

STM and UV-vis Studies of Co Porphyrin-Imidazole Complexation

Introduction

Metalloporphyrins are used in semiconductors, optoelectronics, and catalysis because of their electronic and optical properties. These properties can be modulated by axial ligands and their bonding geometries. In this study, the ligand binding reaction of cobalt (II) octaethyl porphyrin (CoOEtP) and imidazole (Im) was examined using scanning tunneling microscopy (STM) and ultraviolet visible (UV-vis) spectroscopy in nonpolar solvents.

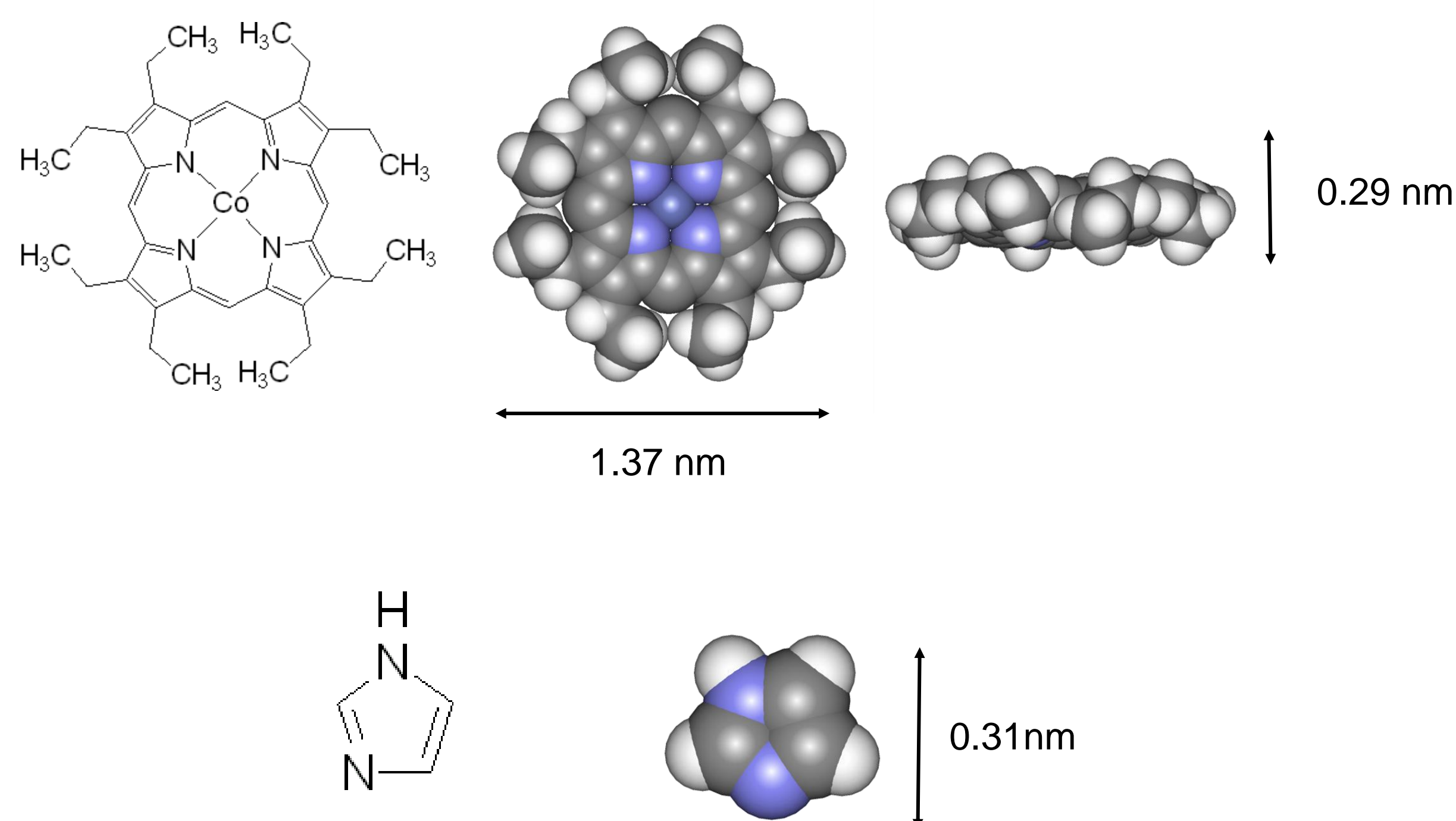


Figure 1: Molecular structure and CPK models of cobalt (II) 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine (CoOEtP) and Imidazole and (Im). In the CPK model of CoOEtP the ethyl groups are in the plane of the macrocycle.

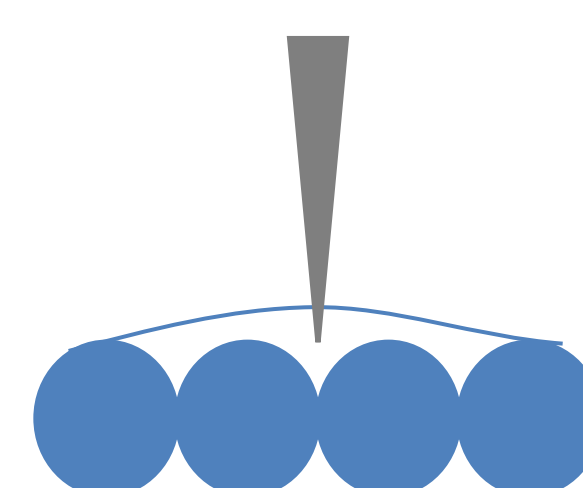
UV-vis spectroscopy measures the absorption of a molecule at different wavelengths in the ultraviolet and visible spectrum caused by the excitation of electrons from the highest molecular orbital (HOMO) to the lowest molecular orbital (LUMO). Shifts in peak locations and changes in absorbance intensity can give information about the kinetics of a chemical reaction, as well as changes in optical and electronic properties.

Scanning tunneling microscopy produces atomic scale images of sample surfaces. A conducting tip, formed by a single atom, is scanned across a surface. Differences in conductivity cause the tip to change vertical position in order to maintain a constant current, producing a surface profile. STM images can be used to determine the size and structural arrangement as well as electronic properties of molecules adsorbed on surfaces.¹

Experimental

A 10^{-5} M stock solution of Co Etioporphyrin was prepared using methylene chloride. Imidazole solutions of differing concentrations were also prepared using methylene chloride. UV-vis spectroscopy was performed 2 minutes after combining 1 mL CoOEtP and 3 mL of imidazole solution in a small vial. The diluted concentration of CoOEtP in all CoOEtP:Imidazole ratio solutions was 10^{-6} M. The Shimadzu UV-2501PC UV-visible spectrophotometers was used.

10^{-6} M CoOEtP in n-octylbenzene was placed on highly ordered pyrolytic graphite (HOPG) for STM imaging at the liquid-solid interface. A drop of 10^{-4} M imidazole and methylene chloride solution was added directly to the CoOEtP and HOPG interface for post reaction imaging. All images were taken under ambient conditions with PicoSTM from Agilent using a 1μ scanner.



STM tip at the solid-liquid interface

Results

UV-vis studies of CoOEtP plus Im (with different stoichiometric ratios) indicate a sequential coordination at the 5th (fast) and 6th (slow) position on the cobalt (Figure 4) resulting in a shift of the Soret band to longer wavelengths (Figure 3).

STM images of CoOEtP at the liquid – HOPG interface show a well-ordered monolayer (Figure 5) with a significant enhancement in the apparent height at the center of molecule associated with tunneling through the half-filled d_{z^2} orbital of the Co^{2+} ion (Figure 2). Images acquired after addition of Im to the CoOEtP STM sample, show a marked depression in the central region of the molecule signaling a decrease in conductivity at the ligated metal ion site (Figure 6).

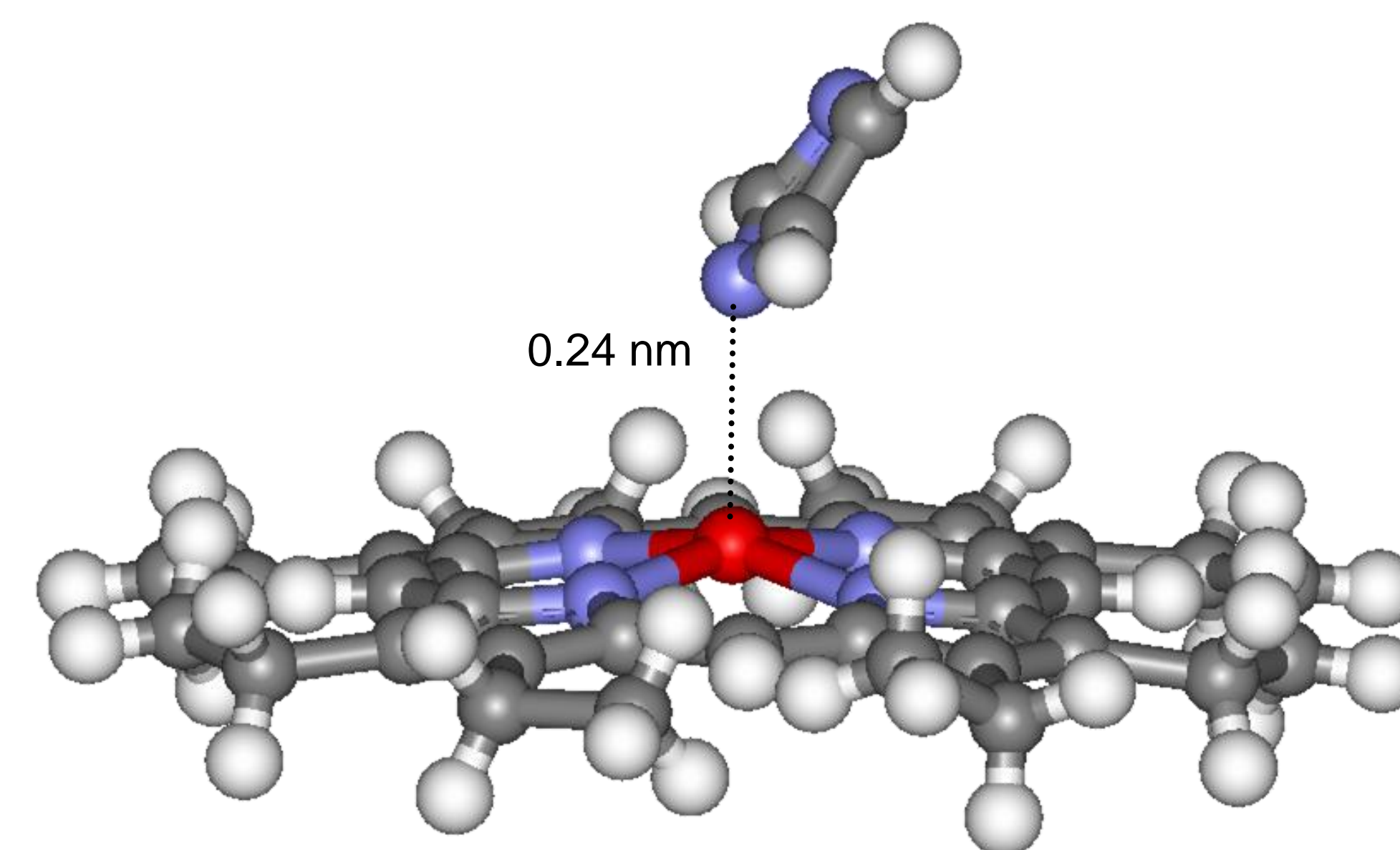


Figure 2: Structural model of the 1:1 CoOEtP:Im adduct. The metal ligand distance is 0.24nm based on the crystal structure measurements.² The Co ion is displaced ~ 0.1 nm above the porphyrin ring.^{2,3}

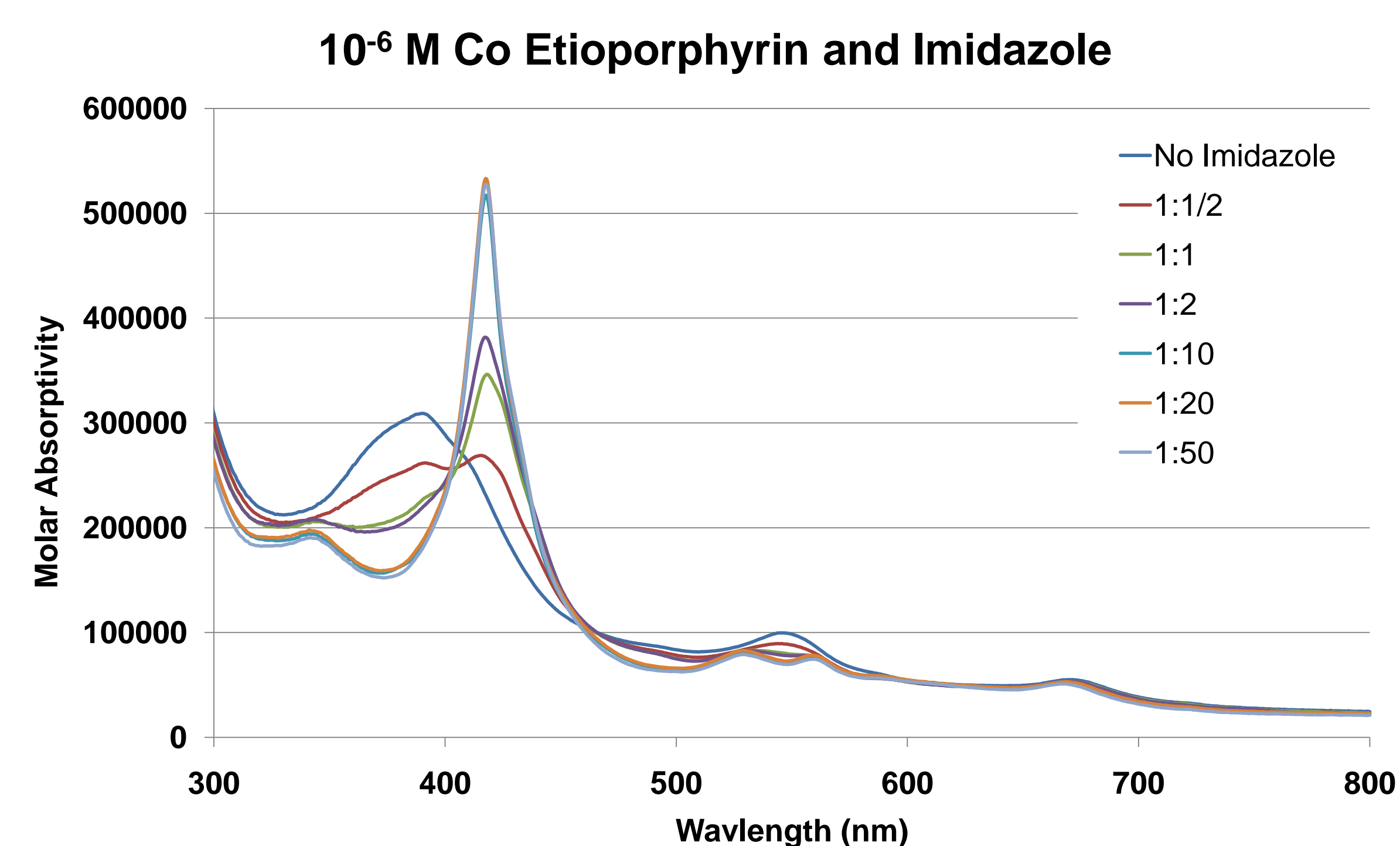


Figure 3: UV-vis spectroscopy plot of CoOEtP and Im at different stoichiometric ratios resulting in a shift of the Soret band.

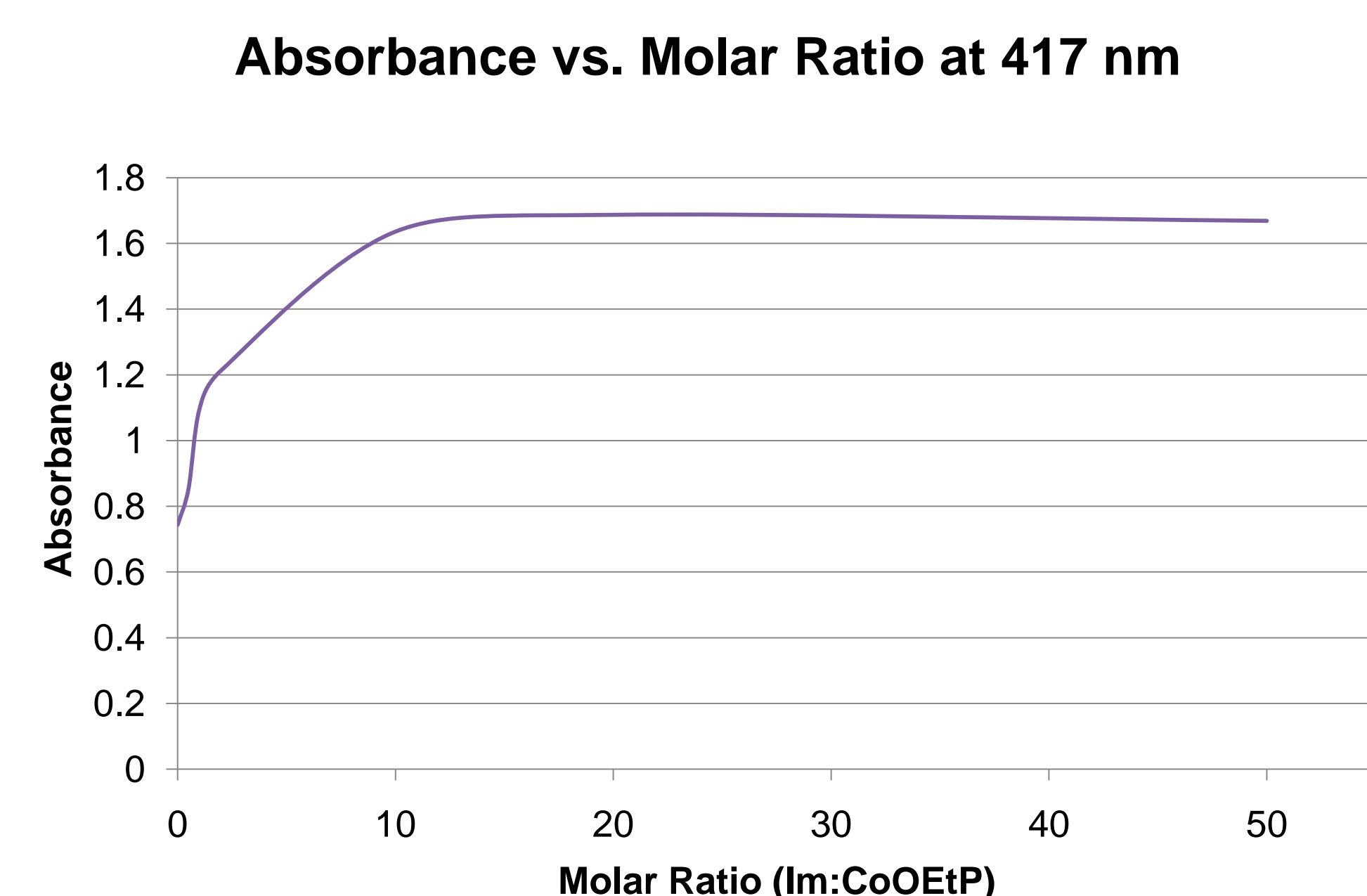


Figure 4: UV-vis plot indicating the coordination of the 5th and 6th position of Co (II). The coordination of the ligand on the 5th position occurs much faster than the 6th, as shown by the steeper slope on the plot.³

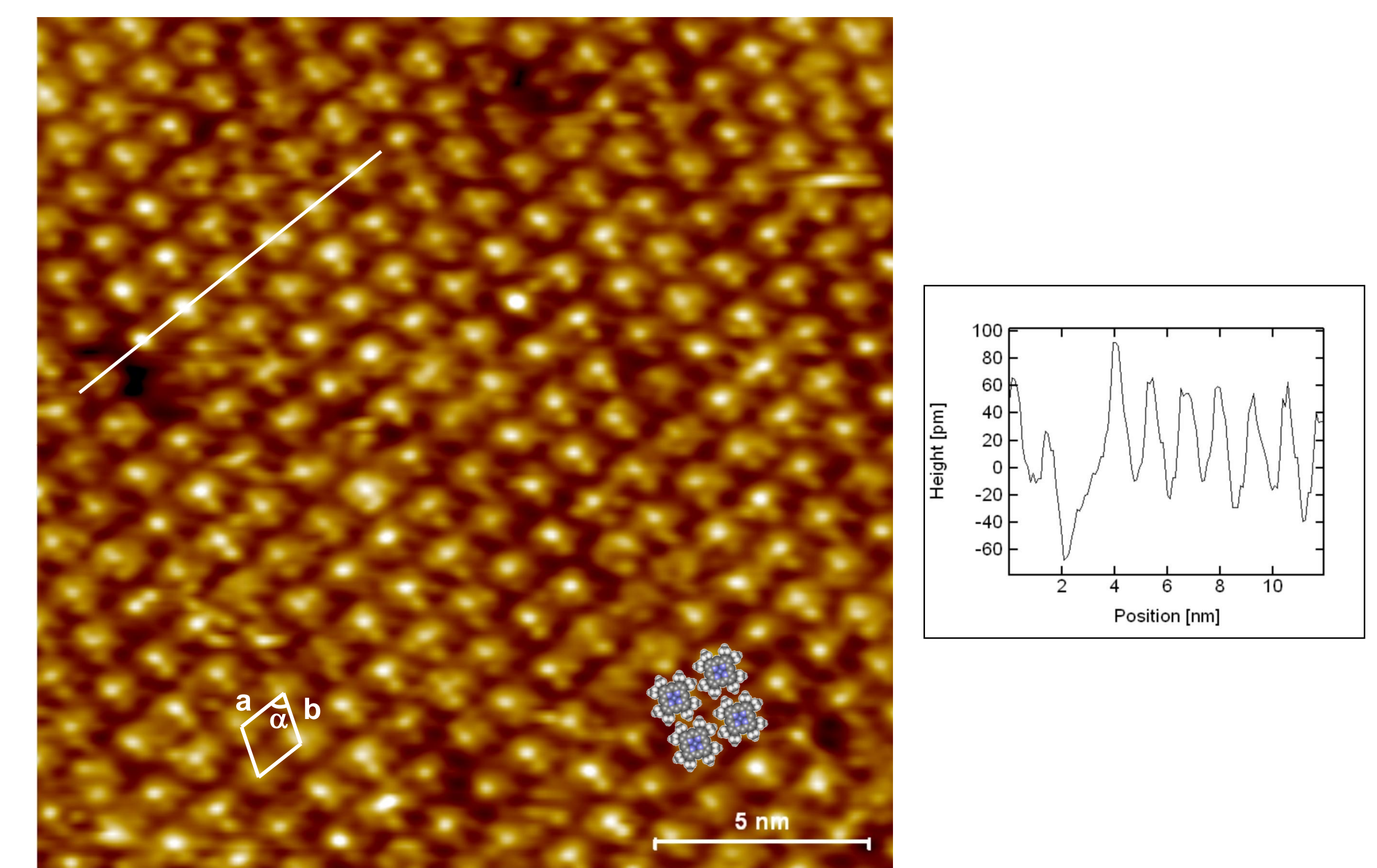


Figure 5: 20 nm^2 image of CoOEtP before the addition of Im. Image acquired at 700 mV bias and 30 pA tunneling current. The figure on the right is a cross sectional diagram. An oblique unit cell is shown with lattice parameters: $a = 1.32 \pm 0.02 \text{ nm}$; $b = 1.30 \pm 0.02 \text{ nm}$; $\alpha = 70.3 \pm 0.3^\circ$. The ethyl groups are most likely sticking up away from the surface.⁴

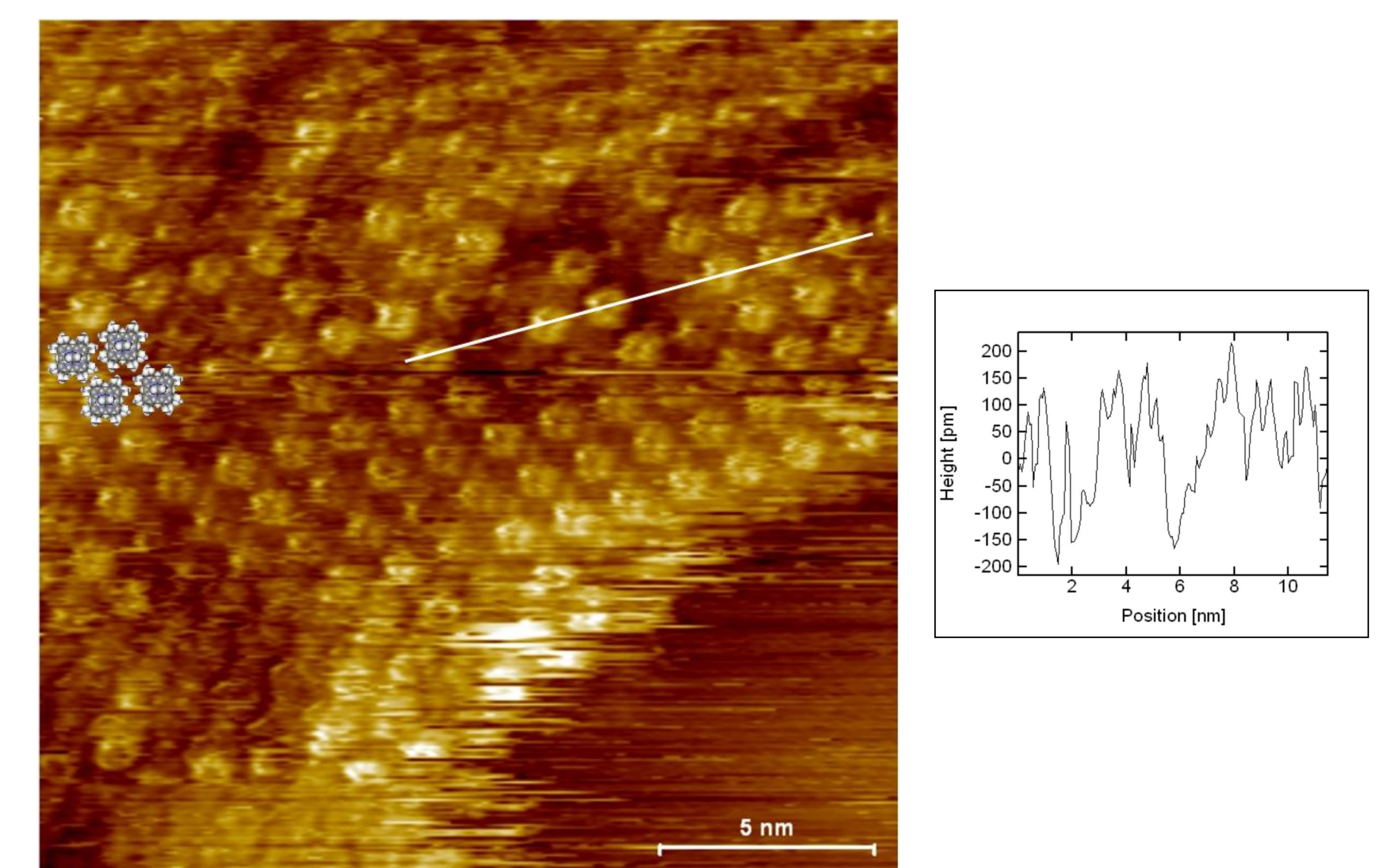


Figure 6: 20 nm^2 image of CoOEtP after the addition of Im. Image was acquired at 1.2 V bias and 30 pA tunneling current. The intermolecular spacing for CoOEtP:Im is $\sim 1.35 \text{ nm}$. Note that while the average CoOEtP is $\sim 130 \text{ pm}$ high, the CoOEtP:Im adduct is nearly 350pm tall.

Conclusions

STM and UV-vis studies have shown that a binding reaction occurs between CoOEtP and Im. Changes in electronic and optical properties were observed upon the addition of the Im ligand, indicating the potential of this compound to be used in future semiconductor and optoelectronic devices.

Oxygen is known to play a significant role on the rate of binding of amine ligands to Co(II) porphyrins. In the future, the effects of O_2 concentration on the CoOEtP+Im reaction will be investigated by STM and UV-vis.

References

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