

Enzyme-Like Selectivity on Metalloporphyrin-Catalyzed Oxidation by a Linear Homopolymer

Sergio A. V. Jannuzzi^{1,2}, Eduardo G. R. Arruda¹, Frederico A. Lima³, Marcos A. Ribeiro¹, César Brinatti¹, André L. B. Formiga^{1*}

¹*Institute of Chemistry, P.O. Box 6154, University of Campinas – UNICAMP, 13083-970, Campinas, SP, Brazil,* ²*Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium,* ³*Centro Nacional de Pesquisa em Energia e Materiais, Laboratório Nacional de Luz Síncrotron, Rua Máximo Solfaro 10000, 13083-970, Campinas, SP, Brazil*

*e-mail: formiga@iqm.unicamp.br

The influence of linear homopolymers on manganese porphyrin-catalyzed oxidation of cyclohexene and phenol in solution was investigated in this work.[1] Our study shows that cyclohexene was epoxidized in the presence of poly(acrylic acid) (PAA) and H₂O₂, however the epoxide was the exclusive product when the reaction was catalyzed by *meso*-tetrakis-(pentafluorophenyl)porphyrinatomanganese(III). The regioselectivity of phenol and methoxybenzene oxidation in the presence of *m*CPBA was calculated as the molar ratio between *para* and *ortho* dioxygenated products. The selectivity for oxidation of phenol in the *para* position increased from 9.6±0.2 to 13.5±0.3 in the presence of PAA, however the same is not observed when PAA-substrate hydrogen bonding is hampered in oxidation of methoxybenzene (from 5.9±0.2 to 7.0±1.0) under the same conditions. Substrate hydrogen bonding (investigated by isothermal titration calorimetry) indicates that the supramolecular strategy of natural enzymes takes place in our artificial approach, as suggested in Figure 1. Unlike other bio-inspired systems, the PAA polymer chain is not covalently bound to the metalloporphyrin, and no evidences of interaction was observed neither by UV-vis nor X-ray absorption spectroscopy. In spite of that, the system still promotes chemo- and regioselectivity. The catalytic data points to active participation of the polymeric chain in epoxidation reaction in order to change the active oxidizing agent in the presence of the manganese porphyrin. The PAA chain also acts as a supramolecular directing agent, which binds phenol via hydrogen bond providing a favorable orientation for regioselective oxidation in the *para* position. The subtle balance of intermolecular interactions between catalyst, auxiliary structure and substrate are key to recognition, spatial orientation, and ultimately important for development of supramolecular catalysts inspired in natural enzymes.

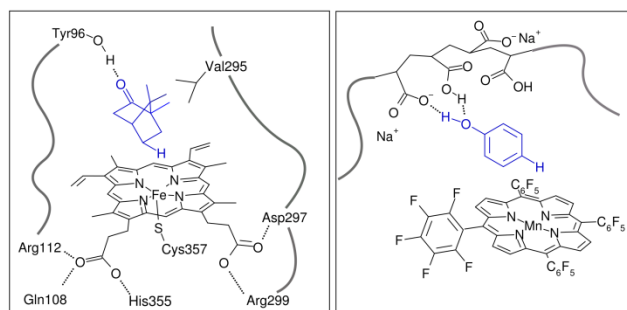


Figure 1. Cartoon of the crystal structure of the natural CYP450cam with bound camphor (left) and our proposed model to address regioselective oxidation owing to intermolecular interactions (right).

Reference: [1] Jannuzzi, S. A. V.; Arruda, E. G. R. d.; Lima, F. A.; Ribeiro, M. A.; Formiga, A. L. B.; *ChemSelect*, **2016**, accepted. DOI: 10.1002/slct.201600597