Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Organic solvent-free production of colloidally stable spherical lignin nanoparticles at high mass concentrations

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Table S1, Figures S1–S9

Table S1. Characterization data for the lignins.

Lignin type	M_w, Da	Ph-OH, mmol/g	Aliph-OH, mmol/g	COOH, mmol/g	Dispersity, Đ (Mw/Mn)	Klason Lignin (Acid insoluble lignin) %	Ref.
SKL	5250	4.21	1.93	0.56	4.4	92	[1]
Lignosulfonate DS10	10482	0.83	3.27	0.74	5.2	96	[2]
Organosolv beech	3433	2.14	4.075	0.65	n.a.	88.56	[3]
Lignosulfonate Sigma Aldrich	~52,000	2.28 (SO3H: 1.86)	2.18	0.18	7.42	~90	[4] [5]
Soda lignin, protobind 2400	~4323	2.71	1.34	0.59	7.5	90	[6] [7]

References

1. Moreno, A., Morsali, M. & Sipponen, M. H. Catalyst-Free Synthesis of Lignin Vitrimers with Tunable Mechanical Properties: Circular Polymers and Recoverable Adhesives. *ACS Applied Materials and Interfaces* **13**, 57952–57961 (2021).
2. Abbadessa, A., Oinonen, P. & Henriksson, G. Characterization of Two Novel Bio-based Materials from Pulping Process Side Streams: Ecohelix and CleanFlow Black Lignin.
3. Lê, H. Q. *et al.* Solubility of Organosolv Lignin in γ-Valerolactone/Water Binary Mixtures. *ChemSusChem* **9**, 2939–2947 (2016).
4. Lignosulfonic acid average Mw 52,000, average Mn 7,000 8061-51-6. https://www.sigmaaldrich.com/SE/en/product/aldrich/471038.
5. Musl, O. *et al.* Mapping of the Hydrophobic Composition of Lignosulfonates. *ACS Sustainable Chemistry and Engineering* **9**, 16786–16795 (2021).
6. Liu, J. *et al.* Fully Biobased Photothermal Films and Coatings for Indoor Ultraviolet Radiation and Heat Management. *ACS Applied Materials and Interfaces* **14**, 12693–12702 (2022).
7. Adjaoud, A., Dieden, R. & Verge, P. Sustainable Esterification of a Soda Lignin with Phloretic Acid. *Polymers 2021, Vol. 13, Page 637* **13**, 637 (2021).

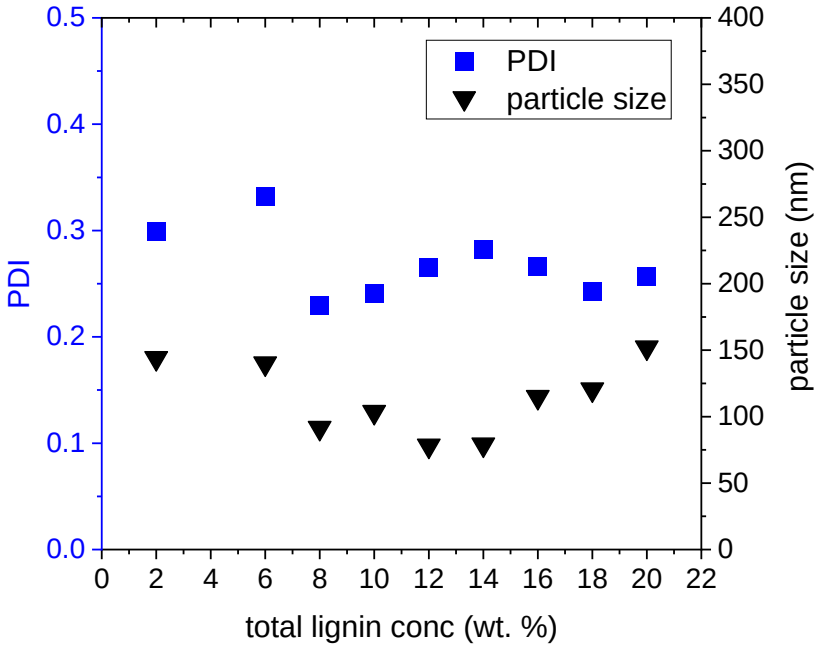

Figure S1: Polydispersity indices (PDI) and particle diameter as a function of lignin concentration in the mixed colloidal dispersion at a constant LS to SKL ratio of 4:1 (w/w).

Figure S2: Visual appearance of LS-SKL (5 to 1 w/w) mixtures in 2 M NaOH at different total lignin concentrations.

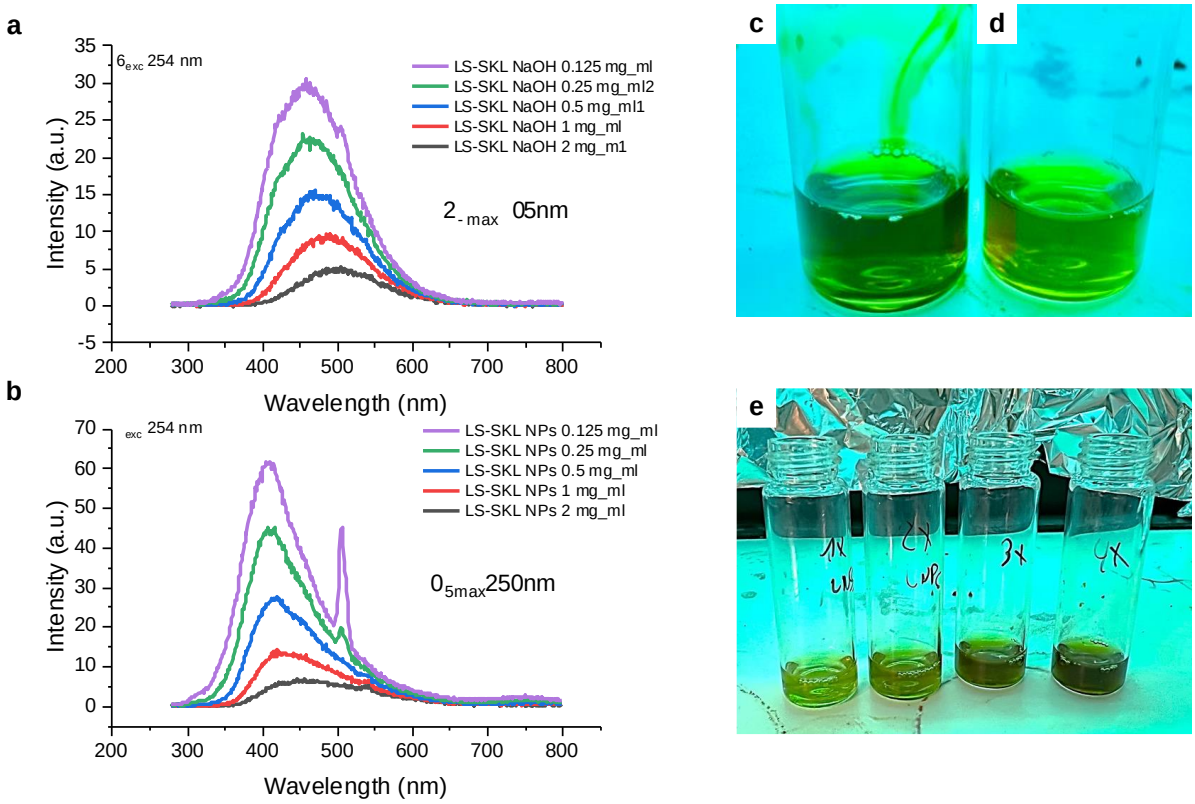

Figure S3: Fluorescence spectra of LS-SKL mixtures in 2M NaOH (a) and of dialyzed LS-SKL NPs (b) and their photographs taken under UV-light (254 nm) (c) and (d), respectively, and (e) photographs of LS-SKL NPs at concentrations increasing from left to right.

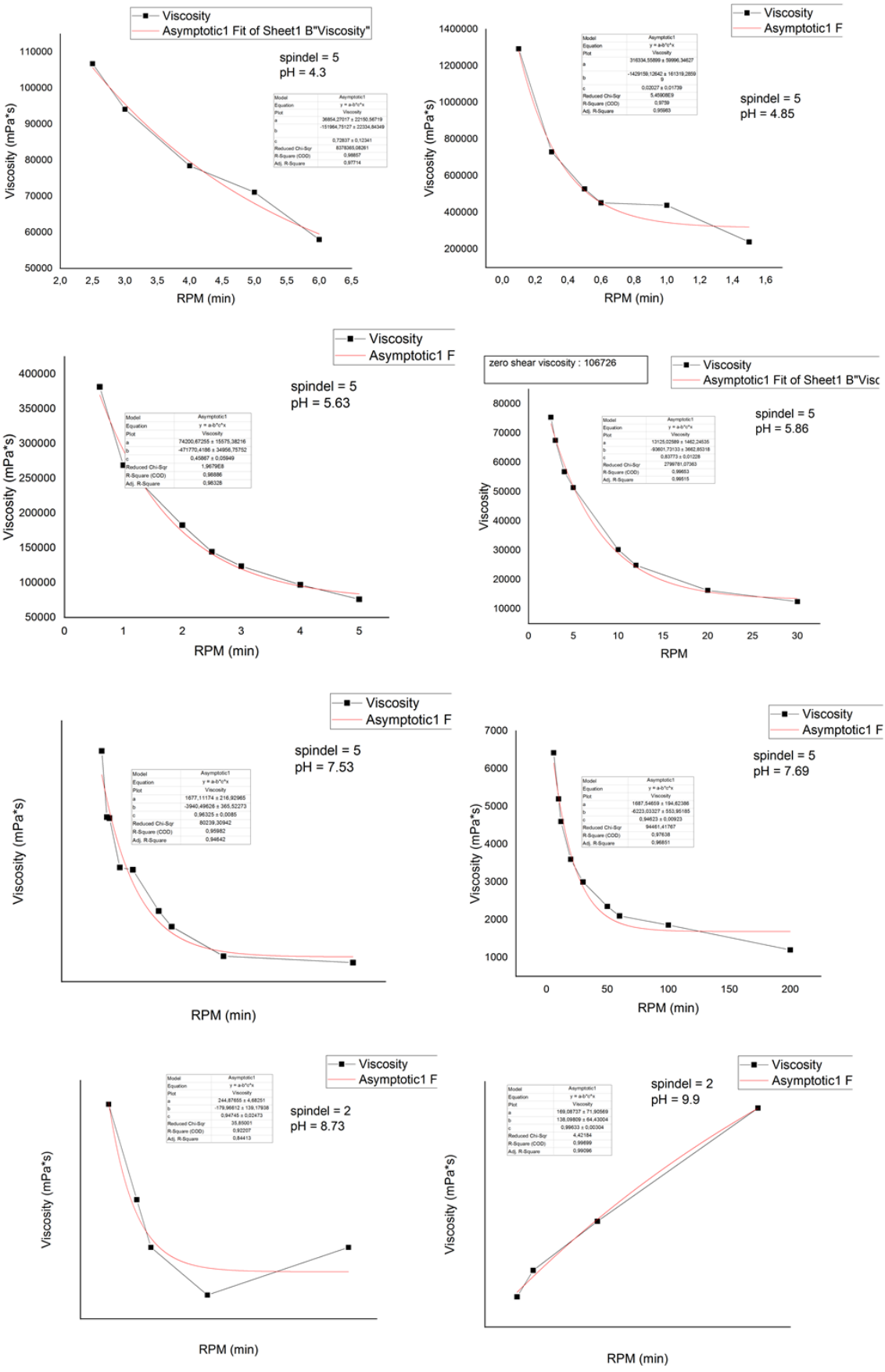

Figure S4: Dynamic viscosity data used to calculate values in Figure 3.

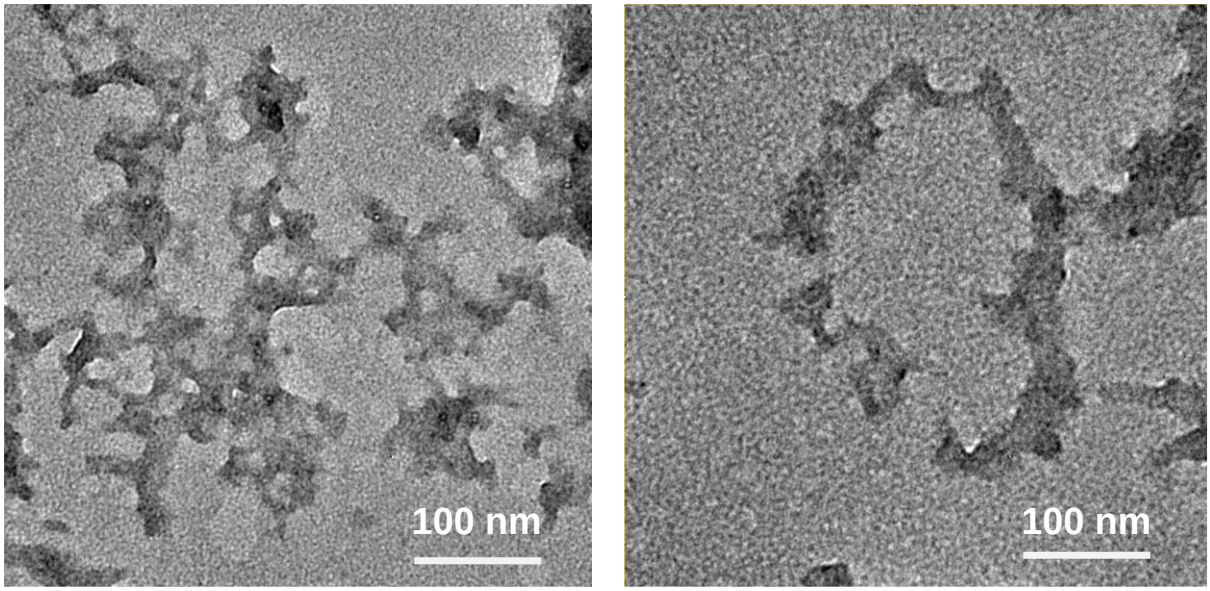

Figure S5: TEM micrographs of precipitating lignin aggregates of LS and SKL at weight ratio below the optimum.

pH 4.3 4.9 5.6 5.9 7.5 8.7 9.9

Figure S6. Appearance of the LS:SKL (5:1 w/w) dispersions at various pH levels studied.

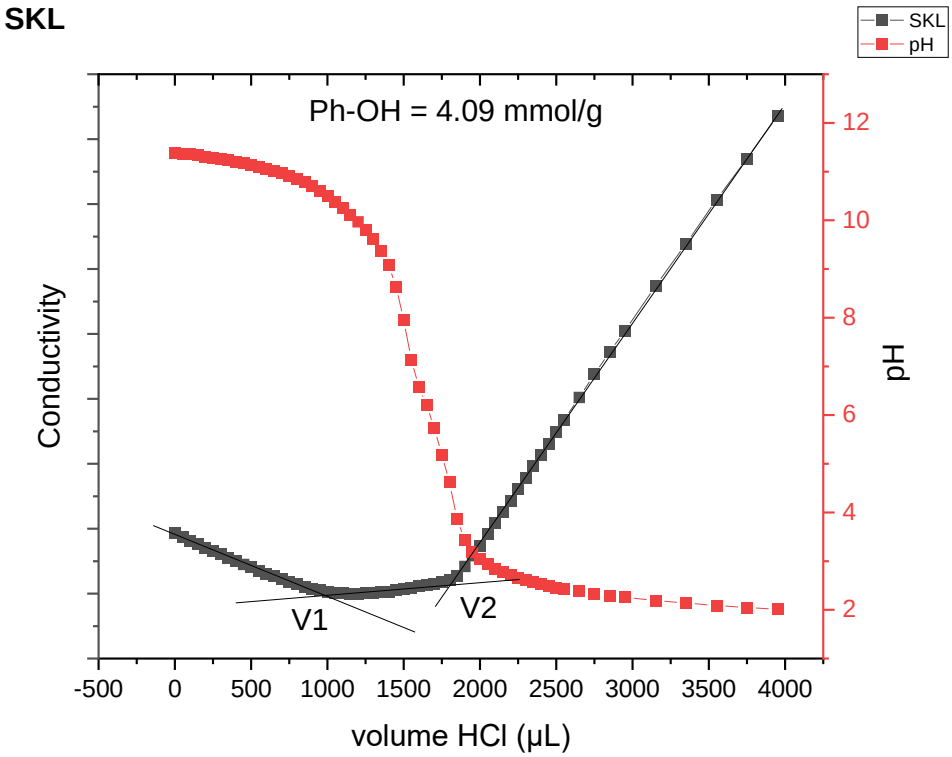

Figure S7. pH and conductometric titration curves of SKL solution.

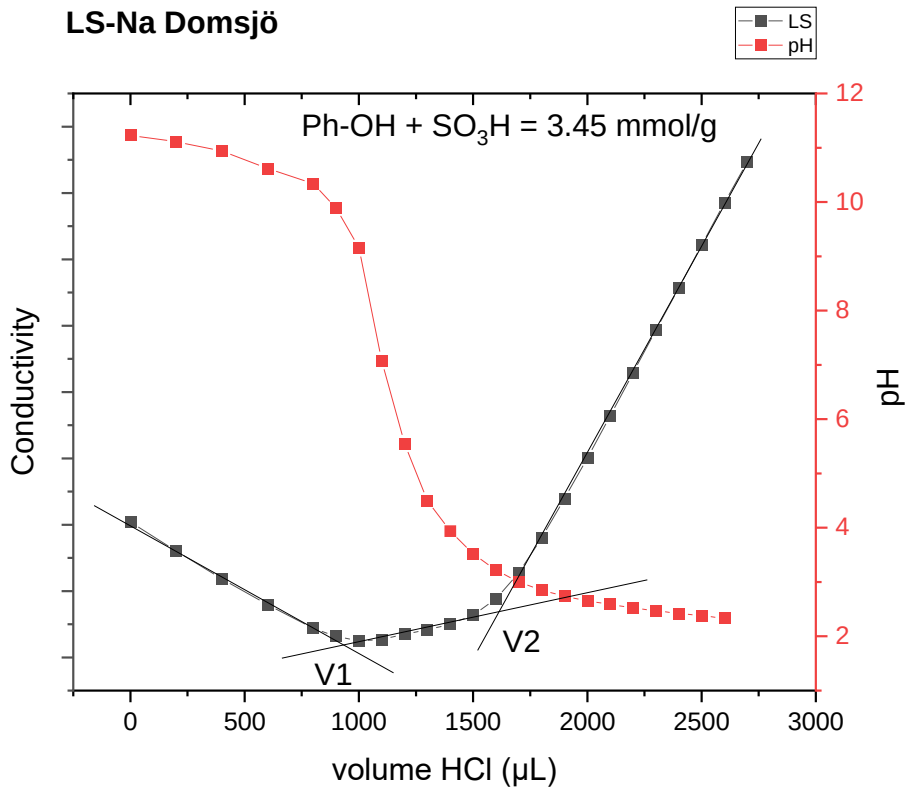

Figure S8. pH and conductometric titration curves of sodium lignosulfonate solution (LS Domsjö).

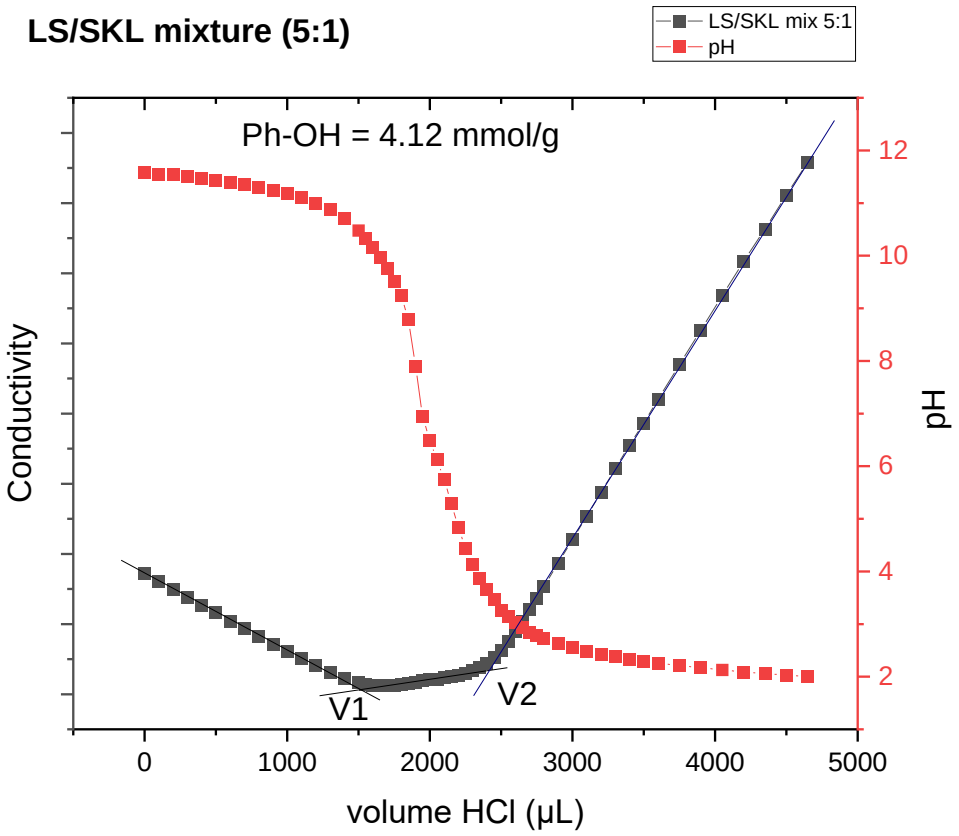

Figure S9. pH and conductometric titration curves of a aqueous mixture of SKL and sodium lignosulfonate solution (LS Domsjö) with 5 to ratio.