Supporting Information for

Aminated and amidated structures introduced by ethylenediamine pretreatment endow lignin with bright fluorescence

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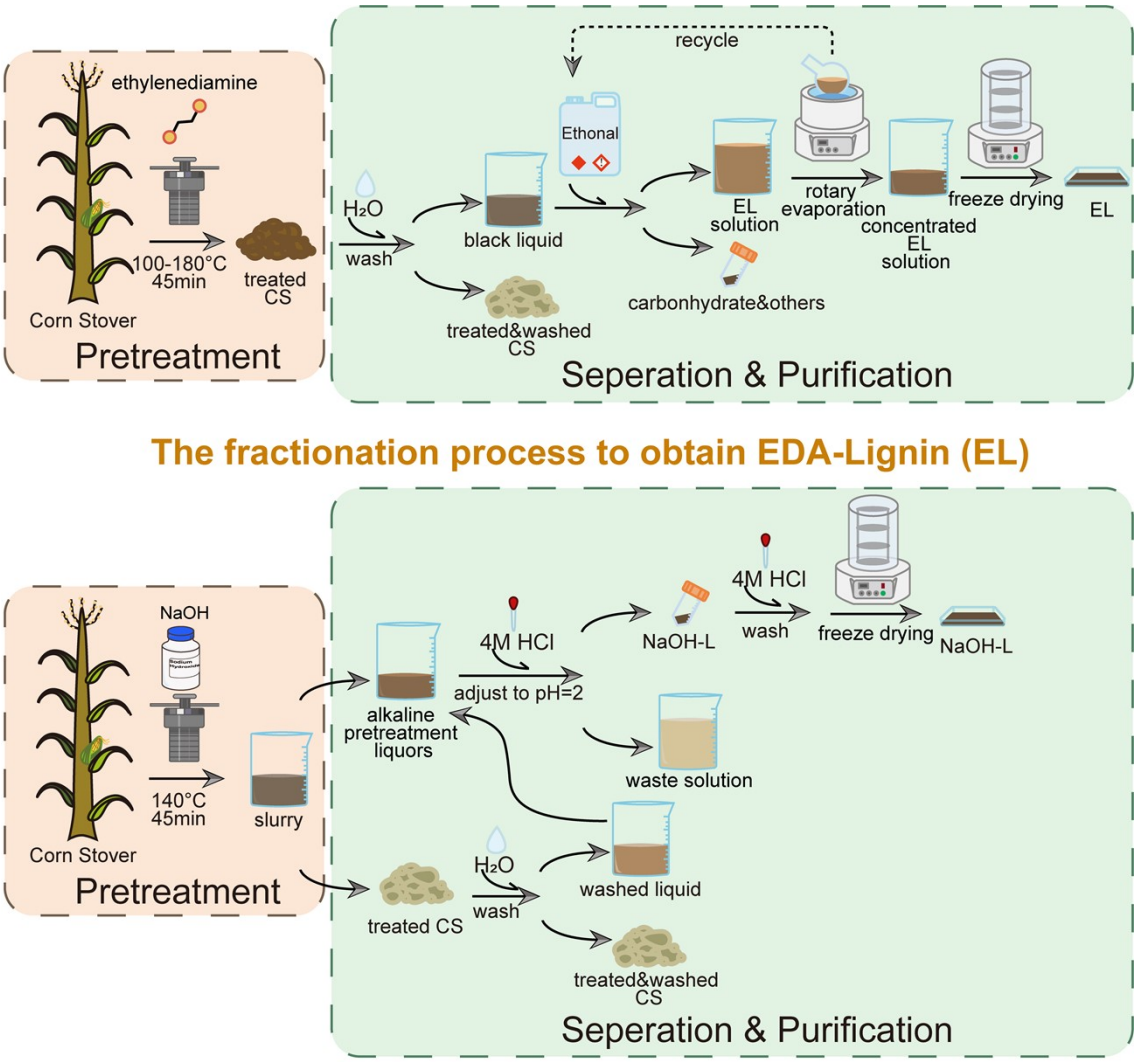

Fig. S1 The pretreatment processes to prepare different lignin samples.

Fig. S2 Appearance of aminated lignin (120EL), which presents in a brown to black sheet-like solid form.

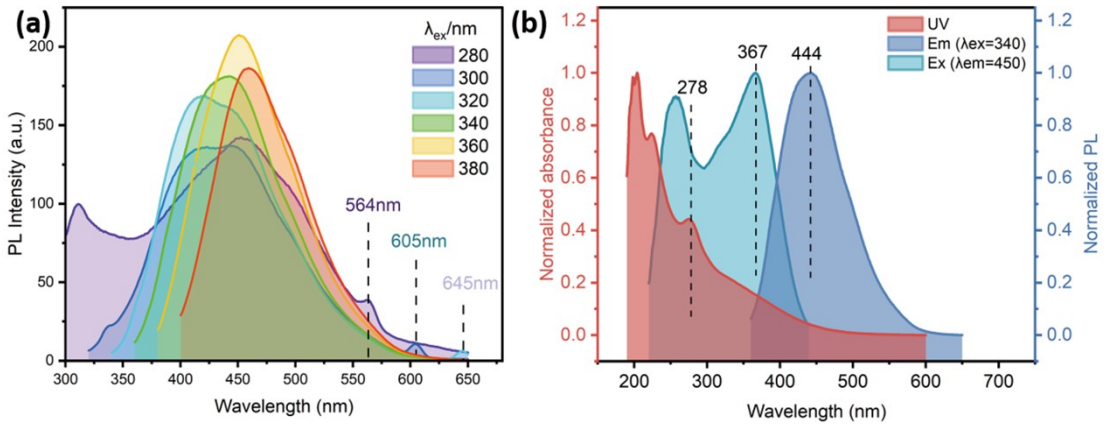

Fig. S3 a) Emission spectrum excited at difference λ_{ex} and **b)** excitation spectrum emitted at 340 nm, PL spectra excited at 340 nm, and UV-vis spectrum of 180EL (c= 0.1g/L).

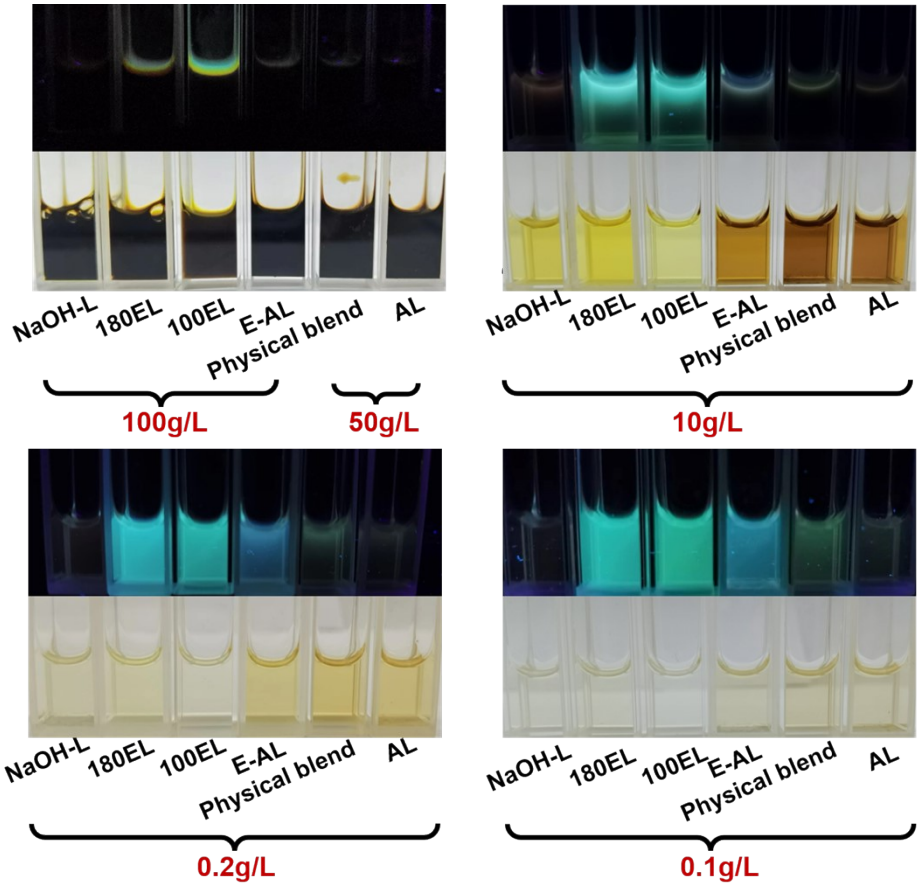

Fig. S4 Fluorescent images of lignin aqueous solutions taken under 365 nm UV light (from a top light);

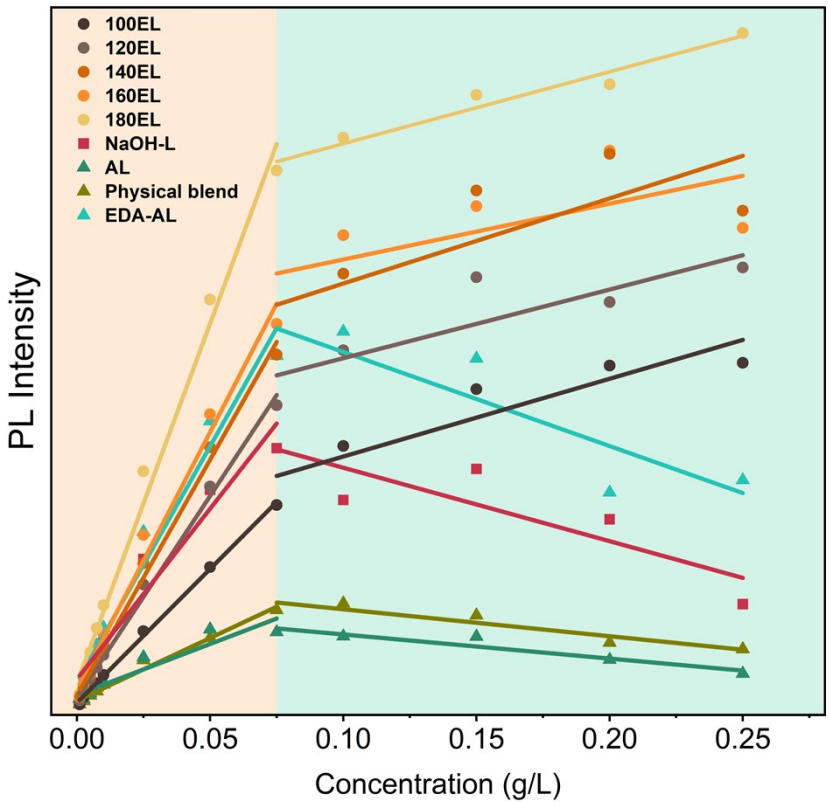

Fig. S5 Two stages of linear regions of concentration-fluorescence intensity; related parameters were shown in tables S1 and S2.

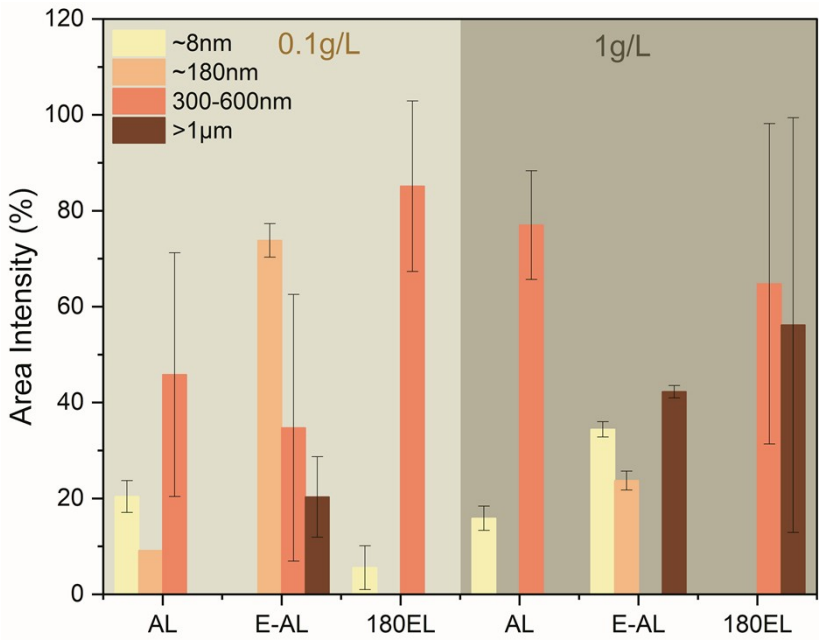

Fig. S6 Particle diameter distribution at two different concentrations (0.1g/L and 1g/L).

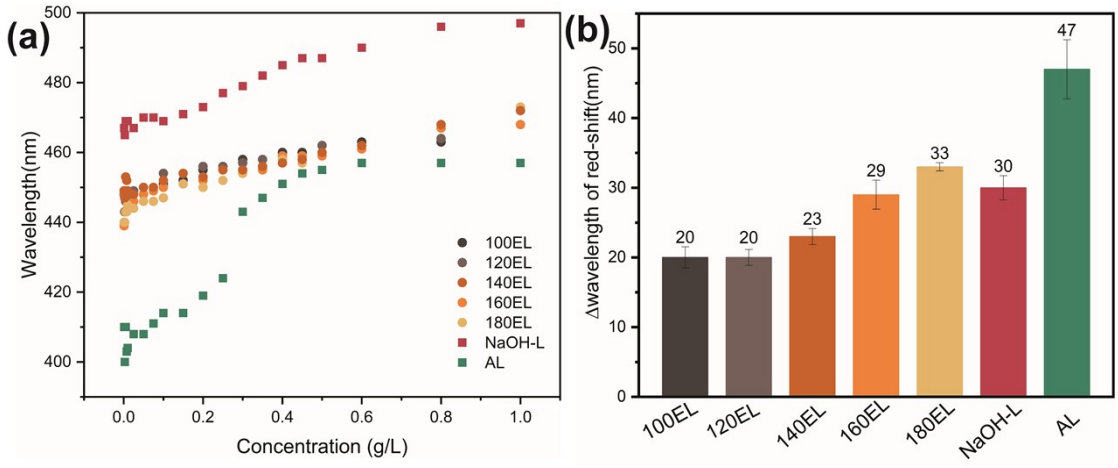

Fig. S7 Red-shift of max emission wavelength affected by increasing concentration.

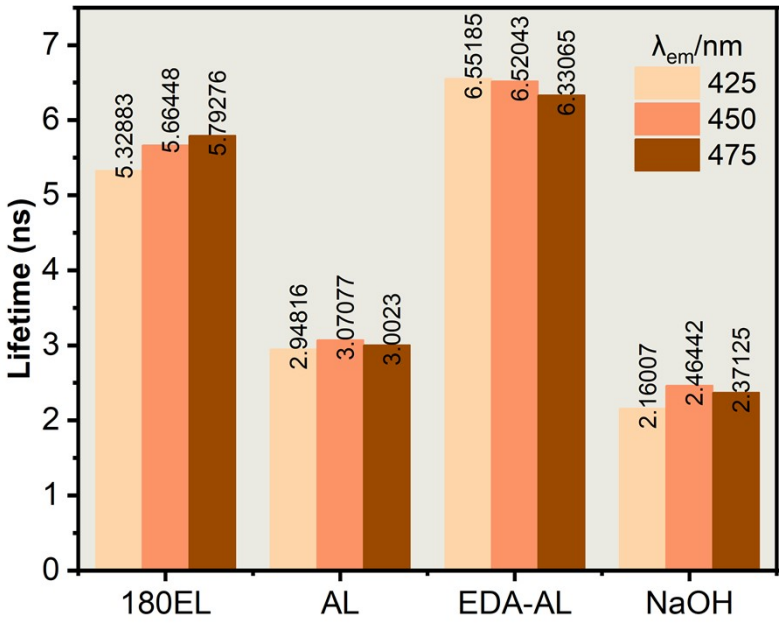

Fig. S8 PL lifetimes at different emission wavelength (c= 0.1g/L)

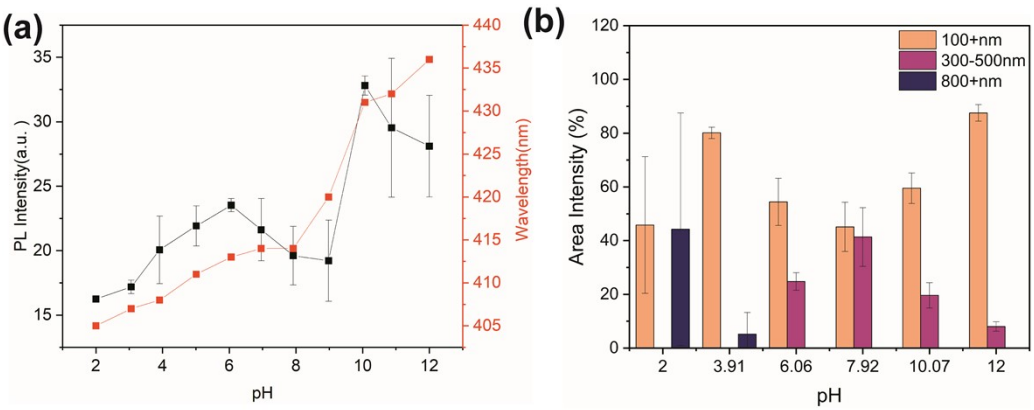

Fig. S9 PL intensity of AL in different pH solution. a) Max fluorescence intensity of AL in different pH and emission wavelengths, b) Size distributions in three ranges (100+ nm, 300-500nm and 800+ nm) of AL (c=0.1 g/L) solution at different pH values.

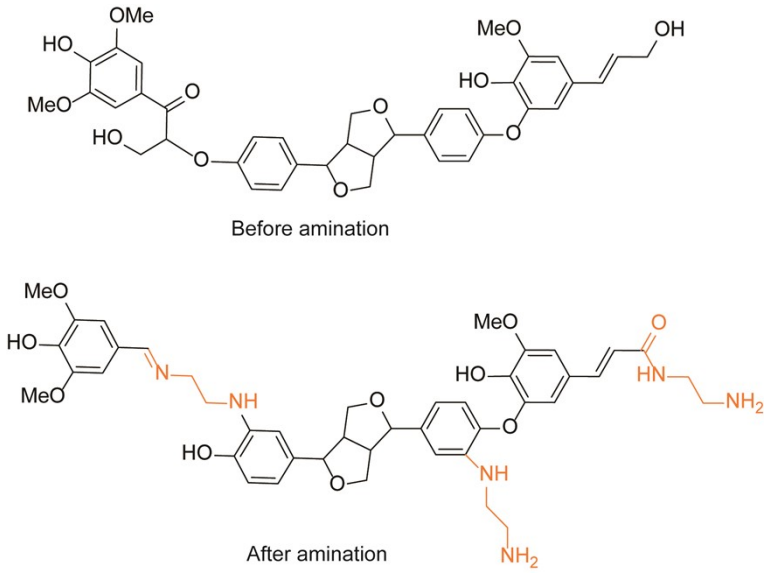

Fig. S10 Molecular structures of model lignin used in theoretical calculations. The aminated molecule contains 4 different types of N-containing groups (-NH2, -NH-, -C=N-, and -CR-NH-), shown in orange color.

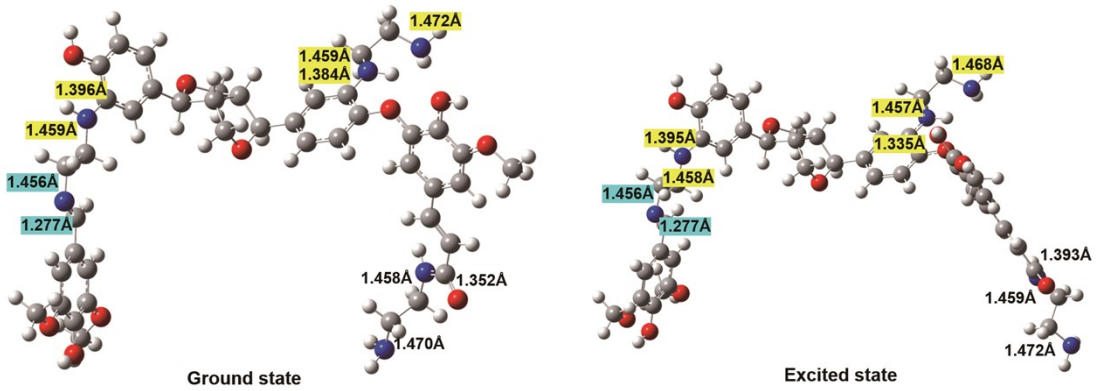

Fig. S11 Bond length of N-C at the ground state and excited state respectively. Yellow ones were shorter after excitement, while blue ones remained unchanged.

Table S1. Parameters of Linear fit in concentration-fluorescence intensity (stage 1: cluster formation).

sample	Intercept	Slope	R-Square (COD)
NaOH	8.03 ± 3.03	984.16 ± 90.51	0.95171
AL	1.82 ± 0.66	361.63 ± 19.88	0.9822
E-AL	6.98 ± 3.12	1365.88 ± 93.36	0.97273
AL	3.51 ± 1.39	293.69 ± 41.69	0.89212
100EL	1.20 ± 0.42	772.93 ± 12.69	0.99839
120EL	2.67 ± 1.14	1165.17 ± 34.10	0.99489
140EL	3.35 ± 1.37	1360.50 ± 41.06	0.99456
160EL	5.16 ± 2.28	1483.74 ± 68.07	0.98753
180EL	6.89 ± 2.96	2075.58±88.63	0.98918

Table S2. Parameters of Linear fit in concentration-fluorescence intensity (stage 2: increase of cluster numbers).

sample	Intercept	Slope	R-Square (COD)
NaOH	89.76 ± 19.75	-209.50 ± 107.50	0.65505
AL	39.56 ± 2.84	-95.16 ± 15.47	0.94977
E-AL	142.69 ± 20.10	-334.78 ± 109.39	0.82403
AL	29.63 ± 3.30	-78.04 ± 17.98	0.90404
100EL	63.69 ± 9.11	157.52 ± 49.60	0.83454
120EL	95.15 ± 13.47	129.00 ± 73.30	0.60764
140EL	121.48 ± 23.73	130.40 ± 129.20	0.33747
160EL	137.12 ± 21.45	44.60 ± 116.78	0.06797
180EL	146.08 ± 5.62	187.40 ± 30.60	0.94939

Table S3. The comparison of calculated and experimental values based on model lignin molecules.

samples	Calculated results		Experimental results	
	absorption	emission	absorption	emission
Un-aminated lignin	286 nm	403 nm	242 nm	420 nm
Aminated lignin	321 nm	486 nm	201 nm	447 nm