

A Highly Efficient, Environmentally Friendly Lignin-based Flame Retardant Used in Epoxy Resin

Peng Dai^{‡1}, Mengke Liang^{‡1}, Xiaofeng Ma^{1,2}, Yanlong Luo^{1,2}, Ming He^{1,2}, Xiaoli Gu³, Qun Gu⁴,
Imtiaz Hussain¹, Zhenyang Luo ^{*1,2}

1. College of Science, Nanjing Forestry University, 159 Longpan Road, Nanjing 210037, P. R. China

2. Institute of Polymer Materials, Nanjing Forestry University, 159 Longpan Road, Nanjing 210037, P. R. China

3. College of Chemical Engineering, Nanjing Forestry University, 159 Longpan Road, Nanjing 210037, P. R. China

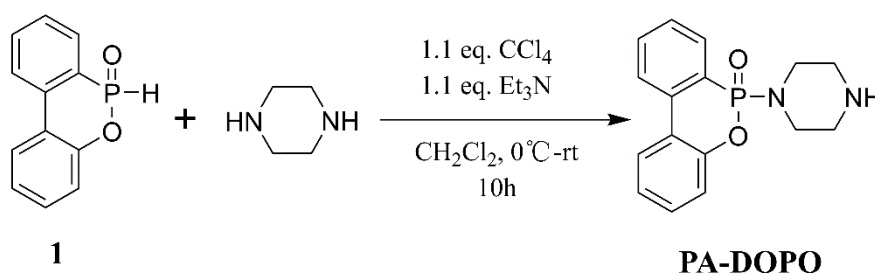
4. Department of Chemistry, Edinboro University of Pennsylvania, 230 Scotland Rd, Edinboro 16444, United States

**Corresponding author. E-mail address: luozhenyang@njfu.edu.cn (Z. Luo)*

‡ P. Dai, and M. Liang equally contributed to this paper.

1. Preparation of PA-DOPO

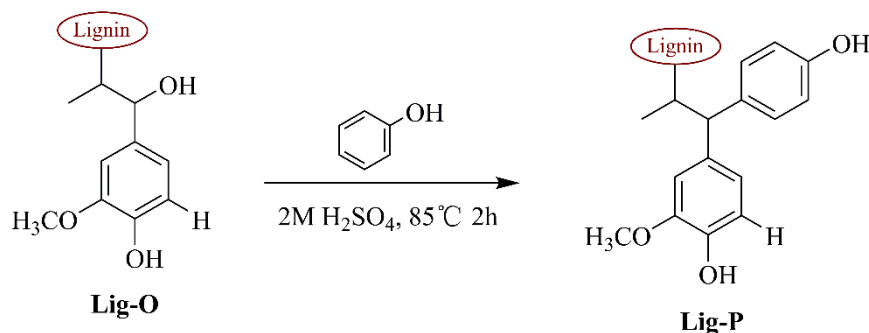
Firstly, piperazine, carbon tetrachloride, triethylamine, and methylene dichloride were mixed in a three-neck flask (solution 1). Secondly, DOPO was dissolved in methylene dichloride and the solution was transferred to a dropping funnel, from which the mixture was added dropwise into solution 1 (with constant stirring) under N₂ atmosphere at 0°C. Then, the reaction mixture was left for 10 hours at room temperature. The molar ratio of DOPO, triethylamine, carbon tetrachloride, and piperazine is 1:1.1:1.1:10. Piperazine is overwhelmingly excessive to ensure minimal by-product. After completion of the reaction, the mixture was filtered and the solid product was washed 3 times with DI water to obtain purified PA-DOPO (yield: 20.5 %).



Scheme S1. Synthetic route of the intermediate (PA-DOPO)

2. Preparation of Lig-P

First, the lignin is purified according to the method described in the literature¹ to obtain an originally purified lignin, Lig-O. Then, Lig-O is subjected to phenolation process according to the method of Jacob Podschun² to obtain Lig-P (yield: 80.5 %).



Scheme S2. Synthetic route of the Lig-P

3. Characterization of PA-DOPO

¹H NMR (CDCl₃, 300K, Bruker Biospin 600 MHz) δ (ppm): 8.02-8.00 (t, 1H, J = 6.1 Hz), 7.95-7.94 (d, 1H, J = 7.8 Hz), 7.83-7.79 (q, 1H, J = 7.2 Hz), 7.70-7.67 (t, 1H, J = 7.8 Hz), 7.51-7.48 (m, 1H), 7.48-7.36 (t, 1H, J = 34.5 Hz), 7.35-7.22 (m, 2H), 3.43-3.41 (m, 4H), 3.18 (s, 4H). NMR data confirmed successful grafting of PA to DOPO.

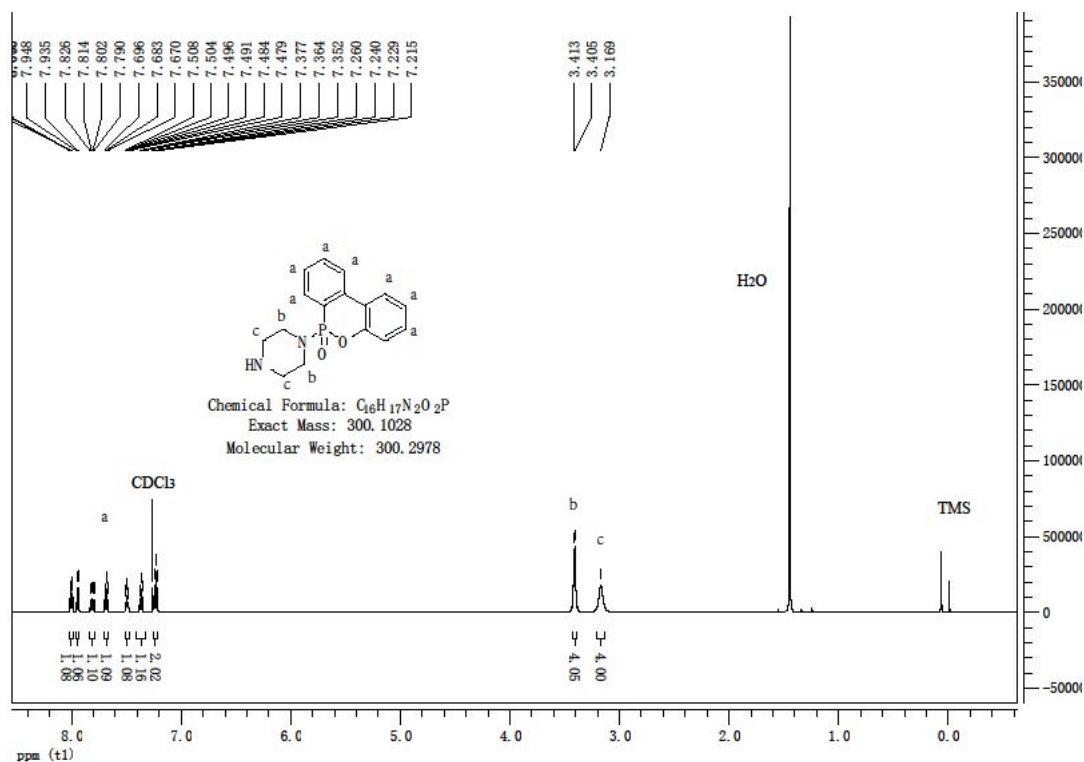


Figure S1. 1H NMR of PA-DOPO

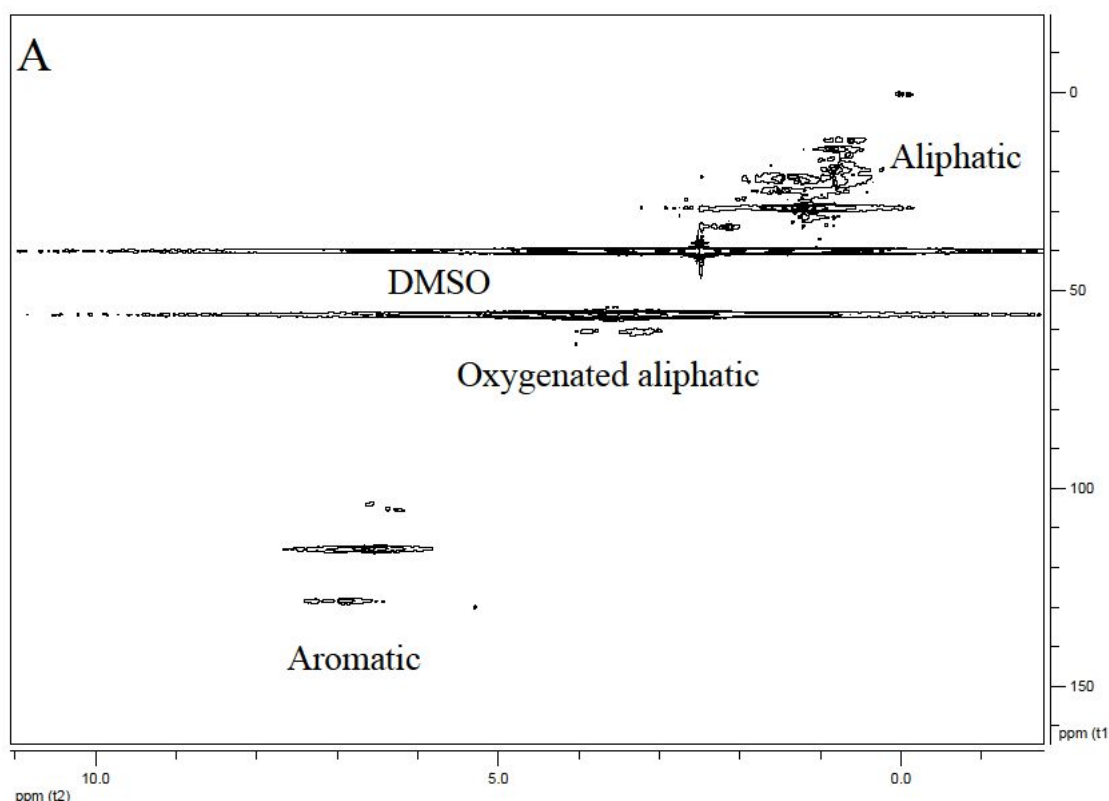
4 Characterization of pretreated lignin (Lig-P)

4.1 Qualitative analysis of phenolated lignin

Two-dimensional NMR (DMSO- d_6 , 300 K, Bruker Biospin 600 MHz) is used to characterize changes in chemical structure from purified lignin (Lig-O) to pretreated lignin (Lig-P). Conditions for the (Heteronuclear Single Quantum Coherence) HSQC analysis were as follows: 1.5 s pulse delay (d1), and acquisition of 160 times.

The HSQC spectrum in Figure S2 (A) shows three regions of Lig-O associated with aliphatic, oxyaliphatic and aromatic ^{13}C - 1H of Lig-P. For

Lig-P, a signal for phenol at δ_C/δ_H 21.9/2.43 ppm is shown in the aliphatic region. The enhancement of the lignin phenol signal after pretreating is evident. In the oxygen-containing aliphatic region, both Lig-O and Lig-P show a cross-signal with methoxyl (δ_C/δ_H 56.0/3.70 ppm) and side chains in the β -O-4' structure. In the aromatic signal region, both lignins display benzene ring signals in guaiac units (δ_C/δ_H 115.4/6.72 ppm), which corroborates the reaction unit of lignin in Scheme S 2, while the signal region in FigureS2 (B) (δ_C/δ_H 106.7/7.36 ppm) is attributed to the phenol. This also proves that phenol was successfully grafted onto lignin³.



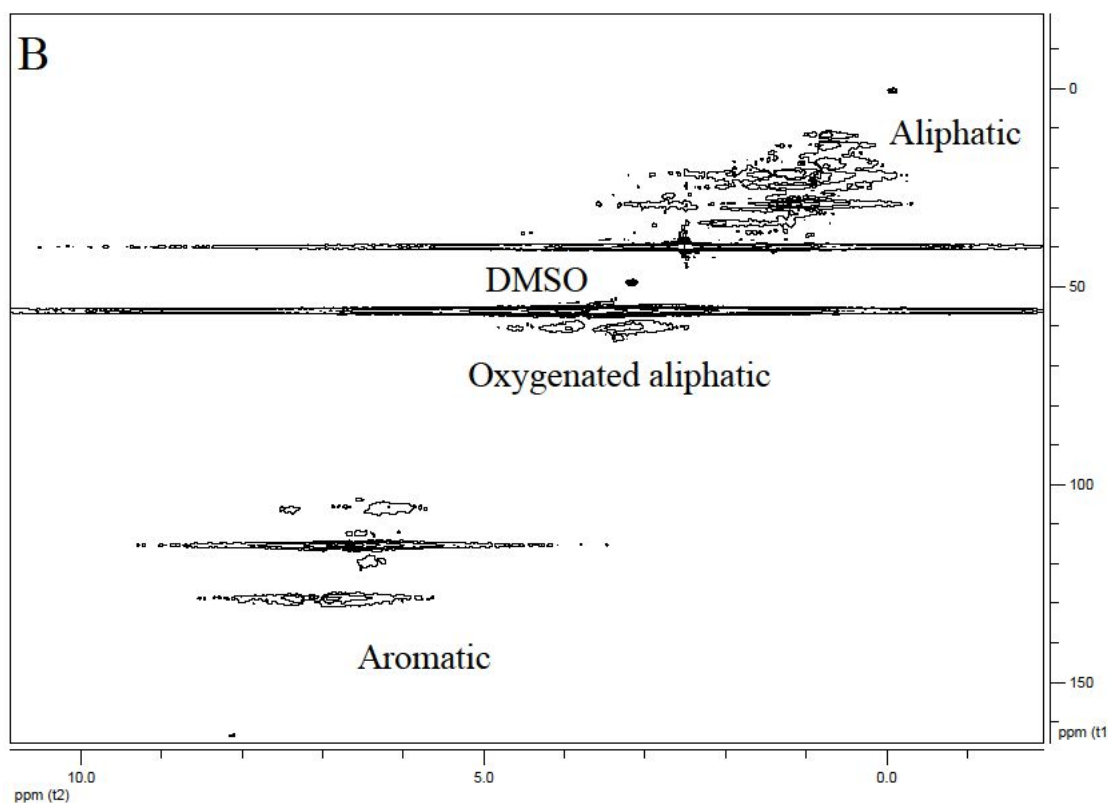


Figure S2. Total HSQC 2D NMR spectra of (A) Lig-O, and (B) Lig-P

4.2 Quantitative analysis of phenolated lignin

Non-aqueous phase potentiometric titration was used to determine the extent of phenolic hydroxyl in lignin samples by using the method of Pobiner⁴. The phenolic hydroxyl content of lignin increased from 2.8 mmol/g to 4.5 mmol/g after the phenolation, which helped the subsequent Mannich reaction to graft more PA-DOPO onto Lig-P. This process also facilitates the grafting of more DOPO onto Lig-M through nucleophilic reactions, to modulate the P content in the lignin, which enhances the flame-retardant efficiency.

5 Effective Heat of Combustion

Figure S3 shows the effective heat of combustion (EHC) of epoxy resin and Lig/EP composite, and the average effective heat of combustion (AEHC) data are shown in Table S1. AEHC of shows a decreasing trend from Lig-P to Lig-M to Lig-F. The Lig-F/EP shows a significant decrease of AEHC comparing to EP.

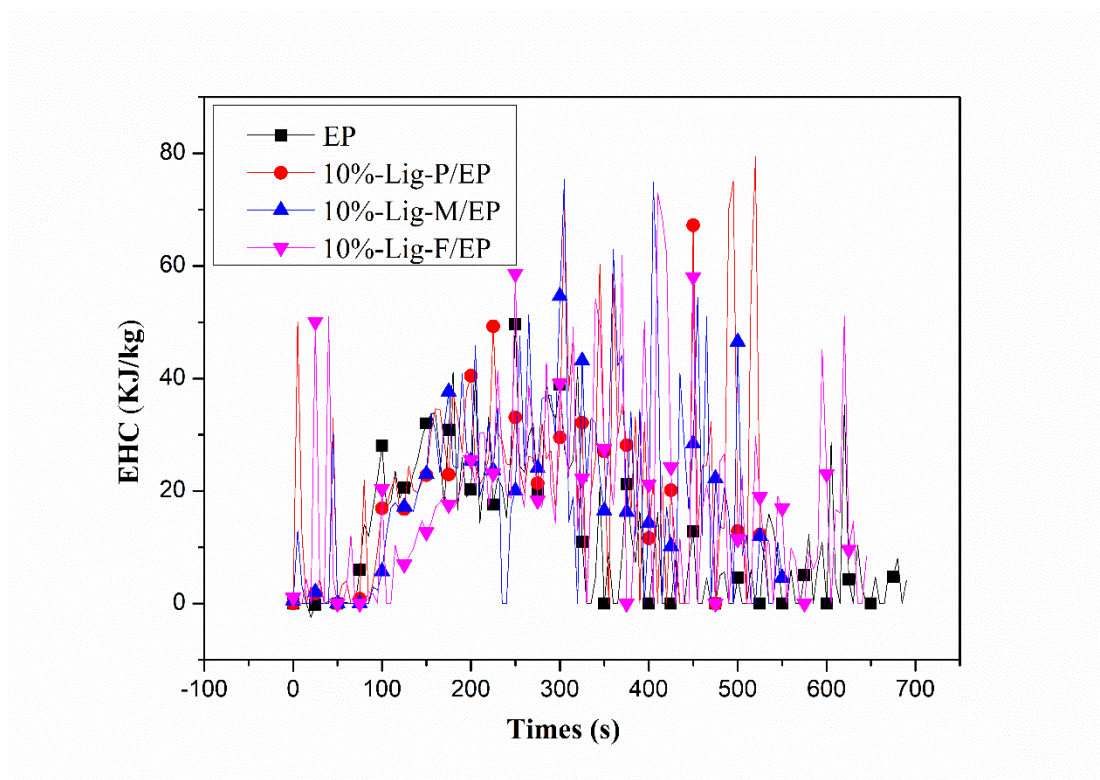


Figure S3. Effective heat of combustion: EP, composites of 10%-Lig-P/EP, 10%-Lig-M/EP, and 10%-Lig-F/EP (dimension of each sample: $100 \times 100 \times 3$ mm; heat flux of 35 kW/m^2)

Table S1 Average effective heat of combustion of EP & Lig/EP Composites

Samples	AEHC (kJ/kg)
EP	22.4
10%-Lig-P/EP	24.3
10%-Lig-M/EP	23.2
10%-Lig-F/EP	20.7

6 Analysis of Mechanical Properties of Lig-F

As shown in Figure S4, with increasing wt% of Lig-F in the composites, the tensile strength and elongation of epoxy resin composite presented a downward trend.

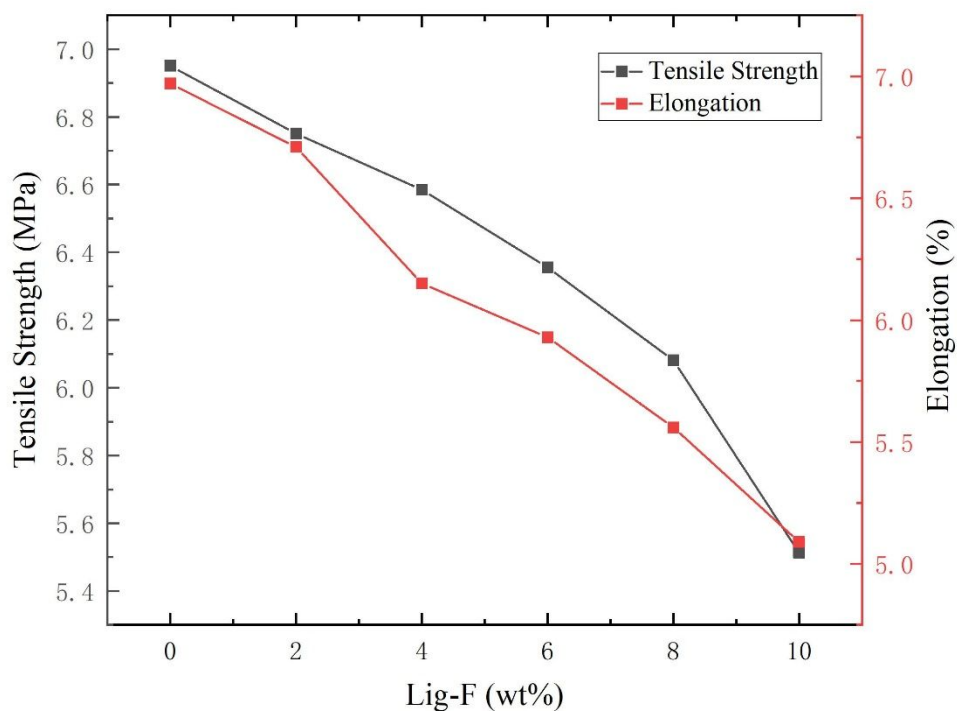


Figure S4. Tensile strength and elongation of EP composites with different Lig-F (wt%)

Reference

1. Liu, L.; Qian, M.; Song, P. A.; Huang, G.; Yu, Y.; Fu, S., Fabrication of Green Lignin-based Flame Retardants for Enhancing the Thermal and Fire Retardancy Properties of Polypropylene/Wood Composites. *ACS Sustainable Chemistry & Engineering* **2016**, 4, (4), 2422-2431.
2. Podschun, J.; Saake, B.; Lehnen, R., Reactivity enhancement of organosolv lignin by phenolation for improved bio-based thermosets. *European Polymer Journal* **2015**, 67, 1-11.
3. Ibarra, D.; Isabel Chavez, M.; Rencoret, J.; Del Rio, J. C.; Gutierrez, A.; Romero, J.; Camarero, S.; Martinez, M. J.; Jimenez-Barbero, J.; Martinez, A. T., Lignin modification during Eucalyptus globulus kraft pulping followed by totally chlorine-free bleaching: A two-dimensional nuclear magnetic resonance, fourier transform infrared, and pyrolysis-gas chromatography/mass spectrometry study. *Journal of Agricultural and Food Chemistry* **2007**, 55, (9), 3477-3490.

4. Harvey, P., Improved inflection points in the non-aqueous potentiometric titration of acid functionalities in lignin chemicals by using internal standardization and ion exchange. *Analytica Chimica Acta* **1983**, 155, 57-65.