Supporting Information for:

Novel Deep Eutectic Solvents with Different Functional Groups towards Highly Efficient Dissolution of Lignin

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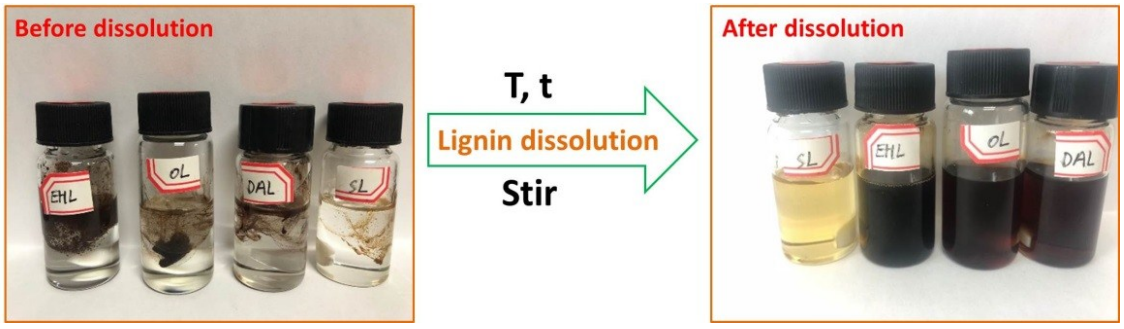

Scheme S1. The dissolution of different types of lignin in the designed DESs.

Table S1. The viscosity (η) of the prepared DESs at different temperatures.[a]

DESs	HBA:HBD (molar ratio)	Viscosity (MPa·s)			
		298.15 K	308.15 K	318.15 K	328.15 K
ChCl-NMTU	1:2	----	----	1443.90	598.42
ChCl-LA	1:1	432.79	226.64	128.81	79.22
	1:2	176.18	95.84	56.574	36.31
BTMAC-LA	1:1	3329.70	1157.50	472.41	223.78
	1:2	598.30	250.82	119.76	65.51
BTEAC-LA	1:1	----	2568.80	934.00	397.20
	1:2	1133.70	431.59	191.05	98.18
ATMAC-NMTU	1:1	3226.30	1082.20	429.98	195.25
	1:2	1437.20	1264.20	447.67	188.91
ATMAC-LA	1:1	226.39	121.64	71.85	46.60
	1:2	126.33	69.15	42.39	27.71

[a]Standard uncertainties u were $u(\eta) = 0.05$, and $u(T) = 0.03$ K.

Herein, it should be pointed out that the uncertainties for the viscosity of DESs were estimated to be ±0.05 (Table S1), and the relative higher uncertainties may be originated from the high viscosity of DESs, which was similar with some systems with ionic liquids.[S1]

S1. J. J. Fillion, H. Xia, M. A. Desilva, M. Quiroz-Guzman and J. F. Brennecke, *J. Chem. Eng. Data*, 2016, **61**, 2897.

Table S2. The density (ρ) of the prepared DESs at different temperatures.[a]

DESs	HBA:HBD (molar ratio)	Density (g cm^{-3})			
		298.15 K	308.15 K	318.15 K	328.15 K
ChCl-NMTU	1:2	1.1702	1.1644	1.1586	1.1527
ChCl-LA	1:1	1.1616	1.1559	1.1501	1.1444
	1:2	1.1751	1.1687	1.1623	1.1561
BTMAC-LA	1:1	1.1406	1.1345	1.1285	1.1226
	1:2	1.1547	1.1482	1.1416	1.1350
BTEAC-LA	1:1	1.1278	1.1215	1.1152	1.1089
	1:2	1.1415	1.1347	1.1279	1.1216
ATMAC-NMTU	1:1	1.1073	1.1014	1.0955	1.0897
	1:2	1.1318	1.1256	1.1195	1.1135
ATMAC-LA	1:1	1.0985	1.0926	1.0868	1.0809
	1:2	1.1266	1.1203	1.1135	1.1069

[a]Standard uncertainties u were $u(\rho) = 4 \times 10^{-4}$ g/m^{-3} and u(T) = 0.01 K, and the $u(\rho)$ originated from the measurement processes.

Table S3. The phase-transition temperatures of DESs.[a]

DESs	HBA:HBD (molar ratio)	T_g (°C)
ChCl-NMTU	1:1	-46
	1:2	-63
ChCl-LA	1:1	-72
	1:2	-83
BTMAC-LA	1:1	-46
	1:2	-49
BTEAC-NMTU	1:1	-15
	1:2	-22
BTEAC-LA	1:1	-41
	1:2	-52
ATMAC-NMTU	1:1	-56
	1:2	-63
ATMAC-LA	1:1	-77
	1:2	--

[a]Standard uncertainties u were $u(T_g) = 2$ °C.

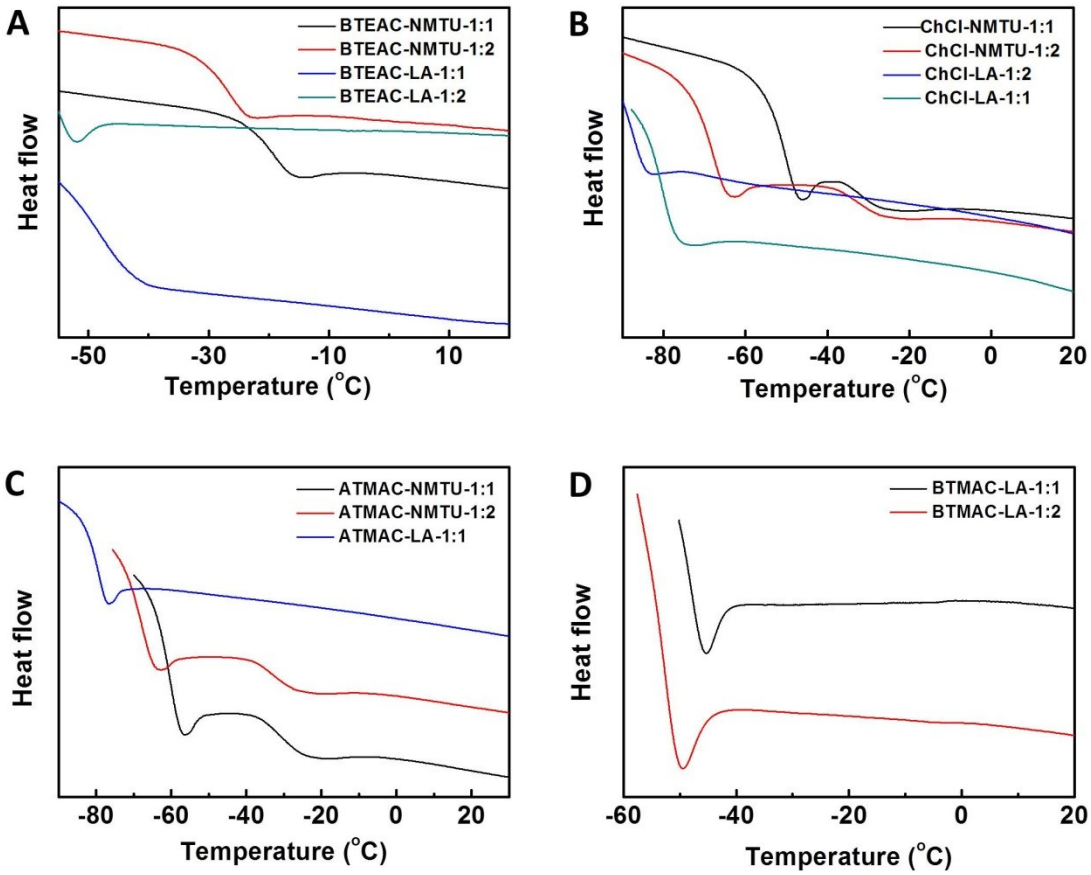

Fig. S1. Glass transition temperature (T_g) of all the prepared DESs analyzed by differential scanning calorimetry (DSC).

Table S4. Solubility (wt%) of EHL at different temperatures.[a]

DESs	Dissolution temperature (K)[b]			HBA/HBD	DES formation
	303.15	323.15	343.15	molar ratio	temperature (K)
ChCl-LA	< 0.3	16.3 (±1.2)	29.4 (±2.3)	1:1	298.15
	< 0.3	30.5 (±1.7)	44.8 (±1.3)	1:2	298.15
ChCl-NMTU	< 0.3	< 0.3	31.6 (±1.9)	1:1	333.15
	< 0.3	< 0.3	37.3 (±2.8)	1:2	333.15
BTMAC-LA	< 0.3	1.8	15.6 (±0.7)	1:1	333.15
	< 0.3	26.9 (±2.1)	35.4 (±1.5)	1:2	303.15
BTEAC-LA	< 0.3	11.1 (±1.7)	18.4 (±0.6)	1:1	333.15
	8.7 (±1.1)	37.8 (±1.2)	44.8 (±1.1)	1:2	298.15
BTEAC-NMTU	< 0.3	< 0.3	2.5	1:1	333.15
	< 0.3	< 0.3	10.5 (±1.7)	1:2	333.15
ATMAC-LA	15.4 (±1.2)	30.3 (±2.1)	42.8 (±2.4)	1:1	298.15
	23.1 (±1.7)	40.8 (±0.9)	48.5 (±1.6)	1:2	298.15
ATMAC-NMTU	< 0.3	23.7 (±3.1)	33.9 (±0.8)	1:1	318.15
	< 0.3	29.4 (±1.5)	39.5 (±2.3)	1:2	333.15

[a]Standard uncertainties u for the temperature were $u(T) = 0.2$ K. [b]The solubility value was the average of twice measurements, and the values in the parentheses were the half of the range of replicate results. Meanwhile, "< 0.3" meant that 1 g of the corresponding DES could not dissolve 3 mg lignin.

Table S5. Solubility (wt%) of DAL at different temperatures.[a]

DESs	Dissolution temperature (K)[b]			HBA/HBD	DES formation
	303.15	323.15	343.15	molar ratio	temperature (K)
ChCl-LA	1.3	3.9	28.8 (±1.9)	1:1	298.15
	13.5 (±2.1)	33.1 (±1.2)	42.7 (±2.7)	1:2	298.15
ChCl-NMTU	< 0.3	0.9	3.3	1:1	333.15
	< 0.3	22.3 (±1.9)	33.1 (±0.9)	1:2	333.15
BTMAC-LA	< 0.3	< 0.3	8.9 (±1.5)	1:1	333.15
	1.9	11.9 (±2.8)	19.1 (±2.0)	1:2	303.15
BTEAC-LA	10.1 (±1.0)	22.7 (±2.1)	37.4 (±1.3)	1:1	333.15
	15.7 (±0.4)	28.8 (±1.8)	36.1 (±0.5)	1:2	298.15
BTEAC-NMTU	< 0.3	< 0.3	21.8 (±1.9)	1:1	333.15
	< 0.3	< 0.3	33.6 (±2.8)	1:2	333.15
ATMAC-LA	11.1 (±1.7)	28.4 (±1.6)	48.6 (±2.2)	1:1	298.15
	22.5 (±0.6)	39.5 (±1.9)	47.7 (±1.4)	1:2	298.15
ATMAC-NMTU	< 0.3	16.4 (±1.3)	45.3 (±2.2)	1:1	318.15
	< 0.3	21.8 (±1.7)	33.7 (±0.8)	1:2	333.15

[a]Standard uncertainties u for the temperature were $u(T) = 0.2$ K. [b]The solubility value was the average of twice measurements, and the values in the parentheses were the half of the range of replicate results. Meanwhile, "< 0.3" meant that 1 g of the corresponding DES could not dissolve 3 mg lignin.

Table S6. Solubility (wt%) of SL at different temperatures.[a]

DESs	Dissolution temperature (K)[b]			HBA/HBD	DES formation
	303.15	323.15	343.15	molar ratio	temperature (K)
ChCl-LA	1.7	4.2	28.1 (±0.8)	1:1	298.15
	4.4	15.8 (±2.5)	36.4 (±1.3)	1:2	298.15
ChCl-NMTU	< 0.3	2.4	4.1	1:1	333.15
	< 0.3	< 0.3	1.5	1:2	333.15
BTMAC-LA	< 0.3	9.7 (±0.7)	23.9 (±1.9)	1:1	333.15
	3.7	33.2 (±1.5)	48.6 (±0.8)	1:2	303.15
BTEAC-LA	< 0.3	25.8 (±0.4)	36.1 (±1.7)	1:1	333.15
	8.8 (±1.1)	17.4 (±1.7)	38.7 (±3.1)	1:2	298.15
BTEAC-NMTU	< 0.3	< 0.3	< 0.3	1:1	333.15
	< 0.3	< 0.3	13.7 (±2.3)	1:2	333.15
ATMAC-LA	2.5	21.3 (±2.8)	29.6 (±1.5)	1:1	298.15
	7.9 (±2.3)	31.3 (±1.5)	38.2 (±1.9)	1:2	298.15
ATMAC-NMTU	< 0.3	15.1 (±2.4)	45.7 (±0.5)	1:1	318.15
	< 0.3	8.5 (±1.6)	25.3 (±1.4)	1:2	333.15

[a]Standard uncertainties u for the temperature were $u(T) = 0.2$ K. [b]The solubility value was the average of twice measurements, and the values in the parentheses were the half of the range of replicate results. Meanwhile, "< 0.3" meant that 1 g of the corresponding DES could not dissolve 3 mg lignin.

Table S7. Solubility (wt%) of OL at different temperatures.[a]

DESs	Dissolution temperature (K)[b]			HBA/HBD	DES formation
	303.15	323.15	343.15	molar ratio	temperature (K)
ChCl-LA	7.7 (±0.8)	24.1 (±1.9)	31.3 (±2.5)	1:1	298.15
	10.4 (±0.4)	36.7 (±1.1)	41.2 (±1.4)	1:2	298.15
ChCl-NMTU	< 0.3	1.7	7.3 (±1.4)	1:1	333.15
	< 0.3	3.9	18.5 (±1.6)	1:2	333.15
BTMAC-LA	1.7	12.7 (±3.1)	26.8 (±1.3)	1:1	333.15
	7.3 (±1.1)	26.5 (±2.5)	36.7 (±0.7)	1:2	303.15
BTEAC-LA	1.3	16.1 (±2.4)	27.6 (±1.7)	1:1	333.15
	11.8 (±0.5)	35.8 (±1.2)	37.1 (±2.8)	1:2	298.15
BTEAC-NMTU	< 0.3	< 0.3	17.2 (±2.1)	1:1	333.15
	< 0.3	< 0.3	22.9 (±1.9)	1:2	333.15
ATMAC-LA	14.6 (±1.2)	25.7 (±0.5)	35.7 (±1.6)	1:1	298.15
	37.2 (±2.4)	44.7 (±1.8)	48.4 (±0.9)	1:2	298.15
ATMAC-NMTU	< 0.3	9.2 (±1.1)	15.3 (±0.8)	1:1	318.15
	< 0.3	19.6 (±2.3)	26.1 (±1.7)	1:2	333.15

[a]Standard uncertainties u for the temperature were $u(T) = 0.2$ K. [b]The solubility value was the average of twice measurements, and the values in the parentheses were the half of the range of replicate results. Meanwhile, "< 0.3" meant that 1 g of the corresponding DES could not dissolve 3 mg lignin.

Table S8. The solvatochromic parameters of DESs.

DESs	π*	α	β	α-β	HBA/HBD molar ratio
ChCl-LA	1.003 (±0.002)	1.305 (±0.003)	-0.849 (±0.003)	2.154	1:1
BTMAC-LA	0.282 (±0.003)	0.083 (±0.002)	1.832 (±0.004)	-1.749	1:1
BTEAC-LA	0.786 (±0.002)	1.040 (±0.004)	1.205 (±0.005)	-0.165	1:1
ATMAC-LA	0.720 (±0.004)	1.149 (±0.005)	-4.816 (±0.002)	5.965	1:1
ChCl-LA	0.852 (±0.004)	1.335 (±0.004)	0.503 (±0.003)	0.832	1:2
BTMAC-LA	1.042 (±0.006)	1.354 (±0.003)	0.590 (±0.004)	0.764	1:2
BTEAC-LA	0.931 (±0.004)	1.219 (±0.003)	0.175 (±0.003)	1.044	1:2
ATMAC-LA	0.792 (±0.005)	1.298 (±0.003)	-5.196 (±0.004)	6.494	1:2

[a]The value of the corresponding solvatochromic parameter was the average of twice measurements, and the values in the parentheses were the half of the range of replicate results.

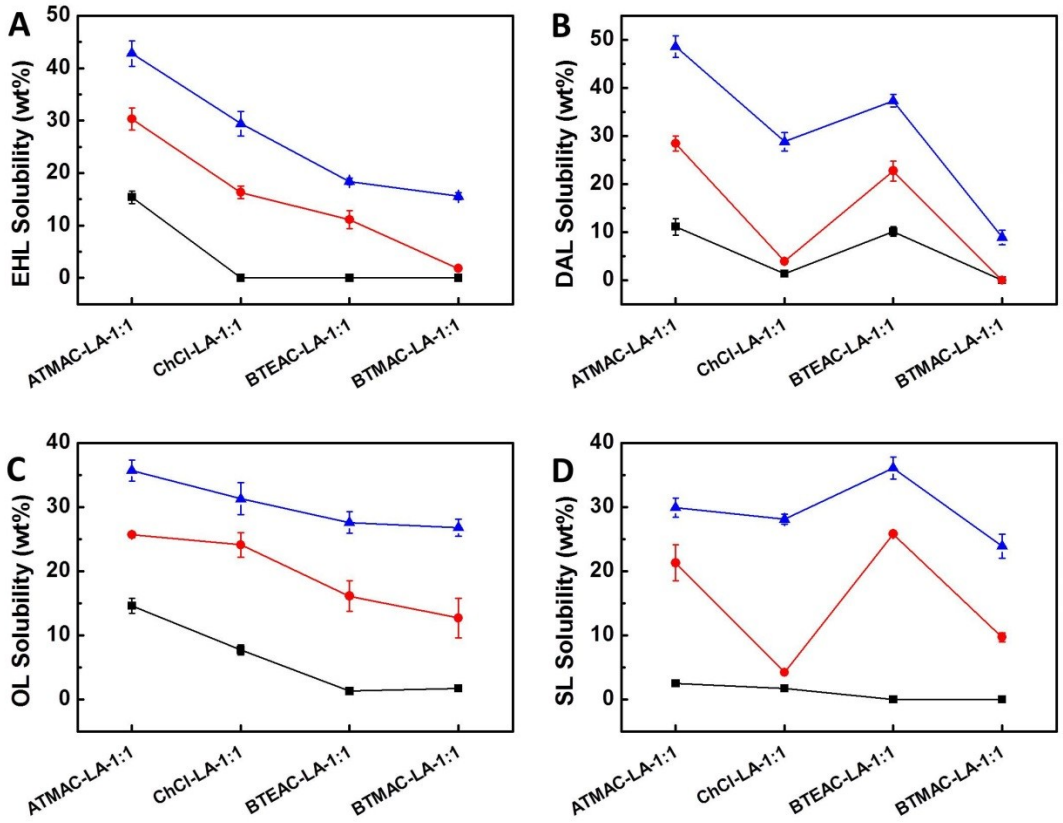

Fig. S2. The correlation between the lignin solubility and the value of β. The black, the red, and the blue lines represented the experiments conducted at 303.15, 323.15, and 343.15 K, respectively. Meanwhile, the β values for ATMAC-LA-1:1, ChCl-LA-1:1, BTEAC-LA-1:1, and BTMAC-LA-1:1 were -4.816, -0.849, 1.205, and 1.832, respectively. Additionally, it should be pointed out that the solubility value was the average of twice measurements, and the errors for the solubility were the half of the range of replicate results.

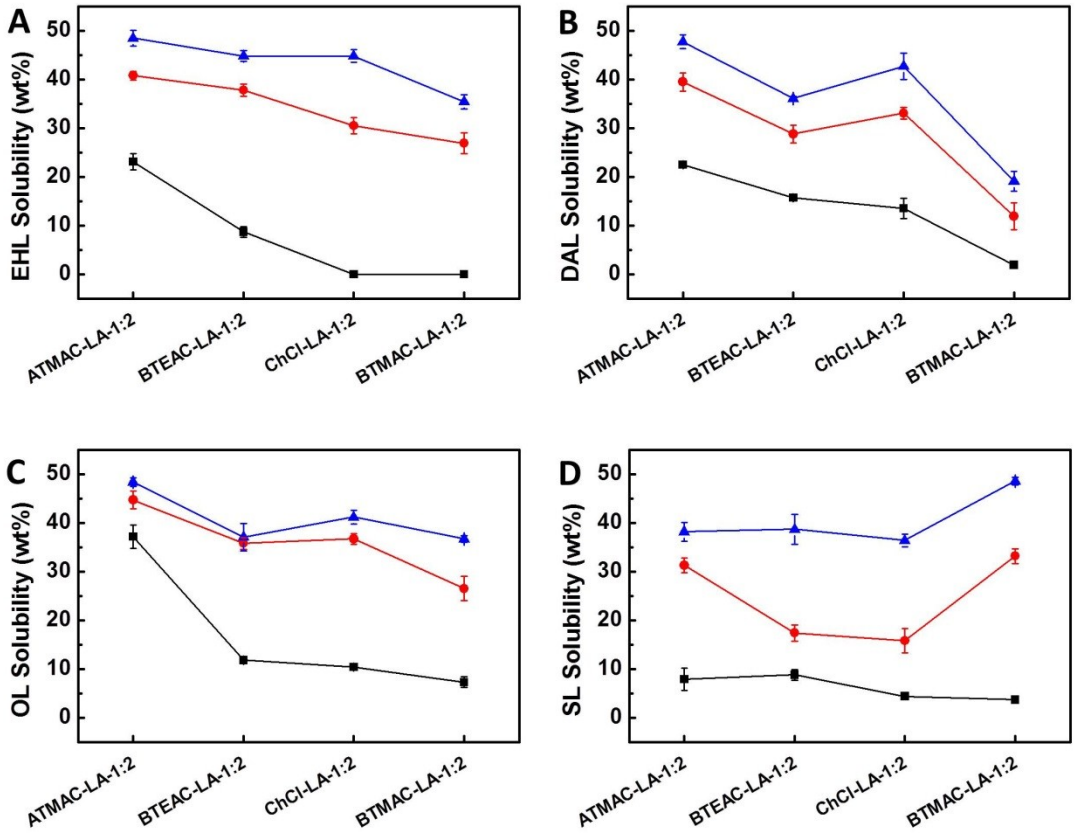

Fig. S3. The correlation between the lignin solubility and the value of β. The black, the red, and the blue lines represented the experiments conducted at 303.15, 323.15, and 343.15 K, respectively. Meanwhile, the β values for ATMAC-LA-1:2, BTEAC-LA-1:2, ChCl-LA-1:2, and BTMAC-LA-1:2 were -5.196, 0.175, 0.503, and 0.590, respectively. Additionally, it should be pointed out that the solubility value was the average of twice measurements, and the errors for the solubility were the half of the range of replicate results.