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Synthesis of a mimetic of the enzyme lytic polysaccharide monooxygenase (LPMO) to catalyse the polysaccharide hydrolysis reaction.

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In this work, a mimetic of the LPMO enzyme, a mononuclear copper enzyme coordinated to two histidine residues, was synthesized. The goal was to study its catalytic activity for application in the segregation of polysaccharides to produce non-polluting energy derived from biomass through oxidative hydrolysis reactions[1].

The project was divided into four organic synthesis steps to obtain the ligand followed by the coordination of copper to the ligand. The ligand was obtained from esterification of L-proline, generating product (1). Alkylation of (1) with bromo methyl pyridine resulted in compound (2), which was hydrolyzed in an alkaline solution to obtain compound (3). Coupling (3) and anthranilic ester, the ligand (LH) was obtained, which was coordinated with the Cu^{2+} ion to form the [CuL] complex.

Complex [CuL] was characterized by UV-vis and FTIR spectrophotometry, microanalysis, cyclic voltammetry, High Resolution Mass Spectroscopy and electron paramagnetic resonance (EPR) spectroscopy. The UV-vis spectrum revealed non-linearity of the molar absorptivity upon increase in concentration, evidencing a dynamic equilibrium between species in solution. EPR spectroscopy revealed that two main complexes co-exist in solution in equimolar concentrations. The increase in the solution pH favors one of them, indicating that the isomers are formed upon a deprotonation/protonation step. Catalytic tests were carried out using colorimetric methods with p-nitrophenyl-β-D-glucopyranoside as a cellulose mimetic[2]. The catalytic efficiency increased with the concentration of H_2O_2, due to the higher concentration of oxidizing agent in the reaction. The kinetic constant at 1.6 mM H_2O_2 was 1.96 x 10^{-3} s^{-1}, while at 10 mM H_2O_2 it was 2.4 x 10^{-3} s^{-1} (Figure 1). Additional studies will be performed using dioxygen as a co-substrate to evaluate the potential of [CuL] in the polysaccharide degradation.

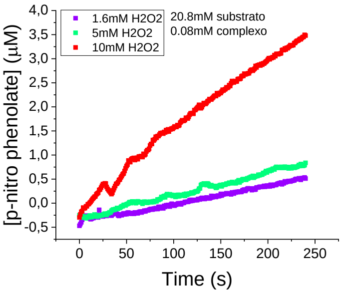

Figure 1. Comparison of the catalytic activity kinetics of [CuL] using colorimetric methods with p-nitrophenyl-β-D-glucopyranoside.

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References

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