A p p e n d i x   B

WORK WITH MAYRA SHEIKH

While working on this project, I had the opportunity to work with Mayra Sheikh, an undergraduate student at Caltech, both as a SURF co-mentor and as a graduate supervisor for her Chem 10 work. During this time, three different projects were attempted. The first, measuring quantum yields of many of the corroles discussed herein, has been presented in Chapter 4. Results from the other two projects will be summarized here.

The first of these remaining projects had the eventual goal of producing a water-soluble chromium corrole complex. Previous work in the group by Dr. Alexandre Meier had shown the chromium corrole capable of acting as an oxidation catalyst for some compounds[72]. While this was limited to phosphines in the initial work, it was hoped that moving to an aqueous system would allow a greater range of substrates. Initial work in this area, performed by Meier and repeated by Sheikh in the beginning stages of her project, had attempted to metallate **2** by the same method used to metallate **1**, refluxing with $Cr(CO)_6$ or $CrCl_2$[73]. This method did not yield the desired results, however, as it appeared to cause the dissociation of at least one sulfonate group from **2** and resulted in a compound that was not water soluble.

The second method attempted in this project was to prepare the chromium version of **1** as detailed in the literature[73] and to use that compound as the starting point for the corrole

sulfonation reaction in place of **1**. While the reaction did produce green products characteristic of sulfonated corroles, mass spectrometry and EPR spectrometry did not confirm the presence of the desired compound.

While it was not determined why these reactions would not produce the desired bis-sulfonated chromium corrole, it was decided to attempt a different method for a water-soluble chromium corrole. It had been seen earlier that the para-fluorines of **1** could be substituted with pyridine, which was then methylated to form a water-soluble corrole, 5,10,15-tris(4-(2-(1-methylpyridyl))tetrafluorophenyl)corrole (**4**, see figure B.1)[11]. While the synthesis of this free-base was attempted, it proved to be extremely sensitive to any change in reaction conditions, and the compound was not made. However, other projects in the group had made use of an imidazole substitution reaction in the para position of decafluorobiphenyl[74]. It was therefore decided to attempt a combination of these two reactions to produce an imidazole substituted corrole.

1 was dissolved in THF under argon, followed by addition of 7 equivalents of imidazole and 14 equivalents of K_2CO_3, and stirred for 6 hours. A mass spectrum of the mixture revealed the main component of the solution to be unreacted free-base. However, peaks were observed for addition of one, two, and three imidazole groups to the corrole (at 42%, 13%, and 1% peak intensity relative to the unreacted starting material, respectively. See figure B.2a). Column separation of this solution (with 4:1 hexanes:dichloromethane as eluent) provided the unreacted free-base and a mixture of the various substituted imidazole
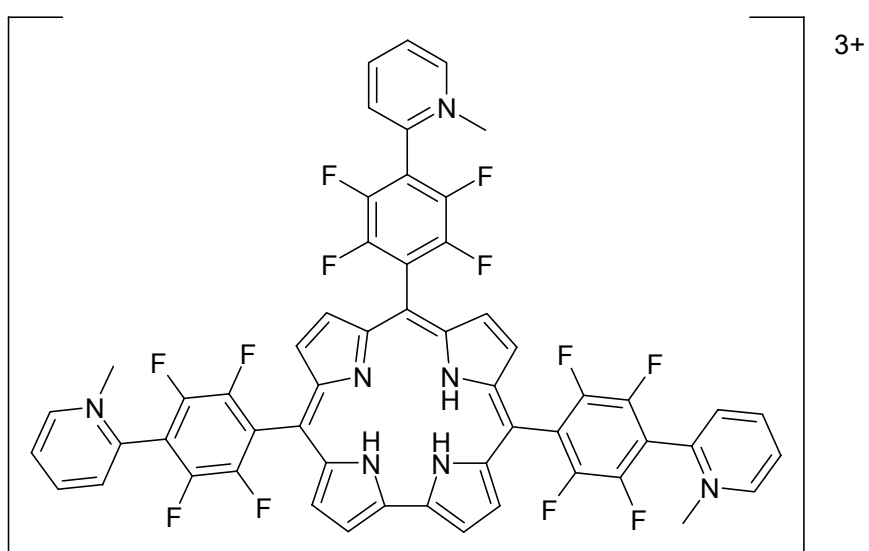
Figure B.1. Previously reported 5,10,15-tris(4-(2-(1-methylpyridyl))tetrafluorophenyl)corrole, **4**.
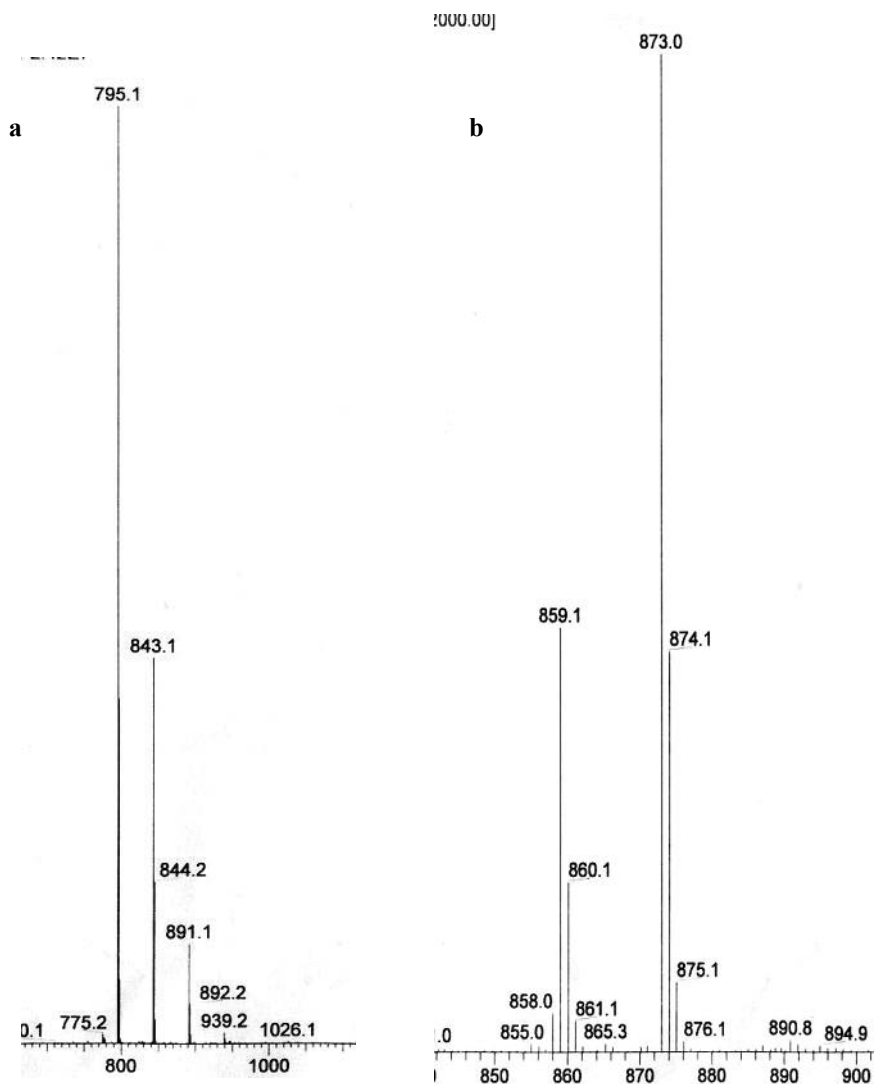
Figure B.2. a) Mass spectrum of reaction mixture from imidazole substitution reaction, negative ions. Unreacted free-base is seen at 795 m/z. Substitution of a fluorine atom by an imidazole molecule adds 48 mass units. Mono, bis, and tris substituted peaks can be observed. B) Mass spectrum of methylation reaction, positive ions. Main peak at 873 corresponds to a dimethyl-monoimidazole corrole, with a peak at 859 corresponding to a monomethyl-monoimidazole corrole.

corroles. Optimization of this reaction to provide a greater portion of triply substituted corrole, as well as separation conditions to resolve the isomers, is ongoing.

While the previous reaction was being optimized, the isomer mixture was used as a starting point for the methylation reaction to ionize the corrole. The isomer mixture was dissolved in distilled DMF and placed under argon. An excess of iodomethane was added, and the solution stirred for three hours at 70 $^{\circ}$C. A mass spectrum of the reaction mixture (see figure B.2b) showed primarily a bismethylated-monoimidazole corrole, with a monomethylated corrole at approximately 45% relative to the bismethylated. Two possible structures for the bismethylated molecule are shown in figure B.3. When the DMF from the reaction solution was evaporated, the solid remaining proved to be water soluble, indicating the creation of a new water-soluble corrole. As with the imidazole substitution reaction, optimization of this reaction is ongoing, but again the crude reaction mixture was used as a starting point for the next step, metallation with a chromium salt to provide a water-soluble chromium corrole.

This reaction was performed in the same manner as metallation of **1** with chromium hexacarbonyl. The ionized free-base corrole was refluxed in THF, and 5-10 mg aliquots of $Cr(CO)_6$ were added every 15 minutes. The reaction was monitored by UV-vis and appeared to be complete after 3 hours. While a separation method for the solution is still being determined, the main peak in the mass spec of the crude reaction mixture shows a surprising result (see figure B.4). The peak at 971 m/z corresponds to a chromium(III)
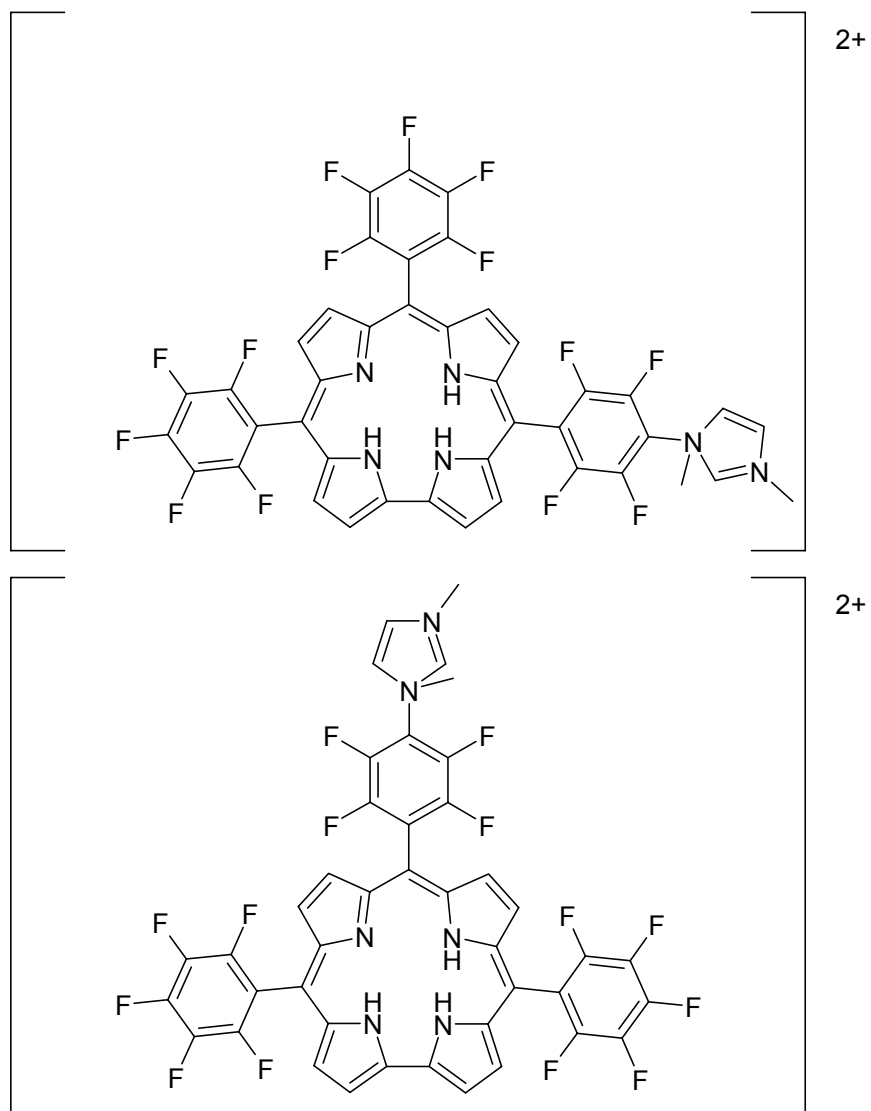
Figure B.3. Two possible structures for the observed
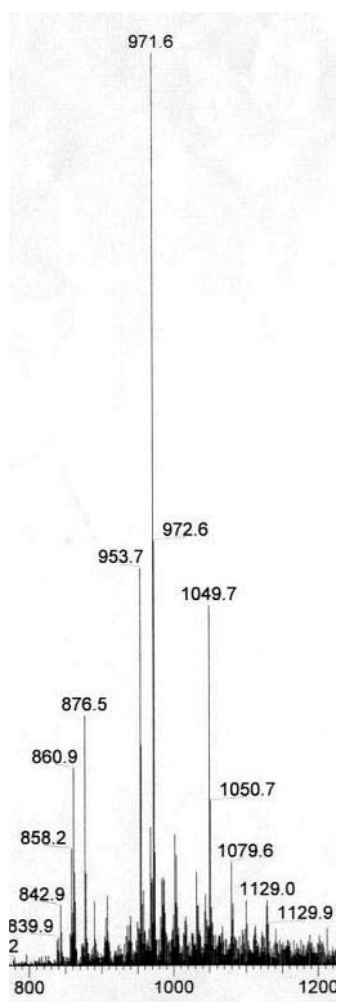bismethylated-monoimidazole corrole.

Figure B.4. Mass spectrum of crude reaction mixture
from chromium insertion reaction.

corrole with two imidazole groups and two methyl groups. Analysis and full characterization of the products from this reaction are pending.

The final project with Sheikh was the synthesis of a water-soluble manganese nitrido corrole. Work by other groups had shown it was possible to synthesize a nitridomanganese(V) version of **1**[75], so we attempted to use those methods to obtain a nitrido derivative of **2-Mn**.

In the procedure, **2-Mn** is stirred with sodium azide in acetonitrile while being irradiated with an arc lamp. Mass and UV-vis spectra provided evidence that a Mn(V) nitrido complex was formed; it remains to optimize the reaction conditions to obtain pure product.