Supplementary Material for

Multiscale exploration of lignin dissolution mechanism based on novel ternary deep eutectic solvents incorporating p-hydroxybenzoic acid

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Content

1. Experimental sessions

1.1 Chemical composition analysis

The component analysis was based on the acid hydrolysis method of The National Renewable Energy Laboratory (NREL). A sample of 1 g of absolute dry mass was weighed into a pressure flask, and 3 mL of sulfuric acid (mass fraction 72%) was immediately added. The pressure flask was then placed in a 30°C water bath oscillator for a duration of 60 minutes to ensure complete hydrolysis of the raw material. After the concentrated acid hydrolysis, 84 mL of deionized water was added to the pressure flask and mixed evenly, diluting the sulfuric acid concentration to 4%. The pressure flask was sealed and reacted in an autoclave at 121 ℃ for 60 min. After the reaction, the pressure flask was cooled to room temperature. After the two-step acid hydrolysis, the residual undissolved solid consists of acid-insoluble lignin (AIL). The formula for calculating the content of AIL is presented as follows:

$$AIL = \frac{m_{final}}{m_{initial}} \times 100\% \tag{1}$$

Where, $m_{initial}$ is absolute dry mass of raw material (g); m_{final} is mass of the freeze-dried sample after DES treatment (g).

The content of acid-soluble lignin (ASL) was quantified using ultraviolet spectrophotometry. The ultraviolet spectrophotometer (UV-Vis, 756S, Lengguang Technology, China) was powered on, adjusted to the required wavelength of 320 nm, and allowed to stabilize for 30 minutes. Took 2 mL of the supernatant of the acid-hydrolyzed sample and diluted it until the absorbance of the ultraviolet spectrophotometer was below 1 A at the time of initial detection. With deionized water as blank sample, the UV-Vis was set to zero, and then the sample absorbance was detected. The calculation formula of ASL content is as follows:

$$ASL = \frac{A_{sample} V df}{\lambda \varepsilon_{Lignin} m_{sample}} \times 100\% \tag{2}$$

Where, A_{sample} is absorbance (A); V is acidolysis liquid volume (L); df is dilution ratio; λ is light path (cm); ε_{Lignin} is lignin absorptivity, and its value is 30 L/(g·cm). m_{sample} is mass of the sample (g).

The calculation formula of lignin component content in raw materials and DES treated samples is as follows:

$$Total\ Lignin = (ASL + AIL) \times 100\% \quad (3)$$

After DES treatment, the calculation formula of the delignification rate of the sample is as follows:

$$Delignification = (1 - \frac{Lgnin\ content\ in\ solid\ residue}{Lignin\ content\ in\ xylose\ residue\ (g) \times Solid\ recovery}) \times 100\% \quad (4)$$

1.2 Analysis methods

The pH value of DESs were measured using a pH meter (PHS-3C, LeiCi, China). The electrode was immersed in a container holding 10 mL of the DES, and the data were recorded after the pH meter had fully stabilized.

The ORP of DESs were measured using a pH meter (PHS-3C, LeiCi, China). The electrode was immersed in a container holding 10 mL of the DES, and the data were recorded after the ORP potential had fully stabilized.

The conductivity of DESs were measured using a benchtop conductivity meter (DDS-307, LeiCi, China). The conductivity electrode was immersed in a container holding 10 mL of DES for measurement, and the data were recorded after the conductivity meter had fully stabilized.

The viscosity of DESs were measured by a rotary viscometer (DV-79, Pingxuan, China). 15 mL of DES to be measured was added to the rotary viscometer, a suitable rotor was selected for viscosity measurement, and the data was recorded after the measurement value of the viscometer was stable.

The functional group changes of DES, raw materials, and DES treated samples were analyzed using Fourier transform infrared spectroscopy (FT-IR, Nicolet iS10, Thermo Fisher Scientific, USA). The infrared region range of FT-IR is 400-4000 cm^{-}

[1], and the solid powder is detected and analyzed by KBr tablet method. The liquid sample pool method was used to detect and analyze the liquid.

The thermal stability of the raw material and DES treated samples were measured using thermogravimetric analysis (TGA 8000, PerkinElmer, USA). Approximately 5 mg of sample was placed in an alumina crucible and heated from ambient temperature to 600 ℃ with a heating rate of 10 ℃/min.

The morphological features of the raw material and DES treated samples were analyzed using transmission electron microscope (TEM, JEM2100, JEOL, Japan), and TEM images were captured at an acceleration voltage of 200 kV.

70 mg of lignin samples were dissolved in DMSO-d_6. Prior to the characterization, the samples were sufficiently ultrasonicated to enable the lignin samples to dissolve in DMSO-d_6. 2D-heteronuclear single quantum correlation nuclear magnetic resonance (2D-HSQC NMR, Bruker Biospin AVANCE III HD 600 MHz, Switzerland) spectroscopy was employed to acquire the NMR spectra of lignin samples at 25°C. The acquisition parameters for the 2D ^{1}H-^{13}C HSQC spectrum were set as follows: 190 ppm spectral width in F1 (^{13}C) dimension with 256 data points and 12 ppm spectral width in F2 (^{1}H) dimension with 1024 data points, a 1.0 s pulse delay (D1), and 128 scans (NS).

2. Tables and Figures

2.1 Tables

Table S1 Detailed information on the chemical components of DES.

DES	Molar ratio	HBA		HBD			
		Abbreviation	CAS	Abbreviation	CAS	Abbreviation	CAS
ChCl-EG	1:2	ChCl	67-48-1	EG	107-21-1	\	\
ChCl-LA	1:2	ChCl	67-48-1	LA	50-21-5	\	\
ATMAC-EG	1:2	ATMAC	1516-27-4	EG	107-21-1	\	\
ATMAC-LA	1:2	ATMAC	1516-27-4	LA	50-21-5	\	\
ChCl-EG-PB	1:2:0.5	ChCl	67-48-1	EG	107-21-1	PB	99-96-7
ChCl-LA-PB	1:2:0.5	ChCl	67-48-1	LA	50-21-5	PB	99-96-7
ATMAC-EG-PB	1:2:0.5	ATMAC	1516-27-4	EG	107-21-1	PB	99-96-7
ATMAC-LA-PB	1:2:0.5	ATMAC	1516-27-4	LA	50-21-5	PB	99-96-7

\- Not available.

Table S2 Chemical composition and pretreatment performance of samples.

Samples	Molar ratio	Solid recovery (%)	ASL (%)	AIL (%)	Lignin (%)	Delignification (%)
Raw material	\	\	2.01±0.02	17.40±0.78	19.41±0.77	\
ChCl-LA	1:2	68.24±0.84	1.40±0.13	27.88±0.81	29.28±0.67	33.38±2.23
ChCl-LA-PB	1:2:0.5	77.78±5.05	0.98±0.09	18.02±1.17	19.01±1.13	61.91±3.62
ChCl-EG-PB	1:2:0.5	75.54±3.27	1.28±0.07	22.26±1.20	23.54±1.24	51.42±4.67
ATMAC-LA-PB	1:2:0.5	70.78±2.90	1.16±0.04	22.27±1.01	23.44±0.97	48.44±3.85
ATMAC-EG-PB	1:2:0.5	67.10±1.97	1.30±0.07	21.79±1.05	23.09±1.10	46.55±0.93

ASL-Acid solution lignin.

AIL-Acid insoluble lignin.

\- Not available.

Table S3 Physical property parameters of different DES.

Samples	Molar ratio	pH	Viscosity (mPa·s)	ORP (mV)	Conductivity (μS/cm)
ChCl-LA	1:2	1.01	355	60.7	2340
ChCl-EG	1:2	3.55	204	34.6	7460
ATMAC-LA	1:2	1.19	343	53.6	1903
ATMAC-EG	1:2	3.93	183	21.5	8160
ChCl-LA-PB	1:2:0.5	0.46	387	268	1101
ChCl-EG-PB	1:2:0.5	2.44	270	108	2660
ATMAC-LA-PB	1:2:0.5	0.53	382	161	2670
ATMAC-EG-PB	1:2:0.5	2.5	267	14.3	4160

ORP-Oxidation-reduction potential.

Table S4 Semiquantitative analysis of functional group in lignin.

Samples	A_{1164}/A_{1513}	A_{834}/A_{1513}
Raw Material	0.950	1.103
ChCl-LA	0.961	1.101
ChCl-LA-PB	0.968	1.101
ChCl-EG-PB	0.893	1.077
ATMAC-LA-PB	0.973	1.039
ATMAC-EG-PB	0.938	1.128

Table S5 RESP atomic charge of lignin dimer molecule.

Lignin dimer	Residue	Type	Atom name	RESP charge
4-O-5	1	CG2R61	C	-0.4016158011
	2	CG2R61	C	0.4380994856
	3	CG2R61	C	-0.1775717242
	4	CG2R61	C	0.4369249228
	5	CG2R61	C	-0.3954923813
	6	CG2R61	C	-0.0985670030
	7	HGR61	H	0.1754736573
	8	HGR61	H	0.1728140663
	9	HGR61	H	0.1524435437
	10	OG301	O	-0.1669184289
	11	CG2R61	C	0.0782726506
	12	CG2R61	C	-0.3227003077
	13	CG2R61	C	0.1984453597
	14	CG2R61	C	0.1797754780
	15	HGR61	H	0.1691581343
	16	CG2R61	C	0.0959334179
	17	CG2R61	C	-0.2187237423
	18	HGR61	H	0.0919041862
	19	OG311	O	-0.4573024090
	20	HGP1	H	0.3444589477
	21	OG301	O	-0.1932656699
	22	OG301	O	-0.2193694496
	23	OG301	O	-0.2204311489
	24	CG331	C	-0.1025751356
	25	HGA3	H	0.0882607127
	26	HGA3	H	0.0882607127
	27	HGA3	H	0.0882607127
	28	CG331	C	-0.0802108222
	29	HGA3	H	0.0747175478
	30	HGA3	H	0.0747175478
	31	HGA3	H	0.0747175478
	32	CG331	C	-0.0978749264
	33	HGA3	H	0.0784967981
	34	HGA3	H	0.0784967981
	35	HGA3	H	0.0784967981
	36	CG2DC1	C	-0.2502539879
	37	HGA4	H	0.1404411446
	38	CG2DC1	C	-0.2549859698
	39	HGA4	H	0.1173641565
	40	CG321	C	0.4109493904
	41	HGA2	H	0.0024243554
	42	HGA2	H	0.0024243554

	43	OG311	O	-0.6617029243
	44	HGP1	H	0.3878294039
5-5	1	CG2R61	C	0.1532435117
	2	CG2R61	C	-0.4569641267
	3	CG2R67	C	0.1661554857
	4	CG2R61	C	0.0334170730
	5	CG2R61	C	0.2366278552
	6	CG2R61	C	-0.3814925174
	7	HGR61	H	0.1837858830
	8	HGR61	H	0.1828648466
	9	CG2R67	C	0.1775531706
	10	CG2R61	C	-0.4623712970
	11	CG2R61	C	0.0243536782
	12	CG2R61	C	0.1560750548
	13	HGR61	H	0.1850115143
	14	CG2R61	C	0.2442938897
	15	CG2R61	C	-0.3898518463
	16	HGR61	H	0.1857301918
	17	OG311	O	-0.3995467182
	18	HGP1	H	0.3136766267
	19	OG311	O	-0.4022515217
	20	HGP1	H	0.3143911847
	21	OG301	O	-0.2106209128
	22	OG301	O	-0.2096463904
	23	CG331	C	-0.0721930600
	24	HGA3	H	0.0742186389
	25	HGA3	H	0.0742186389
	26	HGA3	H	0.0742186389
	27	CG331	C	-0.0749410219
	28	HGA3	H	0.0751737255
	29	HGA3	H	0.0751737255
	30	HGA3	H	0.0751737255
	31	CG321	C	0.0460621935
	32	HGA2	H	0.0327493797
	33	HGA2	H	0.0327493797
	34	CG321	C	0.0400353231
	35	HGA2	H	0.0346067865
	36	HGA2	H	0.0346067865
	37	CG2D1	C	-0.0552796397
	38	HGA4	H	0.1159145875
	39	CG2D2	C	-0.5367415300
	40	HGA5	H	0.1960846615
	41	HGA5	H	0.1960846615
	42	CG2D1	C	-0.0541101087

	43	HGA4	H	0.1157711066
	44	CG2D2	C	-0.5354152426
	45	HGA5	H	0.1957020040
	46	HGA5	H	0.1957020040
β-1	1	CG2R61	C	0.2159476807
	2	CG2R61	C	-0.1890053109
	3	CG2R61	C	-0.2515950291
	4	CG2R61	C	-0.0747763492
	5	CG2R61	C	-0.2539309732
	6	CG2R61	C	0.1924196995
	7	HGR61	H	0.1663134660
	8	HGR61	H	0.1215751789
	9	HGR61	H	0.1475415823
	10	CG311	C	0.1974812161
	11	HGA1	H	-0.0065336742
	12	CG311	C	0.1455078448
	13	HGA1	H	0.0219756006
	14	CG2R61	C	0.0856458301
	15	CG2R61	C	-0.2544491682
	16	CG2R61	C	-0.2318606518
	17	CG2R61	C	0.2488668063
	18	HGR61	H	0.1310367256
	19	CG2R61	C	-0.2876958328
	20	HGR61	H	0.1563314191
	21	CG2R61	C	0.1883467641
	22	HGR61	H	0.1521209619
	23	CG321	C	0.1164373478
	24	HGA2	H	0.0154309503
	25	HGA2	H	0.0154309503
	26	CG321	C	0.2528645802
	27	HGA2	H	-0.0235117414
	28	HGA2	H	-0.0235117414
	29	OG311	O	-0.6578184309
	30	HGP1	H	0.4157128274
	31	OG311	O	-0.6805394011
	32	HGP1	H	0.4092528246
	33	OG311	O	-0.5121076326
	34	HGP1	H	0.3972341535
	35	OG311	O	-0.5110192334
	36	HGP1	H	0.3799498625
	37	OG301	O	-0.3015295894
	38	OG301	O	-0.2846602396
	39	CG331	C	0.0516917300
	40	HGA3	H	0.0471692990

	41	HGA3	H	0.0471692990
	42	HGA3	H	0.0471692990
	43	CG331	C	0.0547303626
	44	HGA3	H	0.0410635789
	45	HGA3	H	0.0410635789
	46	HGA3	H	0.0410635789
β-5	1	CG2RC0	C	0.1195400651
	2	CG2RC0	C	-0.0723114070
	3	CG2R61	C	0.4147408959
	4	CG2R61	C	-0.3473647075
	5	CG2R61	C	-0.1662650591
	6	CG2R61	C	-0.2708414350
	7	HGR61	H	0.1641135707
	8	HGR61	H	0.1400195540
	9	HGR61	H	0.1606269996
	10	CG3C51	C	-0.1503534458
	11	HGA1	H	0.0448135374
	12	CG3C51	C	0.7635138124
	13	HGA1	H	-0.0749921852
	14	OG3C51	O	-0.4052131708
	15	CG2R61	C	-0.7091366313
	16	CG2R61	C	0.5256794509
	17	CG2R61	C	0.4931541915
	18	CG2R61	C	-0.5462089857
	19	CG2R61	C	-0.6075541317
	20	CG2R61	C	0.5077344242
	21	HGR61	H	0.2242676054
	22	HGR61	H	0.1847752489
	23	CG321	C	0.3297401973
	24	HGA2	H	-0.0547219399
	25	HGA2	H	-0.0547219399
	26	OG301	O	-0.2983211963
	27	OG301	O	-0.1128536817
	28	OG301	O	-0.2467760282
	29	OG311	O	-0.6075067331
	30	HGP1	H	0.3806133213
	31	OG311	O	-0.5647982397
	32	HGP1	H	0.4135813070
	33	CG331	C	-0.1345552677
	34	HGA3	H	0.0815099166
	35	HGA3	H	0.0815099166
	36	HGA3	H	0.0815099166
	37	CG331	C	-0.0824470367
	38	HGA3	H	0.0747471220

	39	HGA3	H	0.0747471220
	40	HGA3	H	0.0747471220
	41	CG331	C	0.0951158924
	42	HGA3	H	0.0253806775
	43	HGA3	H	0.0253806775
	44	HGA3	H	0.0253806775
	45	CG2RC0	C	0.1195400651
β-β	1	CG3C52	C	-0.0340327349
	2	OG3C51	O	-0.3335320208
	3	CG3C51	C	0.1770702417
	4	CG3RC1	C	-0.0237130884
	5	CG3RC1	C	-0.0610777771
	6	HGA2	H	0.0701736849
	7	HGA2	H	0.0701736849
	8	HGA1	H	0.0612115001
	9	CG3C51	C	0.3447679999
	10	CG3C52	C	0.2778890905
	11	OG3C51	O	-0.4448085432
	12	HGA1	H	0.0227088881
	13	HGA1	H	0.0447540482
	14	CG2R61	C	-0.1801049713
	15	CG2R61	C	0.1511613105
	16	CG2R61	C	-0.0390741363
	17	CG2R61	C	0.3597483836
	18	CG2R61	C	-0.3931715017
	19	CG2R61	C	-0.0294397819
	20	HGR61	H	0.1111393267
	21	HGR61	H	0.1540795877
	22	OG301	O	-0.3267436889
	23	OG311	O	-0.3543230743
	24	HGP1	H	0.3032507046
	25	OG301	O	-0.1596952712
	26	CG331	C	0.1308061868
	27	HGA3	H	0.0195111996
	28	HGA3	H	0.0195111996
	29	HGA3	H	0.0195111996
	30	CG331	C	-0.2101436824
	31	HGA3	H	0.1154128983
	32	HGA3	H	0.1154128983
	33	HGA3	H	0.1154128983
	34	HGA2	H	-0.0135808117
	35	HGA2	H	-0.0135808117
	36	CG2R61	C	-0.2975694817
	37	CG2R61	C	-0.1871886555

	38	CG2R61	C	-0.0682601588
	39	CG2R61	C	-0.2006840190
	40	CG2R61	C	0.2724704291
	41	CG2R61	C	0.1886283515
	42	HGR61	H	0.1635301409
	43	HGR61	H	0.1344845530
	44	HGR61	H	0.1383809825
	45	HGA1	H	0.0220401567
	46	OG301	O	-0.3352527078
	47	OG311	O	-0.4557279689
	48	HGP1	H	0.3735833973
	49	CG331	C	0.1171104070
	50	HGA3	H	0.0225898459
	51	HGA3	H	0.0225898459
	52	HGA3	H	0.0225898459
β-O-4	1	CG2R61	C	-0.1162303511
	2	CG2R61	C	-0.2777943054
	3	CG2R61	C	-0.0610821212
	4	CG2R61	C	-0.1972251167
	5	CG2R61	C	0.1704439456
	6	CG2R61	C	0.1794667893
	7	HGR61	H	0.1466114328
	8	HGR61	H	0.1571697107
	9	HGR61	H	0.1519328879
	10	CG311	C	0.3770623740
	11	HGA1	H	0.0160136687
	12	CG311	C	0.2450380700
	13	HGA1	H	-0.0406164694
	14	CG321	C	0.0961324576
	15	HGA2	H	0.0345425100
	16	HGA2	H	0.0345425100
	17	OG301	O	-0.3756613697
	18	OG311	O	-0.6658557807
	19	HGP1	H	0.3959150692
	20	OG311	O	-0.6217398119
	21	HGP1	H	0.4140235387
	22	OG311	O	-0.4940996020
	23	HGP1	H	0.3595380203
	24	OG301	O	-0.2381577909
	25	CG331	C	-0.0681790598
	26	HGA3	H	0.0769972433
	27	HGA3	H	0.0769972433
	28	HGA3	H	0.0769972433
	29	CG2R61	C	0.5119145418

30	CG2R61	C	-0.5523251497
31	CG2R61	C	-0.3788705293
32	CG2R61	C	0.5175779236
33	HGR61	H	0.1912684365
34	CG2R61	C	-0.0777605953
35	HGR61	H	0.1692251279
36	CG2R61	C	-0.3782310091
37	HGR61	H	0.1382481101
38	HGR61	H	0.1590015738
39	OG301	O	-0.3410304815
40	CG331	C	0.0902812514
41	HGA3	H	0.0326392879
42	HGA3	H	0.0326392879

Table S6 RESP atomic charge of Ch^+, LA and PB.

Molecule	Residue	Type	Atom name	RESP charge
Ch^+	1	CG334	C	-0.3427485572
	2	HGP5	H	0.1876820890
	3	HGP5	H	0.1876820890
	4	HGP5	H	0.1876820890
	5	CG334	C	-0.4144232513
	6	HGP5	H	0.2059417305
	7	HGP5	H	0.2059417305
	8	HGP5	H	0.2059417305
	9	CG334	C	-0.3423703244
	10	HGP5	H	0.1875454494
	11	HGP5	H	0.1875454494
	12	HGP5	H	0.1875454494
	13	NG3P0	N	0.0468555347
	14	CG324	C	-0.0754922022
	15	HGP5	H	0.1400792013
	16	HGP5	H	0.1400792013
	17	CG321	C	0.2535724856
	18	HGA2	H	0.0097575240
	19	HGA2	H	0.0097575240
	20	OG311	O	-0.6082879348
	21	HGP1	H	0.4397129923
LA	1	CG2O2	C	0.6434646576
	2	CG311	C	0.4342605151
	3	HGA1	H	-0.0518923551
	4	OG2D1	O	-0.5624228138
	5	OG311	O	-0.5522838795
	6	HGP1	H	0.4168535241
	7	OG311	O	-0.6457860737
	8	HGP1	H	0.4026471905
	9	CG331	C	-0.3839657941
	10	HGA3	H	0.0997083430
	11	HGA3	H	0.0997083430
	12	HGA3	H	0.0997083430
PB	1	CG2R61	C	0.4369576912
	2	CG2R61	C	-0.3558120676
	3	CG2R61	C	-0.0856409014
	4	CG2R61	C	-0.0275691125
	5	CG2R61	C	-0.1394322294
	6	CG2R61	C	-0.2422541519
	7	HGR61	H	0.1564318660
	8	HGR61	H	0.1550134575
	9	HGR61	H	0.1524277279

10	HGR61	H	0.1693832438
11	CG2O2	C	0.6516836956
12	OG2D1	O	-0.5507293125
13	OG311	O	-0.5546307912
14	HGP1	H	0.4087543776
15	OG311	O	-0.6028071871
16	HGP1	H	0.4282236940

Table S7 Assignments of ^{13}C-^{1}H correlated signals in the HSQC spectra of the lignin from xylose residue.

Structure	δ_C/δ_H(ppm)	Assignment
B_β	53.1/3.11	C_β-H_β in resinol substructures (B)
C_β	53.4/3.51	C_β-H_β in phenylcoumaran substructures (C)
-OCH_3	55.7/3.73	C-H in methoxyls
A_γ	59.8/3.60	C_γ-H_γ in β-O-4 substructures
X_5	62.6/3.39	C_5-H_5 β-D-xylopyranoside substructures (X)
C_γ	63.5/3.69	C_γ–H_γ in phenylcoumaran (C)
A'_γ	65.5/4.06	C_γ-H_γ in γ-acylated β-O-4' substructures (A')
A_α	72.2/5.08	C_α-H_α in β-O-4 substructures (A)
X_2	73.7/3.19	C_5-H_5 β-D-xylopyranoside substructures (X)
$S_{2,6}$	103.8/6.69	$C_{2,6}$-$H_{2,6}$ in syringyl units (S)
G_2	110.7/7.12	C_2-H_2 in guaiacyl units (G)
FA_2	111.3/7.31	C_2-H_2 in ferulate (FA)
G_{5e}	113.7/6.37	C_{5e}-H_{5e} in guaiacyl units (G)
G_6	115.5/6.83	C_6-H_6 in guaiacyl units (G)
FA_6	118.3/6.78	C_6-H_6 in ferulate (FA)
$H_{2,6}$	122.9/7.11	$C_{2,6}$-$H_{2,6}$ in *p*-hydroxyphenyl units (H)
$pCA_{2,6}$	128.3/7.08	$C_{2,6}$-$H_{2,6}$ in *p*-coumarate (PCA)
pCA_α+FA_α	144.9/7.57	C_α-H_α in *p*-coumarate (PCA) and ferulate (FA)

2.2 Figures

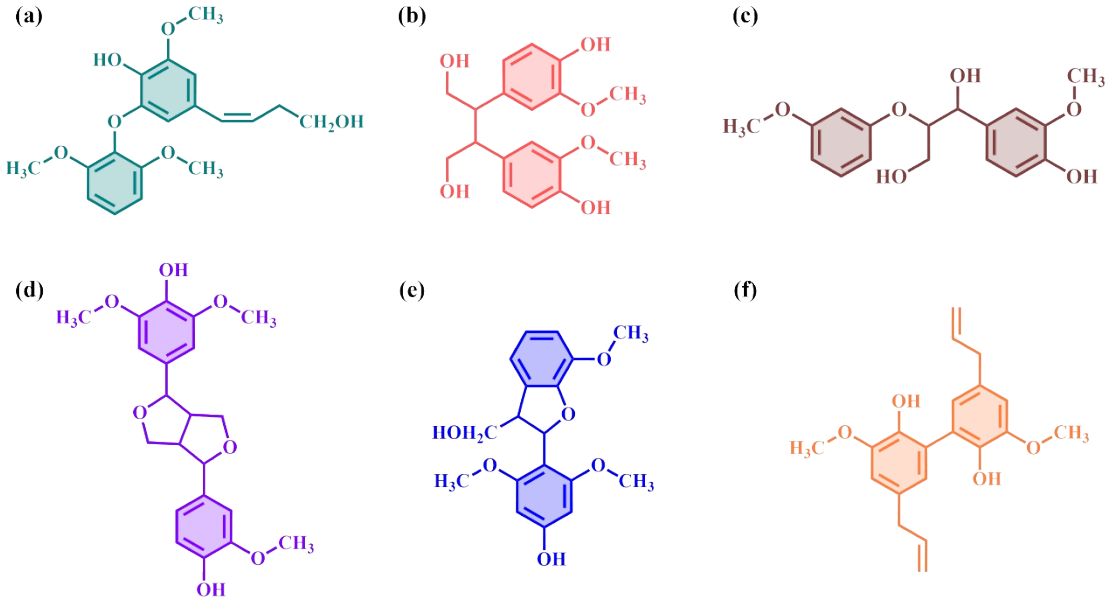

Fig. S1 Two-dimensional molecular structure diagram of lignin dimer: (a) 4-O-5; (b) β-1; (c) β-O-4; (d) β-β; (e) β-5; (f) 5-5.

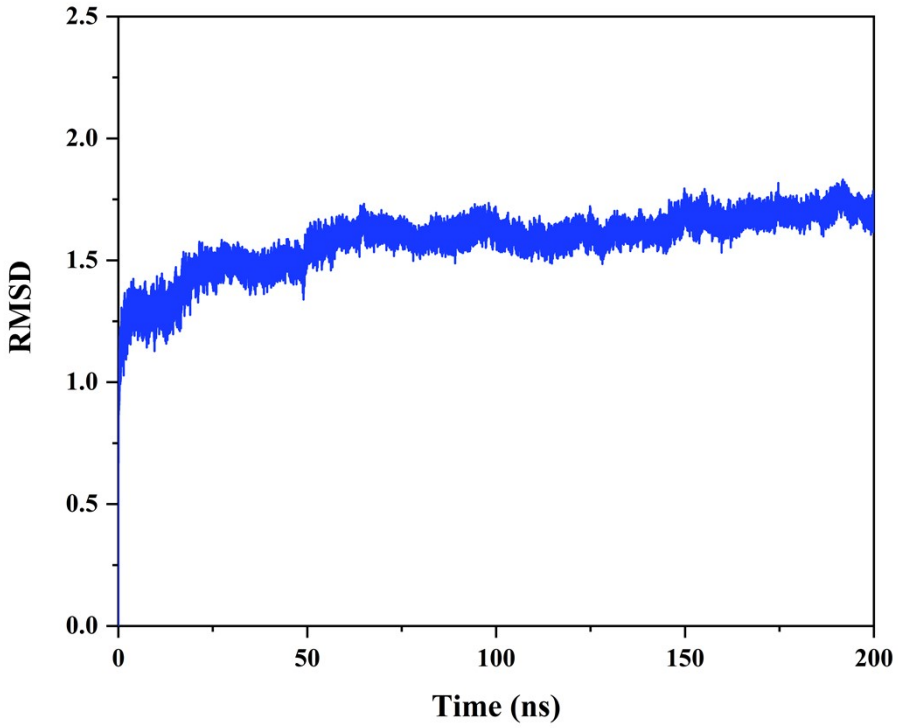

Fig. S2 Root mean square deviation (RMSD) of molecular dynamics simulation.

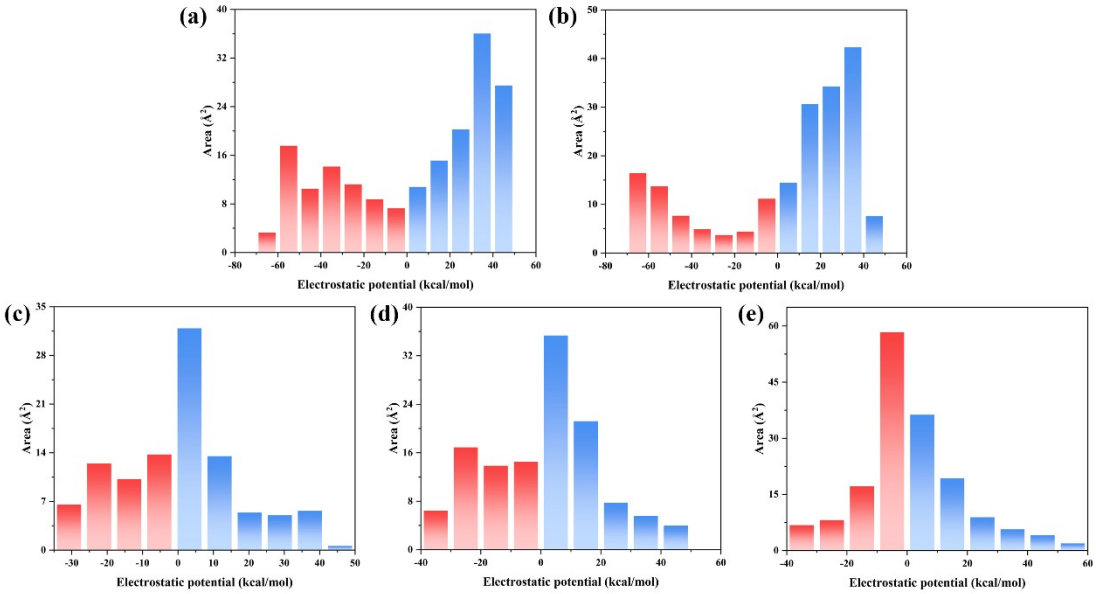

Fig. S3 Electrostatic potential area distribution range plots of DES components: (a) ATMAC; (b) ChCl; (c) LA; (d) EG; (e) PB (Blue: positive potential region; Red: negative potential region).

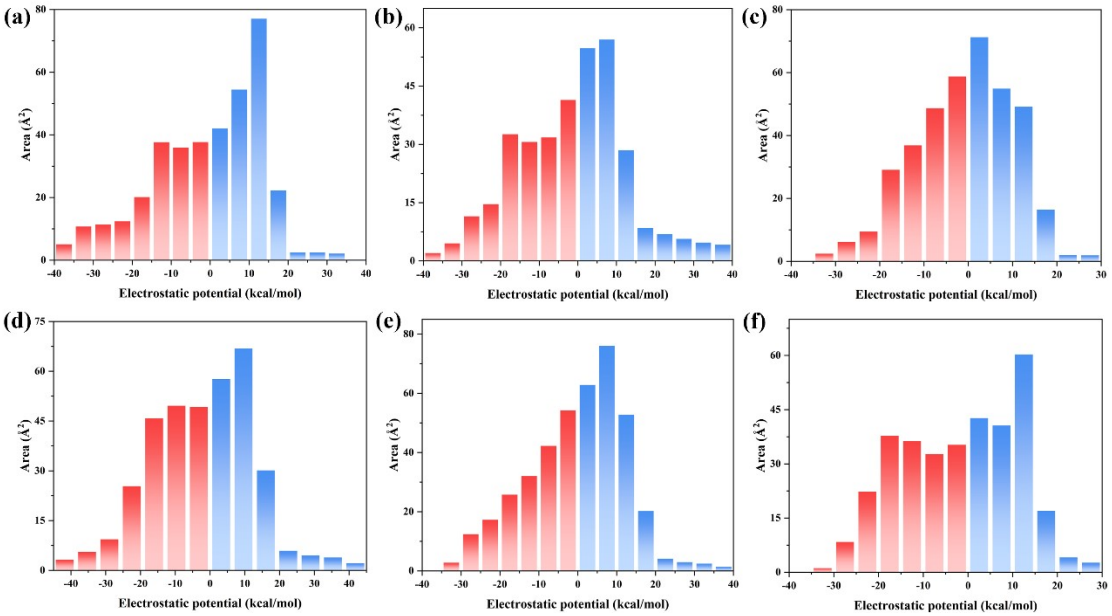

Fig. S4 Electrostatic potential area distribution range plots of lignin dimer: (a) 4-O-5; (b) β-1; (c) 5-5; (d) β-5; (e) β-β; (f) β-O-4 (Blue: positive potential region; Red: negative potential region).

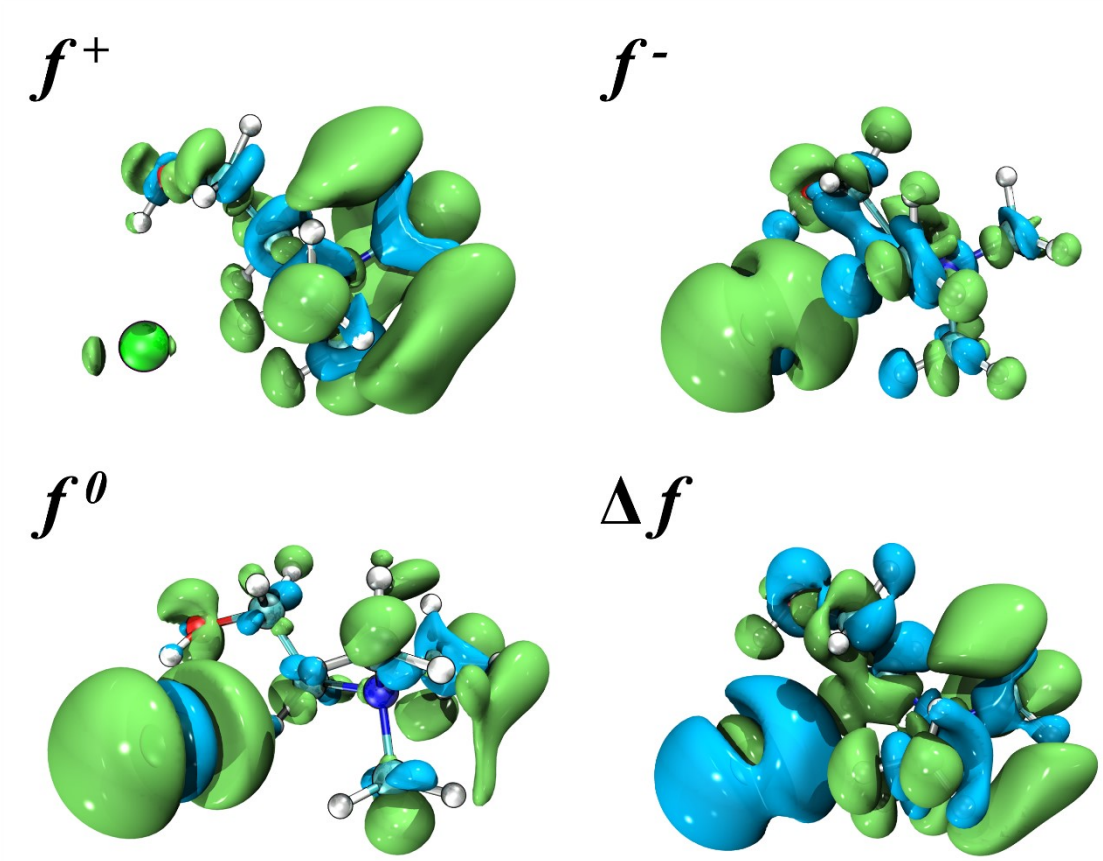

Fig. S5 Fukui function and orbital-weighted dual descriptor plots of ATMAC (Green: positive values; Cyan: negative values).

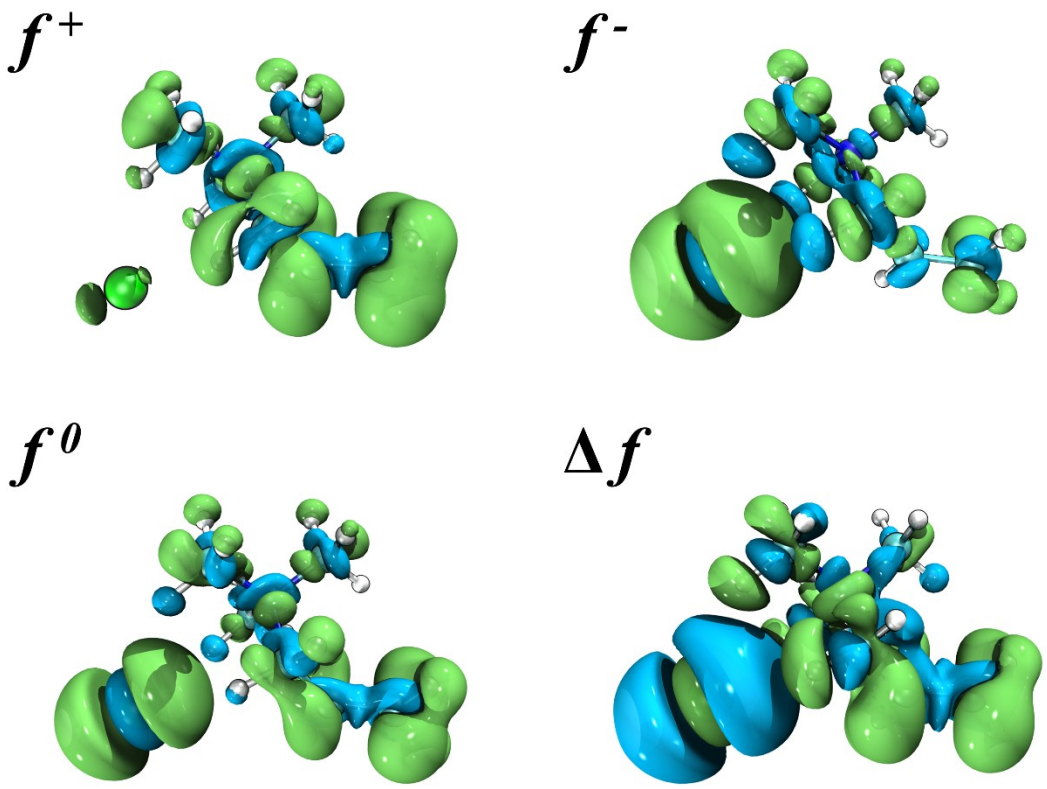

Fig. S6 Fukui function and orbital-weighted dual descriptor plots of ChCl (Green: positive values; Cyan: negative values).

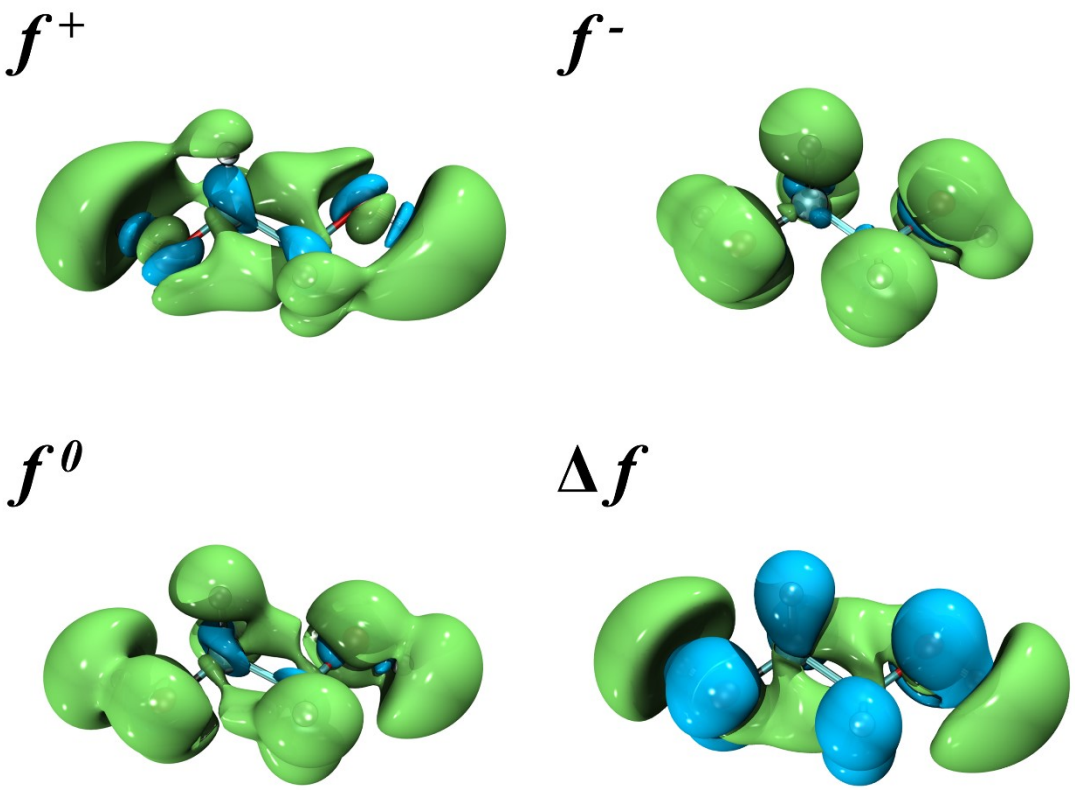

Fig. S7 Fukui function and orbital-weighted dual descriptor plots of EG (Green: positive values; Cyan: negative values).

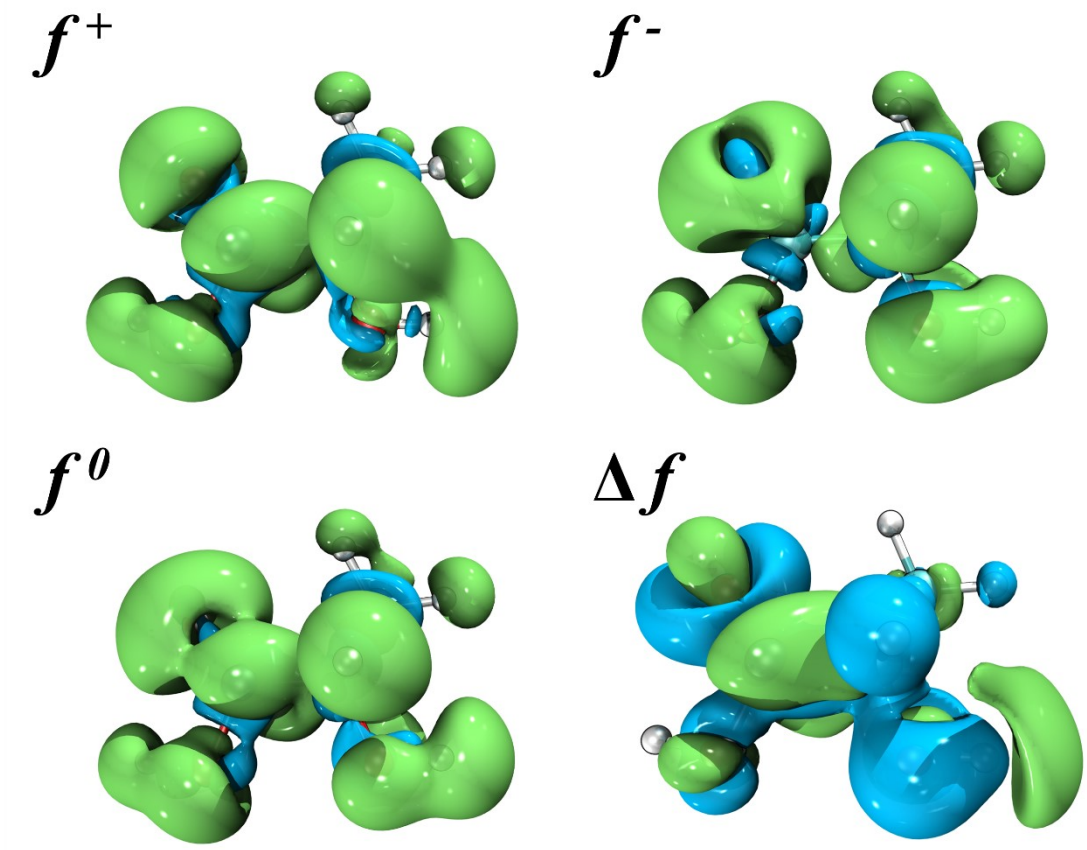

Fig. S8 Fukui function and orbital-weighted dual descriptor plots of LA (Green: positive values; Cyan: negative values).

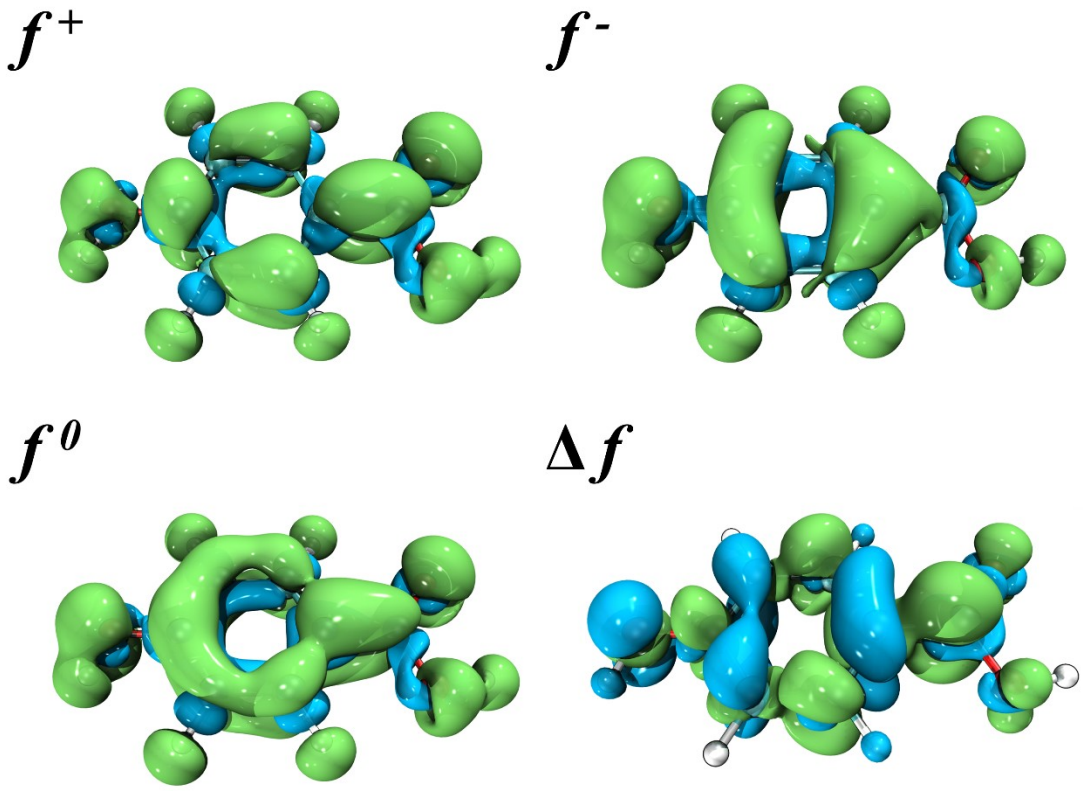

Fig. S9 Fukui function and orbital-weighted dual descriptor plots of PB (Green: positive values; Cyan: negative values).

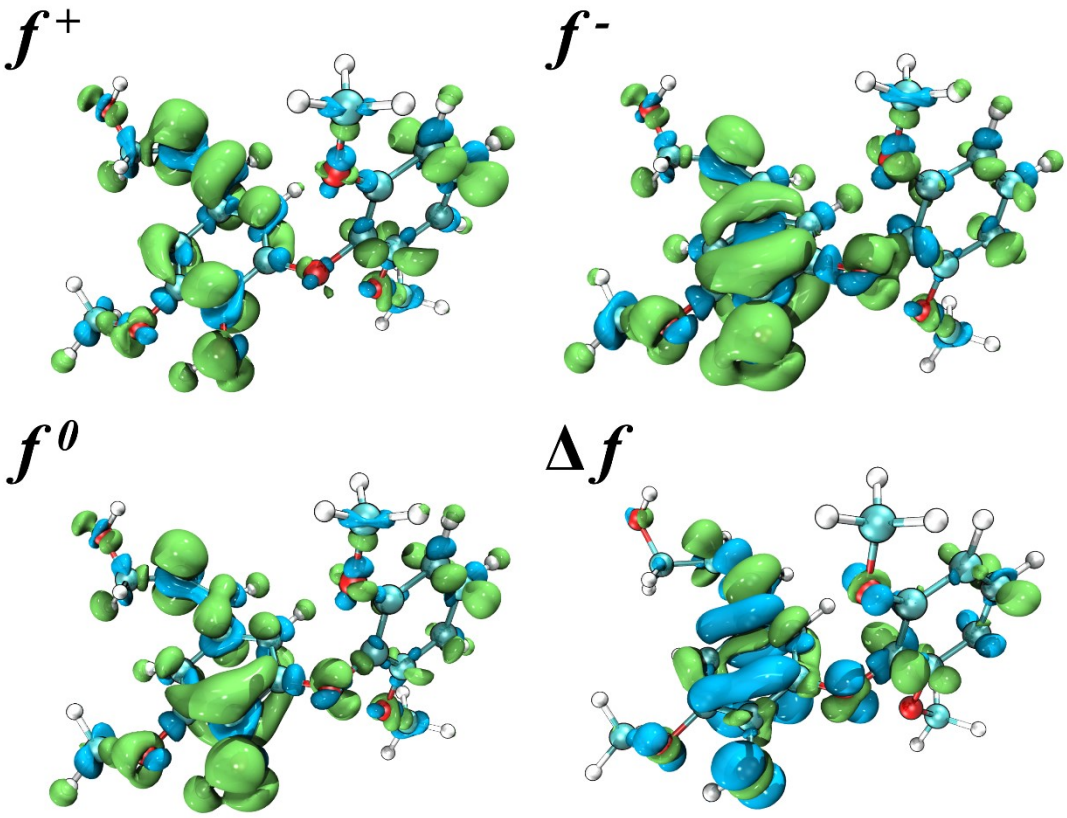

Fig. S10 Fukui function and orbital-weighted dual descriptor plots of 4-O-5 (Green: positive values; Cyan: negative values).

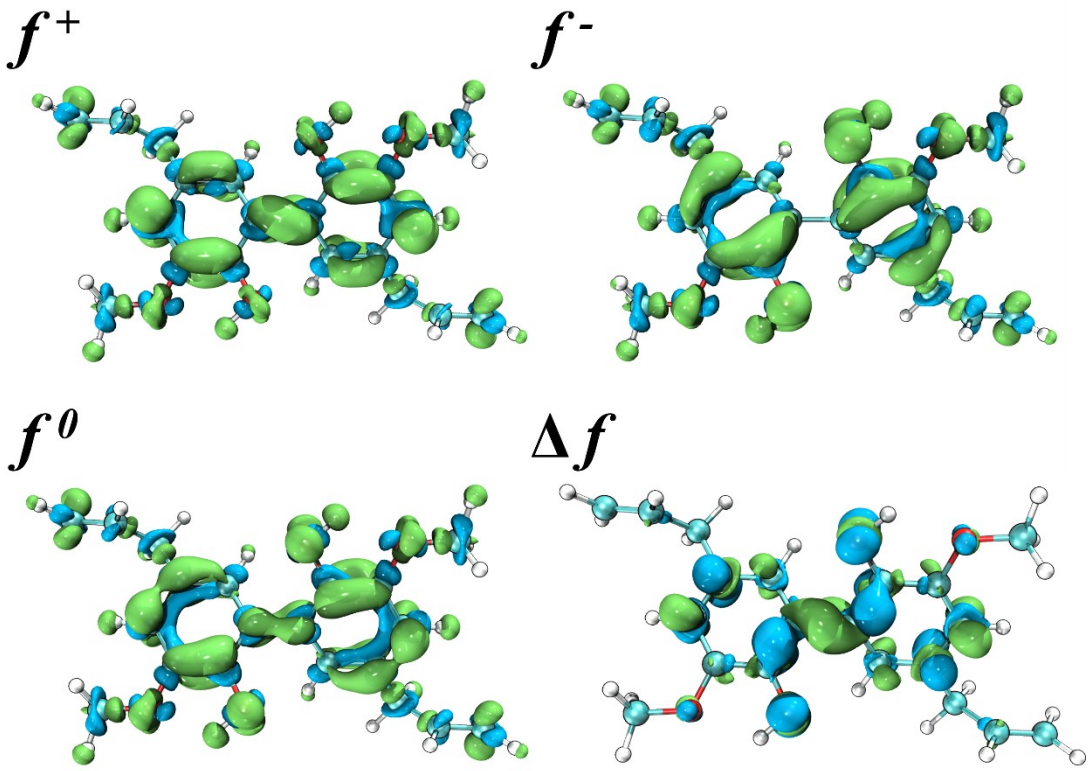

Fig. S11 Fukui function and orbital-weighted dual descriptor plots of 5-5 (Green: positive values; Cyan: negative values).

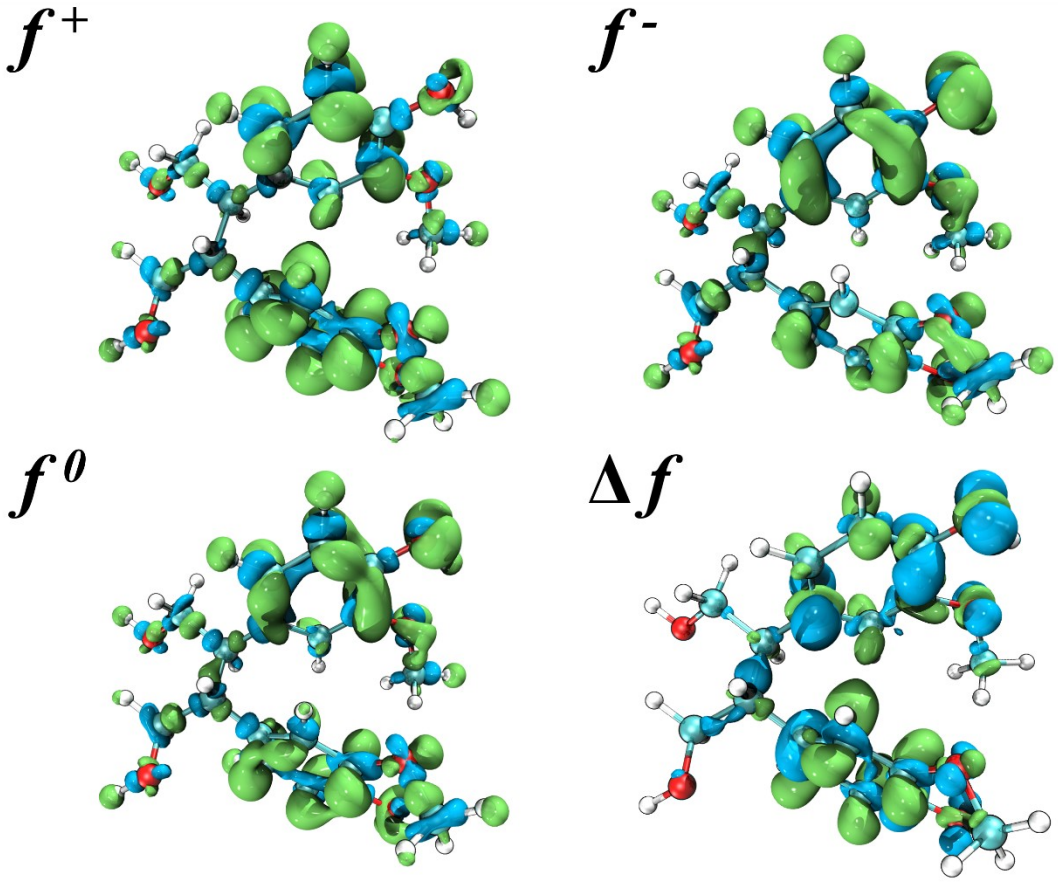

Fig. S12 Fukui function and orbital-weighted dual descriptor plots of β-1 (Green: positive values; Cyan: negative values).

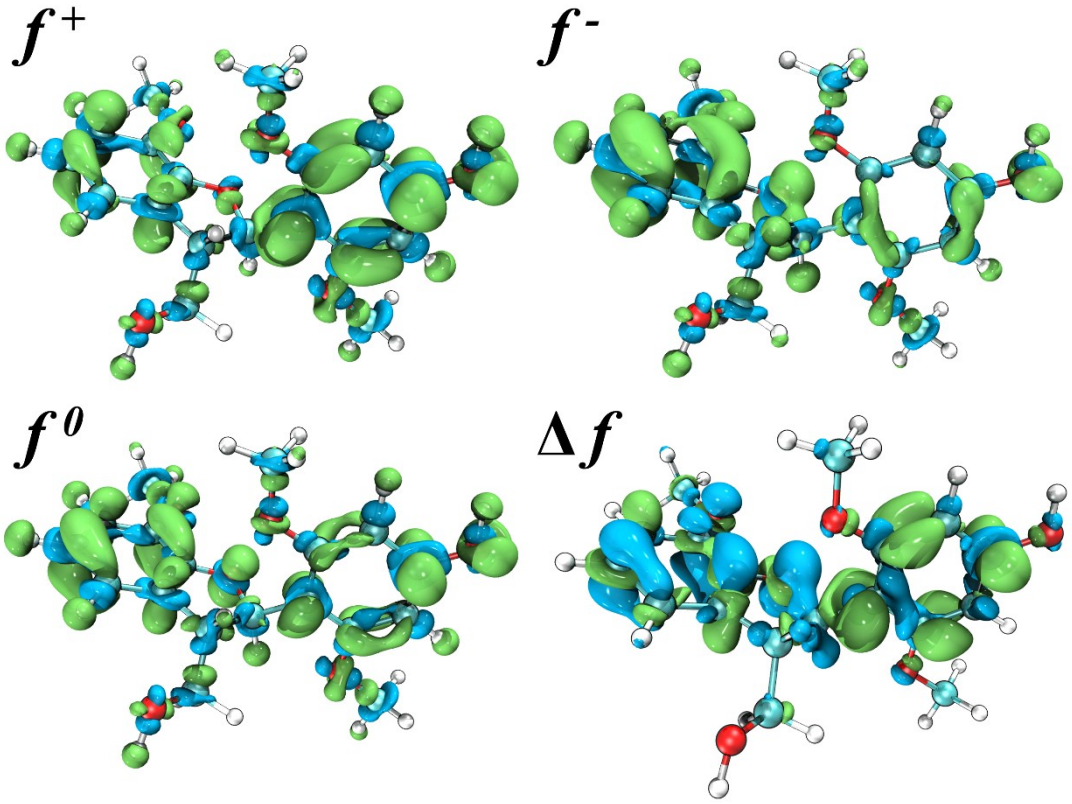

Fig. S13 Fukui function and orbital-weighted dual descriptor plots of β-5 (Green: positive values; Cyan: negative values).

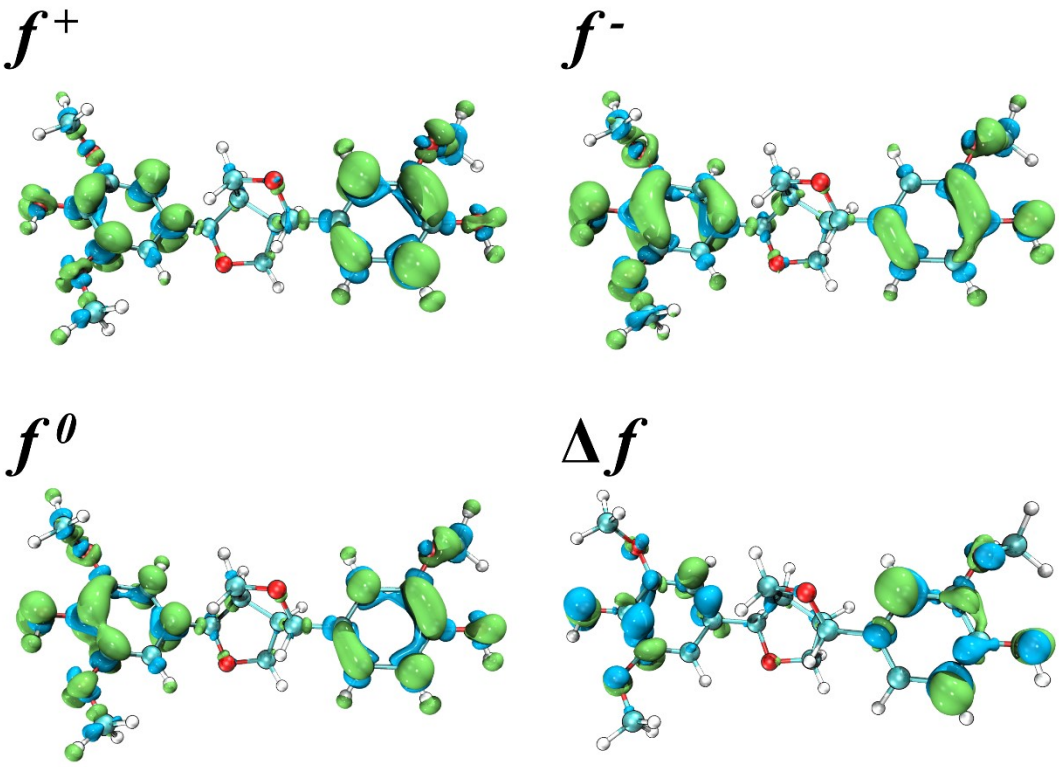

Fig. S14 Fukui function and orbital-weighted dual descriptor plots of β-β (Green: positive values; Cyan: negative values).

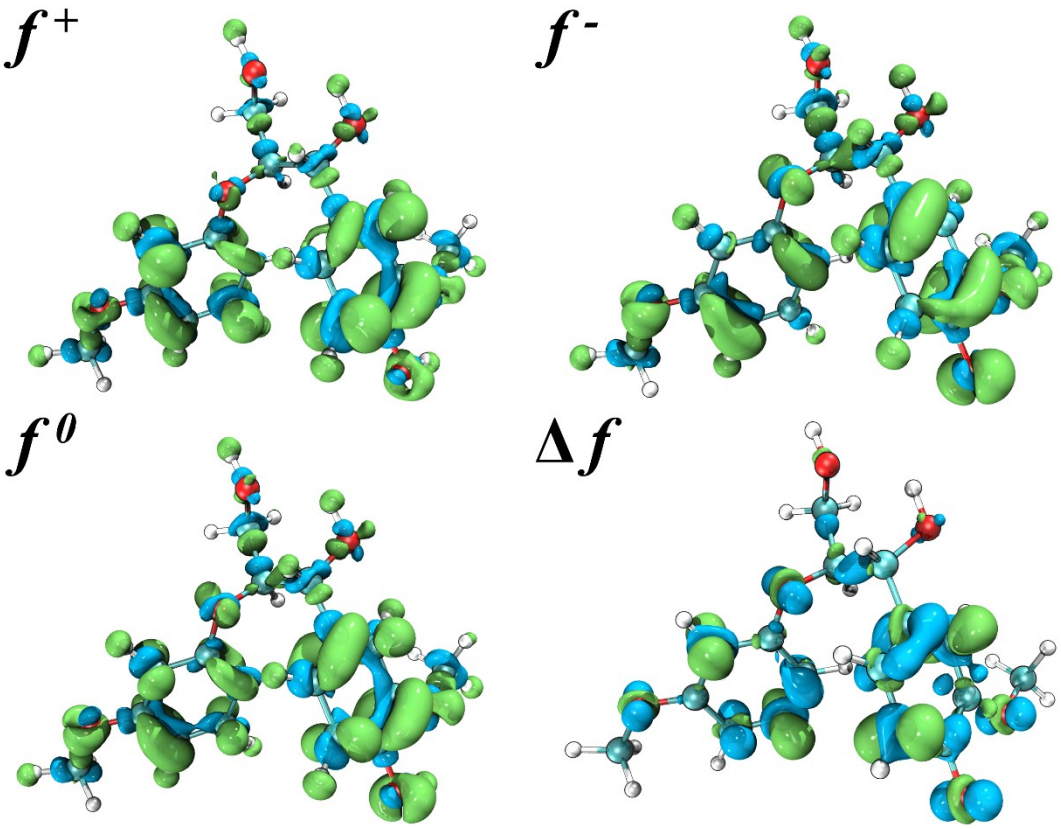

Fig. S15 Fukui function and orbital-weighted dual descriptor plots of β-O-4 (Green: positive values; Cyan: negative values).

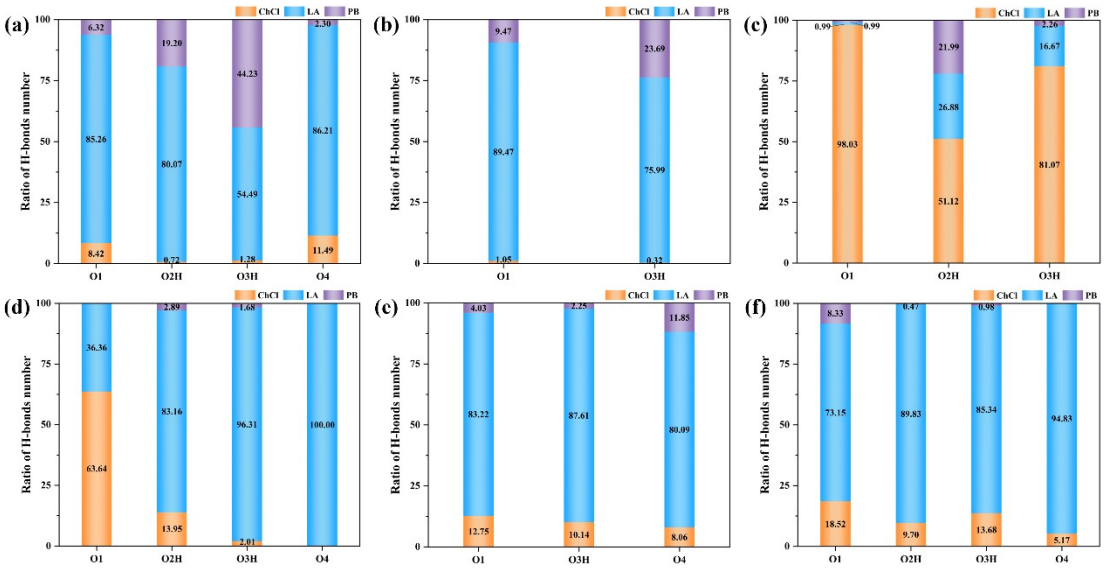

Fig. S16 Percentage of H-bonds between DES components and different lignin dimer: (a) 4-O-5; (b) 5-5; (c)β-1 ; (d) β-5; (e) β-β; (f) β-O-4.