Supplementary information

Eco-friendly conversion between n- and p-type carbon nanotubes based on rationally functionalized lignin biopolymers

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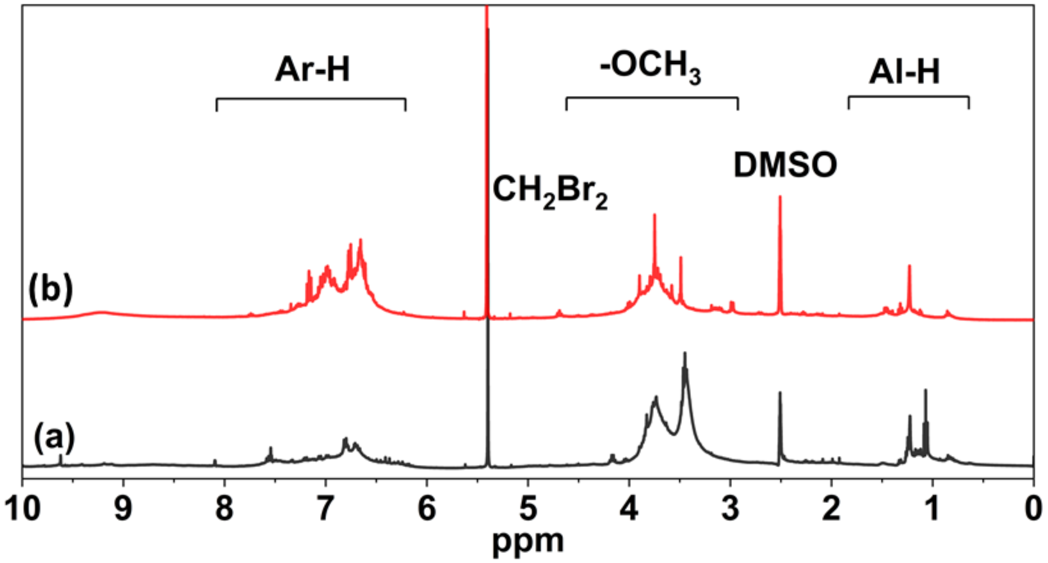


Fig. S1. ^{1}H NMR of (a) orgnosolv lignin and (b) phenolated lignin. The increase in Ar-H indicates the phenyl group's attachment to the lignin backbone structure.

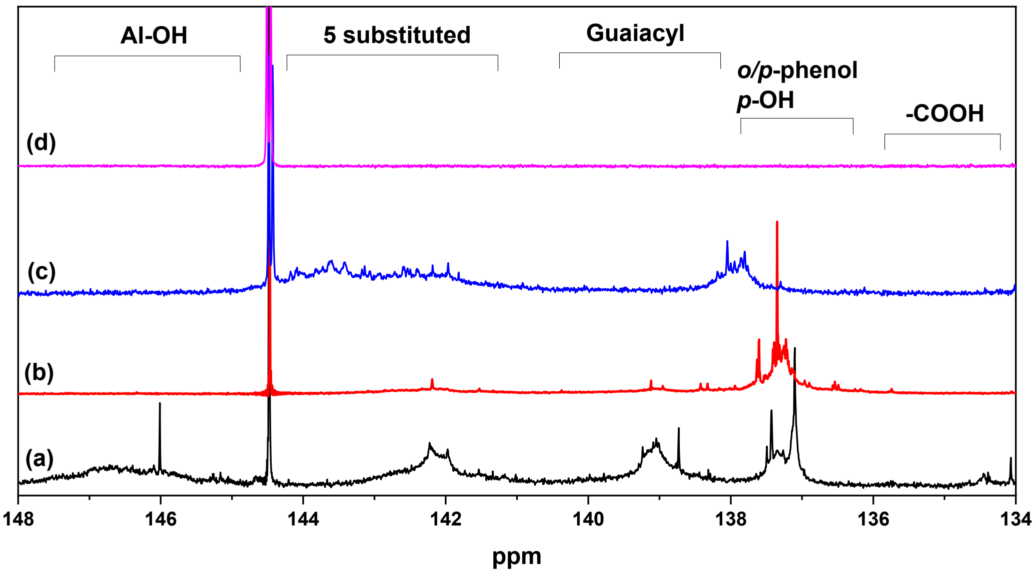


Fig. S2. ^{31}P NMR of (a) orgnosolv lignin and (b) phenolated lignin, (c) aminated lignin, and (d) fluorinated lignin.

Signal assignment:

The peak at 144.5 ppm is an internal standard (10 mg/mL cyclohexanol).

The peaks in ^{31}P NMR are assigned as following: aliphatic hydroxyl (149.0 to 145.0 ppm), syringyl hydroxyl and 5-substituted ring hydroxyl (144.0 to 140.5 ppm), guaiacyl hydroxyl (140.5 to 138.0 ppm), p-hydroxyl-phenyl and newly attached phenol (138.0 to 136.0 ppm), and carboxyl OH (135.0 – 133.0 ppm).

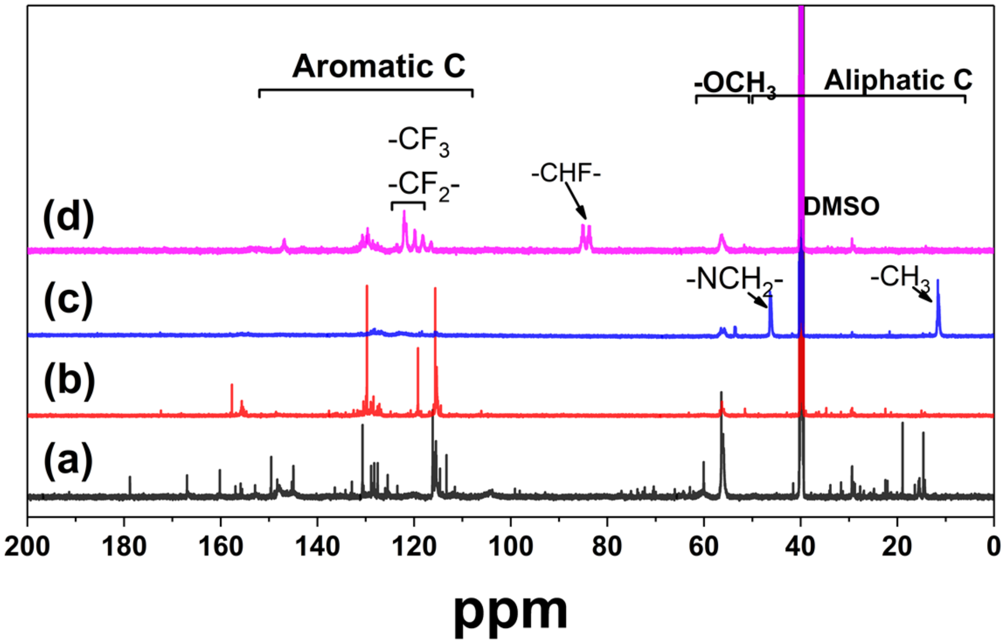


Fig. S3. ^{13}C NMR of (a) organosolv lignin, (b) phenolated lignin, (c) aminated lignin, and (d) fluorinated lignin.

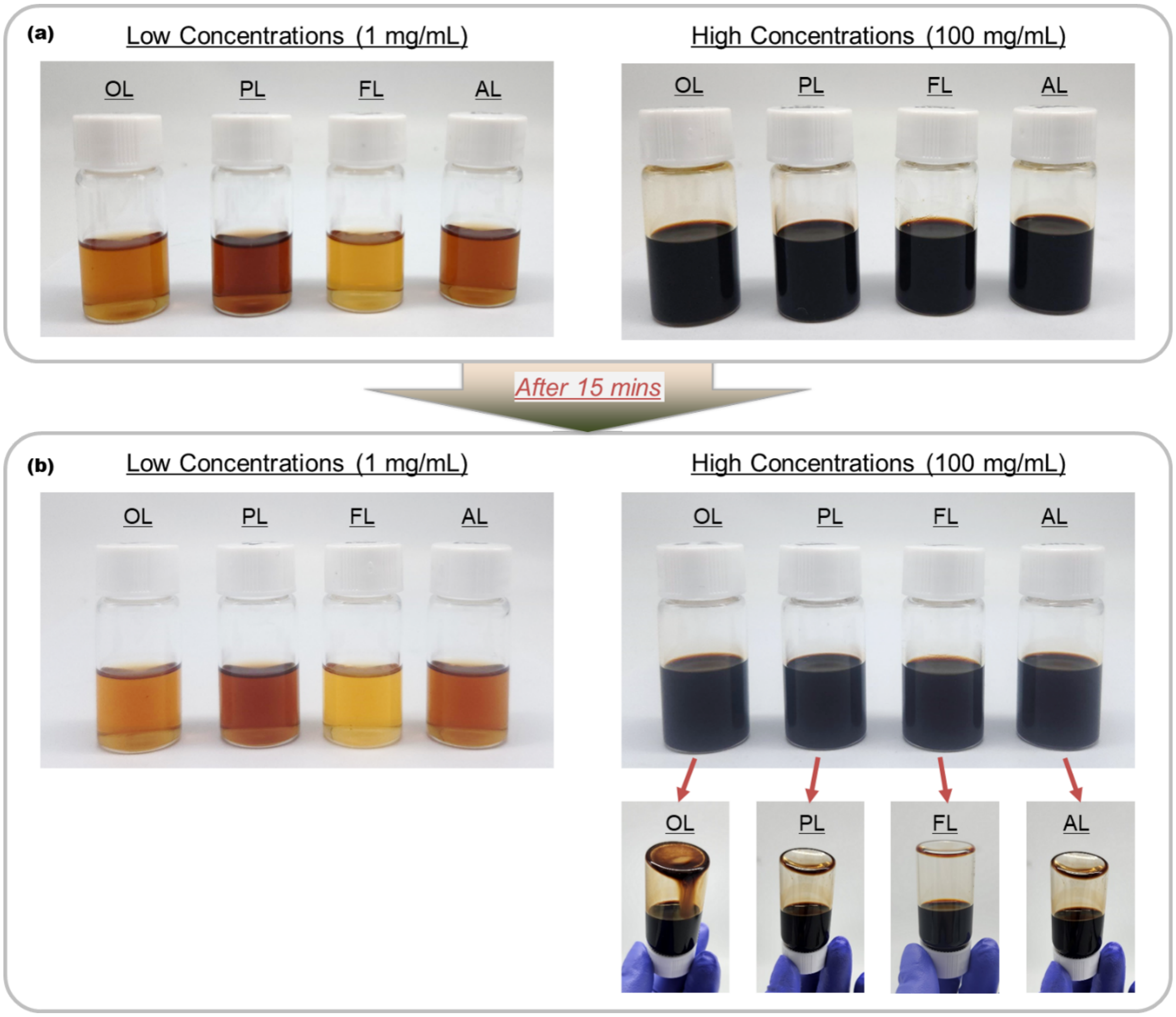
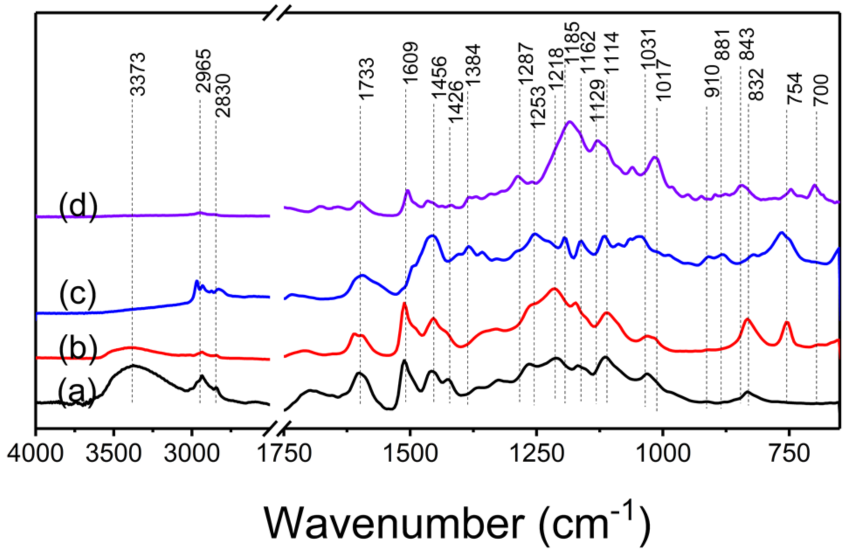


Fig. S4. Photographs showing the solubility of four lignin solutions (OL, PL, FL, and AL) at low concentration (1 mg/mL) and high concentrations (100 mg/mL) (a) right after solution preparation and (b) after 15 mins.



Wavenumber (cm^{-1})	Peak assignment[1-3]
3373	O-H stretching
2965	C-H stretching (aliphatic)
2830	C-H stretching (aliphatic)
1733	C=O stretching (unsaturated)
1609	Aromatic skeletal vibration
1457	C-H deformation (aliphatic)
1426	O-H bending (primary alcohol)
1384	C-H deformation (aliphatic)
1287	C-O-C (alkyl aryl ether), C-O of guaiacyl ring
1253	C-N stretching peak (amine)
1218	C-C, C-O, C=O stretch in Guaiacyl ring
1185	C-F stretching
1162	C-O (alkyl aryl ester)
1129	C-F stretching
1114	Aromatic C-H (Guaiacyl ring)
1031	Aromatic C-H (Guaiacyl ring)
1017	C-F stretching
910	Aromatic C-H bending (1,2,4-trisubstituted)
843	Aromatic C-H bending (1,2,4-trisubstituted)
832	Aromatic C-H bending (disubstituted or tetrasubstituted)
756	Aromatic C-H bending (1,2-disubstituted)
700	Aromatic C-H bending (bezene derivative)

Fig. S5. FT-IR peak assignment of (a) organosolv lignin, (b) phenolated lignin, (c) aminated lignin, and (d) fluorinated lignin.

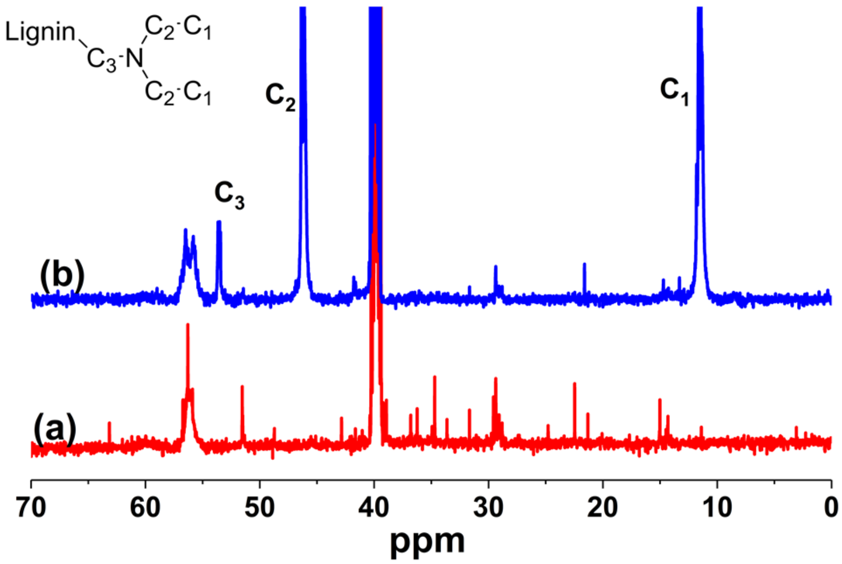


Fig. S6. ^{13}C NMR spectra of (a) phenolated lignin and (b) aminated lignin.

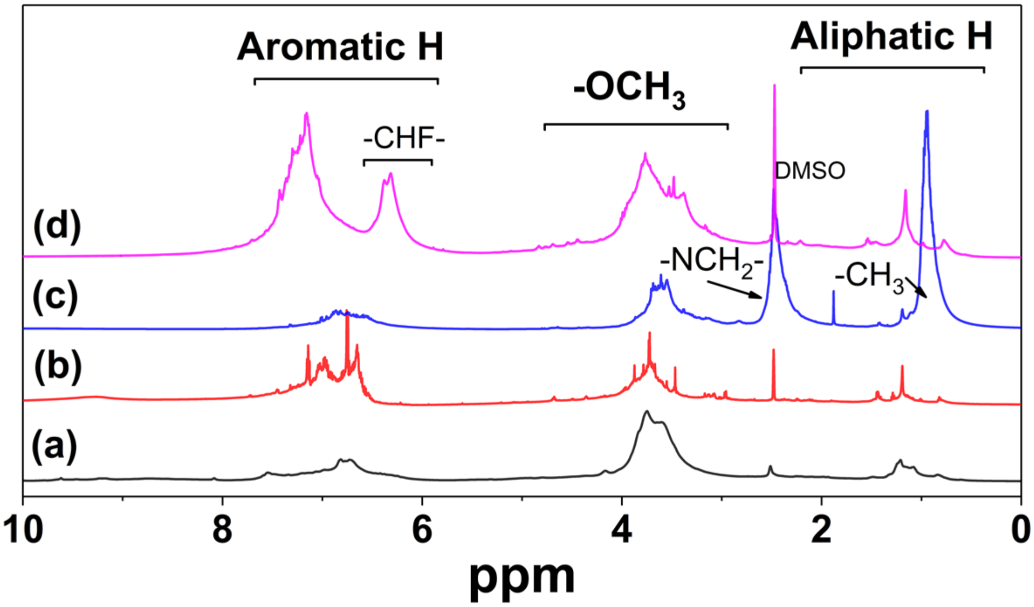


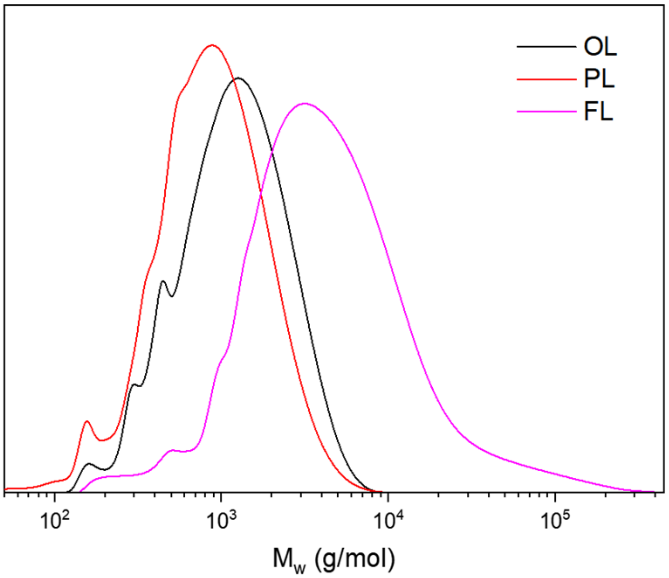
Fig. S7. ^{1}H NMR analyses of (a) organosolv lignin, (b) phenolated lignin, (c) aminated lignin, and (d) fluorinated lignin

Table S1. Hydroxyl contents in lignin samples

mmol/g	Al-OH	5-Substituted	Guaiacyl	*o*/*p*-phenol	-COOH	Total
Organosolv lignin	1.46	1.68	1.46	1.16	0.18	5.77
Phenolated lignin	0.06	1.31	1.29	4.24	0.00	6.90
Aminated lignin	0.00	2.55	0.33	0.95	0.00	3.84
Fluorinated lignin	0.00	0.00	0.00	0.00	0.00	0.00

Table S2. Comparison of nitrogen content in various aminated-lignin materials

	Lignin	Pre-treatment method	Elemental analysis (Weight %)		
			C	H	N
X. Du et al[4]	LignioBoost lignin	Phenolation	-	-	4.88
G. Jiao et al[5]	Biorefinery technical lignin	Phenolation	64.34	7.00	5.44
This research	OrganoSolv Lignin	Phenolation	68.81	8.63	6.19



	Mw (g/mol)	D
OL	1470	1.70
PL	1110	1.76
FL	8820	3.66

Fig. S8. GPC analyses of organosolv lignin (OL), phenolated lignin (PL), and (d) fluorinated lignin (FL).

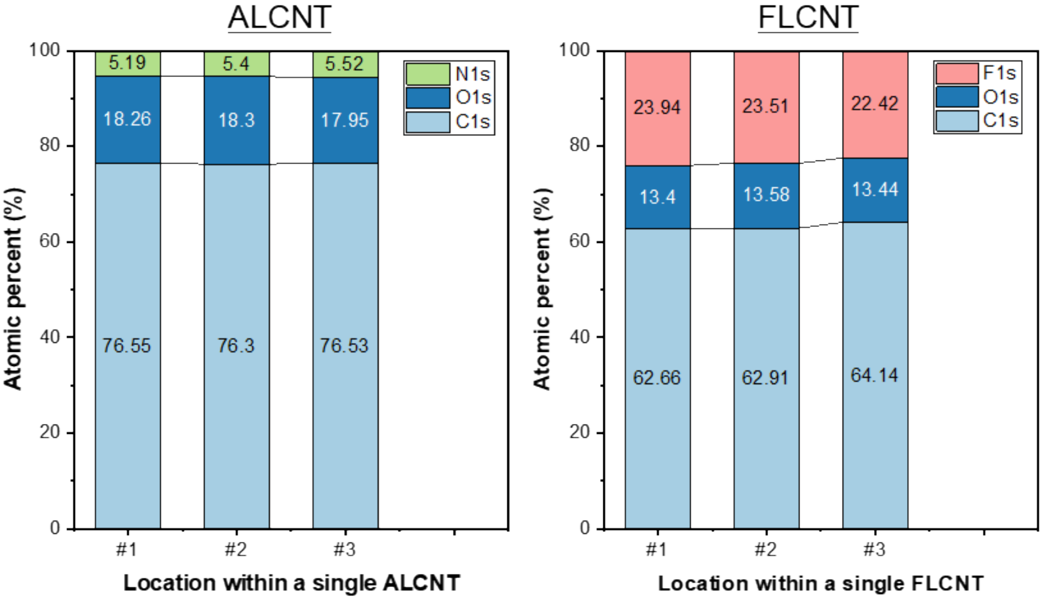


Fig. S9. Atomic percent of AL-(left) and FL-(right) doped DWCNT films analyzed by XPS.

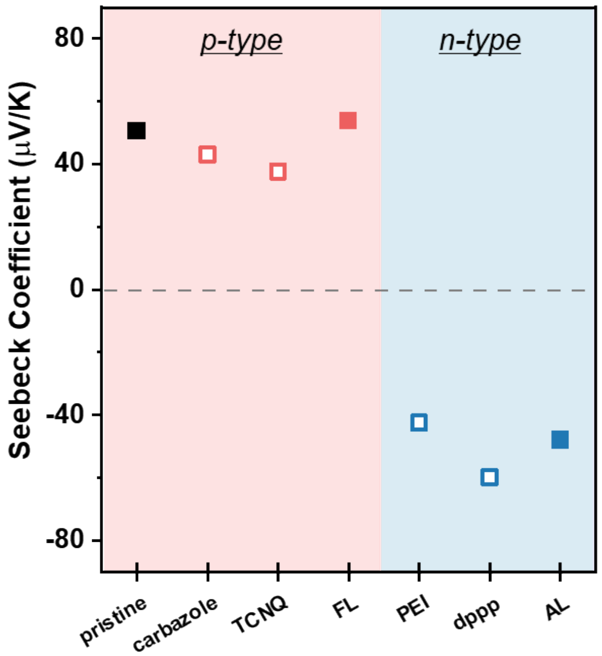


Fig. S10. Comparison of the Seebeck coefficients achieved in this work to those of fossil fuel-based organic dopants including carbazole and TCNQ as *p*-dopants, and PEI and dppp as *n*-dopants.

References

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