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From the study of copper containing enzymes to the development of bioinspired catalysts

Rébecca Leblay,[a] Yongxing Wang,[a] Alessia Munzone,[a] Bruno Faure,[a] Christophe Decroos,[a] Ivan Castillo Perez,[b] Christelle Hureau,[c] Maylis Orio,[a] Marius Réglier,[a] A. Jalila Simaan[a]

[a] iSm2, CNRS, Aix Marseille Univ., Centrale Méditerranée, Marseille, France
[b] Instituto de Química, UNAM, México city, Mexico
[c] Laboratoire de Chimie de Coordination, CNRS, Toulouse, France
Jalila.simaan@univ-amu.fr

Lignocellulosic biomass (composed mainly of polysaccharides and lignin) is increasingly considered as a renewable feedstock to produce bio-sourced chemicals, biomaterials and advanced biofuels. One important step in the valorisation of biomass components into valuable products consists in size reduction of the polymeric recalcitrant components. LPMOs are copper-containing enzymes produced by some bacteria and fungi, among a consortium of enzymes that act collectively to degrade recalcitrant polysaccharides such as cellulose or chitin [1]. LPMO enzymes were shown to oxidatively cleave polysaccharide chains. Notably, LPMOs catalyse the hydroxylation of a strong C-H bond (> 95 kcal/mol) at the glycosidic linkage (either at C1 or C4) leading to glycosidic bond cleavage using either O_2 (and electrons) or H_2O_2 (**Figure 1**) [2]. LPMO active centre is constituted of a mononuclear copper ion ligated by an unusual "histidine-brace" motif consisting of two histidines residues including the *N*-terminal histidine bound in a bidentate fashion.

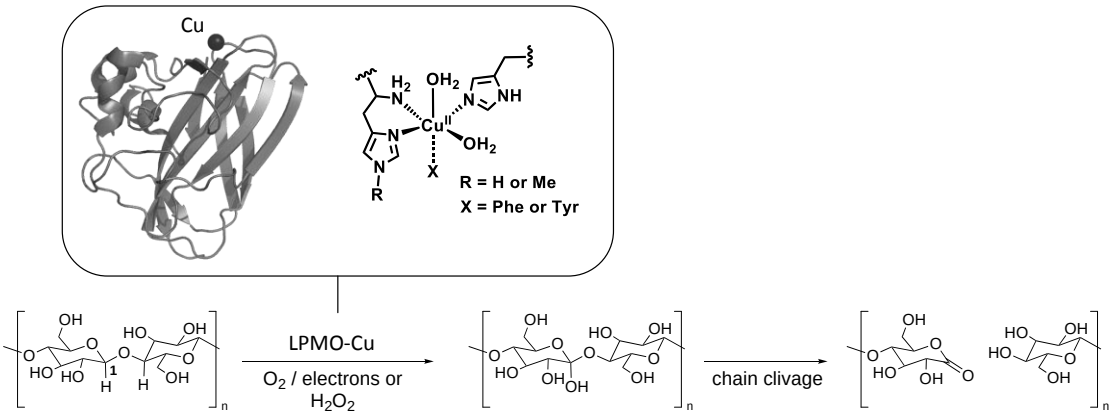

Figure 1: C1 oxidation of cellulose catalysed by LPMO. Structure of a LPMO (PDB ID 6T5Z) with surface exposed copper active-site [3].

Our group combines studies on the enzymatic system to the development of bioinspired copper complexes [3-7]. In particular, we have produced and characterized bacterial LPMOs and evaluated the effect of mutations of active site residues on the physicochemical properties and the reactivity of the enzymes. We have also prepared and characterized bioinspired complexes to get insight into mechanistic pathways allowing strong C-H bonds activation by copper systems. Following this interdisciplinary approach, several functional bioinspired catalysts were prepared and proof-of-concept that bioinspired complexes can oxidatively promote polysaccharide depolymerization was obtained.

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