UV-Vis and STM Studies of the Reaction Between Iron Octaethyl Porphyrin and Imidazole

Kenneth Clark, Krista Nishida, and Ursula Mazur

Department of Chemistry, Washington State University, Pullman, WA 99164-4630

Introduction

Metalloporphyrins serve as models for hemoglobin (Hb) and myoglobin (Mb), proteins that bind O_2, NO, and CO for the purpose of transport, storage, and sensing. It has been well documented spectroscopically that axial coordination of amines enhances the free radical reactivity of iron porphyrins leading to bond formation between the iron ion and O_2. Our goal is to examine the complexation reaction of imidazole (Im) with iron (III) octaethyl porphyrin chloride (FeOEtPCl) and the competition with O_2 for coordination to the metal ion, by scanning tunneling microscopy (STM). The STM approach can provide valuable information about the chemistry taking place in a dynamic environment at a single molecule level.

Here we report the electronic spectra (UV-vis) of FeOEtPCl and Im at different concentrations and with different porphyrin to ligand ratios. The spectra were acquired in a nonprotic solvent with no oxygen present. Reported also are the STM images of FeOEtPCl at n-octylbenzene acquired before the addition of imidazole (Im).

Materials

FeOEtPCl and imidazole were purchased form Aldrich Chemical Co. and used without further purification. All solvents used were reagent grade. Glassware was cleaned in acid and rinsed with deionized water and ethanol and dried before using.

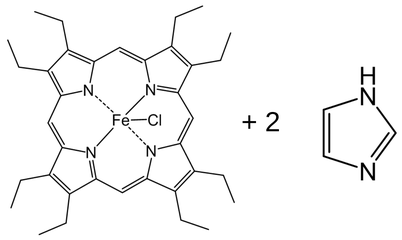
UV-vis

Shimadzu Ultraviolet-visible spectrophotomer was used to record the absorbance spectra. I cm quartz cuvettes were employed. Spectra of FeOEtPCl in chloroform with concentration range of 10^{-4}M -10^{-6}M were measured. Beer's plot was made of the absorbance vs. concentration of the 380nm band of FeOEtPCl in chloroform. Different amounts of imidazole were added to the FeOEtPCl CH_3Cl solution while keeping the concentration the porphyrin concentration constant at 10^{-5}M. Eight different solutions were made with 1:1, 2:1, 10:1, 20:1, 50:1, 100:1, 200:1, and 400:1 Im to FeOEtPCl ratios.

Time dependent reaction absorbance studies were conducted with 1:1, 2:1, 10:1, and 20:1 Im to FeOEtPCl rations in chloroform. For all the ratios studied even after 1 day no changes in the absorbance spectra were observed. Higher concentration of Im need to be employed.

STM

Imaging experiments of FeOEtPCl were performed in n-octylbenzene solution on a graphite substrate at 21 C using a Molecular Imaging Picoscan STM outfitted with a 1 μm scanner. Constant current images are reported after a flattening procedure. STM tips were fabricated from 0.25 mm Pt0.8Ir0.2 wire by electrochemical etching.



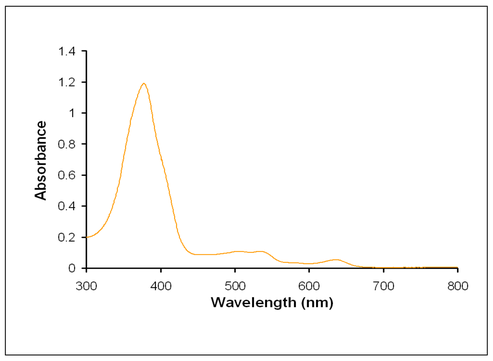


Figure 1. Visible spectrum of 10^{-5} M FeOEtPCl in CH_3Cl.

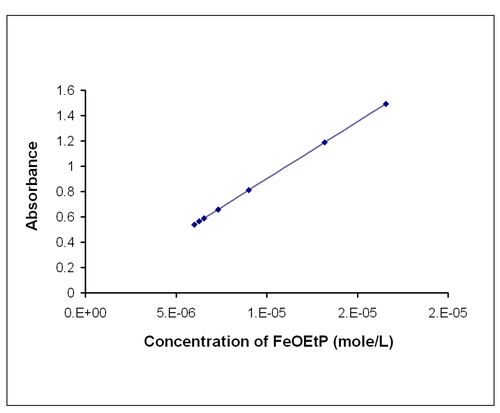


Figure 2. Beer's law plot of 380 nm absorbance vs. concentration of FeOEtPCl in chloroform.

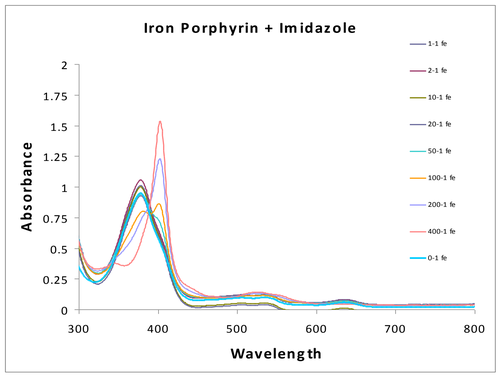


Figure 3. Changes in the visible spectra of 10^{-5}M chloroform solution of FeOEtPCl as a function of Im concentration.

FeOEtPCl	FeOEtPCl-Im$_2$	Assignments[1]
380	404	Soret band
509	528	Q band
543	558	Q band
640	656	Q band

Table 1. Spectral assignment for FeOEtPCl and its Im adduct.

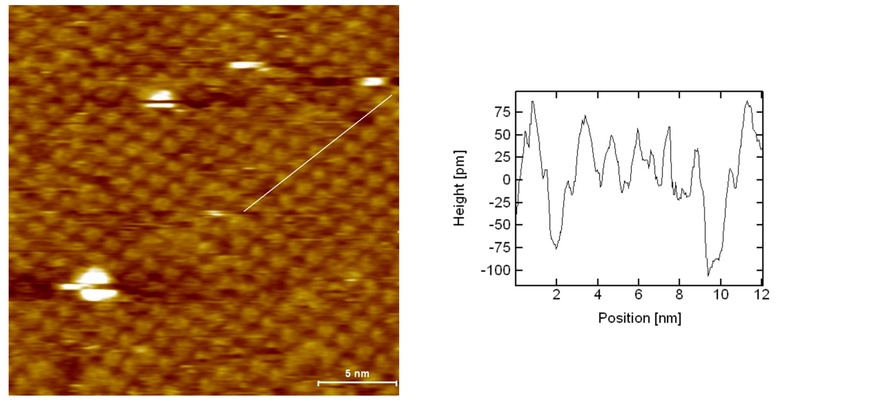


Figure 4: 20 nm^2 image of FeOEtPCl in n-octyl benzene acquired at 1.2 mV bias and 40 pA tunneling current. The figure on the right is a cross sectional diagram showing a ~1.4 nm intermolecular porphyrin spacing.

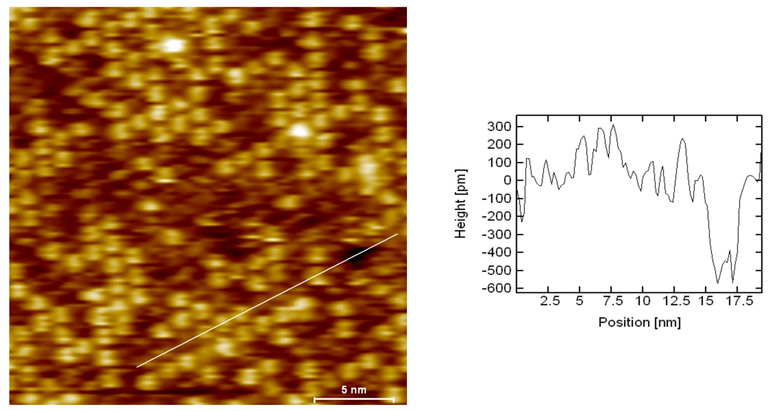


Figure 5: Image of the same sample as in Figure 4 but acquired at -1.5 mV bias and 40 pA tunneling current. The cross section suggest a molecular bilayer formation.

Results and Conclusions

Comparison of our absorbance data with reported spectra[1] , suggests that we are probably not detecting the formation of the 1 :1 complex but the two ligands adduct:

$$FeOEtPCl + 2Im \rightarrow PFe(Im)_2 + Cl^-$$

A well defined isosbestic point at 386 nm is seen in Figure 3. Here both the FeOEtPCl and FeOetPClIm$_2$ have the same molar absorbtivity. The STM images show an interesting bias dependent formation of a FeOEtPCl bilayer. The next step is to image the reaction between imidazole and the iron porphyrin.

References

1. Walker, F. A.; Lo, M.-W.; Ree, M. T. *J. Amer. Chem. Soc.* **1976,** *98, 5552-5560.*
2. Kinetics and mechanisms by J. W. Moore, R. G. Pearson, A. A. Frost, J.W. Moore, and R.G. Pearson. 3rd ed. John Wiley and Sons, **1981**.
3. Vanderkool, G.; Stotz, E. *The Journal of Biological Chemistry* **1966,***241,* 2260-2265

Acknowledgements

I wish to thank Dr. Ursula Mazur and Dr. K. W. Hipps for their guidance on this project. As well as Benjamin Friesen, Bryan Wiggins for their assistance on any issues. This work was supported by the NSF REU Program and grants DMR-0755055 and CHE-0555696.