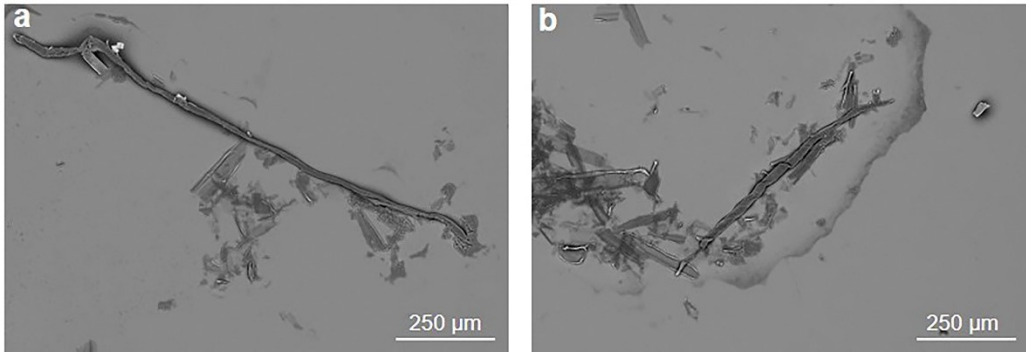
Fig. S3 The SEM images of fibers pretreated at 110 °C (a) and 130 °C (b).
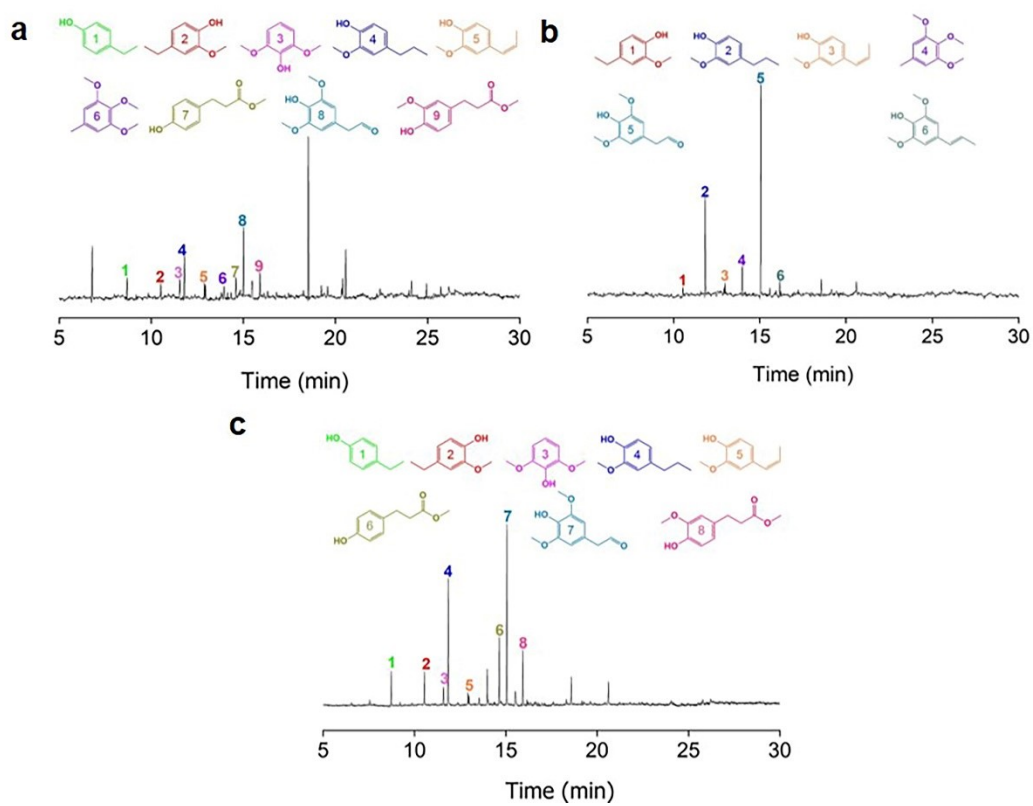
Fig. S4 The original depolymerization images of MWL (a), GSL (b), and LAL (c).
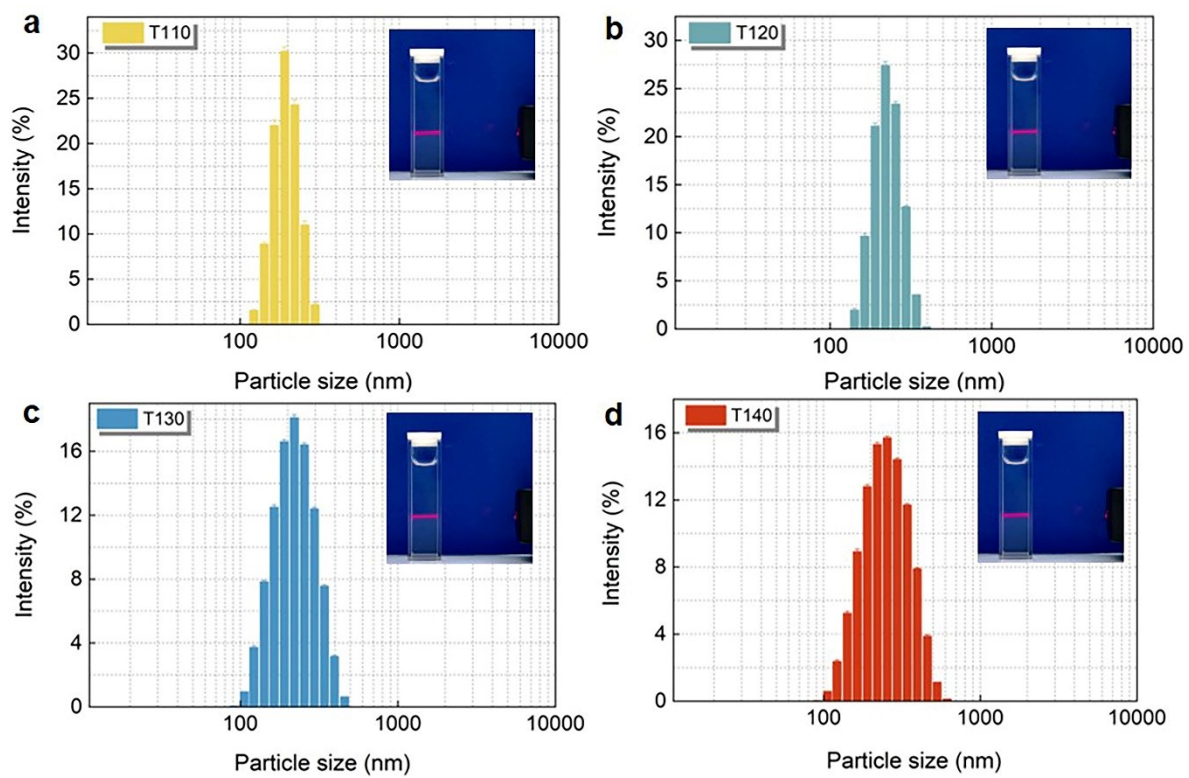
Fig. S5 The size distribution of GSL nanoparticles.
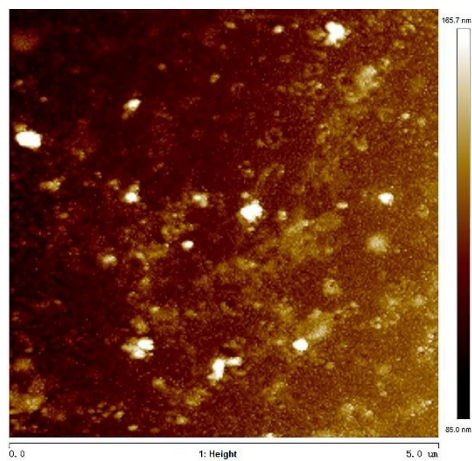
Fig. S6 The AFM image of LNPs.

Table S1 The employed condition in pretreatment process

Sample	Temperature (^{o}C)	Molar ratio	Time (min)
Original	/	/	/
T110	110	ChCl:GA=1:2	60
T120	120	ChCl:GA=1:2	60
T130	130	ChCl:GA=1:2	60
T140	140	ChCl:GA=1:2	60
1:2	130	ChCl:GA=1:2	60
1:3	130	ChCl:GA=1:3	60
1:4	130	ChCl:GA=1:4	60
1:5	130	ChCl:GA=1:5	60
ChCl:GA	130	ChCl:GA=1:4	30
ChCl:LA	130	ChCl:LA=1:4	30
30 min	130	ChCl:GA=1:4	30
60 min	130	ChCl:GA=1:4	60
90 min	130	ChCl:GA=1:4	90
120 min	130	ChCl:GA=1:4	120

Table S2 The main chemical components and solid yield of different pretreated samples

Sample	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Original	43.20 ± 1.96	22.46 ± 2.43	21.53 ± 2.05
T 110	35.76 ± 1.27	11.75 ± 1.09	17.34 ± 1.92
T 120	34.61 ± 1.41	5.82 ± 0.66	8.28 ± 0.96
T 130	34.50 ± 1.78	4.13 ± 0.58	4.32 ± 0.49
T 140	34.14 ± 1.06	2.53 ± 0.40	1.49 ± 0.26
1:2	34.50 ± 1.78	4.13 ± 0.58	4.32 ± 0.49
1:3	33.88 ± 0.99	3.07 ± 0.26	2.03 ± 0.34
1:4	33.48 ± 0.84	2.86 ± 0.31	1.31 ± 0.20
1:5	31.97 ± 1.03	2.54 ± 0.33	0.96 ± 0.16
ChCl:GA	33.71 ± 1.00	3.33 ± 0.54	2.15 ± 0.35
ChCl:LA	34.38 ± 1.26	12.19 ± 2.11	15.36 ± 1.80
30 min	33.71 ± 1.00	3.33 ± 0.54	2.15 ± 0.35
60 min	33.48 ± 0.84	2.86 ± 0.31	1.31 ± 0.20
90 min	32.04 ± 0.73	2.46 ± 0.41	0.84 ± 0.07
120 min	29.59 ± 0.80	2.03 ± 0.29	0.41 ± 0.06

Table S3 The viscosities of DES with different molar ratios at different temperatures

Molar ratio	Viscosity (mPa·s)	Temperature (º C)
ChCl:GA=1:2	2002 ± 11	20
ChCl:GA=1:3	1550 ± 20	20
ChCl:GA=1:4	1064 ± 17	20
ChCl:GA=1:5	996 ± 32	20
ChCl:GA=1:2	91 ± 8	130
ChCl:GA=1:3	75 ± 3	130
ChCl:GA=1:4	54 ± 1	130
ChCl:LA=1:5	49 ± 2	130

Table S4 The physical morphology of collected fibers at various pretreatment conditions

Sample	Length (mm)	Width (um)
T 110	0.48 ± 0.06	44.90 ± 0.71
T 120	0.36 ± 0.02	28.95 ± 0.05
T 130	0.35 ± 0.01	25.30 ± 0.20
T 140	0.37 ± 0.04	25.10 ± 0.20
1:2	0.35 ± 0.01	25.30 ± 0.20
1:3	0.35 ± 0.01	25.40 ± 0.08
1:4	0.39 ± 0.05	25.38 ± 0.25
1:5	0.40 ± 0.09	25.50 ± 0.16
ChCl:GA	0.36 ± 0.01	25.28 ± 0.04
ChCl:LA	0.59 ± 0.07	40.00 ± 1.85
30 min	0.36 ± 0.01	25.28 ± 0.04
60 min	0.39 ± 0.05	25.38 ± 0.25
90 min	0.38 ± 0.02	25.50 ± 0.16
120 min	0.36 ± 0.01	25.10 ± 0.14

Table S5 The pretreatment condition used in enzymatic hydrosis process

Sample	Temperature (^{o} C)	Molar ratio	Time (min)
T110-GA	110	ChCl:GA=1:4	30
T120-GA	120	ChCl:GA=1:4	30
T130-GA	130	ChCl:GA=1:4	30
T130-LA	130	ChCl:LA=1:4	30

Table S6 The main cross-signals and corresponding groups of the benzene ring and side-chain

Label	δ_C/δ_H (ppm)	Assignment
GA_1	96.0/5.11	1,3-dioxane (acetal) structure
$GA\alpha$	82.0/4.63	$C\alpha$-$H\alpha$ in stable lignin structure
$GA\beta$	73.5/4.30~4.40	C_β–H_β in stable lignin structure
$GA\gamma$	67.0/3.82	$C\gamma$-$H\gamma$ in stable lignin structure
$A\alpha$	72.1/4.88	$C\alpha$-$H\alpha$ in β-O-4′substructures (A)
$A\gamma$	60.0/3.72	$C\gamma$-$H\gamma$ in β-O-4′substructures (A)
$A'\gamma$	63.5/4.25	$C\gamma$–$H\gamma$ in γ-acylated β–O–4′substructures (A′)
$A\beta(G)$	84.1/4.35	C_β–H_β in β-O-4' linked to G unit (A)
$A\beta(S)$	87.0/4.13	C_β–H_β in β-O-4' linked to S unit (A)
$B\alpha$	85.2/4.69	$C\alpha$-$H\alpha$ in phenylcoumaran substructures (B)
$B\gamma$	71.9/3.87~4.21	$C\gamma$-$H\gamma$ in phenylcoumaran substructures (B)
$C\beta$	53.8/3.08	C_β-H_β in β-β'resinol substructures (C)
$C\gamma$	62.8/3.85	$C\gamma$-$H\gamma$ in β-β'resinol substructures (C)
$-OCH_3$	56.1/3.76	C-H in methoxyls
$S_{2,6}$	104.2/6.72	$C_{2,6}$-$H_{2,6}$ in syringyl units (S)
G_2	111.1/6.95	C_2–H_2 in guaiacyl units (G)
G_5	116.1/6.81	C_5–H_5 in guaiacyl units (G)
G_6	119.5/6.82	C_6–H_6 in guaiacyl units (G)
$PCA_{2,6}$	130.8/7.50	$C_{2,6}$-$H_{2,6}$ in p-coumaric acid (PCA)
$PB_{2,6}$	131.1/7.57	$C_{2,6}$-$H_{2,6}$ in p-benzoate (PB)

Table S7 The quantification of the major inter-unit linkages in lignin by 2D HSQC NMR spectroscopy

Sample	β-O-4	β-5	β-β	S/G
MWL	85.57%	10.80%	3.63%	3.50
GSL	69.39%	14.83%	15.78%	2.40
LAL	74.64%	21.10%	4.26%	3.61

Table S8 The pretreatment condition used in preparation of lignin nanoparticles

Sample	Temperature (° C)	Molar ratio	Time (min)
T110	110	ChCl:GA=1:4	30
T120	120	ChCl:GA=1:4	30
T130	130	ChCl:GA=1:4	30
T140	140	ChCl:GA=1:4	30

Table S9 The abbreviations used and their detailed explanations

Abbreviation	Explanation
DES	Deep Eutectic Solvent
ChCl	Choline Chloride
GA	Glyoxylic Acid
LA	Lactic Acid
ChCl:GA DES	the DES composed of ChCl and GA
ChCl:LA DES	the DES composed of ChCl and LA
LNPs	Lignin Nanoparticles
SPF	Sun Protection Factor
T130M1:4t30	the pretreatment was carried out under the conditions of $130\,^{\circ}$ C, a molar ratio of ChCl:GA of 1:4, and a pretreatment time of 30 min
MWL	Milled Wood Lignin
GSL	the Extracted Lignin with ChCl:GA DES
LAL	the Extracted Lignin with ChCl:LA DES

SDF movie of GA and MOL.mp4

Movie S1 The SDF movie of GA and MOL**.**

SDF movie of LA and MOL.mp4

Movie S2 The SDF movie of LA and MOL.