Preparation of Photoresponsive Azo Polymers Based on Lignin, a Renewable Biomass Resource

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⑤ *Supporting Information*

ABSTRACT: Lignin-based azo polymers are prepared from alkali lignin, a byproduct in spent liquor from the pulping and papermaking industry, and their structures and photochromic effects are characterized by elemental analysis, Fourier transform infrared, ^{1}H nuclear magnetic resonance, and ultraviolet−visible spectroscopy. Results show that only the 2-(4-nitrophenyl azo) phenol lignin-modified polymer (AL-azo-NO$_2$) shows a significant photochromic effect, and its photoresponsive behavior is evidently slower than that of the synthetic polymer with a similar azo chromophore. For the 2-(4-methoxyphenyl azo) phenol lignin-modified polymer, its photoisomerization behavior was expected to be similar to that of azobenzene-type molecules, but its photoresponse is not obvious. The abnormal photochromic effect of AL-azo polymers is related to strong steric hindrance of lignin backbones. With addition of water (poor solvent), AL-azo-NO$_2$ shrinks gradually, which prevents azobenzene groups from isomerizing and results in a lower isomerization efficiency at higher water contents. Preparation of lignin-based azo polymers offers a novel source of azo polymers and provides a green and sustainable pathway for value-added utilization of lignin biomass recovered from the pulping industry.

KEYWORDS: *Lignin, Azo polymer, Azo coupling reaction, Photoresponse, Photoisomerization*
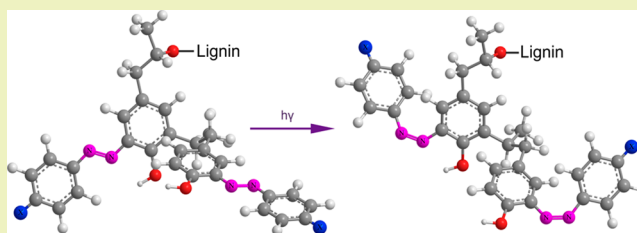
■ INTRODUCTION

Lignin is the one of the most abundant renewable biomass resources. The pulping industry produces >50 million tons of industrial lignin, a byproduct of spent liquor.[1] Alkali recovery and other methods have been used to treat the spent liquor and reduce the level of environmental pollution, but most of the recycled lignin was burned or treated in other low-value methods. With the growth in research on biomass resources and increasing demands of lignin products, the efficient utilization of lignin has attracted worldwide attention.[2] Lignin can be degraded to useful organic components.[3−5] It can also be chemically or biologically modified;[6−10] the corresponding lignin-based products have been widely used in adsorption and dispersion areas,[11,12] such as concrete water reducers,[13] dispersants for water-coal-slurry,[14] and pesticide dispersants.[15]

To broaden the utilization of lignin resources, the discovery of new methods for modifying the alkali lignin and potential applications of polymers based on lignin is encouraged. Properties of some "smart" chemicals can be adjusted by external environment stimuli like light, heat, and pH.[16−18] Introducing these structures or groups of "smart" chemicals into polymers can give them some novel properties. For example, poly[2-(diethylamino)ethyl methacrylate] is well-known to be pH-responsive; the solubility of poly[2-(diethylamino)ethyl methacrylate]-grafed lignin in water can therefore be adjusted by bubbling CO$_2$/N$_2$ (changing pH).[19] Therefore, preparing different stimulus-responsive lignin-based

polymers and then exploiting their applications are meaningful in terms of biomass utilization.

Azo polymers containing azo chromophores draw a great deal of attention because of the unique trans−cis isomerization properties of azo chromophores irradiated with UV or visible light.[20−24] The variation of azo chromophores can trigger many properties such as surface and inner structure changes and would have broad prospects in optical storage and optical control release.[25−30] Azo groups can be introduced into various polymers.[31−34] Besides, many studies have shown that the photoresponsive properties depend on the molecular architecture such as the chemical structure of the backbone, types of azo chromophores, etc. Lignin has a complex but unique benzene structure; introduction of azo groups into lignin backbones and a study of their photoresponsive behaviors have not been reported.

In this work, two lignin-based azo polymers were prepared from alkali lignin. To fully understand the structure−property relationship, their physicochemical properties were explored and compared with those of azo polymers of the other backbone. This synthetic method can be used to prepare different kinds of lignin-based azo polymers with a lignin backbone and different types of azo chromophores.

X: NO₂
    OCH₃
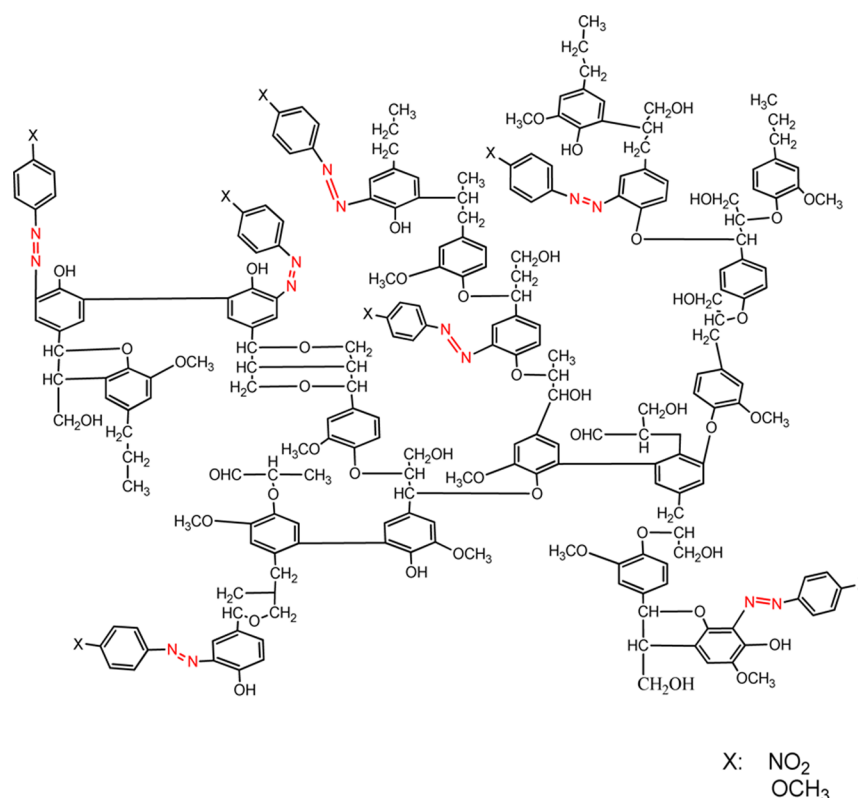
Figure 1. Possible structural formula of lignin-based azo polymers.

EXPERIMENTAL SECTION

Materials. Alkali lignin (AL), separated from poplar pulping black liquor, was supplied by Shixian Paper in Jilin Province, China. The alkali lignin sample was then purified carefully by acidification, filtration, and washing. The acidification was conducted at 55 °C, and the pH was reduced by H_2SO_4; the end pH was 2.0. The M_w of the AL used here was estimated to be 3471 by GPC with a polydispersity index of 1.25. The methoxyl group content is 10.04%.[35] By elemental analysis, the contents of elemental carbon, hydrogen, and oxygen of AL were measured to be 60.03, 5.95, and 33.96 wt %, respectively. On the basis of the results of elemental and functional group analysis, the average phenyl-propanoid unit (C_9 unit) of AL was calculated to be $C_9H_{9.60}O_{3.45}(OCH_3)_{0.62}$, with a monomer molecular weight of 192. *p*-Nitroaniline and *p*-anisidine were analytic grade and purchased from Aladdin Chemistry Co. Ltd. High-performance liquid chromatography grade tetrahydrofuran (THF) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Deionized water (resistivity of ≥18 MΩ/cm) was obtained from a Millipore water purification system and used in our experiments. Other reagents are of analytic grade, and solvents were used as received without further purification.

Preparation of Lignin-Based Azo Polymers. Alkali lignin (1.8 g, ~6 mmol of benzene units) was dissolved in 200 mL of a sodium hydroxide solution (aqueous, 0.004 g/L) and the mixture heated to 85 °C. Then 0.36 g of 30% hydrogen peroxide (aqueous) was added dropwise to the solution and the mixture reacted for 1 h and then cooled to room temperature. The M_w of the oxidated lignin was almost the same as that of alkali lignin.

Before lignin-based azo polymers had been prepared, a diazonium salt was synthesized as follows: 8 mmol of *p*-anisidine (0.985 g) or *p*-nitroaniline (1.10 g) was added to 100 mL of a sulfuric acid solution (12 mmol of sulfuric acid at a concentration of 11.8 g/L) at 0–5 °C while the mixture was being stirred for 20 min, and then a 5 mL solution containing 0.876 g of sodium nitrite was dropwise added while the mixture was being continuously stirred.

The lignin-based azo polymers were synthesized by the azo coupling reaction. The lignin solution obtained as described above and the diazonium salt solution were mixed for reaction for 1 h while being stirred at 0–5 °C, and the solution pH was adjusted to 9.5–10 by addition of a NaOH solution (aqueous, 3 g/L) before the reaction. The final solution was transferred to a dialysis bag (M_w = 1000 Da) and dialyzed in deionized water to remove ions and unreacted aromatic amine. The lignin-based azo polymer solid products were obtained by freeze-drying for 36 h.

Characterization. Infrared spectra were recorded with a PyeUnicamSP2000 spectrometer by incorporating the samples into KBr disks. ^1H nuclear magnetic resonance (NMR) spectra of the products were determined on a Bruker AVANCE Digital 400 MHz NMR spectrometer at 20 °C. Elemental analysis of C, H, O, N, and S was conducted with an Elementar Vario EL cube. UV–vis spectra of the samples were recorded with a Shimadzu UV-2450 spectrometer. The molecular weights and their distribution of alkali lignin and lignin-based polymers were determined by Agilent 1100 series gel permeation chromatography (GPC) with a PL gel, 5 μm, 1000 Å column and a PL gel, 5 μm, 500 Å column. The mobile phase was THF with a flow rate of 1 mL/min. The effluent was monitored by a G1362A RID detector. Polystyrene (PS) was employed as the standard substance to calibrate the instrument.

Photoisomerization Study. The samples were placed 22 cm from a high-intensity 365 nm UV light device (Youwei Co. Ltd., Beijing, China), and the photoisomerization of the azo chromophores was induced by irradiation with the UV light. The light intensity of the UV light was 7000 μW/cm² at a distance of 22 cm, measured with a UV radiometer. The UV–vis spectra of the samples over different irradiation time intervals were recorded with a Shimadzu UV-2450 spectrometer.

RESULTS AND DISCUSSION

Synthesis and Characterization of Lignin-Based Azo Polymers. Two lignin-based azo polymers, 2-(4-nitrophenyl azo) phenol lignin-modified polymer (AL-azo-NO₂) and 2-(4-

methoxyphenyl azo) phenol lignin-modified polymer (AL-azo-OCH$_3$), were prepared by the azo coupling reaction with alkali lignin (AL). The possible structure of the lignin-based azo polymers is shown in Figure 1. The chemical structures of AL-azo-NO$_2$ and AL-azo-OCH$_3$ were verified by ^{1}H NMR, Fourier transform infrared (FT-IR), ultraviolet−visible (UV−vis) spectroscopy and elemental analysis.

Figure 2 shows the ^{1}H NMR spectra of AL-azo-NO$_2$, AL-azo-OCH$_3$, and alkali lignin (AL). Compared with that of AL, those
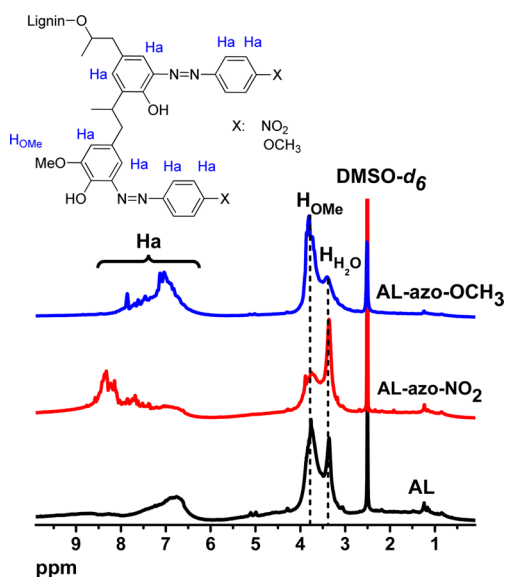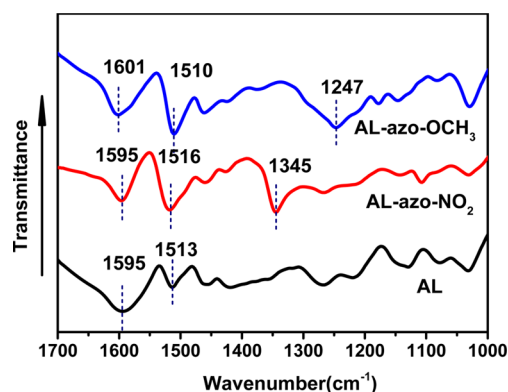

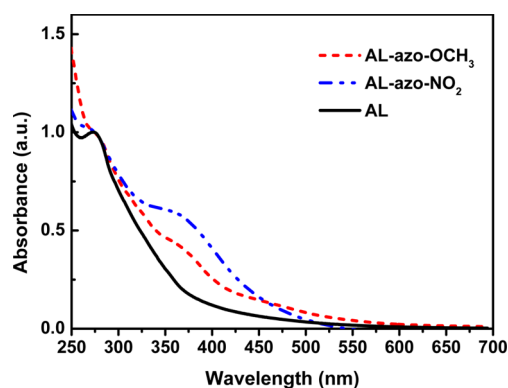**Figure 2.** ^{1}H NMR spectra of alkali lignin and lignin-based azo polymers.

of AL-azo-NO$_2$ and AL-azo-OCH$_3$ show new chemical shifts for aromatic hydrogens (Ar-H), and their exact chemical shifts depend on the type of azo chromophore. For AL-azo-NO$_2$, Ar-H located at the ortho positions of Ar-NO$_2$ (ortho to NO$_2$) has a new resonance at a chemical shift of ∼8.3 ppm and Ar-H (ortho to N=N) has a new resonance at ∼7.8 ppm. It proves that AL-azo-NO$_2$ has been successfully synthesized. AL-azo-OCH$_3$ also has Ar-H (ortho to N=N) that has a resonance at ∼7.8 ppm. Two lignin-based azo polymers have a higher resonance intensity at a lower frequency compared to that of AL. The more electronegative the substituted groups are, the greater the chemical shifts. The chemical shift of Ar-H in AL-azo-NO$_2$ is greater than that in AL-azo-OCH$_3$ because of the lower electronegativity.

Figure 3 shows the IR spectra of AL-azo-NO$_2$, AL-azo-OCH$_3$, and AL. For AL, peaks at 1513 and 1595 cm^{-1} are attributed to the C=C stretching vibration of benzene rings. For AL-azo-NO$_2$, the peak at 1345 cm^{-1} is attributed to the N−O stretching vibration of NO$_2$ groups; for AL-azo-OCH$_3$, the peak at 1247 cm^{-1} is attributed to the C−O stretching vibration of OCH$_3$ groups. After Ar-N=N- is coupled with AL, the intensity ratio of the band at 1510−1516 cm^{-1} to that at 1595−1601 cm^{-1} increases because the N=N stretching vibration is overlapped with the C=C stretching vibration of benzene rings at 1510−1516 cm^{-1}. As shown in Figure 3, the intensity ratio is ∼0.82 for AL but increases to 1.10 for AL-azo-NO$_2$ and 1.16 for AL-azo-OCH$_3$.

The UV−vis spectra of AL-azo-NO$_2$, AL-azo-OCH$_3$,and alkali lignin are shown in Figure 4. The characteristic absorption peak of AL is near 280 nm. Compared with that

Figure 3. FT-IR spectra of alkali lignin and lignin-based azo polymers.

Figure 4. UV−vis spectra of alkali lignin and lignin-based azo polymers dissolved in THF solutions.

of AL, the spectra of AL-azo-NO$_2$ and AL-azo-OCH$_3$ show new characteristic absorption bands in the range of 300−500 nm, indicating that azophenyl has been successfully synthesized in the two polymers. The exact absorption location of the two AL-azo polymers depends on the type of azo chromophore, the degree of functionalization, and the solvent.

By elemental analysis, the contents of nitrogen, carbon, hydrogen, and oxygen of AL, AL-azo-NO$_2$, and AL-azo-OCH$_3$ were measured and are listed in Table 1. The degree of

Table 1. Elemental Analyses of Lignin-Based Azo Polymers

sample	N (%)	C (%)	H (%)	O (%)	DF (%)
AL-azo-NO$_2$	6.2	58.6	4.3	30.7	36.4
AL-azo-OCH$_3$	1.3	61.8	6.3	30.6	9.5

functionalization (DF) of the lignin azo polymers can be approximately calculated from the nitrogen content measured by elemental analysis, according to eq 1. The DF values of AL-azo-NO$_2$ and AL-azo-OCH$_3$ are estimated to be 36.4 and 9.5%, respectively.

$$N\% \approx \frac{DF \times 14 \times n_{azo}}{M_{w,unit} + DF \times M_{w,azo}} \qquad (1)$$

where $N(\%)$ is the mole content of nitrogen in lignin−azo polymers; $M_{w,unit}$ is the molecular weight of the AL unit, which is 192; $M_{w,azo}$ is the molecular weight of the azo end group, which is 150 for -N=N-ph-NO$_2$ and 137 for -N=N-ph-OCH$_3$; and n_{azo} is the number of nitrogen in an azo end group, which is 3 for -N=N-ph-NO$_2$ and 2 for -N=N-ph-OCH$_3$.

Photoisomerization of Lignin-Based Azo Polymers.
The photoisomerization of lignin-based azo polymers in solutions was studied by UV–vis spectroscopy after irradiation with 365 nm UV light. The UV spectra were recorded over different time intervals until the samples reached photostationary states. The spectra of different time intervals changed obviously, and the errors for each time interval are small ($\leq$1%) and depend on repeated experiments. The UV–vis spectra of AL-azo-NO$_2$ solutions varying with irradiation time are given in Figure 5. Upon UV irradiation, the intensity of the π–π^* transition band at 370 nm decreases; this spectral variation is a sign of trans–cis isomerization of the azo chromophores.
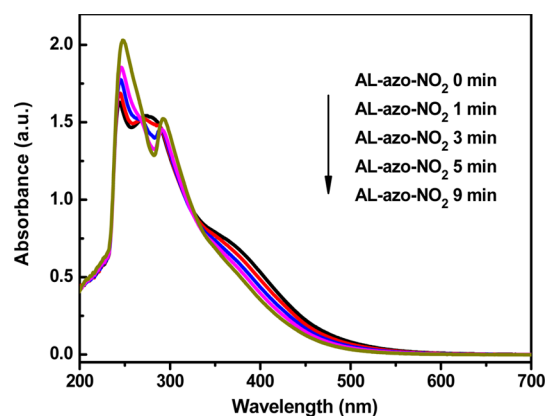
Figure 5. Variation of UV–vis spectra of AL-azo-NO$_2$ in a THF solution induced by the irradiation of UV light.

AL-azo-NO$_2$ shows a significant photochromic effect in THF solutions, while AL-azo-OCH$_3$ shows no obvious photochromic effect under the same condition. The only structural difference between the two types of lignin-based azo polymers is the electron-withdrawing substituent at the 4′ positions of the azobenzene units. The electronegativity of the -NO$_2$ group in AL-azo-NO$_2$ is greater than that of the -OCH$_3$ group in AL-azo-OCH$_3$. This may be why two lignin-based azo polymers show different photochromic effects. The influence of the electron-withdrawing groups appears to be the same in the linear azo polymers and the hyperbranched azo polymers.

Meanwhile, the photochromic effects of the two lignin-based azo polymers are both completely opposite from those of two synthetic azo polymers reported by Wu et al.:[36] poly{2-[4-(4′-nitrophenylazo)phenoxy]ethanol-co-acrylic acid} (PNAPE) and poly{2-[4-(4′-ethoxyphenylazo)phenoxy]ethanol-co-acrylic acid} (PEAPE). As shown in the structural formula (Figure S1 of the Supporting Information), PNAPE has the same azo end group of -N=N-ph-NO$_2$ as AL-azo-NO$_2$ but shows no photochromic effect. PEAPE has an azo end group similar to that of AL-azo-OCH$_3$ but shows a strong photochromic effect.

Typically, azobenzene molecules are categorized into three classes: the azobenzene-type molecules, the amino-azobenzenes, and the pseudostilbenes. Only the azobenzene-type molecules can show an obvious photochromic effect because both trans–cis isomerization and thermal back-relaxation from cis to trans isomerization are slow, but amino-azobenzenes and the pseudostilbenes show no obvious photochromic effect because the thermal back-relaxation from cis–trans isomerization is too fast to detect trans–cis isomerization. For PNAPE, the 4 position of the two phenyl rings is substituted with alkoxy groups, and the 4′ position of the two phenyl rings

is substituted with NO$_2$. PNAPE shows no photochromic effect because it has a structure similar to that of the pseudostilbenes. For AL-azo-NO$_2$, the 4 position of the two phenyl rings is not substituted; however, the 2 position of the two phenyl rings is substituted with OH, and the 4′ position of the two phenyl rings is substituted with NO$_2$. AL-azo-NO$_2$ has a push–pull configuration that is similar to that of PNAPE, but it shows an obvious photochromic effect.

AL-azo-NO$_2$ and PNAPE have the same substituent and are located in the same position but different backbone architectures. The structure of lignin-based azo polymers is different from that of linear azo polymers and hyperbranched azo polymers. Though the lignin backbone structure mainly consists of numerous C$_9$ units, these units [hydroxyphenyl (H), guaiacyl (G), and syringyl (S)] are not completely the same as each other; furthermore, these similar repeated units are randomly linked by several kinds of bonds.[37,38] These factors result in the complex structure, and the complex structure led to strong steric hindrance that makes structures in the polymers not flexible to move.[39] Via comparison of the two backbones of AL-azo-NO$_2$ and PNAPE, it is highly possible that strong steric hindrance of lignin backbones prevents azobenzene from quickly photoisomerizing. That is to say, AL-azo-NO$_2$ has trans–cis photoisomerization behavior much slower than that of PNAPE, and the process can be observed by UV–vis spectroscopy.

For the same reason, AL-azo-OCH$_3$ has trans–cis photoisomerization behavior much slower than that of PEAPE because of the steric hindrance of lignin backbones. AL-azo-OCH$_3$ has a push–pull configuration similar to that of PEAPE but shows no photochromic effect.

As discussed above, the photoresponsive behavior of lignin-based azo polymer AL-azo-NO$_2$ is slower than that of other azo polymers like PNAPE. The trans–cis process lasts several minutes, while that of PNAPE counts by only seconds. Because of the steric hindrance of lignin, azo polymers based on lignin can offer slow photoresponsive functional materials needing slow photoresponsive behavior.

Meanwhile, we have recently successfully prepared the lignin-based polymer (AL-azo-NO$_2$) micelles by self-assembly. Figure 6a shows a TEM image of the colloid spheres obtained from the AL-azo-NO$_2$ micelle solution. AL-azo-NO$_2$ colloid films are also well-prepared through a vertical deposition technique, as shown in Figure 6b. These lignin-based azo micelles and their two-dimensional array offer potential application in control delivery and photoresponsive material areas.
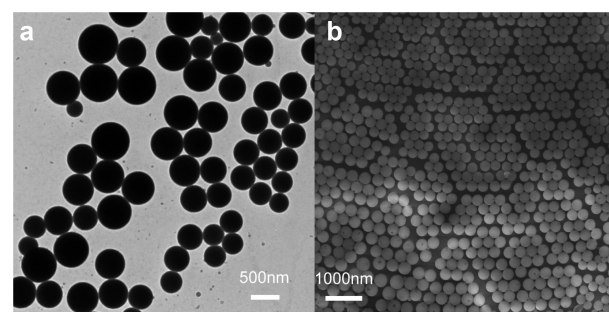
Figure 6. (a) Transmission electron microscopy and (b) scanning electron microscopy images of surface morphology for the colloidal spheres obtained from the AL-azo-NO$_2$ suspension.

■ CONCLUSION

Two novel lignin-based azo polymers (AL-azo-NO_2 and AL-azo-OCH_3) with different azobenzene chromophores have been successfully synthesized from alkali lignin. Only the AL-azo-NO_2 shows a significant photochromic effect. It is interesting to find that the photoresponsive behavior of the lignin-based azo polymers is evidently slower than that of synthetic azo polymers with similar azo end groups because the strong steric hindrance of lignin backbone prevents the azo chromophores from isomerizing. Lignin-based polymer (AL-azo-NO_2) micelles are also prepared by self-assembling, and their two-dimensional array is formed. The lignin-based azo polymer preparation offers an economic method for synthesizing azo compounds and provides potential applications in slow photoresponsive materials. The preparation of a novel lignin product is of great significance for both the utilization of renewable resources and environmental protection.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Structural formulas of PNAPE and PEAPE. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00261.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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