ChemistrySELECT

Supporting Information

Acetylated Lignins: A Potential Bio-Sourced Photosensitizer

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Contents

1. Lignins and other reagents

KL-1 were purchased from Sigma-Aldrich (catalogue number: 80068-05-1). KL-2 were generously donated by the "Université du Québec à Trois-Rivières". Sawdust chestnut tree from which OL is extracted were supplied by Mazières establishment at "La Chapelle-Montbrandeix", Haute-Vienne, France. They were dried in a ventilated oven for three days at 40 °C, crushed and sieved (particle size less than 250 µM). Other reagents and solvents were also purchased from Sigma-Aldrich and used as received without further purification.

2. Extraction of organosolv lignin

Organosolv lignin was obtained as follow: 3.20 g of sawdust chestnut tree were treated with 100 mL of aqueous ethanol solution (65/25, v/v). Concentrated sulfuric acid (8 mmol L^{-1}) was added as a catalyst. The mixture was then stirred at 160 °C during 2 h in a 150 mL sealed pressure reactor (Parr reactor). After completion of the extraction and complete cooling of the mixture, nylon filter was used to separate the black liquor from the pulp. Then, pulp was washed three times with 25 mL of hot aqueous ethanol solution (60 °C, 65/25, v/v). The wash solution were added to the black liquor and 525 mL of deionised water were added to the combined liquor to precipitate the lignin. The solution was then centrifuged at 2740 x g for 20 min at 25 °C and filtered under vacuum on filter paper. Finally, the solid was washed with deionized water and dried at 50 °C for 72 h.

3. Lignin's acetylation

Lignins were acetylated as follow: 1.00 g of oven-dried lignins were dissolved in 40 ml of pyridine-acetic anhydride (1/1, v/v) and stirred for 48 h at 25 °C under argon. Lignin were then precipitated in approximatively 500 ml of deionized water. After filtration, esterified lignins

were dissolve in chloroform, washed tree times with distilled water and the solution was dried over $MgSO_4$. Acetylated lignins were finally obtained by rotary evaporation of the solvent.

4. Lignins' characterisation

Ash content of samples was determined according to NERL/TP-51044622 standard protocol (2008).[1] The weight of ash was calculated as a percentage of the initial dry sample weight and each sample was analysed in triplicate.

Acid-soluble lignin and acid-insoluble lignin of each sample were determined according to the NERL/TP-510-42618 standard protocol.[2] Each sample was analysed in duplicate.

C, H, N, S and O ratio of samples were obtained with a Thermoscientific Flashsmart elemental analyser. Vanadium oxide (V_2O_5) was added to the sample as catalyst for sulphur detection.

Molar mass analysis was performed on an Agilent 1100 series Gel Permeation Chromatography with a PLgel 5 µm MIXED-C 300 x 7.5 mm column. The mobile phase was THF with a flow rate of 1 mL min^{-1}. The effluent was monitored by a UV detector and height polystyrene standards with molar masses from 580 to 1 074 000 g mol^{-1} were employed to calibrate the instrument.

FT-IR spectrum of materials were obtained using a Frontier PerkinElmer spectrometer in the attenuation total reactance analysis mode. Spectra were collected between 600 and 4000 cm^{-1} after placing the pure product on a diamond crystal plate.

NMR analyses were performed at room temperature on a Bruker DPX 500 NMR spectrometer. For the ^{31}P NMR analyses, the method described by Granata and Argypopoulos[3] was used. Cyclohexanol was used as an internal standard and chromium III acetylacetonate as a relaxation agent. NMR tubes were provided with coaxial insert filled with 85% H_3PO_4 and all chemical shifts were reported relative to the signal of phosphoric acid.

Methoxy groups of lignins were quantified by ^1H NMR after acetylation according to the method of Abreu and Freire.[4]

5. EPR analyses

EPR analyses were performed on a Bruker Model ESP300E spectrometer. A lignins' concentration of 2 mg L^{-1} is used in each case and the protocol is that described by Riou et al.,[5] with the only exception that during the detection of $^1O_2$ *N*,*N*-dimethylformamide is employed as solvent and not as phosphate buffer for solubility reasons. Samples were irradiated

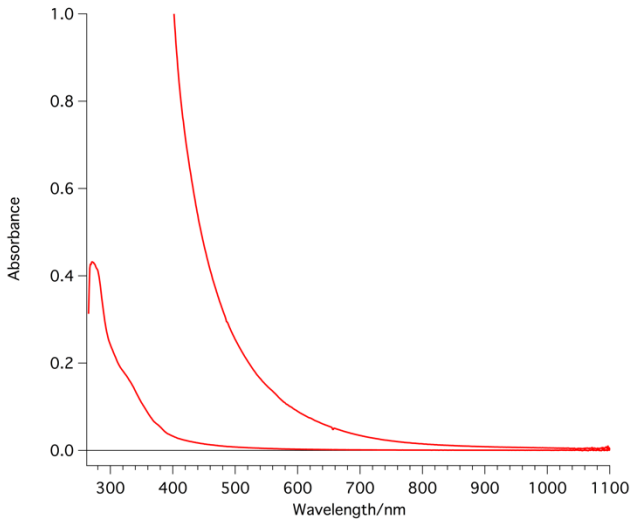
with a halogen source with an intensity of 68 μE s^{-1} m^{-2} for $O_2^{\bullet-}$ detection and of 270 μE s^{-1} m^{-2} for $^1O_2$ detection.

For superoxide anion detection, KL-1 were purified as follow: lignins were solubilized in a soda solution (0.04 mol L^{-1}). Then, sulfuric acid 98% were gradually added up to pH 3 to precipitate the lignins. Finally, KL-1 were washed and separated from water by centrifugation (2700 x g) for 20 minutes.

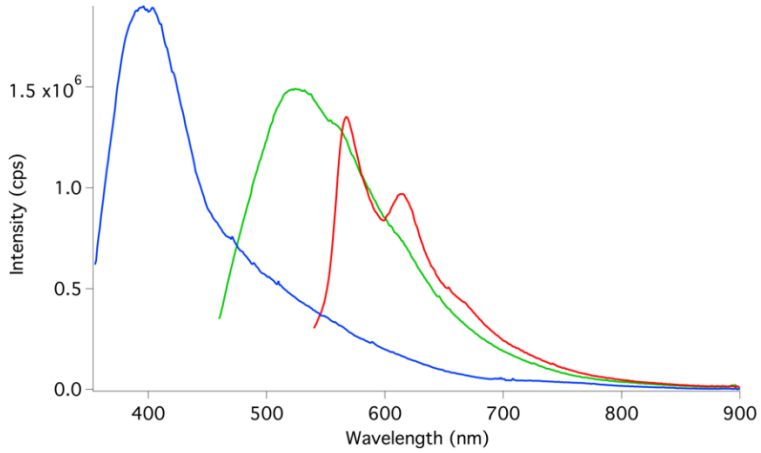
6. Quantum yield determination of singlet oxygen

For the determination of quantum yield of singlet oxygen emission (Φ_Δ), UV–Vis spectra of solutions were recorded in quartz cuvettes (1 cm) with a Hewlett-Packard/Agilent 8453 diode-array UV–Vis spectrophotometer. To record the $^1O_2$ emission at 1270 nm, a highly-sensitive liquid nitrogen cooled InGaAs detector (Electro-Optical Systems DSS series cryogenic receiver, 2 mm InGaAs photodiode) was coupled to a Horiba Jobin Yvon Spex Fluorolog 3 spectrofluorometer. Maximum slits and long integration times (10 s) were used. Sample and reference solutions were optically matched at the excitation wavelength with an absorption value of 0.1 (1 cm). An 850 nm cut-off filter was used in the emission path, to eliminate second order effects of the lignin or ZnPC fluorescence.

UV-Visible absorption and emission of AcOL:



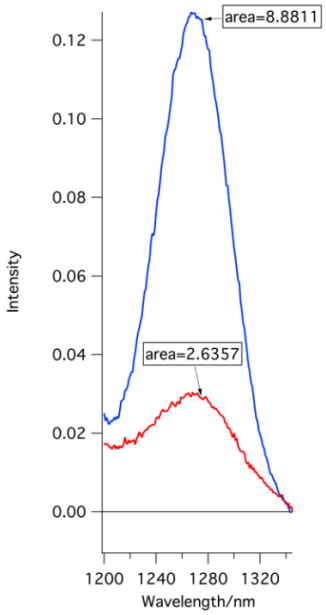
UV-Vis absorption spectra of two DMF solutions of acetylated lignin (OL). A maximum at 271 nm, a shoulder at 332 (diluted sample) and an absorption onset around 900 nm can be observed (high concentration).



Front face emission spectra of acetylated lignin (OL) in DMF using 350 nm (blue), 450 nm (green) and 525 nm (red) excitation. Slits were 1, 2 and 3 nm respectively for excitation path. Slit was 5 nm for emission path for all. Second order effects were suppressed with cut-off filters.

These emission spectra show that there are at least three different types of chromophores present the polymer.

Singlet oxygen emission:



NIR emission spectra displaying singlet oxygen emission generated by ZnPC in DMF (blue) and by acetylated lignin (OL) in DMF (red) obtained from samples with matched absorption of 0.1 at 350 nm. The area under the red spectrum is ca. 30% of that of the blue spectrum. A 850 nm cutoff filter was used in the emission channel.

$\Phi_\Delta = 0.17 \pm 0.03$ in DMF ($\lambda_{ex} = 350$ nm).

7. References

[1] "Determination of Ash in Biomass" A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, Report No. NERL/TP-510-42622, Laboratory Analytical Procedure, **2008**.

[2] "Determination of Structural Carbohydrates and Lignin in Biomass" A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D. Crocker, Report No. NERL/TP-510-42618, Laboratory Analytical Procedure, **2008**.

[3] A. Granata, D. S. Argyropoulos, *J. Agric. Food Chem.* **1995**, *43*, 1538-1544.

[4] H. D. S. Abreu, M. D. F. I. Freire, *An. Bras. Ci.* **1995**, *67*, 379-382.

[5] C. Riou, C. A. Calliste, A. D. Silva, D. Guillaumot, O. Rezazgui, V. Sol, S. Leroy-Lhez, *Photochem. Photobiol. Sci.* **2014**, *13*, 621-625.