

Thiophene-functionalized metalloporphyrin as cytochrome P450 model: synthesis and catalytic activity

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The enzymes belonging to the cytochrome P450 (P450) superfamily have in common the active center Fe^{III}P-IX (iron(III)protoporphyrin-IX), also known as heme group, responsible for promoting a number of specific activities in biosystems under ambient conditions, among which the ability to functionalize C-H bonds and to promote selective oxidations are the most important ones. To take advantage of the catalytic potential of Fe^{III}P-IX-based systems, a number of studies have focused the preparation of several synthetic porphyrins, known as metalloporphyrins (MeP), which are catalytically active, able to mimic the oxidation reactions that occur at P450 enzymes. In this sense, this work investigates the reactivity of thiophene-functionalized metalloporphyrin in biomimetic catalysis of P450, an unexplored system for this kind of application. This porphyrin present four thienyl rings almost co-planar with the core structure, which are responsible for providing interesting electrochemical and chemical properties (chemo- and regio-selective reactions) [1]. Therefore, the meso-tetra(thien-2-yl)porphyrin (H₂TThP) was synthesized according to a literature procedure [1], thereafter the

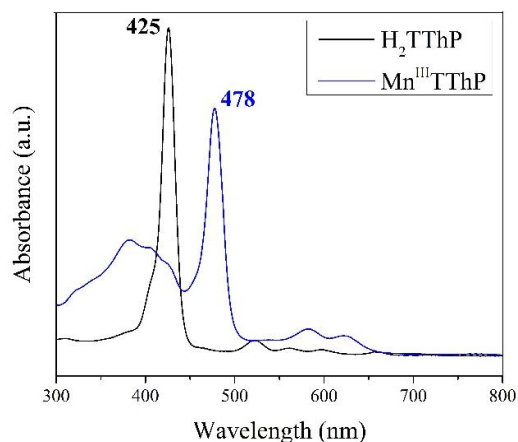


Figure 1: UV/Vis spectra of the H₂TThP and Mn^{III}TThP

H₂TThP was metalated with manganese(III) ion to afford the metalloporphyrin (Mn^{III}TThP) (Figure 1). The catalytic performance of this new MeP was evaluated by hydrocarbon oxidation tests employing the (Z)-cyclooctene and cyclohexane as substrates and iodosylbenzene (PhIO) as oxygen donor. The epoxide yields obtained from the catalytic epoxidation of (Z)-cyclooctene demonstrated that the formation of the active specie (Mn^V(O)P) was effective. The maximum yield of epoxide (100%) was obtained after 75 min reaction time. In the catalytic study with cyclohexane hydrocarbon, the ratio cyclohexanol/cyclohexanone was 1,3. The results with cyclohexane, indicate that Mn^{III}TThP showed a similar selectivity to the alcohol

product (biomimetic product) compared with others MePs widely used in biomimetic catalysis [2,3]. The results show that the new MeP (Mn^{III}TThP) has potential for application in biomimetic catalysis of P450, however, optimizations related to the change in the metal ion and introduction of electron-withdrawing groups in the porphyrin ring should be performed.

[1] Momo, P. B. et al. *Eur. J. Org. Chem.* 2014, 21, 4536.

[2] Zanardi, F. B. et al. *Micropor. Mesopor. Mat.* 2016, 219, 161.

[3] da Silva, V. S. et al. *Appl. Catal. A. Gen.* 2015, 491, 17.