

Supporting Information

Secondary Structures in a Freeze-Dried Lignite Humic Acid Fraction Caused by Hydrogen-Bonding of Acidic Protons with Aromatic Rings

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MATERIALS AND METHODS

A ^{13}C chemical shift anisotropy (CSA) filter was inserted to the multiCP sequence to distinguish components with different chemical shift anisotropies. The multiCP sequence was also combined with recoupled long-range dipolar dephasing to probe the distances between ^{13}C nuclei and their nearest protons.

Table S1. Functional group composition (%) of LC2 based on ^{13}C multiCP NMR.

Sample	ppm						
	215-185	185-160	160-140	140-95	95-65	65-50	50-0
	Ketone	O-C=O, N-C=O	Arom. C-O	Arom. C-C, Arom. C-H	OC	OCH ₃ , NCH	Alkyl C
LC2	3.0	12.7	15.6	42.2	6.3	5.3	14.9
Lignin	4.1	5.2	21.0	29.1	6.4	12.8	21.5

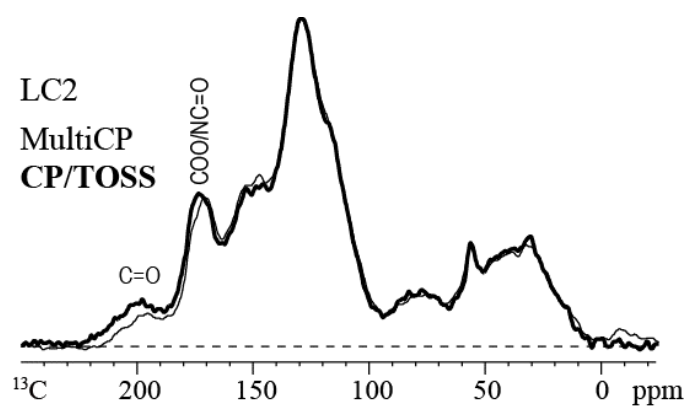


Figure S1. ^{13}C spectra of LC2 obtained by multiple cross polarization (multiCP, thin line) and ^{13}C cross polarization total sideband suppression (CP/TOSS, bold line).

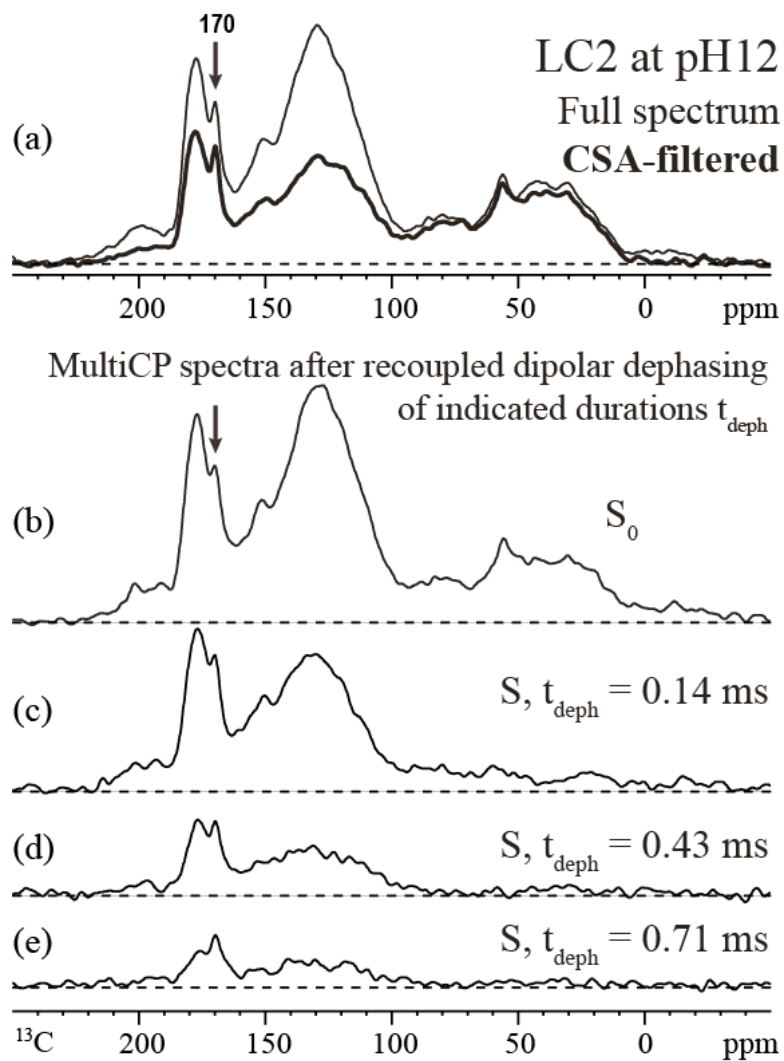


Figure S2. (a) ^{13}C multiCP NMR spectra of LC2 potassium salt (at pH 12) before (thin line) and after inserting a CSA filter (bold line, $t_{\text{CSA}} = 68 \mu\text{s}$). (b-e) ^{13}C multiCP NMR spectra of LC2 potassium salt (at pH 12) after recoupled long-range dipolar dephasing of indicated durations.

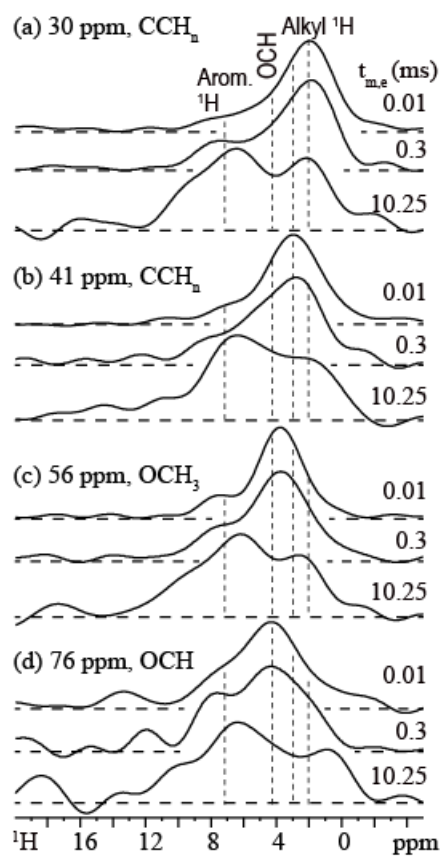


Figure S3. The ^1H spectra extracted at different ^{13}C chemical shifts at different mixing times from 2D HETCOR NMR spectra of LC2.

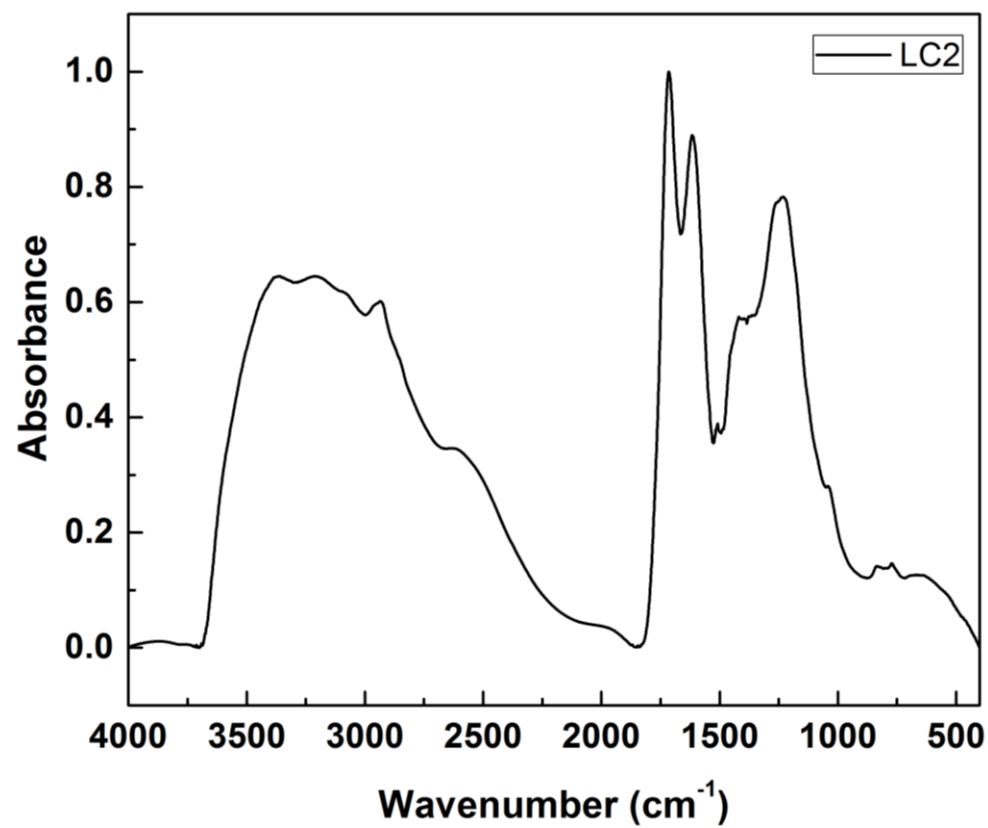


Figure S4. FT-IR spectrum of LC2.