

Introduction

Cytochrome c Oxidase (CcO) is the final enzyme of the respiratory chain. It catalyses the reduction of molecular oxygen to water, without any side products, e.g. H_2O_2 . Since the enzyme itself is rather unsteady to work with, a molecular catalyst with the same catalytical benefits is desirable. A very direct approach to this is to partially imitate the bi-nuclear centre of CcO, specifically the Heme and the copper containing pyridine moiety. The result of that is shown in fig. 1, where both subunits are connected with a backbone, also keeping them at distance. Note that the copper is not yet incorporated.

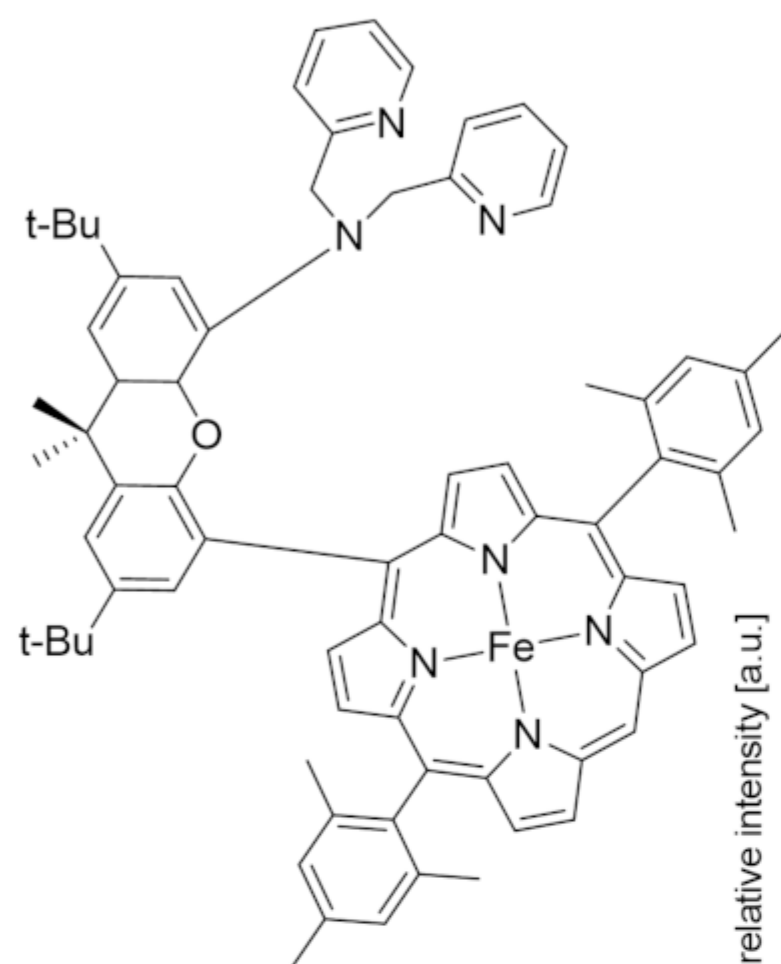


fig. 1: Structure of the molecular catalyst imitating the binuclear centre of CcO without copper at the bi-pyridin unit.

Methods

The molecular catalyst named PyXPFeCl is investigated in solution and in immobilized state. Latter can be achieved by a variety of methods, e.g., drycasting (dc), incubation (inc) casting or incubating it onto a self-assembled Monolayer (SAM). For the catalytic reaction, electrochemical measurements such as cyclic voltammetry (CV) or linear-sweep voltammetry (LSV) are employed. For more information about the mechanism behind resonance Raman (RR) and surface-enhanced Raman (SER) scattering are the methods of choice.

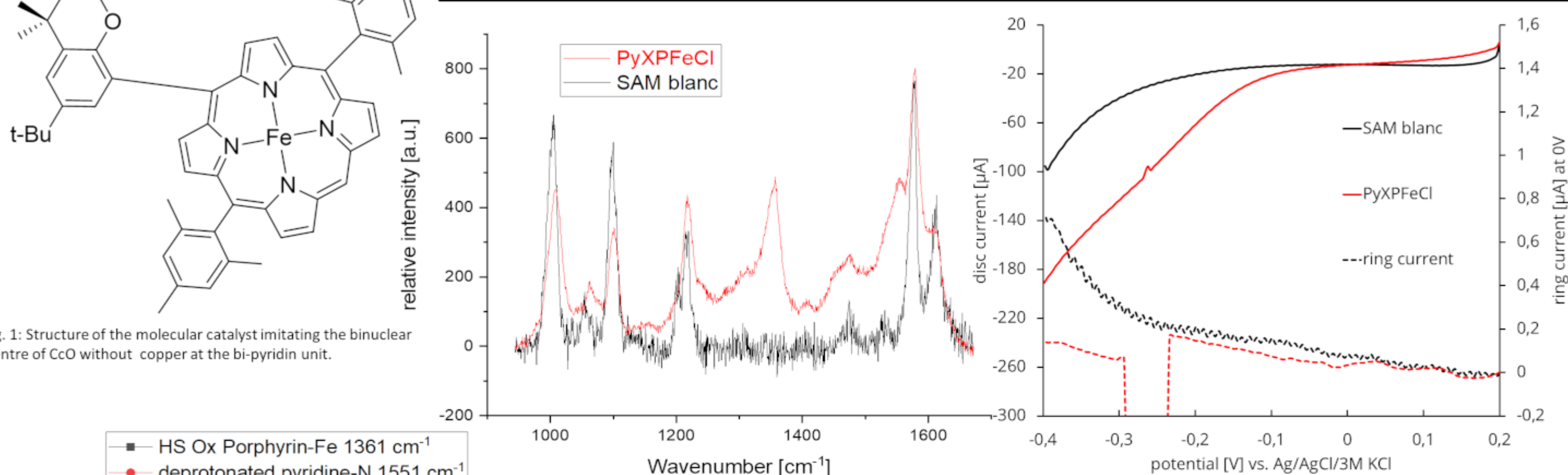


Fig. 2: PyXPFeCl (red) immobilized on a Mercaptopyridine (black) SAM on roughened silver disc electrodes in 0,1M PB pH = 7 @ 1000 rpm. right: LSV data recorded with 100 mV/s on an RRDE with platinum as a ring electrode, held at 0V over the course of the experiment left: SER spectra recorded with the same setup with a 442 nm excitation laser

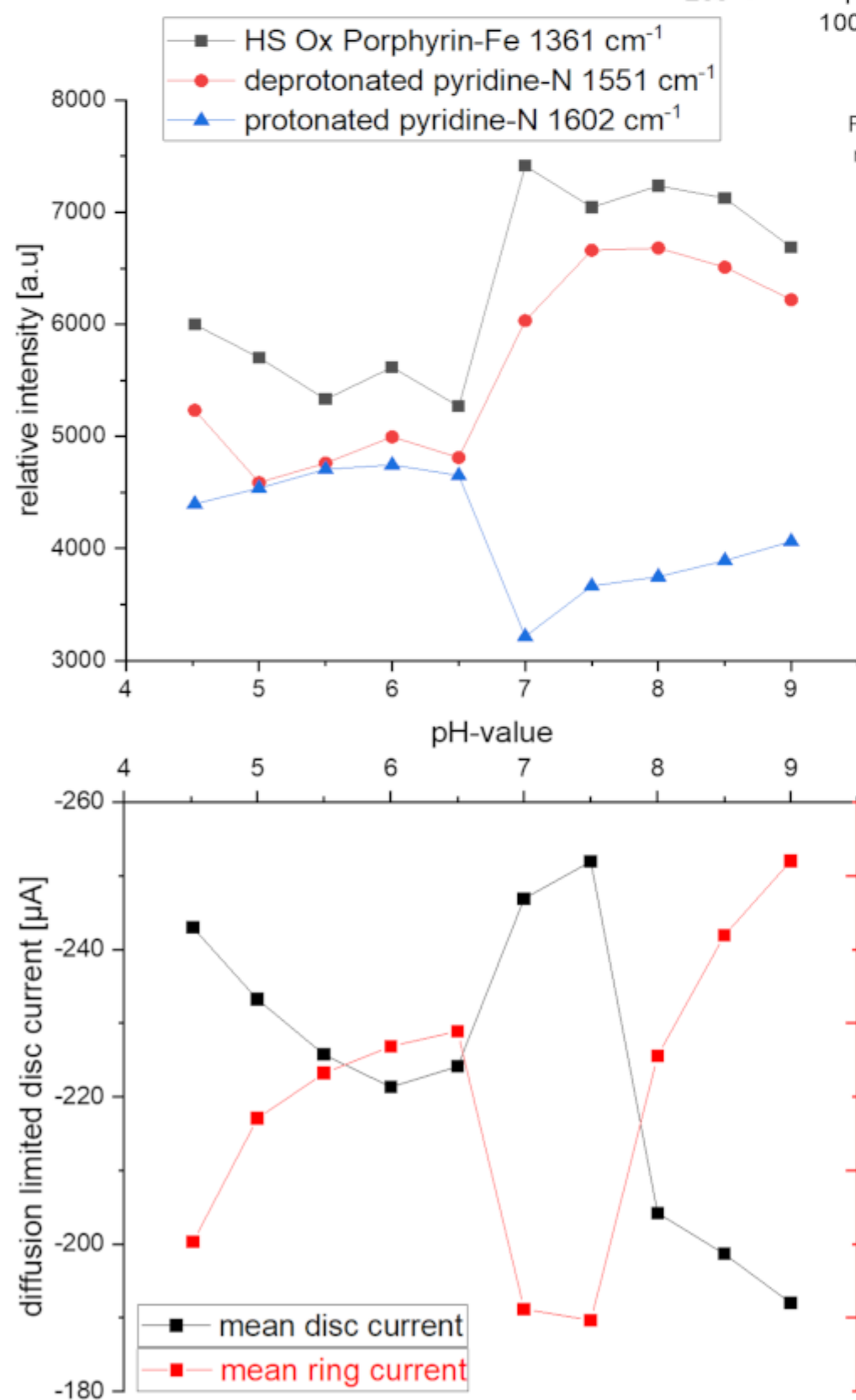


Fig. 3: PyXPFeCl on roughened silver, incubated from DCM. Measurements taken in 0,1 M PB at 1000 rpm top: SER measurements at different pH-values with 442 nm excitation with intensities of different signals indicating pyridine protonation bottom: LSV data from RRDE experiments under different pH-values with average currents given between -0,3 to -0,4 V at 100 mV/s

Results

As shown in fig. 2 the synthetic complex is able to reduce oxygen to water without hydrogen peroxide as unwanted by-product in higher quantities. While the mercaptopyridine SAM strongly reduces the influence of the underlying silver electrode, its SERs spectrum also offer some bands to compare the bi-pyridine part of the catalyst with. As can be deduced from fig. 3 the effect of pH-value goes beyond a simple proton delivery influence. At pH 7,5 to 7 the pyridine ring stretching vibration with deprotonated nitrogen at 1602 cm^{-1} drops in intensity, while the band for the protonated species at 1551 cm^{-1} rises.¹ At the same time the ν_4 band of the porphyrin high spin oxidized species at 1361 cm^{-1} loses intensity also.² The electrochemical data for that region show an increased catalytic current while the corresponding ring current, indicative for H_2O_2 formation drops leading to the assumption of a "sweet spot" for oxygen reduction to water. Since this sample is immobilized via incubation from DCM directly onto the roughened silver electrode, the influence of the electrode itself on this will need further investigation. One of the possibilities is an peroxidase activity of the catalyst, which might be combined with silvers ability to generate hydrogen peroxide. Additionally the incorporation of the copper and its effect on the catalytic process and its mechanism will be included in future research.

References

- ¹ Lewis J. Rothberg and Zhenjia Wang, 2005, J. Phys. Chem B, 209, p. 3387-3391
- ² Inez M. Weidinger et al., 2019, Inorg. Chem. 58, p. 10637-10647