Supporting Information for

Lignin and Phenylenediamine Synergy in Carbon Dots: Deciphering the Origin of Long-Wavelength Photoluminescence and the Carbon Core Growth

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1. Experimental Section

1.1 Materials

p-Phenylenediamine (PPD), formamide (FA), dioxane (Diox), ethanol (EtOH), N,N-dimethylformamide (DMF), ethyl acetate, polyvinyl alcohol (PVA) and polyethylene glycol (PEG) were supplied by Meryer Chemical Technology Co., Ltd. (Shanghai, China) and used without further purification. Industrial alkali lignin was provided by a paper manufacturer and isolated from the black liquor by precipitation at pH 7. NaOH-pretreated lignin and EtOH-pretreated lignin were obtained based on our previous work.[1] Lignin with a molecular weight below 1 kDa (L-lignin) was fractionated using an organic membrane separation apparatus.

1.2 Preparation of CDs

All CDs were prepared via the solvothermal method with lignin and PPD (in a 1.2:1 ratio) as precursors. The processes were as follows: 72 mg of lignin and 60 mg of PPD were dissolved in 10 mL of specific solvents (i.e. FA, Diox, EtOH, DMF) and uniformly dispersed by ultrasonication. The resulting solution was transferred to a Teflon-lined autoclave, heated at 200 °C for 10 h, and then allowed to cool naturally to room temperature. The reaction solution was filtrated through an organic membrane and then dialyzed using a dialysis bag with a molecular weight cut-off of 500 Da. The dialysate was replaced every 6 h until it became colorless. The remaining liquid was freeze-dried in a vacuum lyophilizer to obtain CD powder. Blue, green, white and blue emissive CDs were obtained from FA, Diox, EtOH, DMF, respectively, and named B-CDs, G-CDs, W-CDs, and R-CDs accordingly.

R-CDs-O_2 were prepared using the same procedure as that for R-CDs, except that O_2 was bubbled through the solution for 30 minutes prior to the solvothermal treatment.

R-CDs-N_2 were prepared using the same procedure as that for R-CDs, except that N_2 was bubbled through the solution for 30 minutes prior to the solvothermal treatment.

PPD-R-CDs were prepared using the same method as that for R-CDs, except that PPD was used as the sole carbon source.

L-CDs were prepared using the same method as that for R-CDs, except that lignin was used as the sole carbon source.

PVA-R-CDs were prepared following the same procedure as that for R-CDs, but with lignin replaced by PVA.

PEG-R-CDs were prepared following the same procedure as that for R-CDs, with lignin replaced by PEG.

1.3 Fabrication of the CD-based LED devices

GaN LED chips without a phosphor coating were purchased from Advanced Optoelectronic Technology Co., LTD. The 0.1 mL CD solution (1.0 mg mL^{-1}) was thoroughly mixed with 0.9 mL of epoxy resin, and the mixture was then drop-coated onto GaN LED chips. Subsequently, the LED chips were placed in a 60 °C oven for 2 hours. The emission spectra of LEDs were measured by combining a Spectra scan PR-650 spectrophotometer with an integrating sphere and a computer-controlled Keithley model 2400 voltage current source under ambient conditions at room temperature.

1.4 Separation and purification of R-CDs

The crude product of R-CDs was purified by column chromatography using a gradient elution program with mixtures of methanol and ethyl acetate. Column chromatography was performed with silica gel (400 mesh) as the stationary phase.

The elution flow rate was maintained at approximately 2.0 mL/min throughout the separation process. The methanol-to-ethyl acetate volume ratio was progressively increased from 1:5, 2:5, 3:5, and 4:5, to a final ratio of 1:1, with 10 mL of eluent at each step. The column was then continuously eluted with the 1:1 mixture until elution was complete. Throughout this process, a yellow fraction was the first compound to be eluted and was collected for subsequent investigation. A red fraction, which eluted as the second major component, was also collected. This red fraction was then subjected to two additional purification cycles using the same chromatographic method described above. After a total of three cycles, a high-purity red fraction was obtained.

1.5 Photostability testing

The CD dispersion in ethanol (0.05 mg mL^{-1}) was loaded into a sealed quartz cuvette. The sample was irradiated with UV light directed perpendicularly onto the cuvette, ensuring the beam illuminated the entire volume of the dispersion. At designated time intervals, the fluorescence spectrum of the sample was recorded.

1.6 Instruments and characterization

The crystalline structure and morphological features of the CDs were characterized using high-resolution transmission electron microscopy (HRTEM, JEM-2100F) with samples supported on ultrathin porous carbon films. Elemental analysis was performed with a Vario Micro cube elemental analyzer (Elementar Co., Germany). Chemical structure and functional groups were investigated by Raman spectroscopy (Renishaw England) and Fourier-transform infrared (FTIR) spectroscopy (Bruker ALPHA II spectrometer). FTIR spectra were collected in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} with 16 scans per sample. Surface chemical states of CDs were analyzed by X-ray photoelectron spectroscopy (XPS) on a Thermo Fisher Scientific Nexsa system. The optical properties were evaluated using UV-Vis absorption spectroscopy (Shimadzu UV-3100 spectrophotometer) and steady-state photoluminescence spectroscopy (Edinburgh Instruments FLS980 spectrophotometer equipped with an integrating sphere). Electron paramagnetic resonance (EPR) measurements were carried out on a CIQTEK EPR200-Plus spectrometer.

For LC-MS spectrometric analysis: the reaction solution was diluted 10-fold with a mixture of water, acetonitrile, and trifluoroacetic acid (95/5/0.1, v/v/v) prior to analysis. LC-MS analysis was performed using an Agilent 1290 LC system equipped with a Brucker MicrOTOF-Q II mass spectrometer. Separation was achieved on a C18 column (2.1×150 mm, 1.7 μm) with a mobile phase consisting of (A) of 0.1% formic acid-water and (B) acetonitrile. The eluted compounds were ionized by electrospray ionization (ESI) in positive mode.

For ^{1}H NMR spectroscopic analysis: the purified fluorophore was thoroughly dried under vacuum, and a 5 mg portion was dissolved in 0.5 mL of deuterated DMSO for ^{1}H NMR analysis, which was conducted on a Bruker Ascend 400 MHz spectrometer.

For Two-dimensional ^{1}H–^{13}C heteronuclear single quantum coherence (HSQC) NMR spectroscopic analysis: 0.1 g lignin sample was dissolved in 0.5 mL of deuterated DMSO. HSQC NMR spectra were recorded on a Bruker AVANCE III 600 MHz spectrometer using the standard hsqcedetgpsisp2.2 pulse sequence. The data were collected with 64 scans per increment and 256 increments in the indirect dimension. The internal standard (I_{C9}) was determined based on the sum of the half of the S2/6 signal, the G2 signal, and half of the H2/6 cross-signal.

$Ic9$ units = $0.5I_{S2/6} + I_{G2} + 0.5I_{H2/6}$

where $I_{S2/6}$, I_{G2}, and $I_{H2/6}$ are the integral values of the S2/6, G2 and H2/6 signals, respectively. I_{C9} represents the total integral value corresponding to the aromatic ring.

The content of linkage I_X% can be calculated according to the following formula:

$I_X\% = I_X/I_{C9} \times 100\%$

where I_X is the integral value of α-position of β–O–4, β–β, and β–5 substructures. It is important that all integrations are performed at the same contour level.

For molecular weight analysis: molecular weight distributions of lignin samples were determined by gel permeation chromatography (GPC) using a Waters e2695 system equipped with a TSKgel GMPWxl column and a 2489 UV/Vis detector operating at wavelength of 280 nm and 254 nm, with 0.1 M NaOH as the mobile phase.

For computational details: all quantum chemical calculations were carried out using the Gaussian 09 software package. The ground-state geometries of the relevant structures were fully optimized using density functional theory (DFT) with the B3LYP functional and the 6-311G(d,p) basis set. The first singlet excited state was subsequently optimized using time-dependent DFT (TD-DFT) with the same functional and basis set. The theoretical emission wavelengths were calculated as the energy difference between the ground and the first excited state.

2. Figures and Tables

Table S1 Elemental analysis of R-CDs and PPD-R-CDs

Samples	%C	%H	%N	%O
R-CDs	66.5 ± 0.2	4.7 ± 0.1	13.5 ± 0.1	15.3 ± 0.1
PPD-R-CDs	62.5 ± 0.2	4.6 ± 0.1	19.5 ± 0.1	13.1 ± 0.3

Table S2 Summary of quantum yields of lignin-derived CDs reported in the literature

Precursors	Method	Fluorescence	Quantum yield	Ref
Alkali lignin	Oxidation and solvothermal	Blue	8.0%-9.0%	[2]
		Green		
		Yellow		
		Red		
Hydrolyzed lignin and o-phenylenediamine	Solvothermal	Blue	7.4%	[3]
	Solvothermal and oxidation	Green	2.1%	
	Solvothermal and reduction	Yellow	14.8%	
Alkali lignin	Hydrothermal	Blue	1.0%-3.9%	[4]
Industrial lignin and tyrosine	Hydrothermal	Blue	1.5%	[5]
Industrial lignin and arginine	Hydrothermal	Green	0.9%	
Industrial lignin and sodium hydroxide	Hydrothermal	Yellow	1.2%	
Industrial lignin, urea, tripotassium phosphate and sodium hydroxide	Hydrothermal	Red	4.7%	
Alkali lignin and o-aminobenzenesulfonic acid	Acidolysis and hydrothermal	Blue	23.7%	[6]

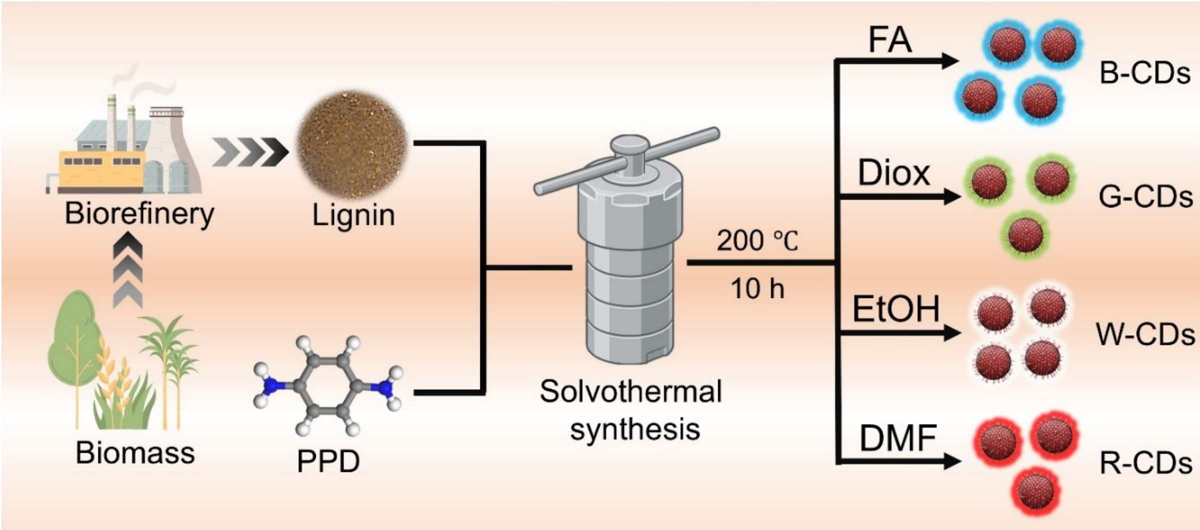

Fig. S1. Synthesis scheme for CDs with white and multi-color emission.

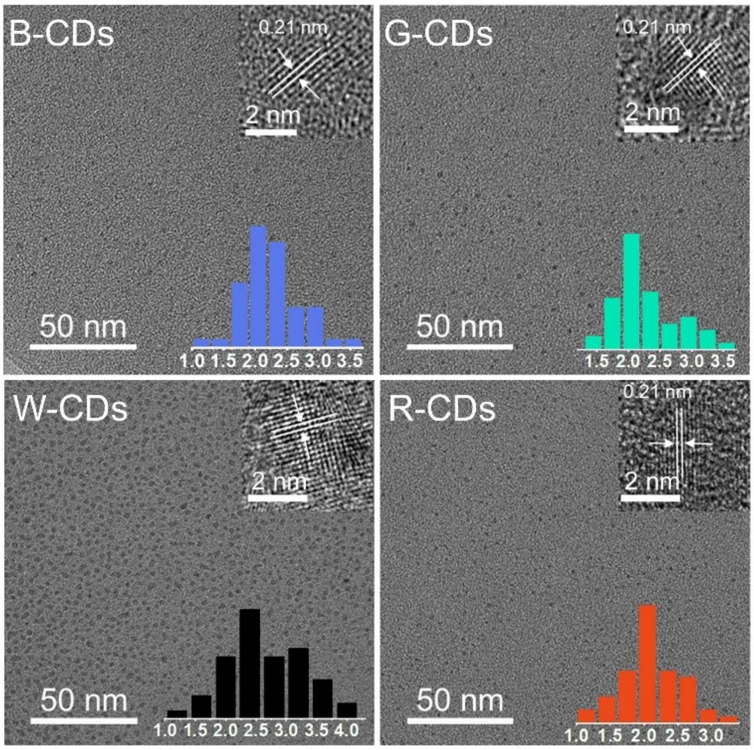

Fig. S2. TEM images of the four CDs. The inserts show the corresponding high-resolution TEM (top right) and particle size distributions (bottom right).

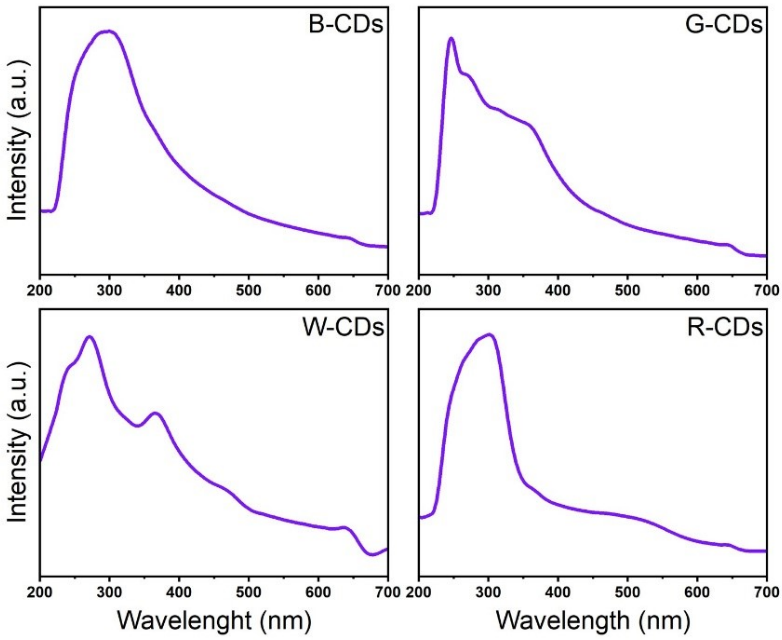

Fig. S3. UV-vis spectra of the four CDs.

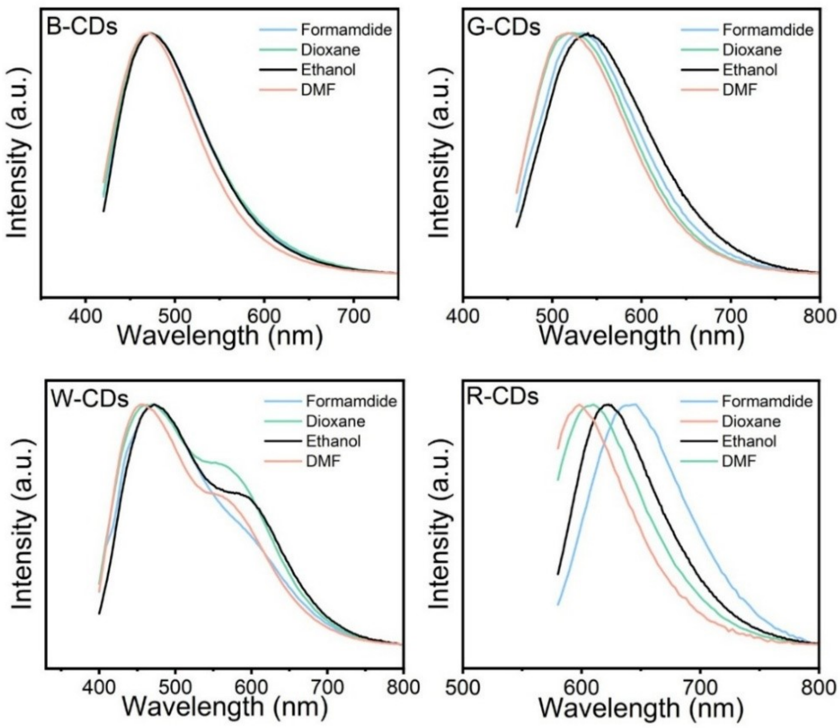

Fig. S4. Normalized PL spectra of the four CDs in different solvents.

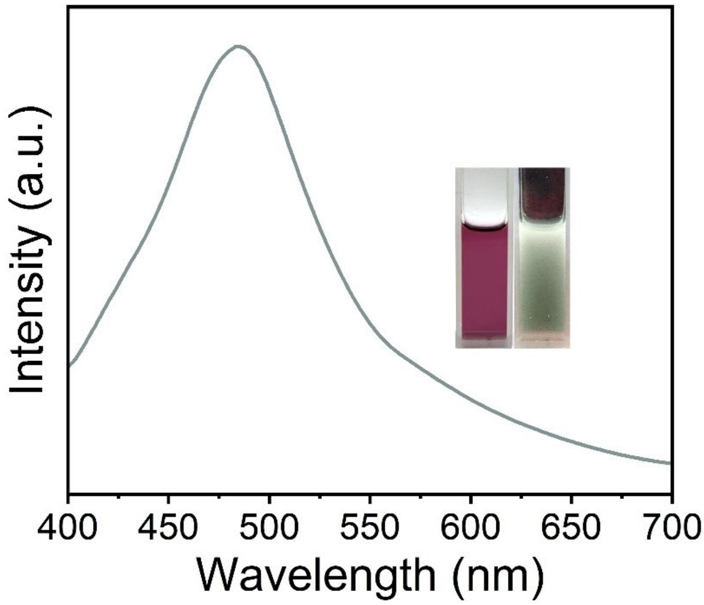

Fig. S5. PL spectra of R-CDs in their protonated form. The corresponding photographs taken under daylight and 365 nm UV light are shown in the left and right insets, respectively.

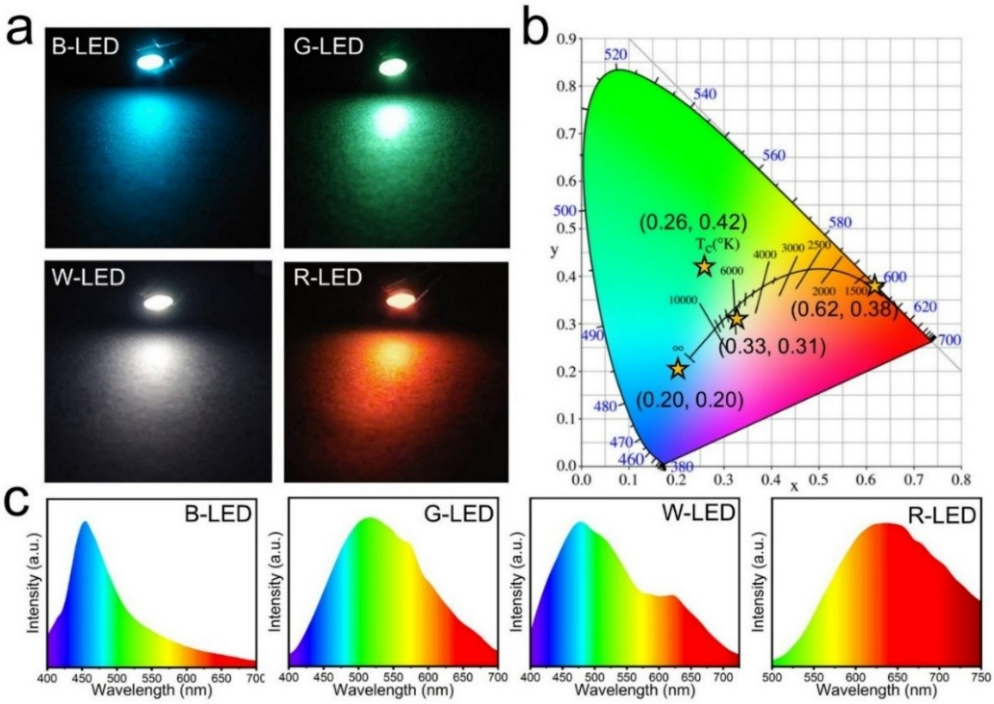

Fig. S6. Performance of the as-synthesized CDs in LED devices. (a) Photograph of the multi-color LEDs. (b) Corresponding CIE color coordinates. (c) PL spectra of the multi-color LEDs.

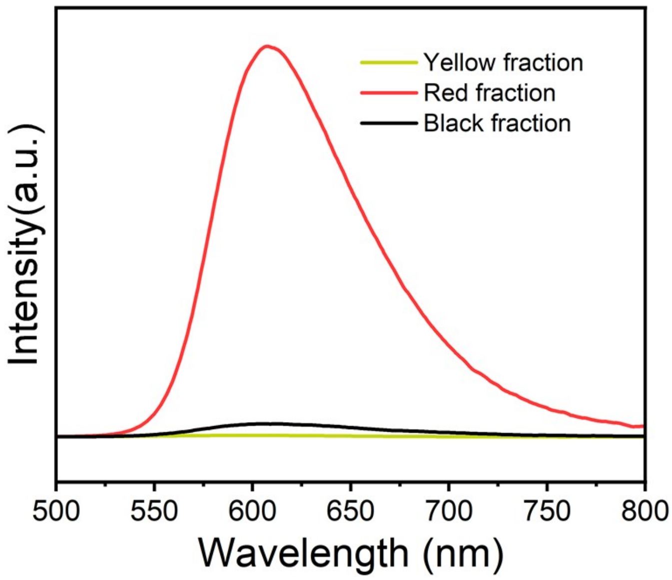

Fig. S7. PL spectra of the three fractions isolated from R-CDs.

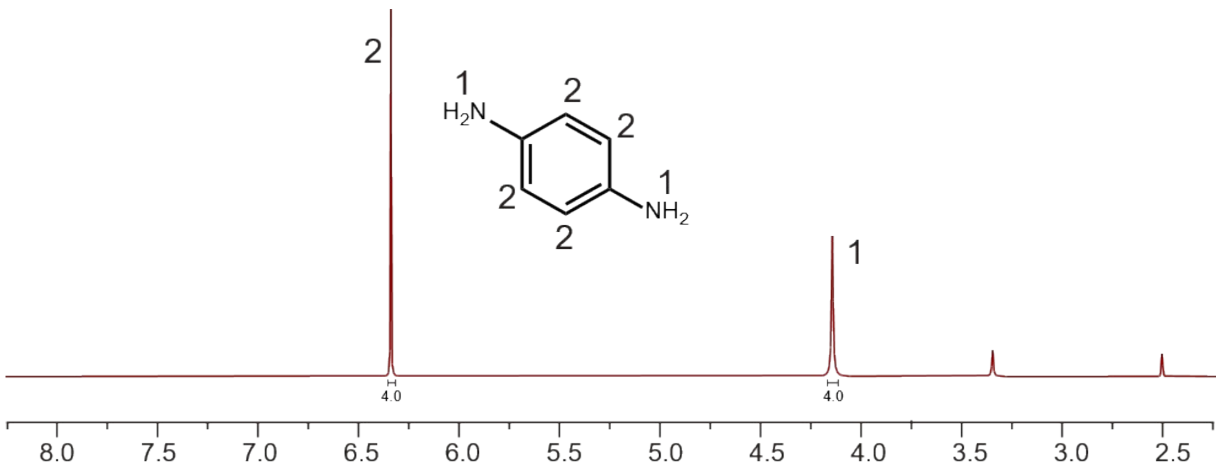

Fig. S8. ^1H NMR spectra of PPD.

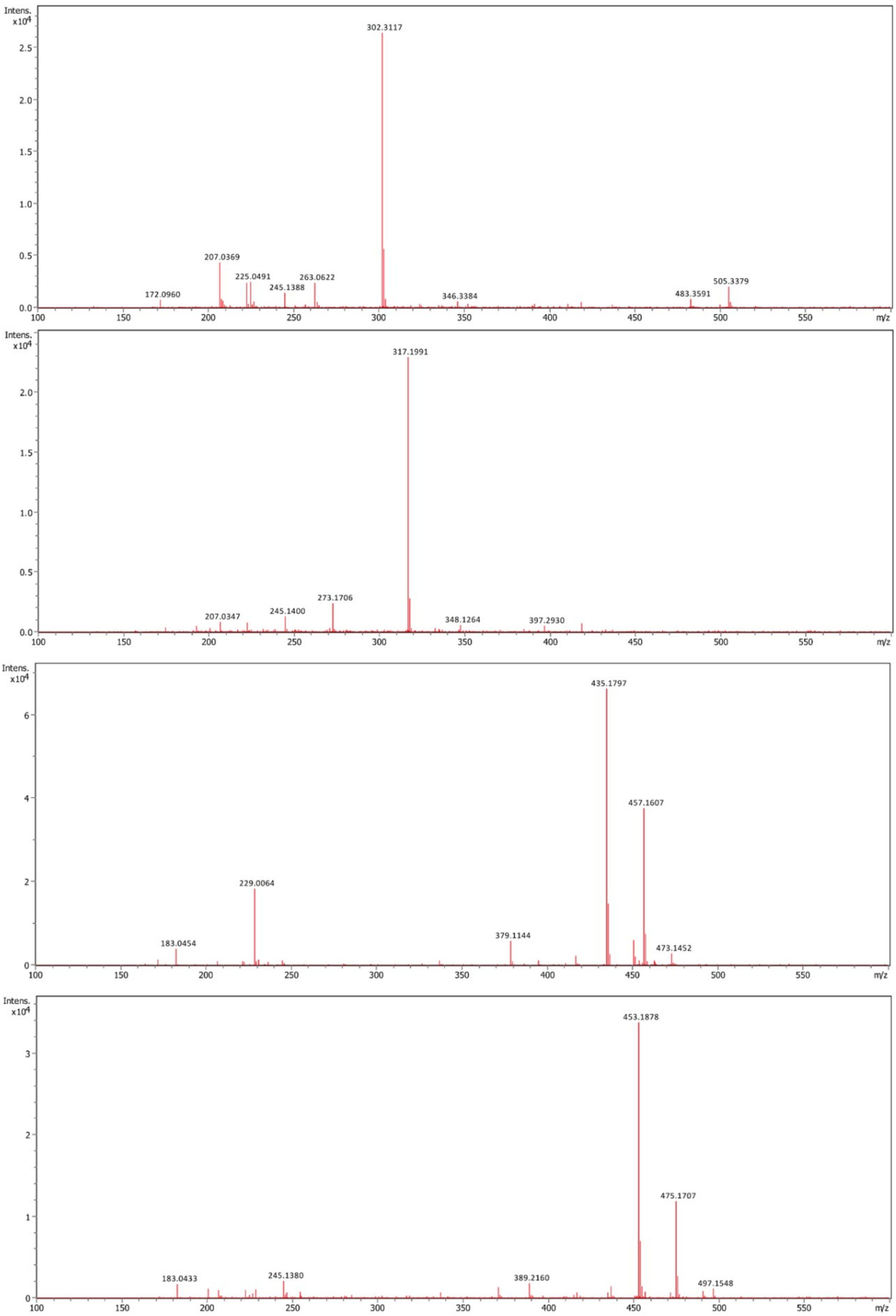

Fig. S9. MS spectra of the black fraction.

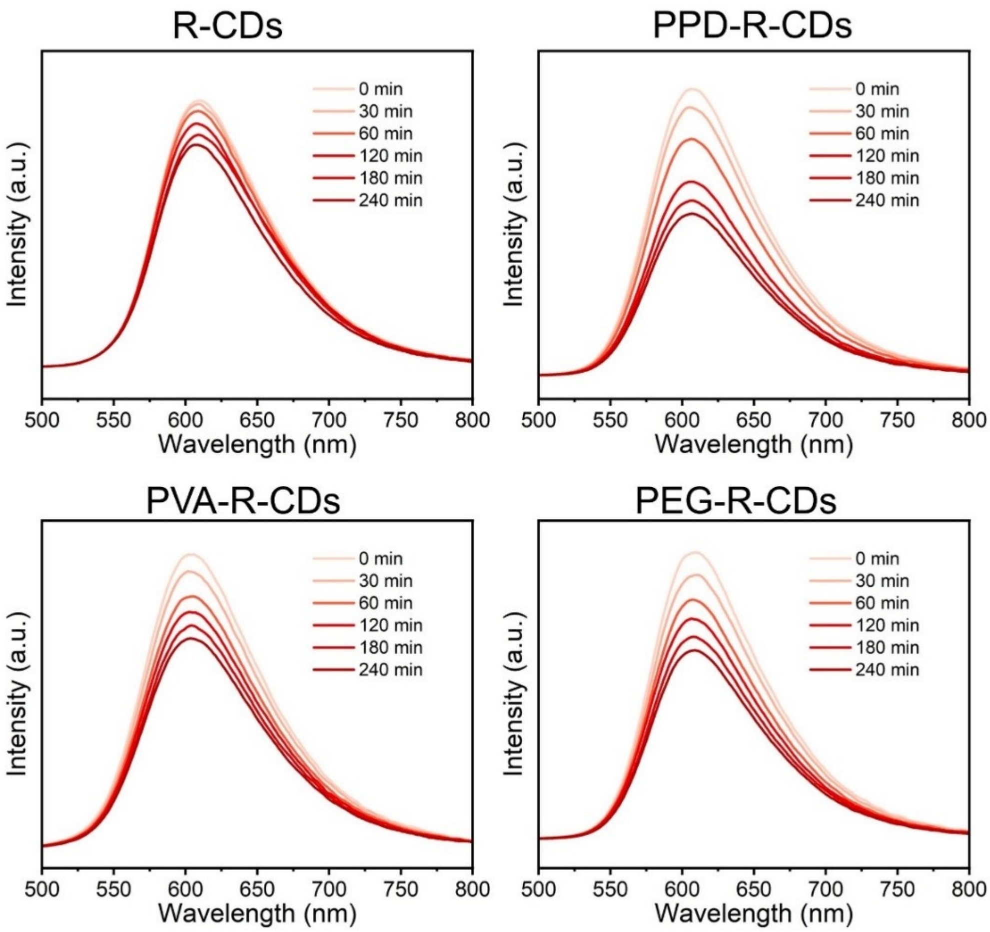

Fig. S10. PL spectra of R-CDs, PPD-R-CDs, PVA-R-CDs and PEG-R-CDs under different UV irradiation times.

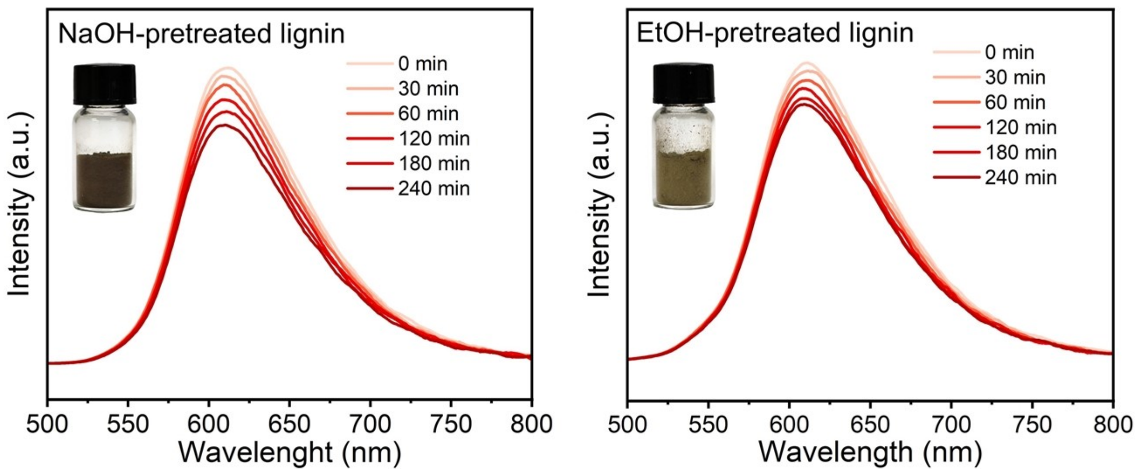

Fig. S11. PL spectra of CDs prepared from NaOH-pretreated lignin or EtOH-pretreated lignin and PPD under different UV irradiation times.

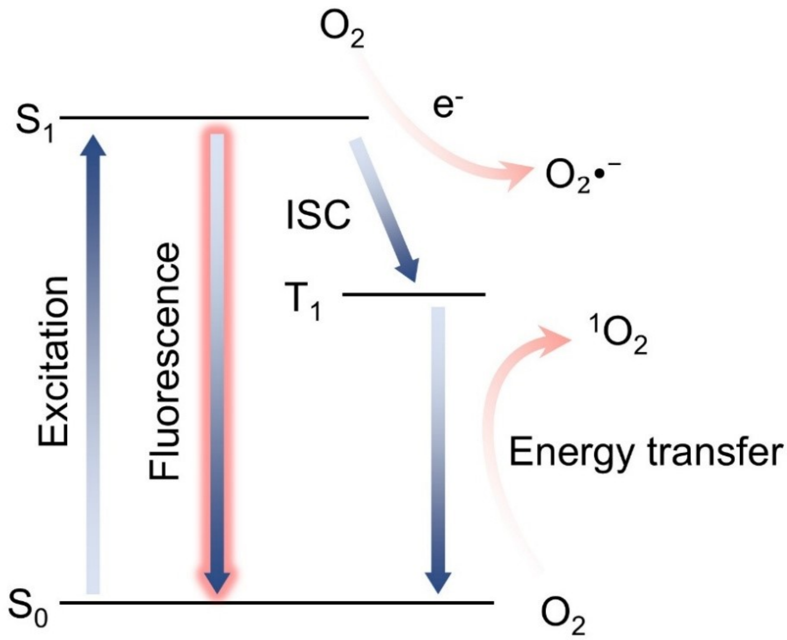

Fig. S12. Schematic illustration of O_2•⁻ and $^1O_2$ production.

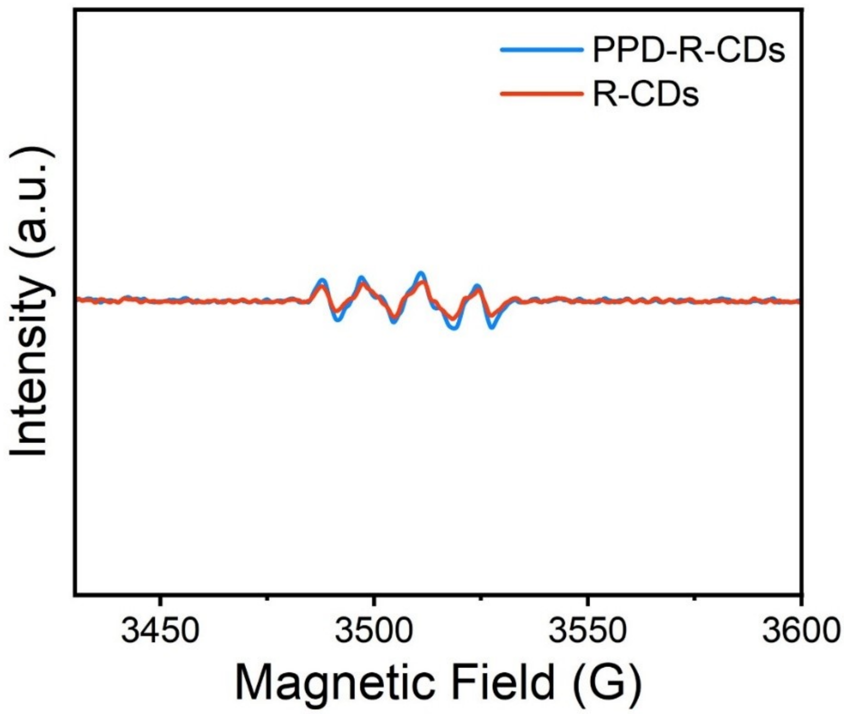

Fig. S13. EPR signal of DMPO-O_2•⁻ in methanol.

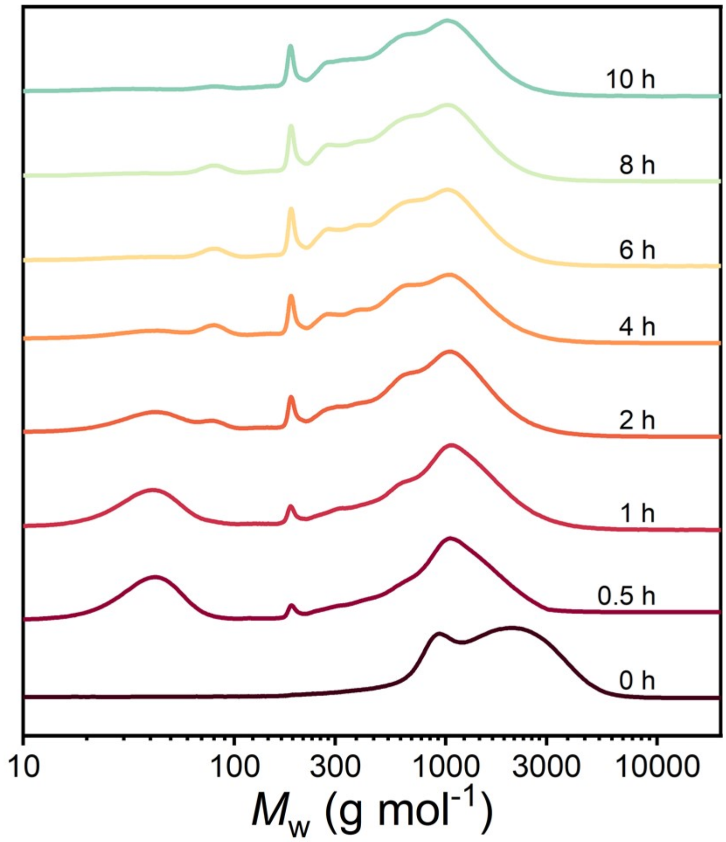

Fig. S14. GPC spectra of lignin at different reaction times.

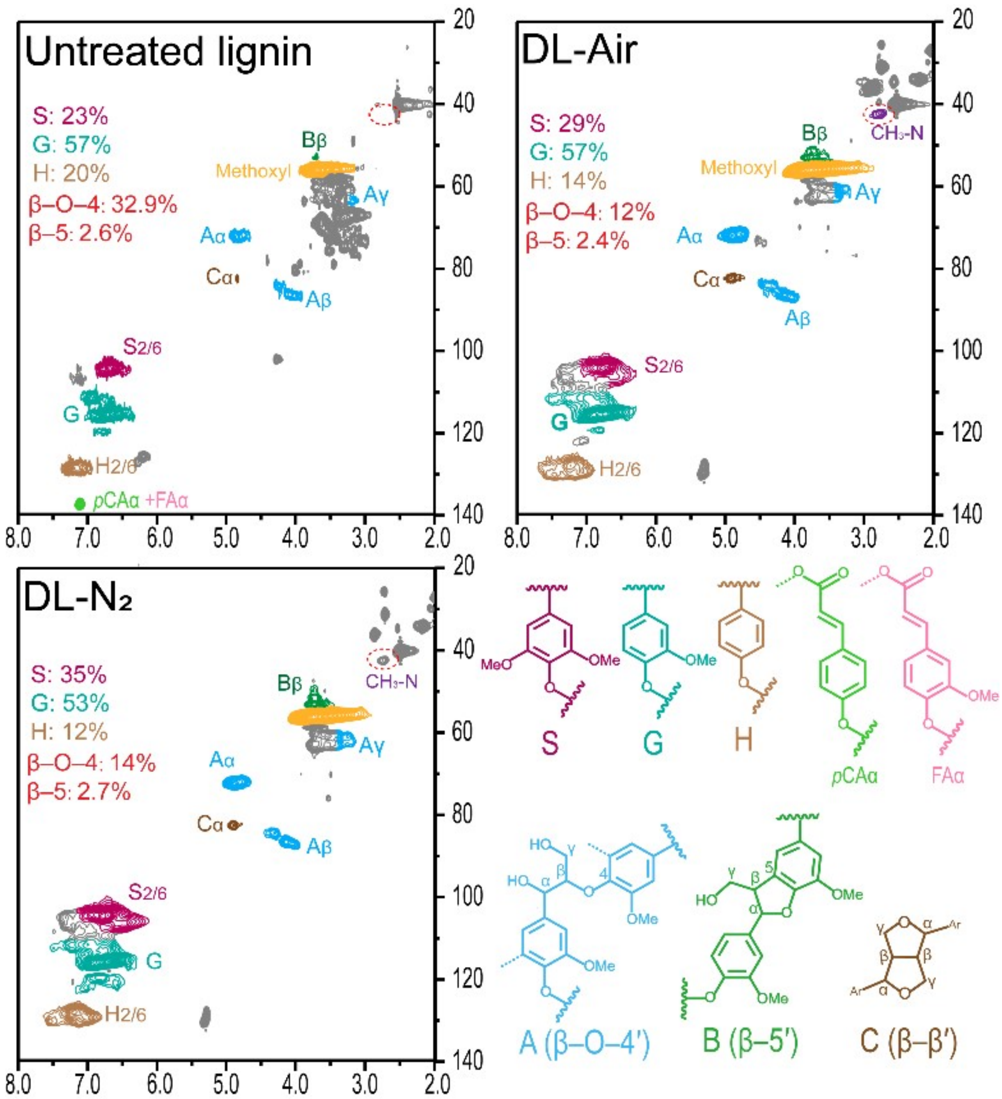

Fig. S15. Structural comparison of technical lignin, depolymerized lignin under air atmosphere (DL-Air), and depolymerized lignin under N_2 atmosphere (DL-N_2): ^{1}H-^{13}C cross signals and semi-quantitative information of interunit linkages and lignin units.

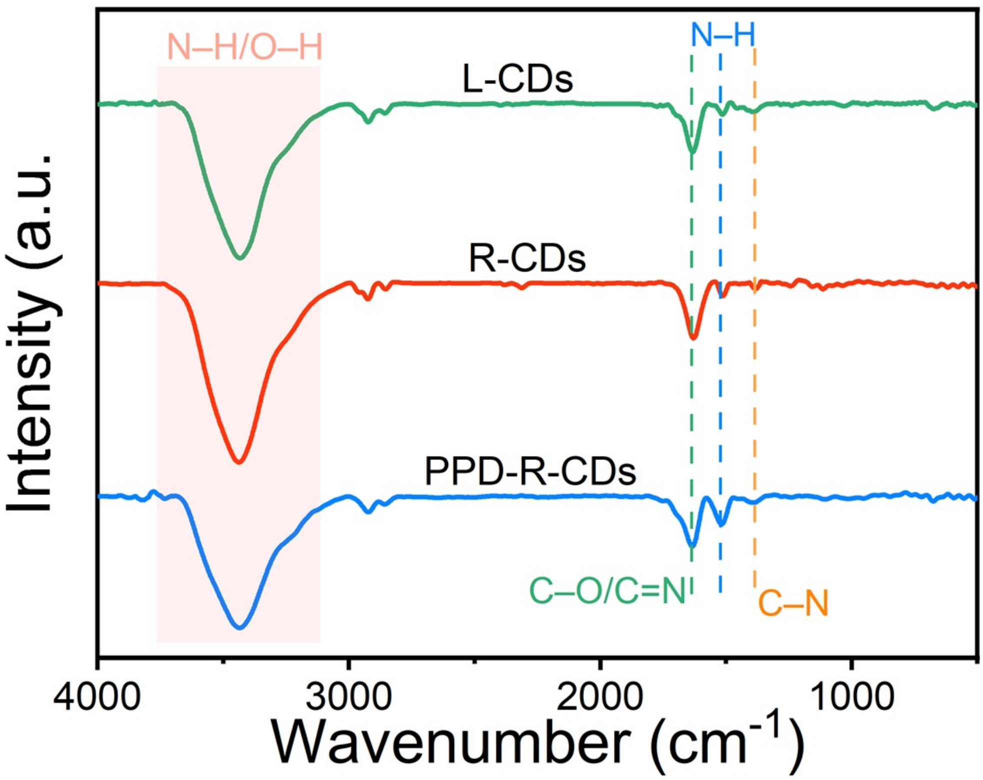

Fig. S16. FTIR spectra of L-CDs, PPD-R-CDs and R-CDs.

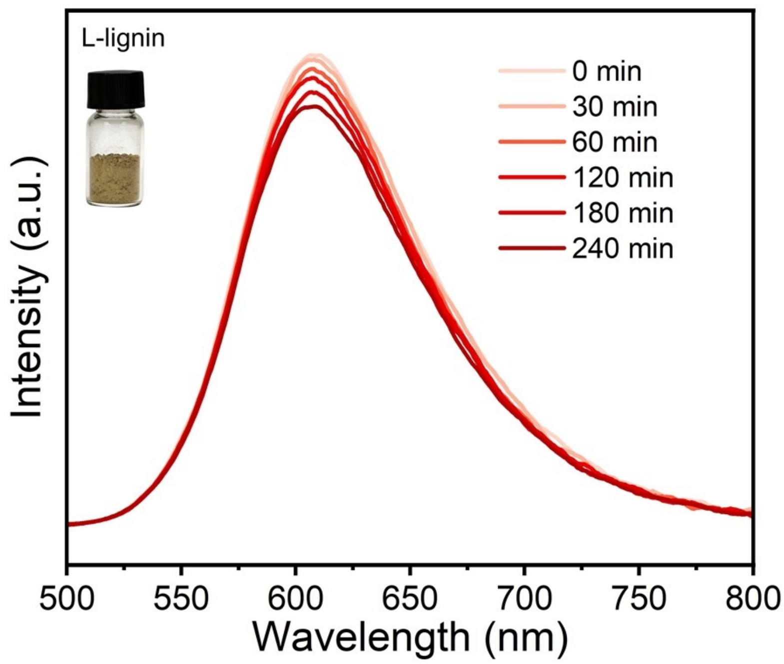

Fig. S17. PL spectra of CDs prepared from L-lignin and PPD under different UV irradiation times.

References

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