

**Supplementary Information for Functional “whitened” lignin  
synthesized via solvent-controlled encapsulation**

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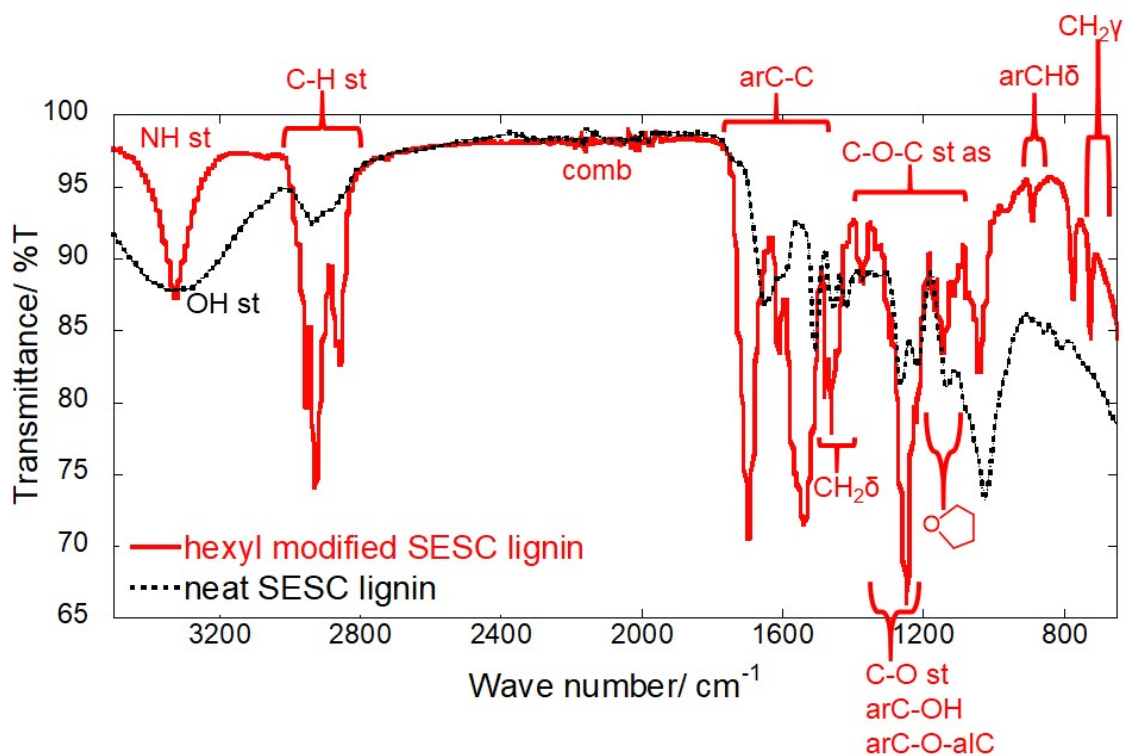
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**Table S1** | The results of the Boehm titration<sup>S1</sup> of SESC lignin and hexyl modified SESC lignin. The Boehm titration was performed as follows; Approximately 0.125-g of sample was weighed into each of three 50-mL polypropylene bottles. One bottle each was filled with 25 mL of 0.05 molar NaOH, NaHCO<sub>3</sub>, or Na<sub>2</sub>CO<sub>3</sub>. A control without sample for each solution also was prepared. Samples and controls were equilibrated on a shaker (R-12, THOMAS KAGAKU Co., Ltd, Japan) for 18 h. The solutions with sample were filtered through 5- $\mu$ L PTFE filters. An aliquot of each solution was titrated with 0.05 molar HCl. The amount of base neutralized by the samples was determined by the difference between the solution containing sample and the control solution.

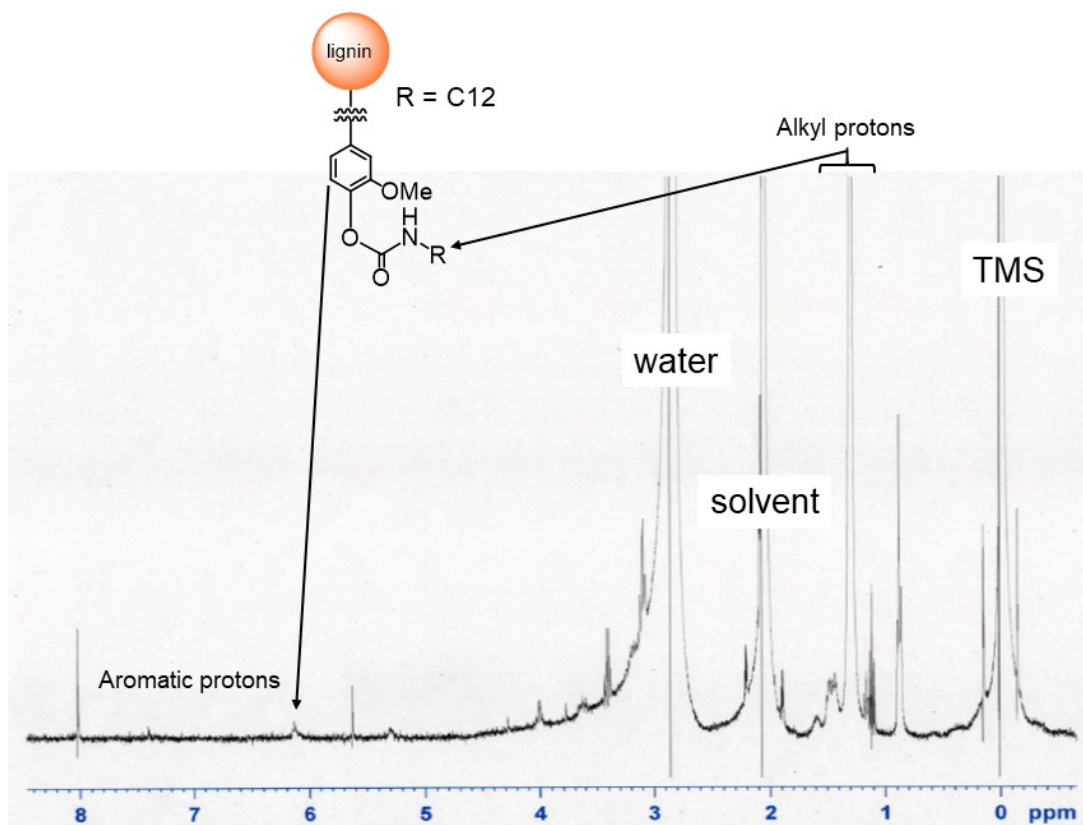
Here, the “**total acidity**” corresponds to the amount of NaOH neutralized and will consist of any organic acids with an acid dissociation constant (pKa) less than 12, and those acids formed when lactones hydrolyze. The amount of neutralized NaHCO<sub>3</sub> is considered to be due to the strongest of the organic acids and is assumed to be primarily carboxylic acids, referred to as “**strong acid**” fraction. The amount of neutralized Na<sub>2</sub>CO<sub>3</sub> is considered to be due to the strong organic acid fraction, and the moderate strength organic acids (low pKa phenols) and lactones fraction. When lactones hydrolyze into carboxylic acids and phenols, the carboxylic acids and some or all of the phenols are expected to be neutralized by the Na<sub>2</sub>CO<sub>3</sub>. The difference between the milliequivalents (meq) of NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> neutralized will be referred to as “**moderate organic acid and lactone**” fraction with the understanding that this category can include the neutralization of the carboxylic acids and phenol components of lactones after hydrolysis. The difference between the milliequivalents of NaOH and Na<sub>2</sub>CO<sub>3</sub> neutralized is composed of the weakest organic acids, assumed to be the high pKa phenols, and is referred to as “**weak acid**” fraction. Some of the phenols could come from the hydrolysis of lactones.<sup>S2</sup>

	total acidity /meq g <sup>-1</sup> *	strong acid /meq g <sup>-1</sup>	moderate acid and lactone /meq g <sup>-1</sup>	weak acid /meq g <sup>-1</sup>
SESC lignin	1.28	0.24	0.56	0.48
hexyl modified SESC lignin	0.32	0	0.18	0.14

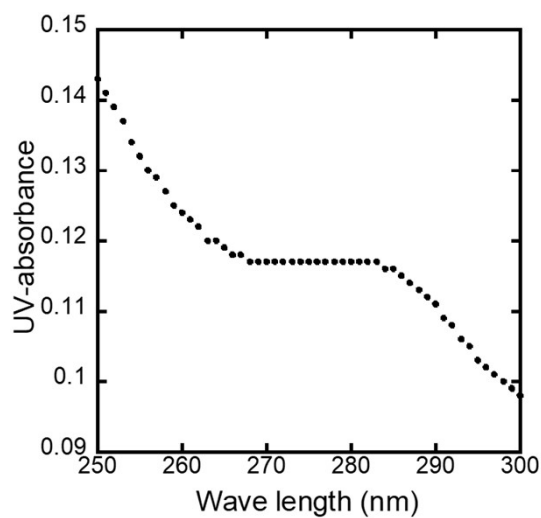
\* meq g<sup>-1</sup>: milliequivalents per gram



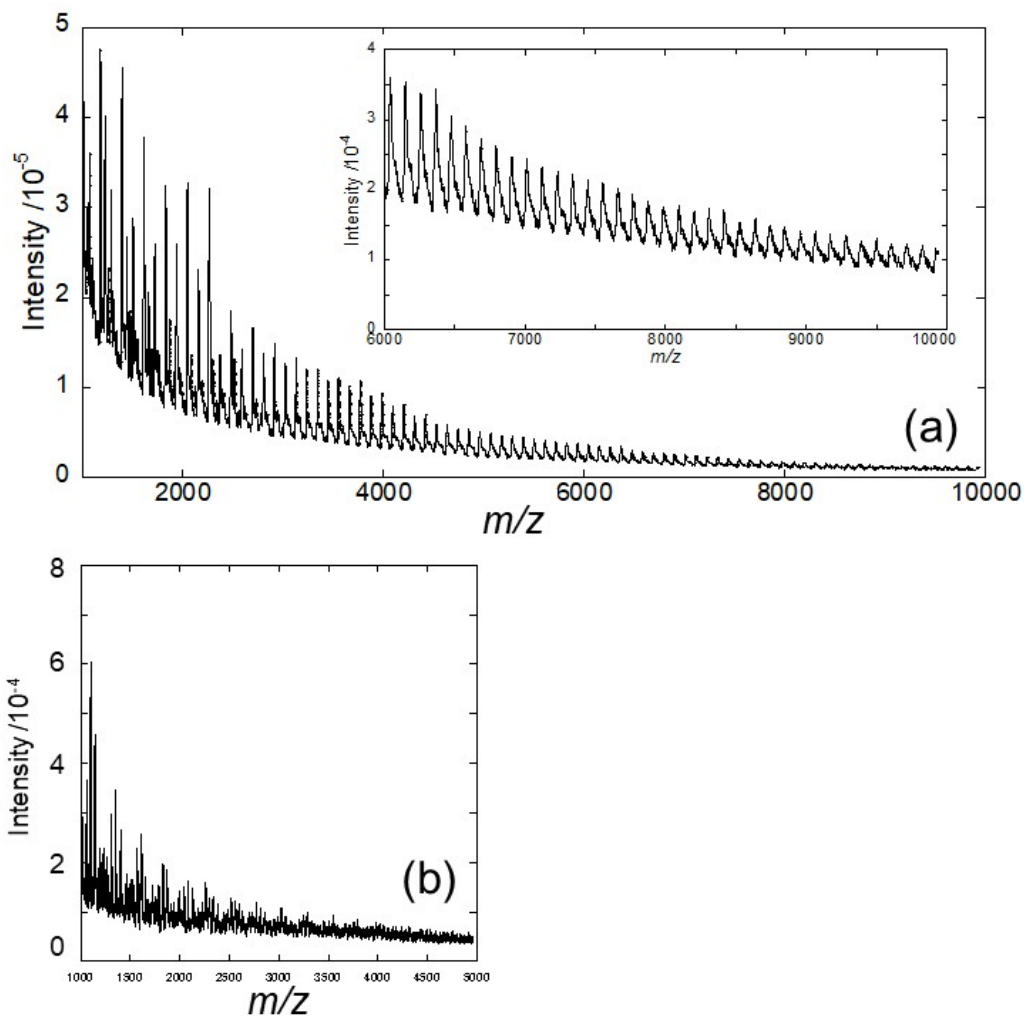
**Fig. S1** | Typical FT-IR spectrum of organic group modified SESC lignin (red line; Here, the modified organic group is a hexyl chain) and neat SESC lignin (black line). FT-IR spectra were recorded on a Thermo Sci NICOLET6700 spectrometer by attenuated total reflection method for lignin powder.



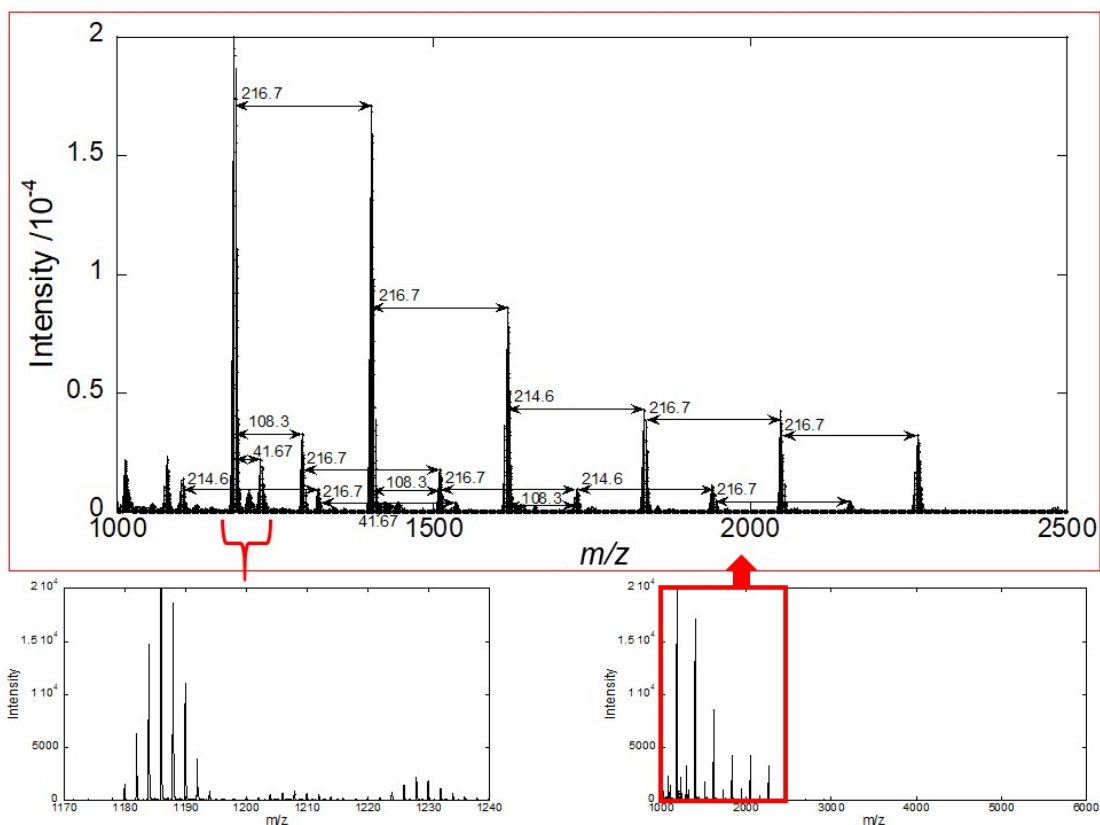
**Fig. S2** | Typical <sup>1</sup>H-NMR spectra of organic group modified SESC lignin solved in acetone-*d*<sub>6</sub>. (Here, the modified organic group is a dodecyl chain) <sup>1</sup>H-NMR spectrum was measured on an Avance 400 NMR spectrometer (Bruker Biospin Co., Inc.) at r.t. Chemical shifts are reported in ppm downfield from SiMe<sub>4</sub>, using the solvent's residual signal as an internal reference.



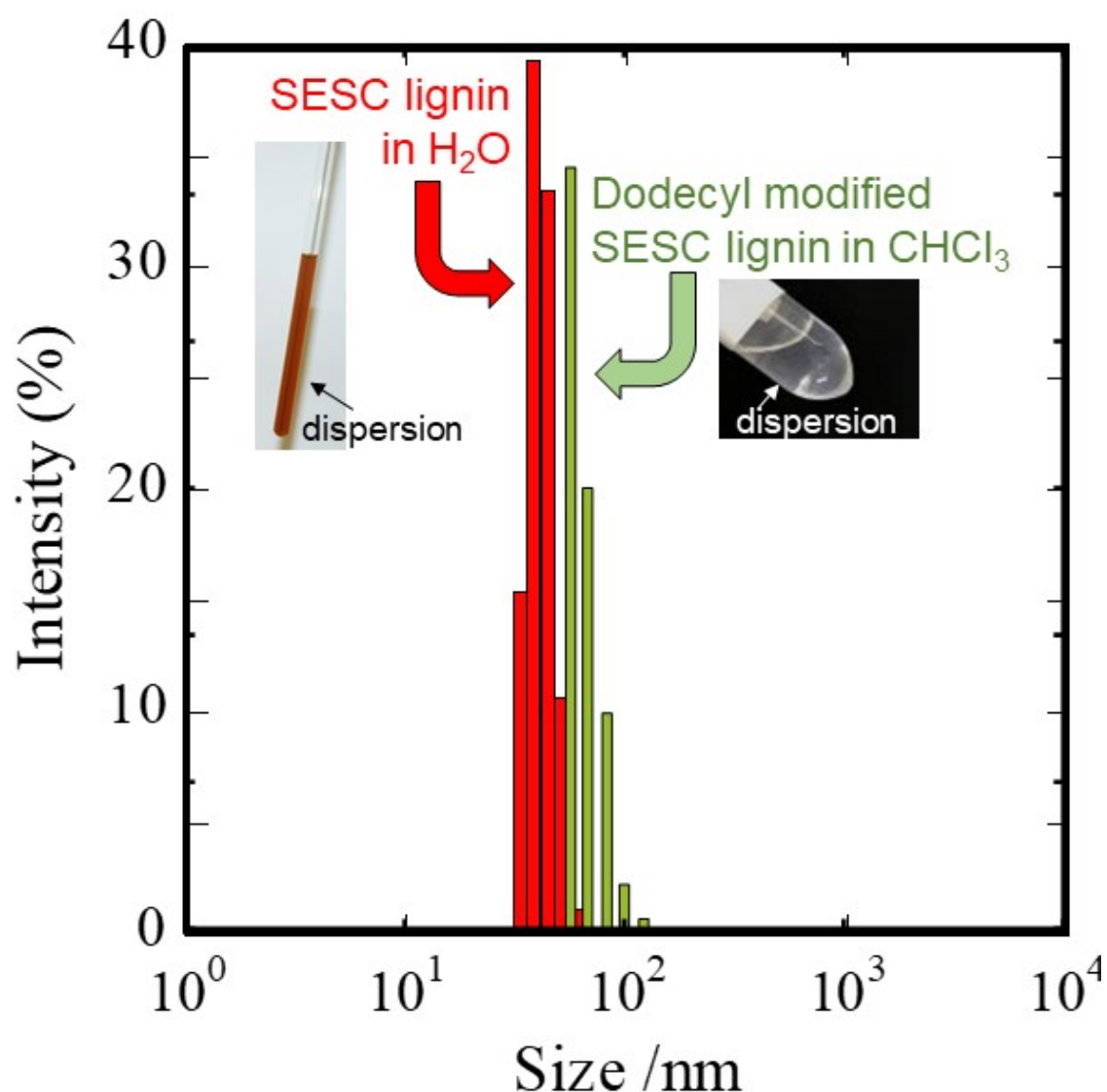
**Fig. S3** | UV-vis absorption spectrum of 3.5 w/v% hexyl modified SESC lignin EtOH solution. The spectrum was estimated in a UV-vis spectrophotometer (U-2910, Hitachi High-Technologies, Co., Japan). The baseline was obtained from neat EtOH. The guaiacyl-type and syringyl-type lignin derivatives show absorption maximum at 280 and 270 nm, respectively.<sup>S3</sup> This absorption causes a shoulder around 270–280 nm in the UV-vis absorption spectrum.



**Fig. S4** | Mass spectra (MS) with a high detection sensitivity of hexyl modified SESC lignin (a) and neat SESC lignin (b) that were measured in the linear detection mode. MS was obtained by laser ionization time-of-flight mass spectroscopy via matrix-assisted laser desorption/ionization (MALDI-TOF/MS), which was measured on an auto-flex speed TOF/TOF MS (Bruker Daltonics Inc.) for a sample mixed with trifluoromethanesulfonic acid silver salt and 2,5-dihydroxybenzoic acid (DHB).

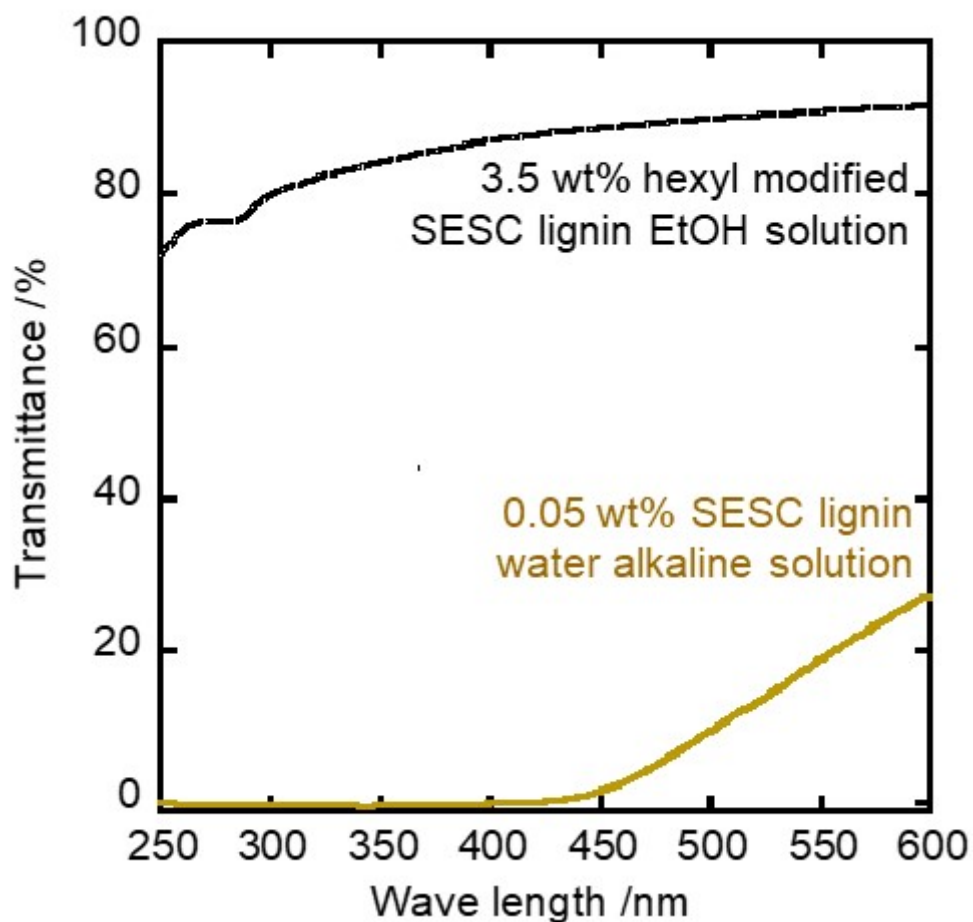


**Fig. S5** | MS with high resolution of hexyl modified SESC lignin that was measured in the reflector detection mode. In the reflector detection mode, the peaks were recognized until  $m/z \approx 2500$  as shown in the lower right chart. The peaks split octet with an interval of  $m/z = 2$ . As shown in the spectrum, the intervals of main peaks are 217, 215, 108, and 41.7. A similar MS pattern was also obtained from heptyl-modified SESC lignin. These values correspond to the fragmented molecules of modified SESC lignin as dehydrogenated coniferyl alcohol with urethane bonding (219) because it has been reported that the dehydrogenated coniferyl alcohol is detected on the MALDI-TOF/MS spectrum of conifer (pine),<sup>S4</sup> 4-methoxy phenyl derivative (106), and a broken piece from ether bonds (42.0), respectively. The precise peak interval of mass spectra in the reflector detection mode indicates a uniform molecular structure of modified SESC lignin.



**Fig. S6** | The histogram of the size distribution of SESC lignin in water (red; from ref S2) and dodecyl modified SESC lignin in chloroform (green). The similar shape of two histograms indicates the same molecular shape (*i.e.*, nanoparticle) of neat SESC lignin and dodecyl modified SESC lignin in solvents. The size distribution of dodecyl modified lignin derivatives in chloroform was measured by dynamic light scattering (DLS). DLS measurements were performed using a DLS-7000 equipped with a 75-mW Ar laser (wavelength = 488 nm) light source (OTSUKA ELECTRONICS Co., LTD, Japan). Inserted photographs are a dispersion of modified SESC lignin and SESC lignin, respectively.











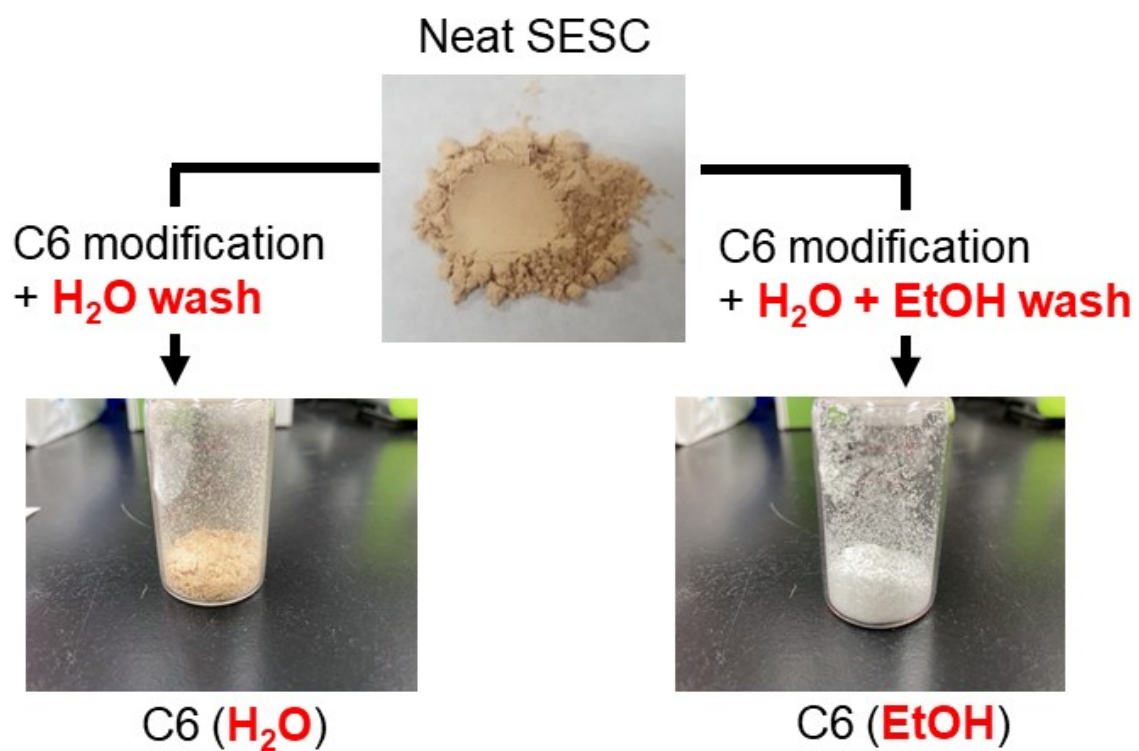
**Fig. S7** | UV-vis transmittance spectra of 3.5 w/v% hexyl modified SESC lignin EtOH solution and 0.05 w/v% SESC lignin water alkaline solution. The spectrum was estimated in a UV-vis spectrophotometer (U-2910, Hitachi High-Technologies, Co., Japan). The baseline was obtained from EtOH or H<sub>2</sub>O. The absorption of visible light on SESC lignin disappeared by its modification via SCE reaction.



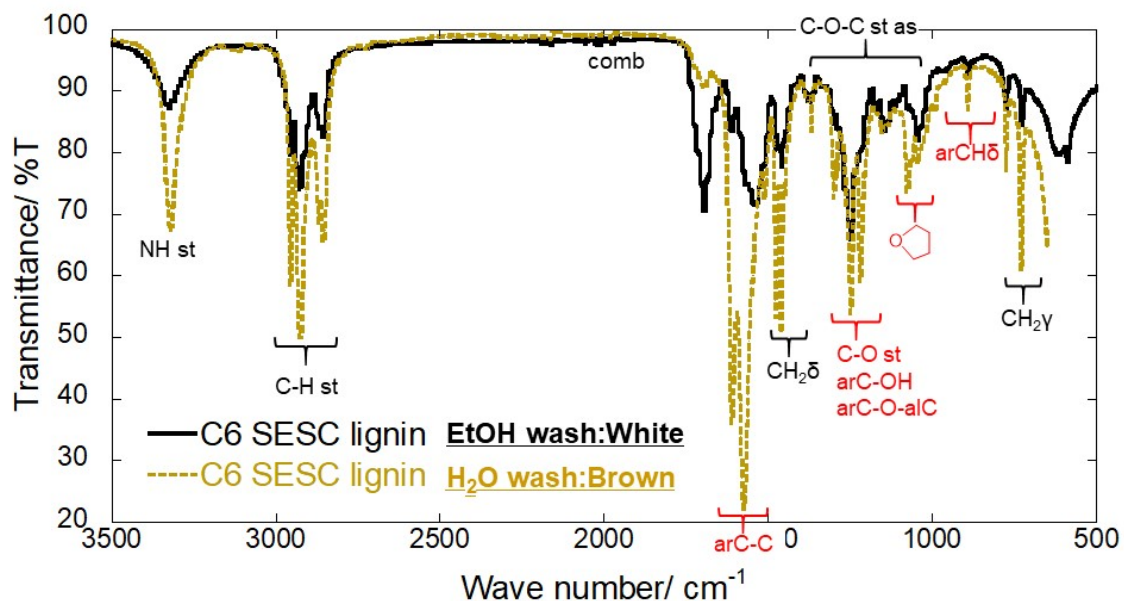
**Fig. S8** | Predicted schematic illustration of the whitened mechanism of SESC lignin. Covering by substituent (*i.e.*, suppression of light absorption), blocking of phenolic hydroxy groups (*i.e.*, diminishing quinoid structure), and assembling to uniform shape (*i.e.*, the reflection of light) would induce whitening SESC lignin nanoparticles.

Modified lignin or unmodified lignin	$L^*$	$a^*$	$b^*$	
<b>2,6-Diisopropylphenyl</b> modified SESC lignin	89.72	0.02	0.96	
<b>Hexyl</b> modified SESC lignin	85.41	-0.17	1.42	
<b>Phenethyl</b> modified SESC lignin	83.81	0.40	8.29	
<b>Dodecyl</b> modified SESC lignin	82.46	0.63	4.22	
<b>Benzyl</b> modified SESC lignin	77.97	2.33	13.05	
SESC lignin	66.84	8.38	19.04	

**Fig. S9** |  $L^*a^*b^*$  (CIELAB) color space and corresponding photographs of various substituent modified lignin derivatives and raw materials. The lignin derivatives with higher or lower  $L^*$  value than approximately 80 exhibited white or brown ~ black coloring, respectively.



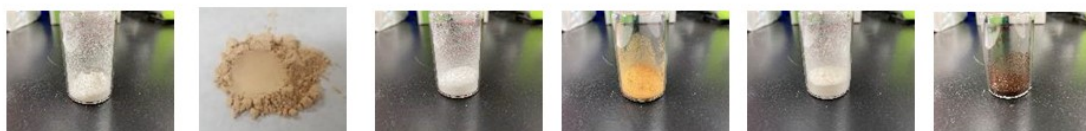
**Fig. S10** | The difference in coloring hexyl modified SESC lignin depending on washing solvent for products. The encapsulation state of lignin (*i.e.*, chromophore in lignin) would change depending on washing-solvent polarity.



**Fig. S11** | FT-IR spectra of hexyl (C6) modified SESC lignin. In the FT-IR spectrum for brown-colored modified lignin (in brown line), the peaks originated from aromatics and cyclic ether of lignin's structural units (instructed by red characters) were emphasized relative to those for white-colored modified lignin (in black line). This tendency implies that aromatic groups of lignin's structural units in the brown-colored modified lignin showed much light absorption relative to that in the white-colored modified lignin because of exposing lignin components on the surface of modified SESC lignin

Modified lignin or unmodified lignin	$L^*$	$a^*$	$b^*$
Dodecyl modified <b>SESC lignin</b> [C12 SESC]	82.46	0.63	4.22
SESC lignin [Neat SESC]	66.84	8.38	19.04
Dodecyl modified <b>lignin sulfonate</b> [C12 LS]	88.59	-0.16	1.78
Lignin sulfonate [Neat LS]	55.09	10.80	28.45
Dodecyl modified <b>soda lignin</b> [C12 soda]	81.49	2.09	8.63
Soda lignin [Neat soda]	28.40	3.69	3.62
Dodecyl modified <b>Kraft lignin</b>	74.19	3.37	4.22
Kraft lignin	45.87	8.51	18.90
Dodecyl modified <b>alkali treated lignin sulfonate</b>	73.83	3.02	12.49
Alkali treated lignin sulfonate	19.12	2.10	1.86

C12 SESC    Neat SESC    C12 LS    Neat LS    C12 soda    Neat soda



**Fig. S12** |  $L^*a^*b^*$  (CIELAB) color space and corresponding photographs of dodecyl modified lignin derivatives and neat lignin derivatives. SESC, LS, and soda are SESC lignin, lignin sulfonate, and soda lignin, respectively.

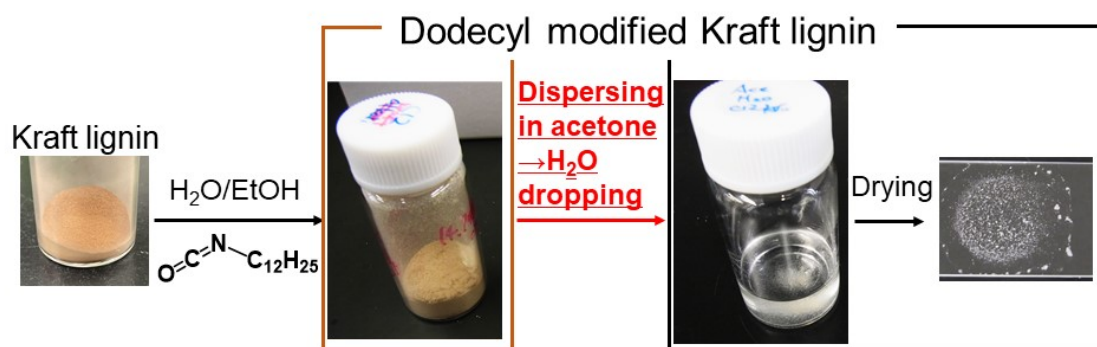


**Fig. S13** | Photographs of powders of hexyl modified SESC lignin (left) before and (right) after about 2 years storing.

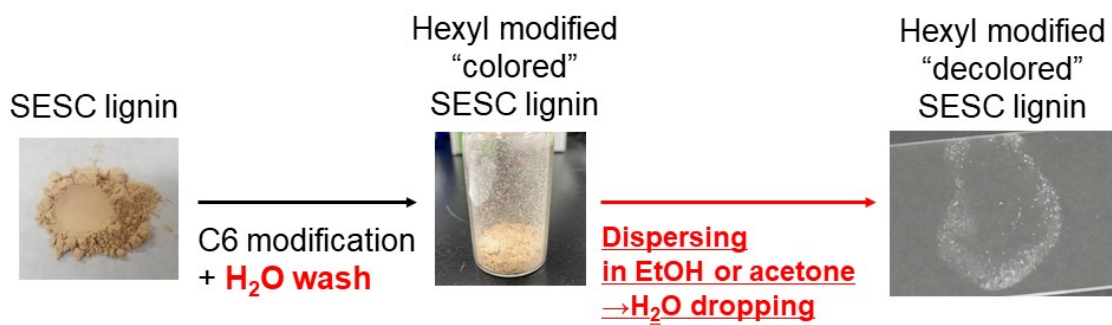


**Fig. S14** | Photographs of powders of dodecyl modified SESC lignin (left) and dodecyl modified Kraft lignin (right).

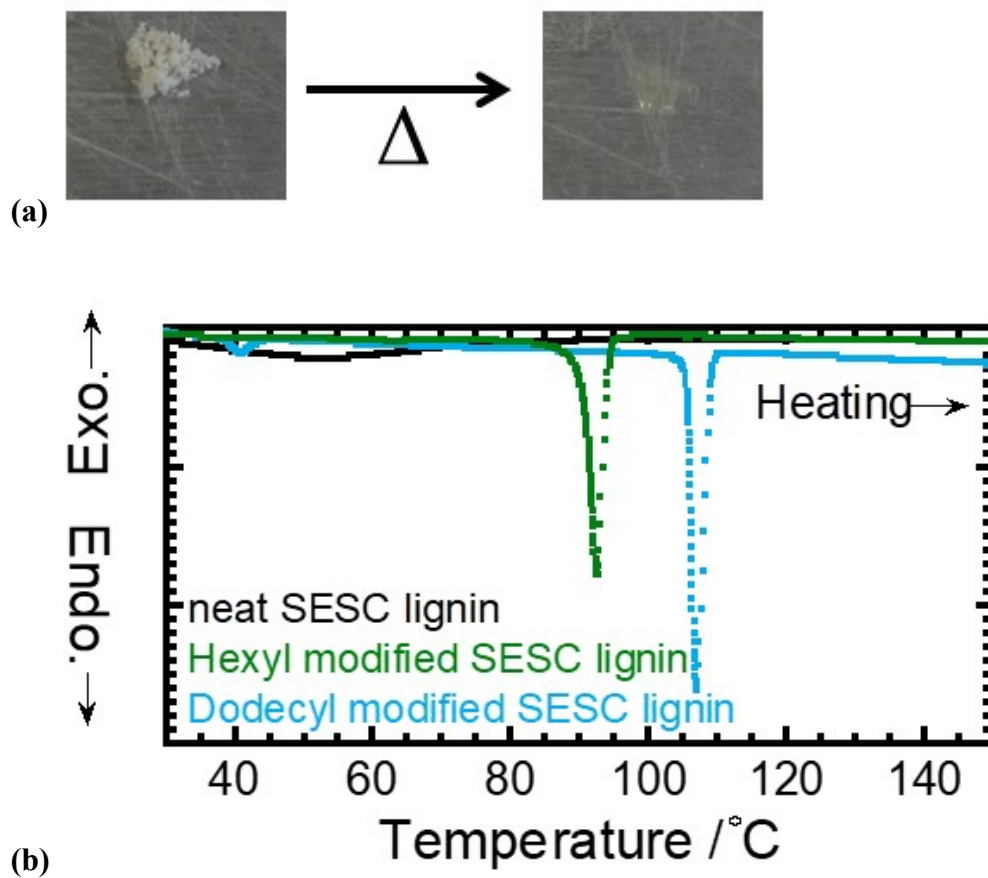




**Fig. S15** | The color change of dodecyl modified Kraft lignin. The brown-colored modified lignin was whitened by dispersing in acetone and following the addition of  $\text{H}_2\text{O}$ . The encapsulation state of lignin (*i.e.*, chromophore in lignin) would change depending on washing-solvent polarity.



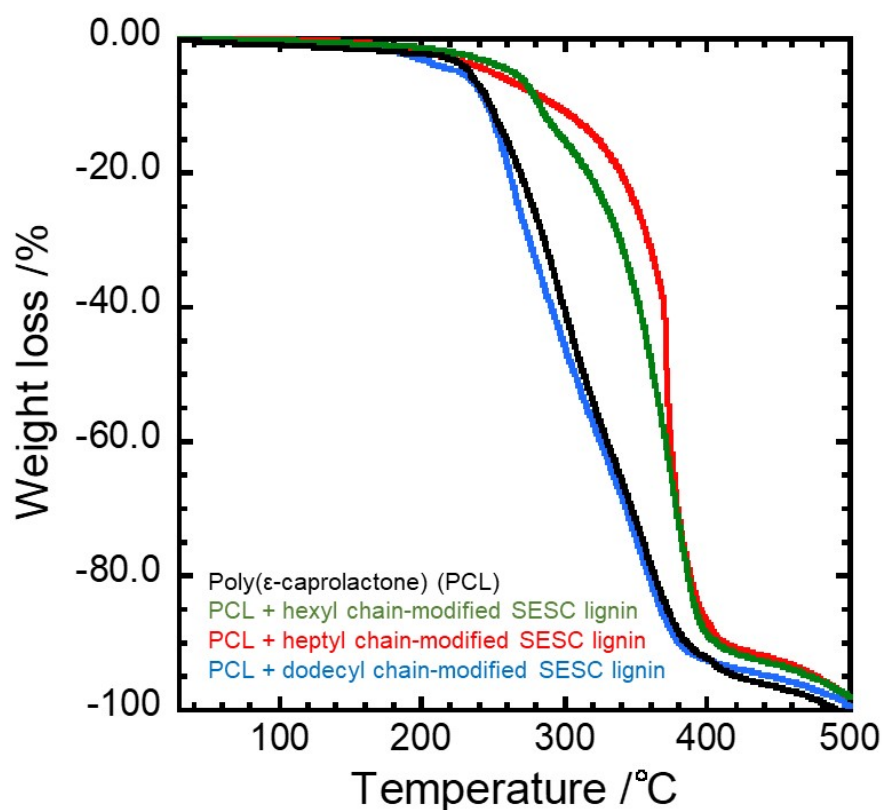
**Fig. S16** | The color change of brown-colored hexyl modified SESC lignin washed with water. The brown-colored modified lignin was whitened by dispersing in ethanol or acetone and following the addition of H<sub>2</sub>O. The encapsulation state of lignin (*i.e.*, chromophore in lignin) would change depending on washing-solvent polarity.



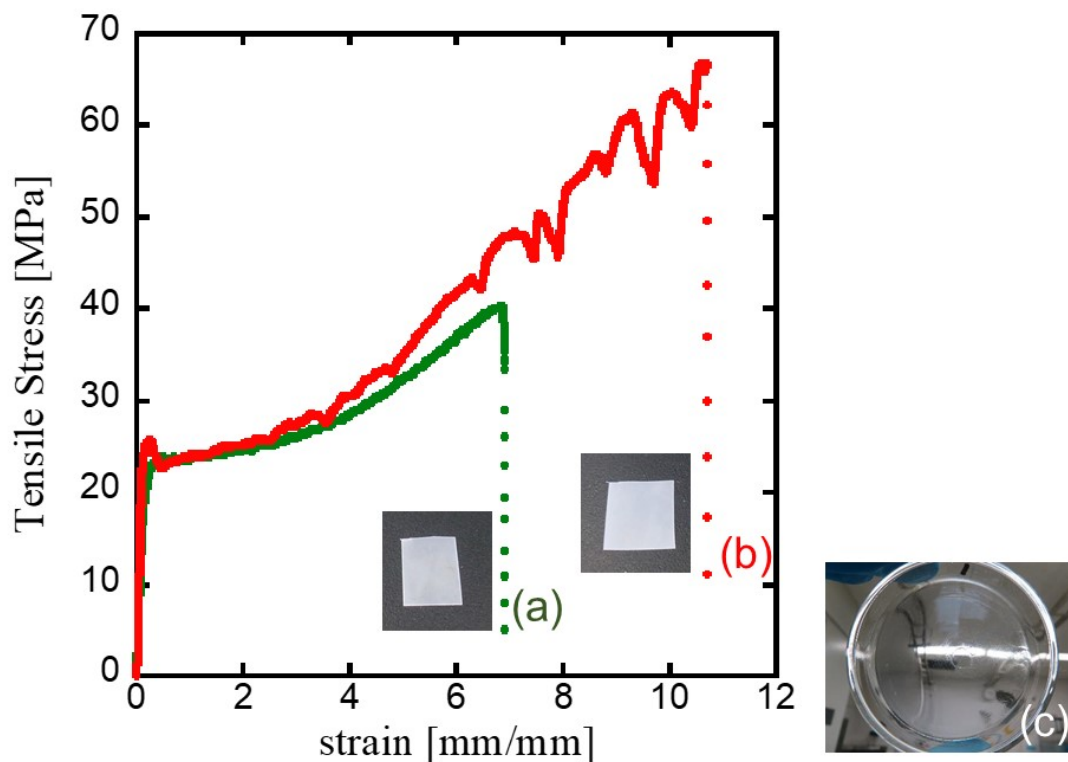
**Fig. S17** | (a) Typical photographs of hexyl modified SESC lignin at r.t. (left) or 70°C (right). (b) Differential scanning calorimetry (DSC) curves of hexyl (green) or dodecyl (blue) modified SESC lignin and neat SESC lignin (black). DSC measurement was performed on a Rigaku Thermo Plus DSC 8230 at 5°C min<sup>-1</sup>.



**Fig. S18** | Photographs of the transparent film consisting of dodecyl modified SESC lignin obtained by hot melting that is sandwiched between two glass plates.



**Fig. S19** | The results of thermo-gravimetric (TG) analysis of a mixture of poly( $\epsilon$ -caprolactone) (PCL;  $M_n = 10,000$ ) and alkyl (hexyl, heptyl, and dodecyl) modified SESC lignin. (PCL : lignin = 95:5 w/w%). Feeding 5 w/w% of hexyl or heptyl modified SESC lignin to poly( $\epsilon$ -caprolactone) increases its 5 and 50% weight decomposition temperature by approximately 20 and 60°C. However, modifying the dodecyl group to SESC lignin spoils its heatproofing nature, *i.e.*, the length of the alkyl chain affects the heatproofing nature of modified SESC lignin to polymers.



**Fig. S20** | Tensile stress–strain curves of (a) a PCL film containing 5 w/w% dodecyl modified SESC lignin and (b) a neat PCL film prepared by kneading and hot-pressing. The tensile stress–strain curves were obtained by a JTT LSC-005/30 type tensile tester (Tokyo Koki Testing Machine Co., Ltd., Japan). Inserted photographs are corresponding samples. (c) Photograph of PCL casting film containing 5 w/w% dodecyl modified SESC lignin on glass petri dish prepared by solvent casting.

## REFERENCES

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S3 K. Takabe, S. Miyauchi, R. Tsunoda and K. Fukazawa, *IAWA Bull. n. s.*, 1992, **13(1)**, 105.

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### Data availability

All data are available in the main Article and Supplementary Information, or from the corresponding author upon reasonable request.