

Summary of Minor Research Project

**FUNCTIONALISED LIGNIN WITH
CHROMOPHORIC GROUPS AS A MATRIX FOR
STABILISING SILVER NANOPARTICLES:
THEORETICAL AND EXPERIMENTAL STUDIES**

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By
Dr. Thomas V. Mathew
ASSISTANT PROFESSOR
RESEARCH POSTGRADUATE DEPARTMENT OF CHEMISTRY
ST. THOMAS COLLEGE, PALA – 686 574 KOTTAYAM, KERALA

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Introduction

Lignin is a natural composite material in all vascular plants, providing the plant with strength and rigidity. The word lignin is derived from the Latin word *lignum* meaning wood. It is a main component of vascular plants. Indeed, lignin is second only to polysaccharides in natural abundance, contributing 24 - 33% and 19 - 28%, respectively, to dry wood weights of normal softwoods and temperate-zone hardwoods. By decreasing water permeation across the cell wall, lignin renders the plant resistant to biodegradation as well as to environmental stresses. Lignin is an amorphous, aromatic, water insoluble, heterogeneous, three-dimensional, and cross-linked polymer with low viscosity. The molecular mass of lignin is high (600 - 1000 kDa), although not uniform, varying greatly within isolated samples. The molecular mass of lignin is thus difficult to determine, and use of a conventional formula is not possible. Lignin is highly reduced and its carbon content is 50% higher than that of polysaccharides, which makes lignin energy-rich [1, 2, 3].

The field of nanoscience has blossomed over the last twenty years and the need for nanotechnology will only increase as miniaturization becomes more important in areas such as computing, sensors, and biomedical applications. They attracted a great deal of attention in recent years due to their optical, physical and chemical properties that differentiates them from bulk material properties. Advances in this field largely depend on the ability to synthesize nanoparticles of various materials, sizes, and shapes, as well as to efficiently assemble them into complex architectures. The synthesis of nanoparticles, however, is a fairly established field as particles of submicron or nanosized dimensions have been synthesized for centuries. The first example of considerable recognition is the Roman Lycurgus Cup, a bronze cup lined with colored glass that dates to the fourth Century AD. The glass scatters a dull green light and transmits red light. According to a study commissioned by the British Museum, who currently displays the cup, the glass contains 70 nm particles that are an alloy of silver (70 percent) and gold (30 percent) [4]. Silver nanoparticles of this size are known to scatter green light and transmit orange, and the addition of Au shifts the absorption band to longer wavelengths.

Among the large varieties of these nano materials, the metal nano particles both in the pure and composite form have been extensively investigated because of their unique optical as well as electronic properties [5, 6, 7]. The noble metals, especially silver and gold, have attracted great attention due to their innumerable applications in various branches of science namely catalysis [8], photonics [9], photography, chemical sensing [10], surface enhanced Raman scattering (SERS) [11] and most importantly in the medicinal field as anti-microbial agents [12].

The present work deals with the development of a series of photoresponsive environment-friendly systems based on lignin. The core systems having free hydroxyl groups were functionally modified with selected photochromic molecules such as 3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid and 4-(1-pyrenyl) butyric acid. The modification was achieved by functional transformation such as esterification. All the chromophoric systems selected for the present study have free carboxyl functions. These carboxylic functional groups were attached to the biopolymeric cores through esterification of the free alcoholic functions of the cores by DCC coupling. The newly developed systems were soluble in polar solvents, "nature friendly" and "Green" in their properties. The esterified products were isolated, purified by column chromatography or membrane dialysis. All the products were characterised by FT IR, UV-Visible, ¹H NMR and fluorescence emission spectroscopic analysis and thermal studies. The systems thus developed are: lignin - 3-((E)-(4-aminophenyl) diazenyl) naphthalen-2-ol carboxylic acid, lignin - 4-(1-pyrenyl) butyric acid. Spectral studies show that all these photochromic systems have successfully introduced into the cores and thermal studies indicate optimum stability for all the products. All the biopolymeric core systems functionalised with photochromic moieties were subjected to UV-Visible absorption studies, light fastening studies, fluorescence emission analysis and thermal analysis. The systems showed excellent light absorption, light stabilisation and fluorescence emission properties.

Chapter 2

Results

The photochemical properties of the chromophoric system is greatly improved when it is attached to biopolymers. For the monomeric system, 3-((E)-(4-aminophenyl) diazenyl) naphthalen - 2 - ol carboxylic acid, a notable absorption at visible region was observed at 479 nm and there was a decrease in the intensity up on irradiation with sun light. The intensity of absorption exhibited by chromophoric system showed a gradual decrease on prolonged irradiation by sunlight. The intensity of absorption was decreased form 1.21 to 1.15 on 6 hours of irradiation under visible light. The absorption band corresponding to $\pi \rightarrow \pi^*$ transition was shifted to a shorter wavelength 318 nm and the band due to the $n \rightarrow \pi^*$ transition appeared at longer wavelength 485 nm when attached to lignin. In the case of chitosan functionalised with 3-((E)-(4-aminophenyl) diazenyl) naphthalen - 2 - ol carboxylic acid, the absorption band corresponding to $\pi \rightarrow \pi^*$ transition was shifted to a shorter wavelength 309 nm and the band due to the $n \rightarrow \pi^*$ transition appeared at longer wavelength 484 nm. A comparison of intensities of chromophore and biopolymer bound chromophore vs time of irradiation is given in 2.1.

(ii) Fluorescence emission properties

The fluorescence emission spectra of lignin functionalized with 3-((E)-(4-aminophenyl) diazenyl) naphthalen - 2 - ol carboxylic acid and the monomeric dye are recorded at room temperature and compared. The fluorescence emission properties were enhanced when the chromophore functionalized with lignin.

2.0.1 Light fastening and fluorescence emission behaviour of functionalised biopolymers with 4-(1-pyrenyl)butyric acid

The light fastening and fluorescence emission behaviour of biopolymer functionalised with 4-(1-pyrenyl)butyric acid were systematically studied.

The photochemical stability of the chromophoric system, 4-(1-pyrenyl)butyric acid, is appreciably increased when it was attached to lignin. For the monomeric system, there was a decrease in the intensity

Table 2.1: Comparison of intensity of absorption vs time of 3-((E)-(4-aminophenyl) diazenyl) naphthalen - 2 - ol carboxylic acid, and its biopolymer bound analogues under visible light irradiation

Compound	0 Hr	1 Hr	2 Hr	3 Hr	4 Hr	5 Hr	6 Hr
Dye	1.21	1.20	1.19	1.18	1.17	1.16	1.15
Lignin - Dye	1.77	1.72	1.68	1.65	1.61	1.58	1.56

Table 2.2: Comparison of intensity of absorption vs time of 4-(1-pyrenyl)butyric acid, and its biopolymer bound analogues under visible light irradiation

Compound	0 Hr	1 Hr	2 Hr	3 Hr	4 Hr	5 Hr	6 Hr
Dye	1.78	1.77	1.76	1.76	1.75	1.73	1.72
Lignin - Dye	1.81	1.80	1.79	1.78	1.77	1.76	1.75

up on irradiation with sun light. The intensity of absorption exhibited by chromophoric system showed a gradual decrease on prolonged irradiation. Lignin functionalised with 4-(1-pyrenyl)butyric acid is photochemically stable systems and there was no appreciable change in the intensity of absorption on several hours of irradiation under visible light. A comparison of intensities of chromophore and biopolymer bound analogue vs time of irradiation is given in 2.2.

Conclusion

We studied the photochemical, photophysical and thermal properties of a series of chromophoric systems attached to biopolymers such as lignin. The chromophoric systems under study are 3-((E)-(4-aminophenyl) diazenyl) naphthalen - 2 - ol carboxylic acid and 4-(1-pyrenyl)butyric acid. The absorption of the azo chromophore 3-((E)-(4-aminophenyl) diazenyl) naphthalen - 2 - ol carboxylic acid at about 320 nm is attributed to the $\pi \rightarrow \pi^*$ transition in *trans* isomer and the band at 479 nm to the $n \rightarrow \pi^*$ transition in *cis* isomer. The $\pi \rightarrow \pi^*$ transition shifted to a shorter wavelength and the $n \rightarrow \pi^*$ transition appeared at longer wavelength when the chromophore attached to biopolymers. Incorporation of chromophoric systems onto biopolymers backbones enhances the stability and light absorption properties of the chromophores. Photoluminescence of azo chromophore 3-((E)-(4-aminophenyl) diazenyl) naphthalen - 2 - ol carboxylic acid was greatly enhanced when attached to biopolymers. Pyrene containing polymers received interest because of their potential use as semiconductors, photoresist materials and fluorescent probes. 4-(1-pyrenyl)butyric acid substituted biopolymers were synthesised and their photochemical and photophysical properties were studied. Light fastening properties were greatly enhanced when attached to biopolymers. The emission behaviour of 4-(1-pyrenyl)butyric acid was monitored and emission at 375 and 395 nm are due to the fuorescence from excited monomeric pyrene and 419 nm from the excimers. Emission from the excimers were slightly red shifted when attached to biopolymers. The difference between the spectra of the monomeric chromophore and polymer bound analogues indicates that pyrene moieties that form excimers had already formed dimers prior to excitation, or that these moieties were different in different environments.

Bibliography

- [1] G. Henriksson. *Lignin in Pulp and Paper Chemistry and Technology*, volume 1. Walter de Gruyter GmbH and Co. KG: 10785 Berlin, 2009.
- [2] B. Xiao, X.F. Sun, and RunCang Sun. The chemical modification of lignins with succinic anhydride in aqueous systems. *Polym. Degr. Stab.*, 71(2):223 – 231, 2001.
- [3] Wim Thielemans and Richard P. Wool. Butyrate kraft lignin as compatibilizing agent for natural fiber reinforced thermoset composites. *Composites : Part A*, 35(3):327 – 338, 2004.
- [4] D. J. BARBER and I. C. FREESTONE. An investigation of the origin of the colour of the lycurgus cup by analytical transmission electron microscopy. *Archaeometry*, 32(1):33–45, 1990.
- [5] Sudipa Panigrahi, Subrata Kundu, Sujit Kumar Ghosh, Sudip Nath, Snigdhamayee Praharaj, Soumen Basu, and Tarasankar Pal. Selective one-pot synthesis of copper nanorods under surfactantless condition. *Polyhedron*, 25(5):1263 – 1269, 2006.
- [6] Michal Lahav, Emily A. Weiss, Qiaobing Xu, and George M. Whitesides. Core-shell and segmented polymer-metal composite nanostructures. *Nano Letters*, 6(9):2166–2171, 2006. PMID: 16968046.
- [7] Günter Schmid and Lifeng F. Chi. Metal clusters and colloids. *Advanced Materials*, 10(7):515–526, 1998.
- [8] L. N. Lewis. Chemical catalysis by colloids and clusters. *Chemical Reviews*, 93(8):2693–2730, 1993.
- [9] G. Carotenuto. Synthesis and characterization of poly(n-vinylpyrrolidone) filled by monodispersed silver clusters with controlled size. *Applied Organometallic Chemistry*, 15(5):344–351, 2001.
- [10] Youngjin Kim, Robert C. Johnson, and Joseph T. Hupp. Gold nanoparticle-based sensing of “spectroscopically silent” heavy metal ions. *Nano Letters*, 1(4):165–167, 2001.
- [11] Shuming Nie and Steven R. Emory. Probing single molecules and single nanoparticles by surface-enhanced raman scattering. *Science*, 275(5303):1102–1106, 1997.

- [12] Abdulkareem Melaiye, Zhaohui Sun, Khadijah Hindi, Amy Milsted, Daniel Ely, Darrell H. Reneker, Claire A. Tessier, and Wiley J. Youngs. Silver(i)-imidazole cyclophane gem-diol complexes encapsulated by electrospun tectophilic nanofibers: formation of nanosilver particles and antimicrobial activity. *Journal of the American Chemical Society*, 127(7):2285–2291, 2005. PMID: 15713108.