Supporting information

Multiple hydrogen bond coordination in three-constituent deep eutectic solvent enhances lignin fractionation from biomass

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Contents

Materials:

Poplar wood powder was used as feedstock and dried at 103 °C for 24 h. ChCl, glycerol, and $AlCl_3 \cdot 6H_2O$ were purchased from Aladdin Reagent Co. Ltd. Acetone were purchased from Kermel Chemical Reagent Co., Ltd. 4-nitroaniline (NH_2), N,N-diethyl-4-nitroaniline (NEt_2), and Nile red (NR) were purchased from Sigma-Aldrich (St. Louis, MO). All the above chemicals and reagents were used without further purification.

Note S1. Measurement of the K–T solvatochromic parameters

The dyes of NR, NEt_2, NH_2, 4-nitroanisole (OMe) and 4-nitrophenol (OH) were considered for measuring the K–T solvatochromic parameters.[1,2] NH_2 was used to determine β.[3] NEt_2 was selected to determine π^*, because this dye will show distinct absorption band for high-polarity DES. NR was used as a solvatochromic indicator to determine α. Reichardt's dye 30 and NR are generally used to determine the α values. But when Reichardt's dye 30 was added in the 3c-DES, the dye faded to colorless immediately. There was no detectable absorption band in the UV spectra (400–700 nm). Therefore, NR was used as solvatochromic probe to calculate α values instead of Reichardt's dye 30.

The dyes were respectively dissolved in methanol and stored in amber glass vials. Each time 5 mL dye solution was added into a 5mL centrifuge tube. The methanol was evaporated by vacuum drying at 40 °C for 2 day. Then, 3 mL DES was put into the dried dye, and was transferred into a 1 cm^2 quartz cuvette. The absorption spectrum of the mixture was checked using UV-visible spectrophotometer (TU-1900, Beijing Purkinje General Instrument Co. Ltd, China) at room temperature in the wavelength range of 300–700 nm.

The calculation of α, β and π^* values use the following equations: [4]

$$\pi^* = 0.314 \times (27.52 - \nu_{NEt2})$$

$$\beta = 11.134 - \frac{3580}{\lambda(NH_2)_{max}} - 1.125\pi^*$$

$$\alpha = \frac{19.9657 - 1.0241\pi^* - \nu_{NR}}{1.6078}$$

Where π^* is normalized to give cyclohexane and DMSO,[5] λ_{max} is the wavelength

corresponding to maximum absorption of dye and $v = 1/(\lambda_{max} \times 10^{-4})$.

Note S2. Calculation of CR, LF and LER

CR (wt%) is the weight percentage of non-dissolved solid residues to the wood feedstock. LF means the DES-extracted lignin which was precipitated with water after the removal of cellulose residues by filtration. LF (wt%) is calculated as the weight percentage of non-dissolved solid residues to the wood feedstock. LER (%) is calculated by the percentage of lignin fractions to the initial lignin content in wood feedstock. The initial lignin content in wood $feedstock$ is measured as 19.12±0.32%.

$$CR\ (wt\%) = \frac{Non\text{ - }dissolved\ solid\ residues}{Wood\ feedstock} \times 100\%$$

$$LF\ (wt\%) = \frac{DES - extracted\ lignin}{Wood\ feedstock} \times 100\%$$

$$LER\ (\%) = \frac{Lignin\ fractions}{Initial\ lignin\ content\ in\ wood\ feedstock} \times 100\%$$

Note S3. Calculation of purity of LF

The content of LF in the DES was determined by the acid hydrolysis method. First, the precipitated lignin by adding water was dried at 80 °C for 24 h. The oven-dried lignin (100 mg) was then reacted with 1.5 mL of 72% H_2SO_4 at room temperature with stirring for 2 h. The solution was diluted with DI water to a 3% H_2SO_4 concentration and refluxed for 2 h. Finally, it was filtered and the acid-insoluble lignin (Klason lignin) was determined by gravimetric analysis. The percentage of acid-insoluble lignin to the DES-extracted lignin was defined as the purity of LF.

Table S1 The electron density (ρ) and density Laplacian ($^{\nabla 2}\rho$) for the ChCl-glycerol and lignin-lignin at the bond critical points calculated at the M06-2X/6-31+G** level

Substance		**Interaction**	$\boldsymbol{\rho}$ (0.002–0.035)	$^{\nabla 2}\boldsymbol{\rho}$ (0.024–0.139)
$Ch^{+}\cdots Glycerol\cdots Cl^{-}$		$Cl_{44}\cdots H_{22}–C_{16}$	0.008	0.0237
		$Cl_{44}\cdots H_{25}–C_{18}$	0.005	0.0141
		$Cl_{44}\cdots H_{7}–O_{1}$	0.021	0.0560
		$Cl_{44}\cdots H_{10}–C_{3}$	0.012	0.0397
		$O_{15}\cdots H_{35}–C_{29}$	0.014	0.0473
		$O_{15}\cdots H_{43}–C_{33}$	0.013	0.0421
Lignin$\cdots$lignin	A1	$O_{23}\cdots H_{46}–O_{45}$	0.022	0.0680
		$O_{50}\cdots H_{19}–O_{18}$	0.021	0.0671
	A2	$O_{38}\cdots H_{19}–O_{18}$	0.021	0.0694
	A3	$O_{45}\cdots H_{19}–O_{18}$	0.027	0.0884
	A4	$O_{45}\cdots H_{14}–C_{12}$	0.009	0.0291
		$O_{38}\cdots H_{19}–O_{18}$	0.024	0.0737

Table S2 Lewis acid strength and K–T parameters of the ChCl/glycerol DES with different metal chlorides

Metal chloride	State	Lewis acid strength[6]	K–T parameters			LF (%)
			α	β	π^*	
NaCl	solid-liquid	–1.3697				
LiCl	liquid	–1.0262	0.99	0.63	1.13	2.02
$CaCl_2$	solid-liquid	–1.3849				
$ZnCl_2$	crystallization	–0.6115				3.38
$MgCl_2 \cdot 6H_2O$	liquid	–0.5429	0.96	0.73	1.17	4.10
$FeCl_3$	liquid	1.4993				11.44
$AlCl_3 \cdot 6H_2O$	liquid	2.4401	1.96	0.66	1.13	18.27

Table S3 Assignment of $^{13}C–^{1}H$ cross-signals in the HSQC spectra of lignin fractions[7]

label	δ_C/δ_H	assignment
OMe	55.7/3.75	C–H in methoxyls
Aγ	59.9/3.28-3.61	$C_\gamma–H_\gamma$ in *β*–O–4' substructures (A)
Aα	71.6/4.81	$C_\alpha–H_\alpha$ in *β*–O–4' substructures (A)
$A_{\beta(G)}$	83.7/4.30	$C_\beta–H_\beta$ in *β*–O–4′ substructures linked to G and H units (A)
$A_{\beta(s)}$	85.9/4.11	$C_\beta–H_\beta$ in *β*–O–4′ substructures linked to S units (A)
Bγ	70.9/3.77and4.15	$C_\gamma–H_\gamma$ in resinol substructures (B)
Bα	84.9/4.68	$C_\alpha–H_\alpha$ in resinol substructures (B)
Bβ	53.5/3.01	$C_\beta–H_\beta$ in resinol substructures (B)
Cγ	62.8/3.65	$C_\gamma–H_\gamma$ in phenylcoumaran substructures (C)
Cα	87.0/5.45	$C_\alpha–H_\alpha$ in phenylcoumaran substructures (C)
Cβ	53.0/3.47	$C_\beta–H_\beta$ in phenylcoumaran substructures (C)
S2,6	103.5/6.01	$C_{2,6}–H_{2,6}$ in etherified syringyl units (S)
G2	110.9/6.90	$C_2–H_2$ in G units (G)
G5	115.0/6.73	$C_5–H_5$ in G units (G)
G6	118.7/6.78	$C_6–H_6$ in G units (G)
X2	70.55/3.06	$C_2–H_2$ in *β*–D–xylopyranoside
X3	74.14/3.28	$C_3–H_3$ in *β*–D–xylopyranoside
PB2,6	131.84/7.69	$C_{2,6}–H_{2,6}$ in p-hydroxybenzoate substructures (PB)

Table S4 M_w, M_n, and polydispersity (M_w/M_n) of MWL and 3c-DESL

	MWL	**3c-DESL**
$\boldsymbol{M_w}$	6838	5466
$\boldsymbol{M_n}$	4550	3270
$\boldsymbol{M_w/M_n}$	1.50	1.67

Table S5 Analysis of carbohydrates that dissolved in the 3c-DES

	Content of carbohydrates (wt%)				
	Glucose	**Xylose**	**Fructose**	**5-HMF**	**Furfural**
Wood[a]	22.7	20.0	-	-	-
3c-DES-extracted[b]	1.95	5.12	1.86	8.31	3.44

Annotation: The glucose, xylose, and fructose content were analyzed by HPLC (LC-1260, refractive index detector RID-G1362A, Agilent, USA). A Bio-Rad Aminex HPX-87P column (300 mm×7.8 mm) was used with the following parameters: mobile phase: ultrapure water; flow rate: 0.6 mL/min; injection volume: 20 μL; column temperature: 80 °C; refractive index detector, retention time: fructose (10.8 min), glucose (11.4 min), and xylose (12.8 min). Furfural and 5-HMF were analyzed by HPLC (Waters 600E, UV detector VMD-2996, USA) using an Acquity BEH C18 column (1.7 μm, 2.1×50 mm), with the following parameters: mobile phase: acetonitrile:water (10:90, v/v); flow rate: 0.8 ml/min; injection volume: 20 μL; column temperature: 30 °C; UV detector: detection wavelength of 280 nm; and retention time: 5-HMF (8.4 min), furfural (13.9 min). **a:** The value of glucose and xylose reported by our previous report[8]. **b:** Liquid phase of 3c-DES after removal of lignin (120 °C, 4h), carbohydrates were calculated by relative mass percentage to wood.

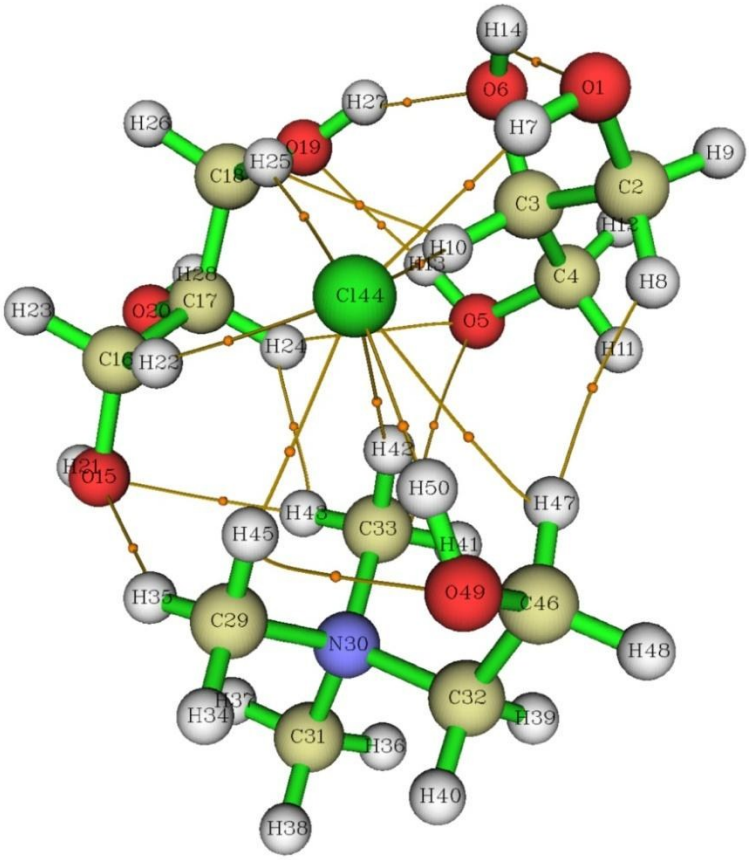

Fig. S1 Topological graph of ChCl-glycerol interactions

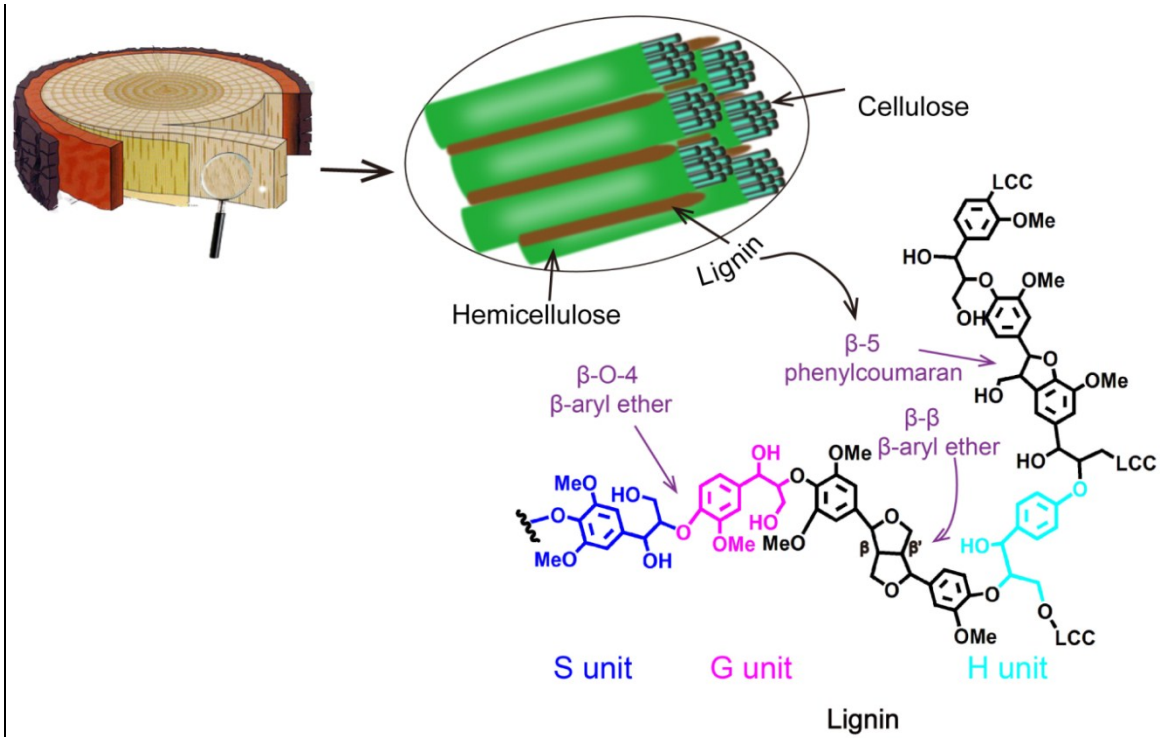

Fig. S2 Typical LCC structure and lignin substructures

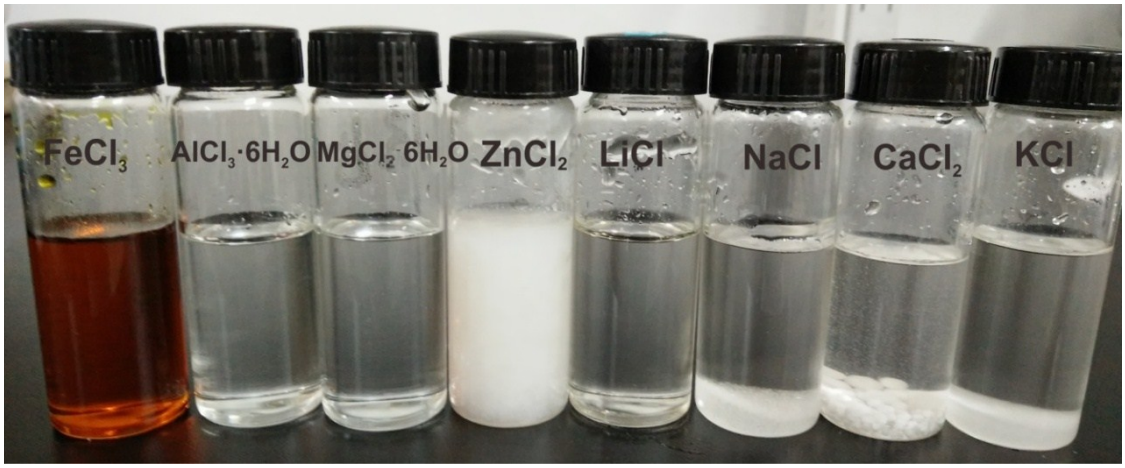

Fig. S3 Photographs of the mixtures formed by adding metal chloride salts in the ChCl/glycerol DES

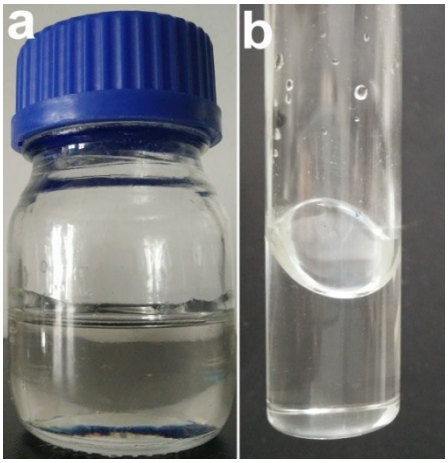

Fig. S4 3c-DES-4 at room temperature and low temperature (–20 ^{o}C)

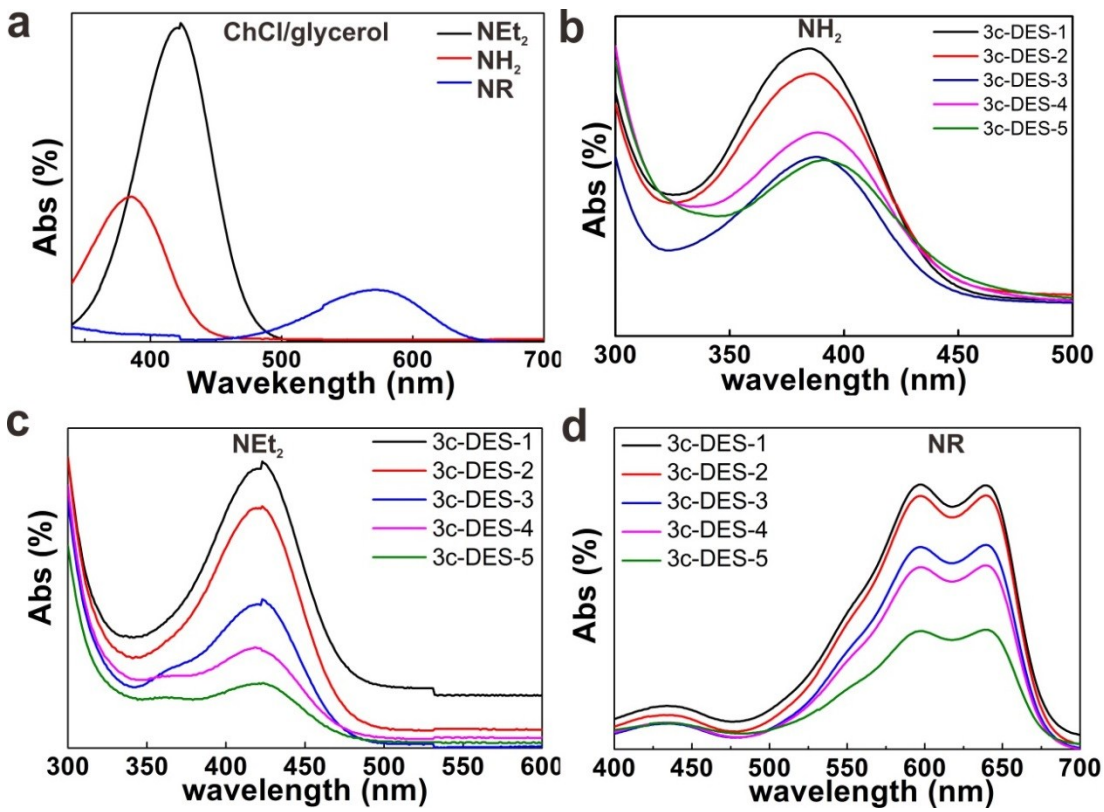

Fig. S5 (a) UV spectra of the K–T dyes: N,N-diethyl-4-nitroaniline (NEt_2), 4-nitroaniline (NH_2) and Nile red (NR) in ChCl/glycerol. UV spectra of the 3c-DESs with K–T dyes (b) NH_2, (c) NEt_2 and (d) NR.

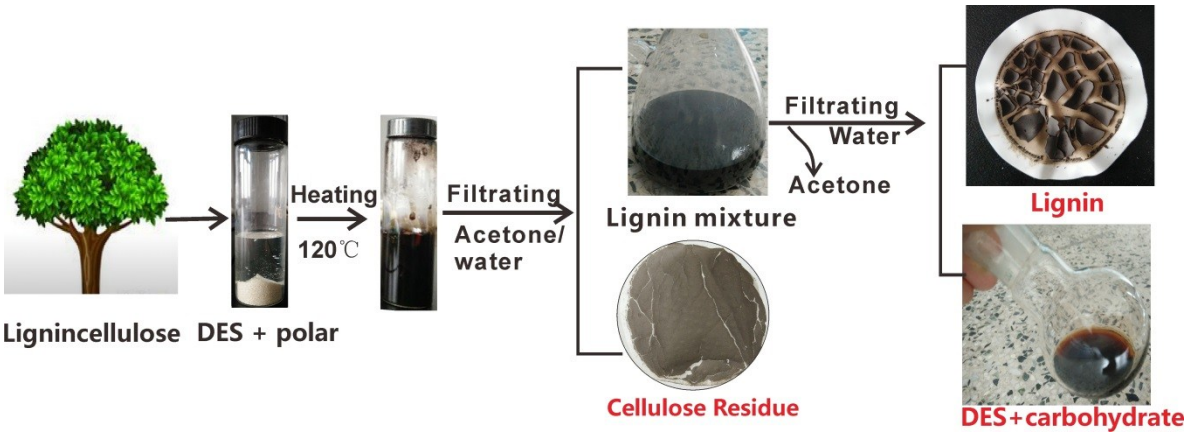

Fig. S6 The fractionation process of wood lignocellulose into CR, LF and dissolved carbohydrates by oil bath heating with the 3c-DES

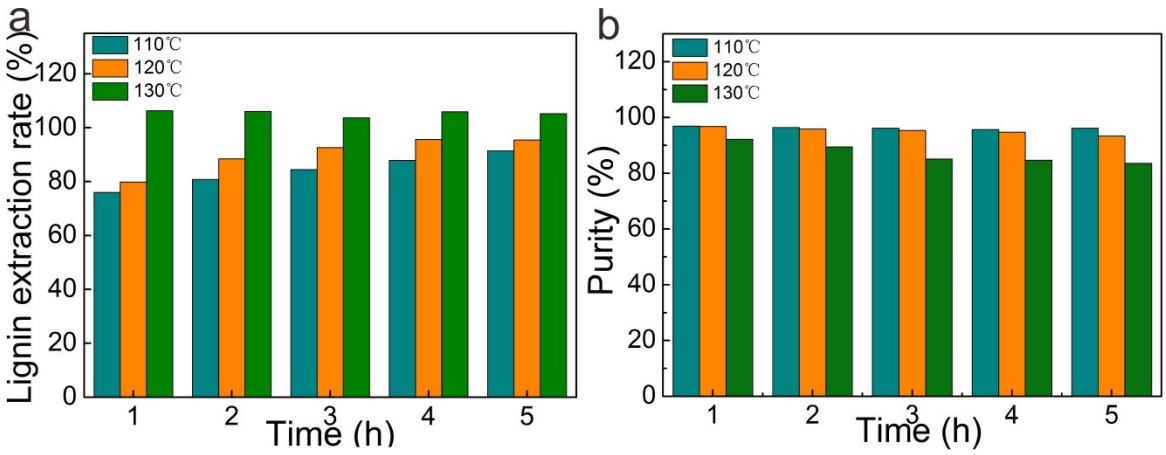

Fig. S7 (a) LER and (b) purity of the LF pretreated with the 3c-DES-4 at different temperatures and with increasing time

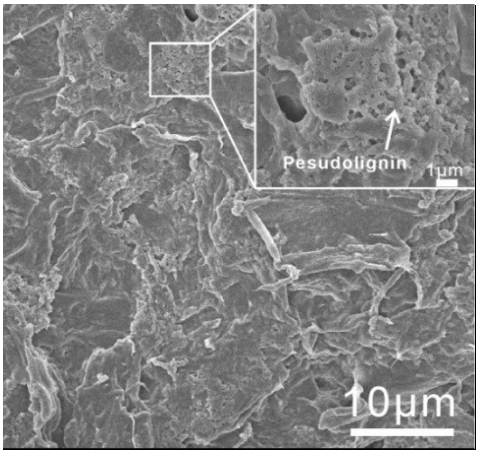

Fig. S8 SEM image of the pseudolignin generated at 120 °C for 4 h.

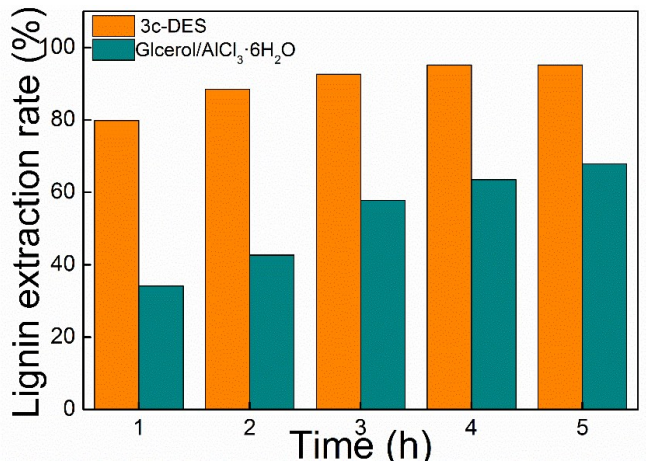

Fig. S9 Comparison of the lignin extraction rates (LERs) between 3c-DES-4 and glycerol/$AlCl_3 \cdot 6H_2O$ (7:1)

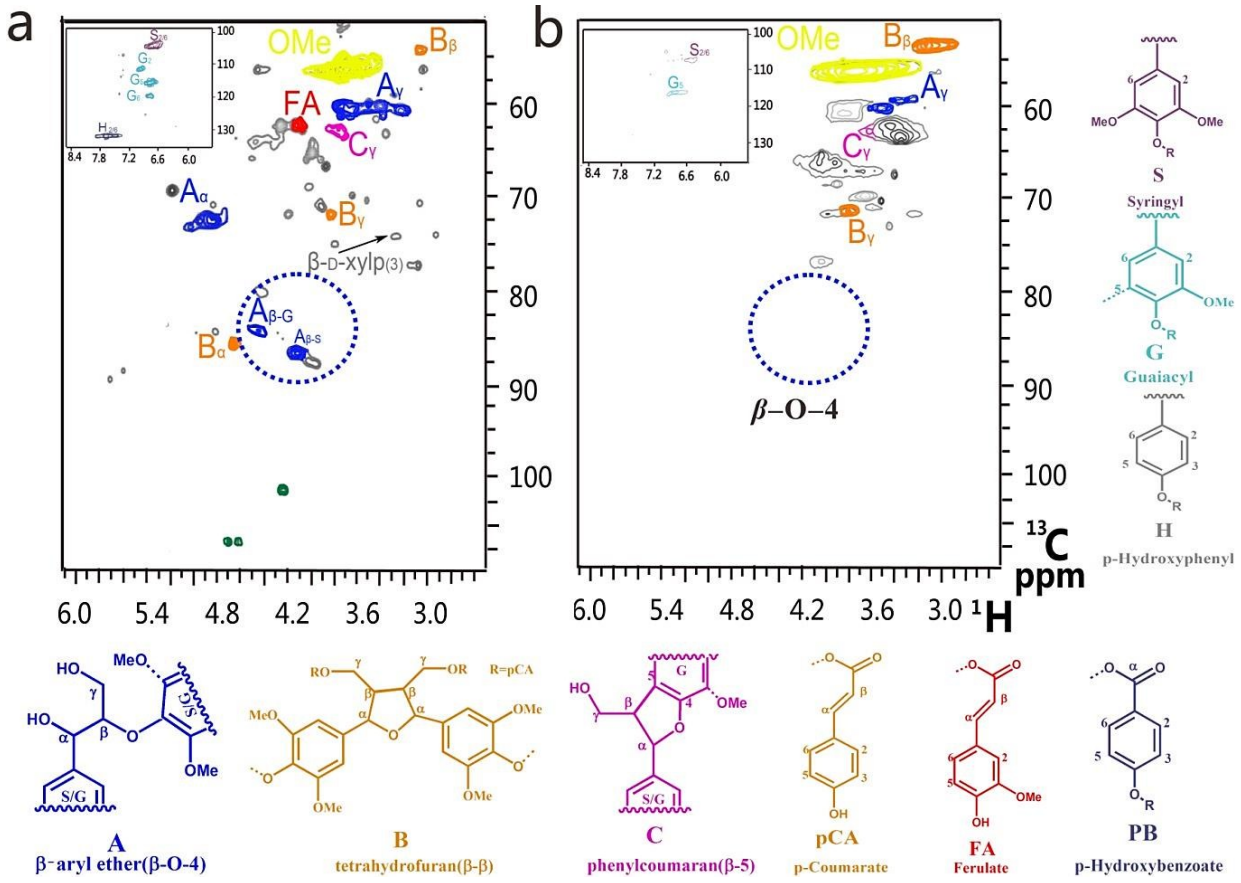

Fig. S10 2D-HSQC NMR spectra of (a) MWL and (b) 3c-DESL in the side-chain region and aromatic region (insets)

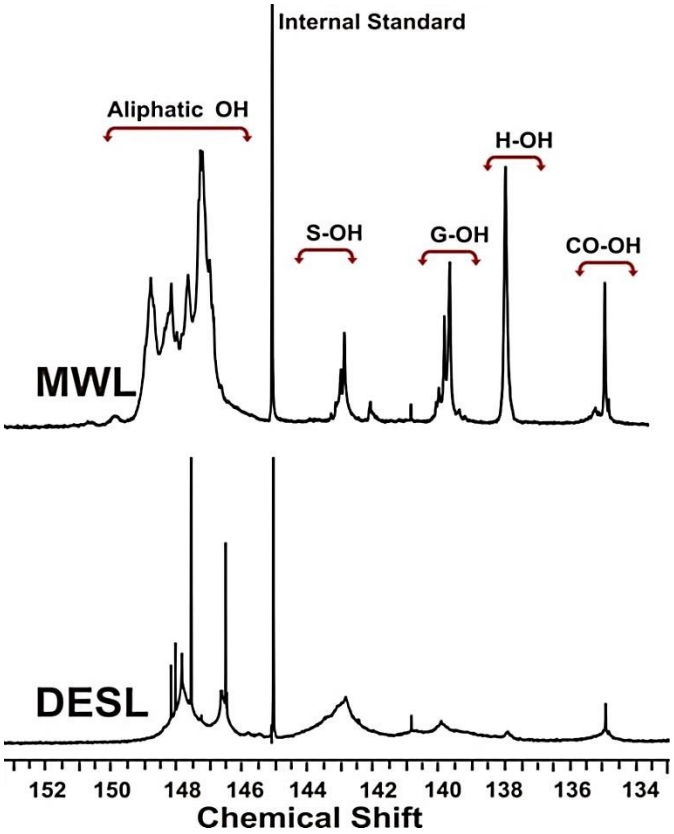

Fig. S11 ^{31}P NMR spectra of MWL and 3c-DESL

References

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