Supporting Information

Computational Modeling-guided Design of Deep Eutectic Solvents for Tailoring Lignin Chemistry during Lignocellulose Pretreatment

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1. Deep eutectic solvent (DES) characterization methods

Fourier transform infrared (FT-IR) spectra of these DES were recorded by a Thermo Scientific Nicolet iS20 instrument during 500~4000 cm^{-1} wavenumber under the conditions of 32 scans and a resolution of 4 cm^{-1}.

2. Lignin characterizations methods

The lignin regenerated from different DES was observed by a Thermo Scientific Nicolet iS20 instrument at the same condition of DES characteristics.

Two-dimensional heteronuclear single quantum coherence nuclear magnetic resonance (2D-HSQC NMR) was performed through a Bruker AscendTM 600 MHz spectrometer. The detailed procedures and acquisition parameters could be referred to in previous publications. The acquisition parameters were as follows: 166 ppm spectral width in F1 (13C) dimension with 256 data points and 12 ppm spectral width in F2 (1H) dimension with 1024 data points, a JC-H of 145 Hz, a 1.0 s pulse delay, and 128 scans.

According to our previous study, the lignin hydroxyl groups were determined by ^{31}P NMR. It was also performed on the Bruker 600 MHz instrument. In brief, ~20 mg of the dried lignin sample was weighed into an NMR tube, and then 0.4 mL anhydrous pyridine and deuterated chloroform (1.6 : 1, v/v) were added to dissolve the samples. Then, 0.15 mL of mixed solution composed of cyclohexanol (internal standard) and chromium acetylacetonate (relaxation) was injected using a Hamilton syringe. An excessive amount (~0.1 mL) of phosphitylation reagent 2-chloro-4,4,5,5-tetramethyl- 1,3,2-dioxaphospholane (TMDP) was introduced to react with the mixture, then the mixture was immediately transferred into the NMR tube and then subjected to the test.

The molecular weight of lignin was measured by gel permeation chromatography (GPC) (Agilent, USA). Before the analysis, 4 mg of samples were first acetylated using 2 mL of the pyridine/acetic anhydride (1: 1, v : v) solvent under magnetic stirring for 24 h. After acetylation, the samples were further dissolved in THF, and then subjected to GPC analysis.

Table S1. Composition of maple wood before and after different DES pretreatments

DES	Solid recovery (%)	Lignin removal (%)	Composition of solid part (%)		
			Cellulose	Hemicellulose	Lignin
[Ch][Cl]-Ethylene Glycol	96.0	26.8	40.0±0.5	13.5±0.3	15.2±0.5
[Ch][Cl]-Catechol	94.0	26.4	43.1±0.3	13.8±0.2	15.7±0.6
[Ch][Cl]-Urea	93.2	32.2	41.2±0.4	12.7±0.2	14.6±0.4
[Ch][Cl]-Lactic Acid	76.1	71.3	67.9±0.7	5.4±0.2	7.6±0.3
[Ch][Cl]-Oxalic Acid	71.2	80.6	69.6±0.6	4.7±0.1	5.3±0.4
DBU-Lactic Acid	87.2	34.6	40.9±0.5	13.1±0.5	15.0±0.4
Betaine-Lactic Acid	96.2	10.4	38.8±0.5	11.6±0.4	18.6±0.5
[BTEA][Cl]-Lactic Acid	70.9	70.7	63.8±0.9	8.9±0.3	8.2±0.2
[TEA][Cl]-Lactic Acid	70.8	62.0	54.1±0.6	6.9±0.2	10.7±0.3
Maple wood	N/A	N/A	35.2±0.4	15.1±0.3	20.4±0.4

Table S2. The β-O-4 and β-5 bond content of lignin and activity coefficients in 9 DES (lignin-carbohydrate complexes models)

			ln r			
DES	**β-O-4**	**β-5**	**glucose-HG-lignin**	**glucose-SS-lignin**	**glucose-GG-lignin**	**glucose-SG-lignin**
[Ch][Cl]: Ethylene Glycol	29	6	0.065197	0.201323	0.114438	-0.01228
[Ch][Cl]: Catechol	28	2.4	-0.15229	-0.02556	-0.11755	0.074755
[Ch][Cl]: Urea	26	0	-0.31169	-0.08055	-0.26356	0.096446
[Ch][Cl]: Lactic Acid	0	3.4	-0.12795	0.051505	-0.08138	0.164747
[Ch][Cl]: Oxalic Acid	0	0	-0.34112	-0.15291	-0.30288	0.007769
DBU: Lactic Acid	47	11.1	-0.02943	0.00023	-0.02561	0.286997
Betaine: Lactic Acid	15	11.6	-0.09647	0.046979	-0.05991	0.137006
[BTEA][Cl]: Lactic Acid	2.4	2.9	-0.29036	-0.11773	-0.25871	-0.01074
[TEA][Cl]: Lactic Acid	2.2	1	-0.29667	-0.12161	-0.26162	-0.01208

Table S3. Multivariate analysis of lignin models

	Pillai	F stats	P-value	Model
x1	0.95263	20.1117	0.04737	HG-lignin
x2	0.60158	1.5099	0.39842	SS-lignin
x4	0.16365	0.1957	0.83635	SG-lignin
x1:x2	0.8119	4.3164	0.1881	HG+SS-lignin
x1:x4	0.51141	1.0467	0.48859	HG+SG-lignin
x5	0.96786	30.1101	0.03214	glucose-HG-lignin
x6	0.91053	10.1768	0.08947	glucose-SS-lignin
x7	0.58959	1.4366	0.41041	glucose-GG-lignin
x8	0.62767	1.6858	0.37233	glucose-SG-lignin
x7:x8	0.96860	30.8496	0.03140	glucose-GG+glucose-SG-lignin

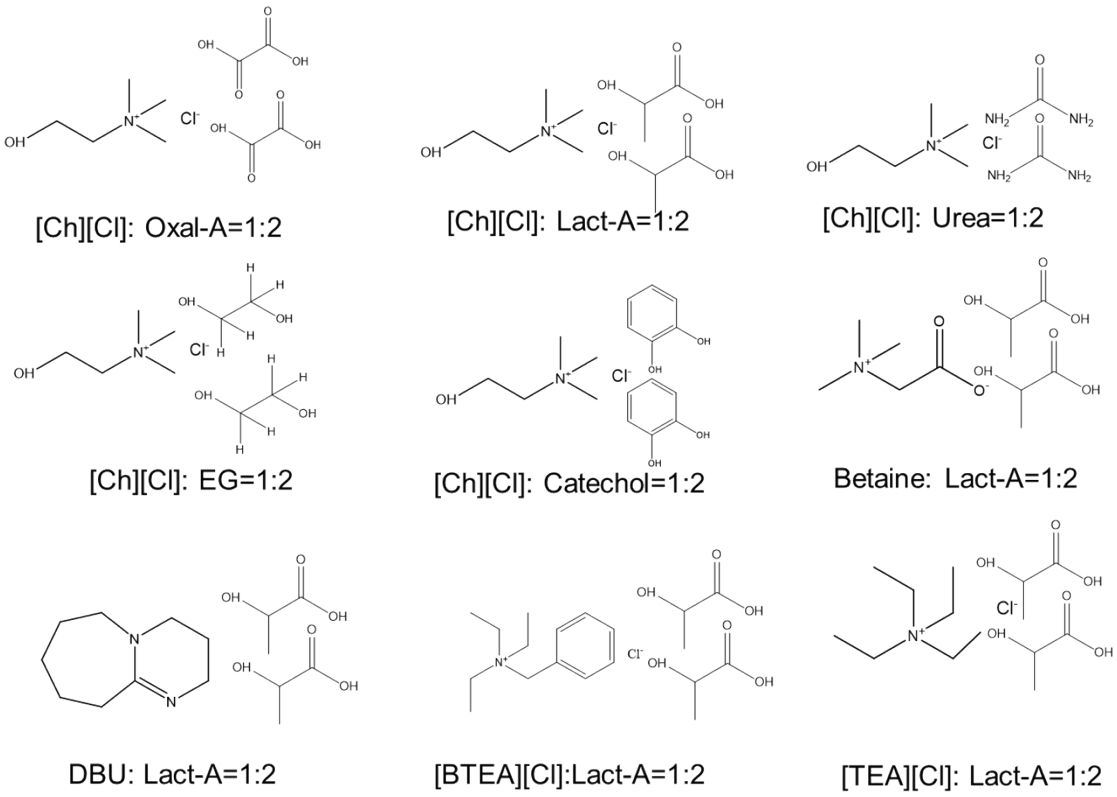

Figure S1. The structures of the synthesized DES.

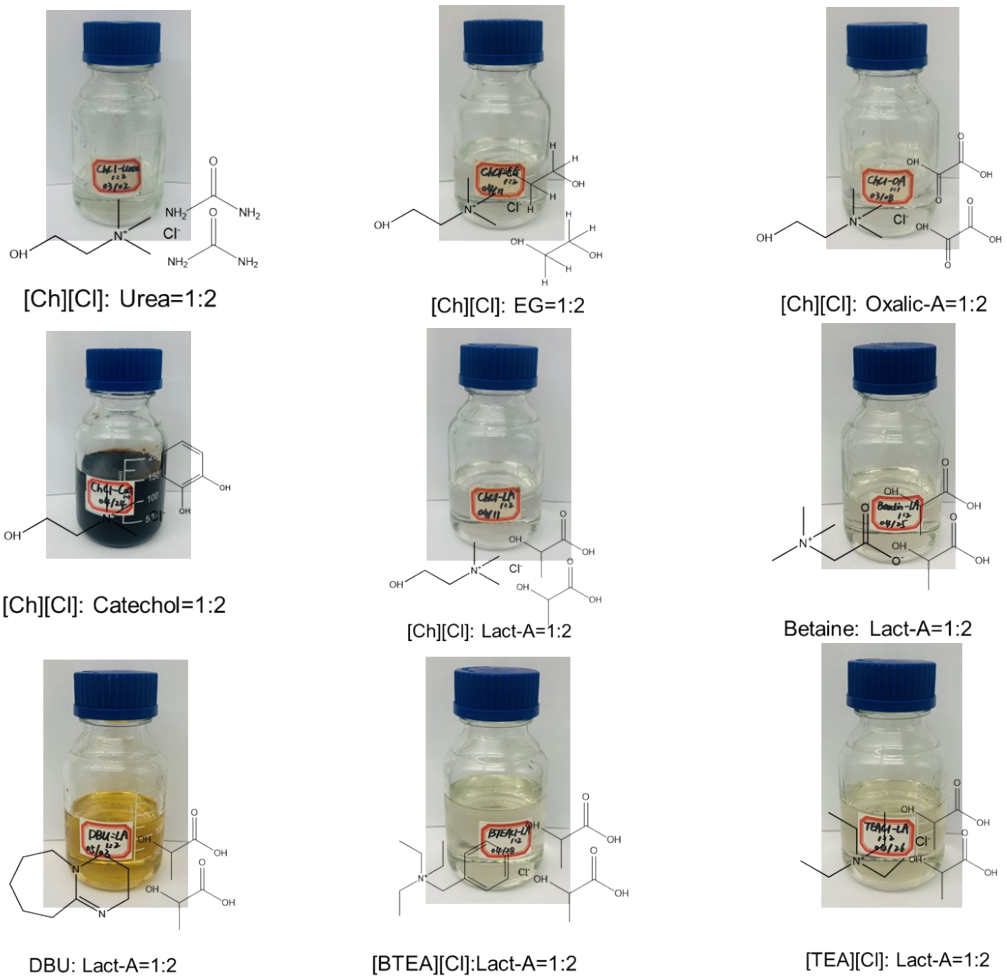

Figure S2. The camera images of the synthesized DES.

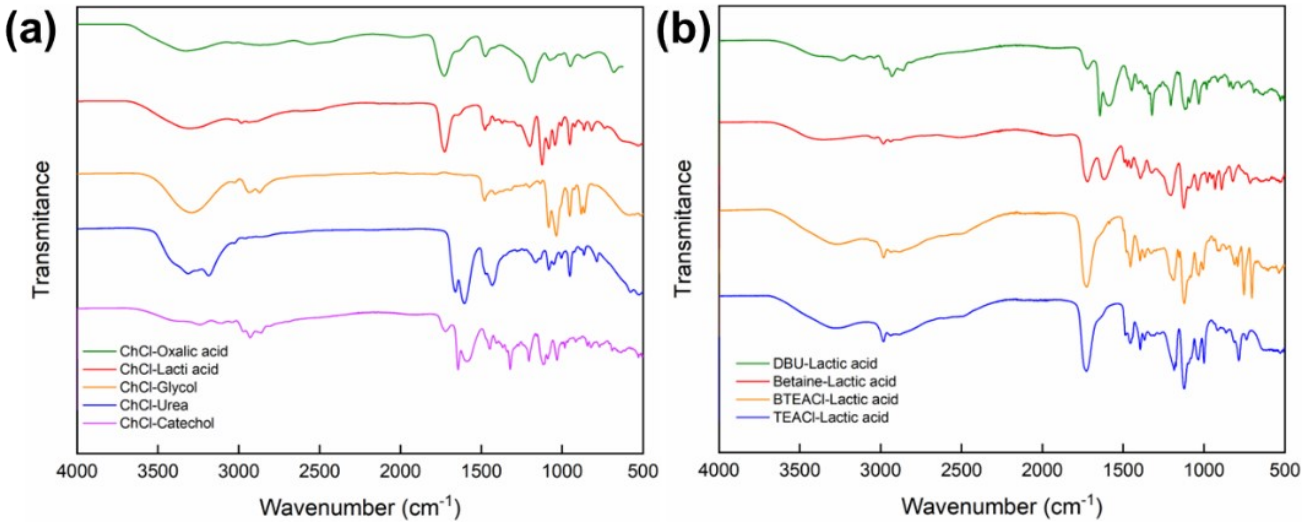

Figure S3. The FT-IR spectra of the synthesized DES.

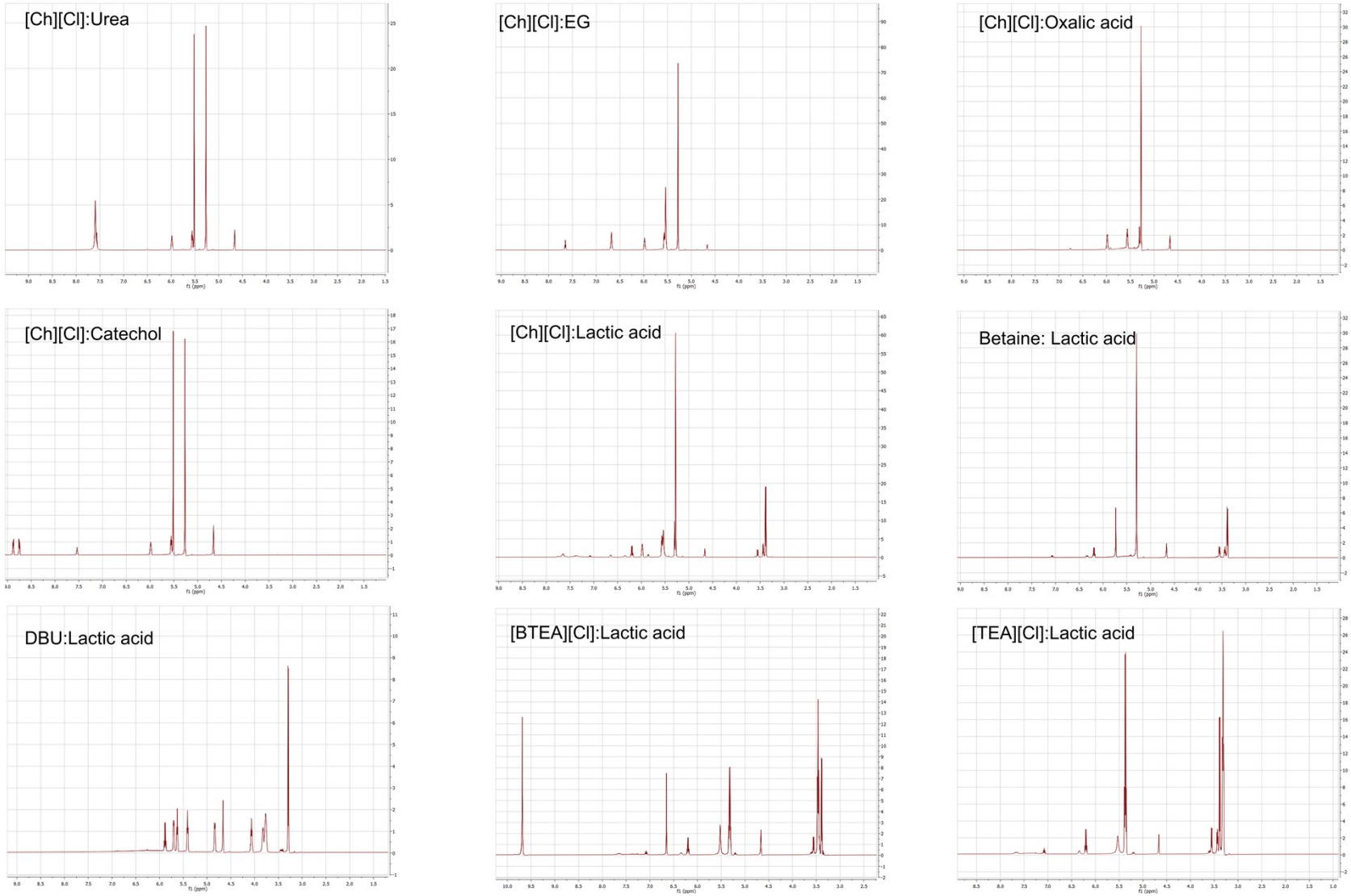

Figure S4. The H NMR spectra of the synthesized DES.

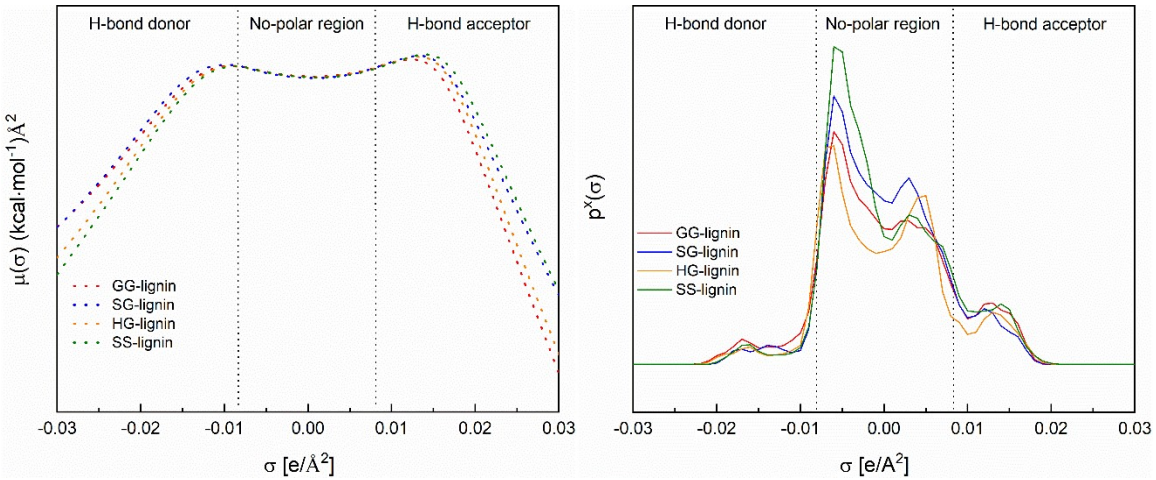

Figure S5. σ potential and σ profiles of the dimer lignin models.

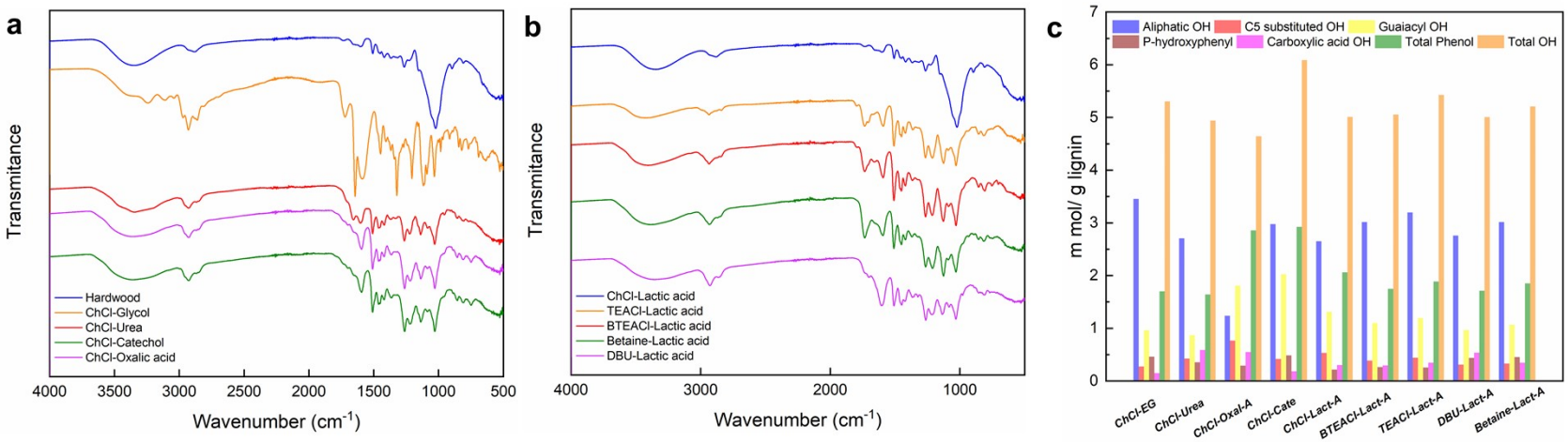

Figure S6. Characterization of lignin structure. **a,b,** FT-IR spectra of lignin regenerated from different DES pretreatment; **c,** Hydroxyl groups of lignin regenerated from different DES pretreatment.

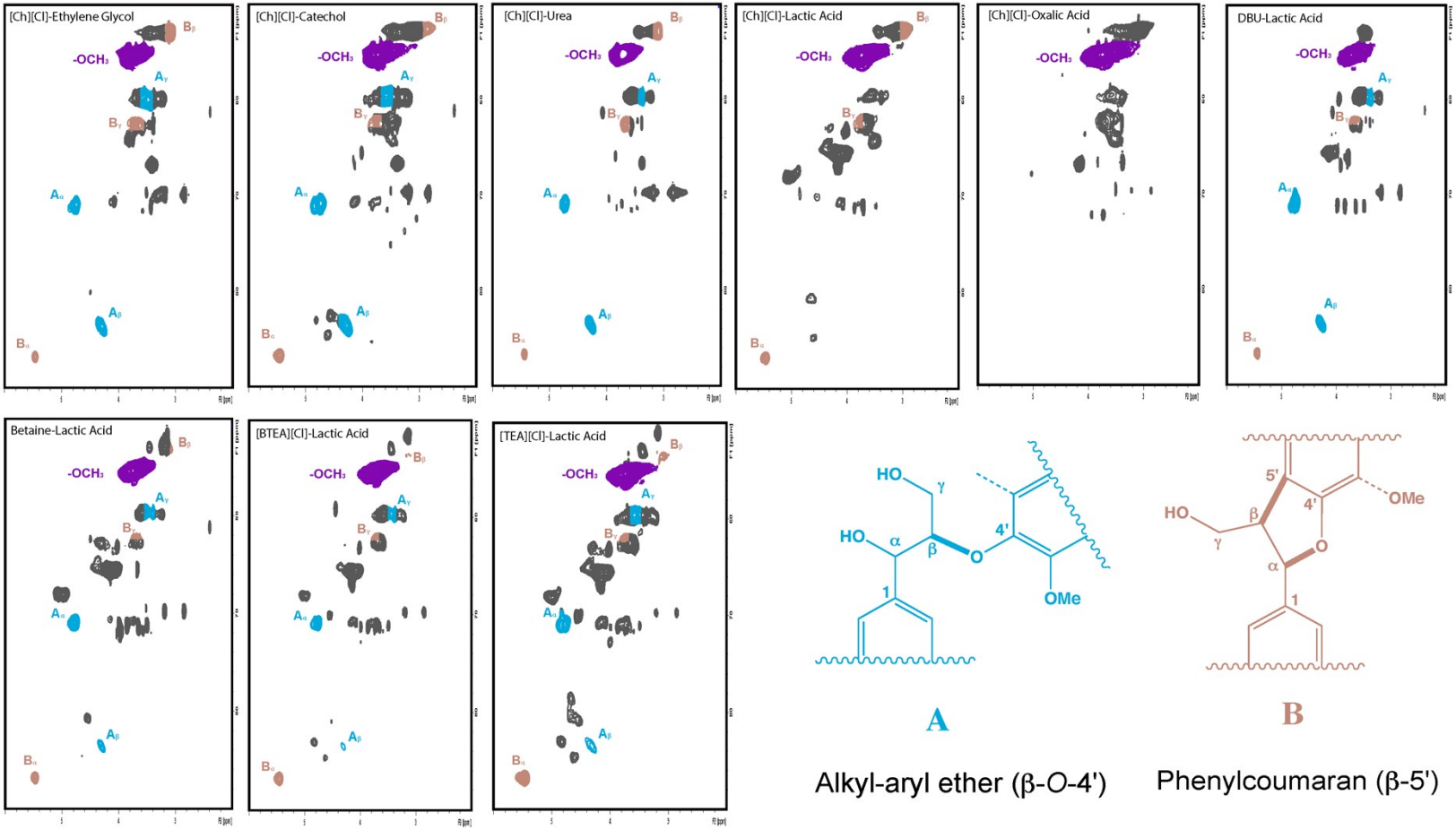

Figure S7. 2D HSQC NMR spectrum of lignin pretreated from different DES.

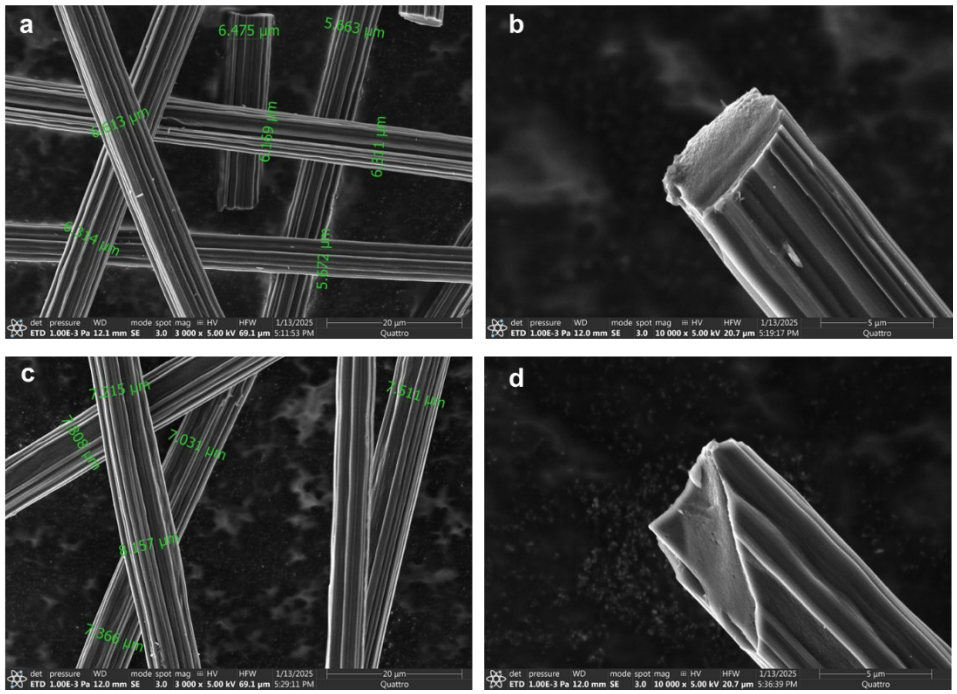

Figure S8. SEM images of lignin carbon fibers. a, b, DBU-LA pretreated lignin carbon fiber; **c,d,** ChCl-LA pretreated lignin carbon fiber.

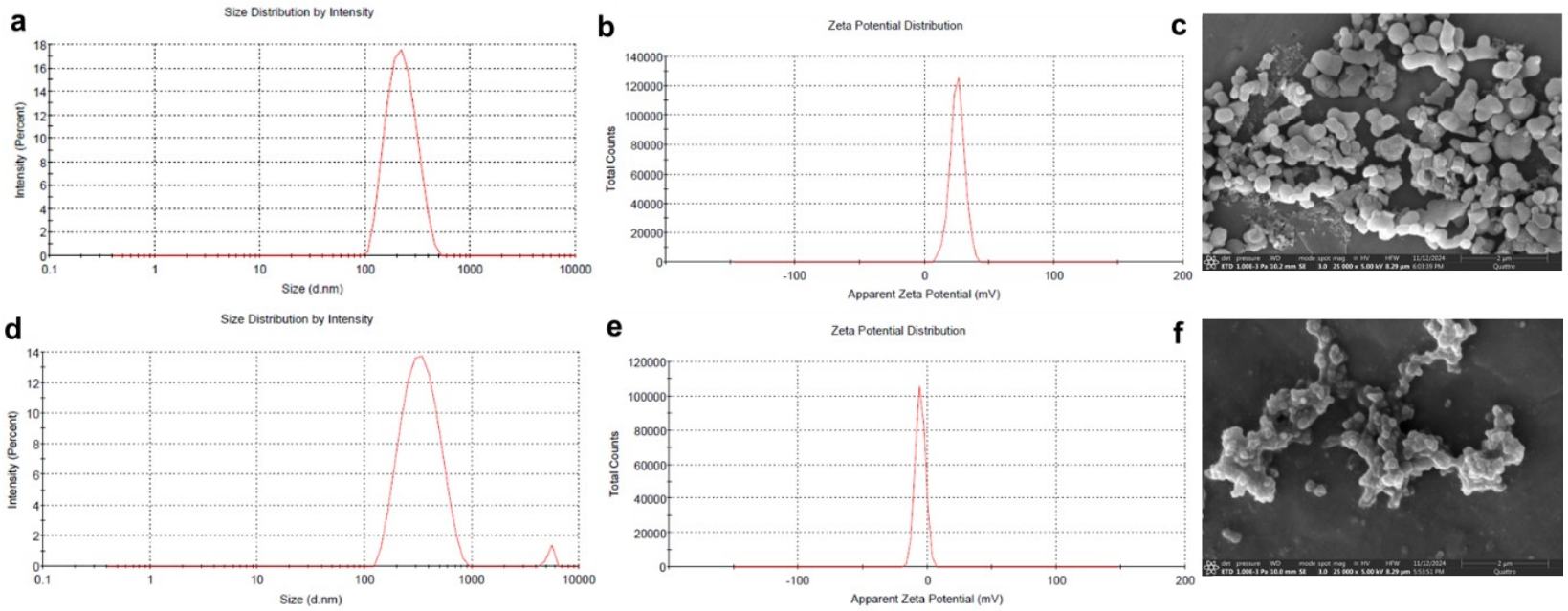

Figure S9. Characterization of the morphology and size of lignin nanoparticles. a, b, c Particle size, zeta potential and SEM image of the lignin nanoparticle from ChCl-LA; **d,e,f** Particle size, zeta potential and SEM image of the lignin nanoparticle from DBU-LA.