Chapter 2

SYNTHESES

While the initial synthesis of corroles was a very long procedure, the advent of a one pot synthesis by Gross and co-workers in 1999 revolutionized the process of making corroles. It is now possible to make hundreds of milligrams of free-base corrole in a single day, compared to weeks or even months of work with the previous methods. Detailed in this chapter are the synthetic methods used for the corroles studied in this work, including two different free-bases; gallium, manganese, and tin complexes of these free-bases; and work done toward the synthesis of an indium corrole.

The particular corrole free-bases used in this study were 5,10,15-tris(pentafluorophenyl)corrole, and 2,17-bis(sulfonato)-5,10-15-tris(pentafluorophenyl)corrole. The structures for these two molecules are shown in figure 2.1.

General Synthetic Procedures

All corroles used in this work are derived from the first of these, 5,10,15-tris(pentafluorophenyl)corrole (**1**), which in turn is synthesized from pyrrole and pentafluorobenzaldehyde. This can be accomplished by different methods, either involving a solid support, an acid to aid the reaction, or neat. All three methods will be described at the end of this chapter. However, in all cases, the synthesis of **1** is a condensation reaction

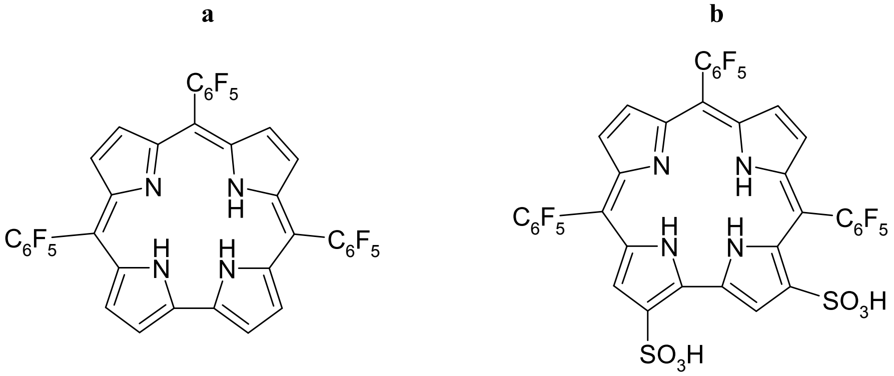


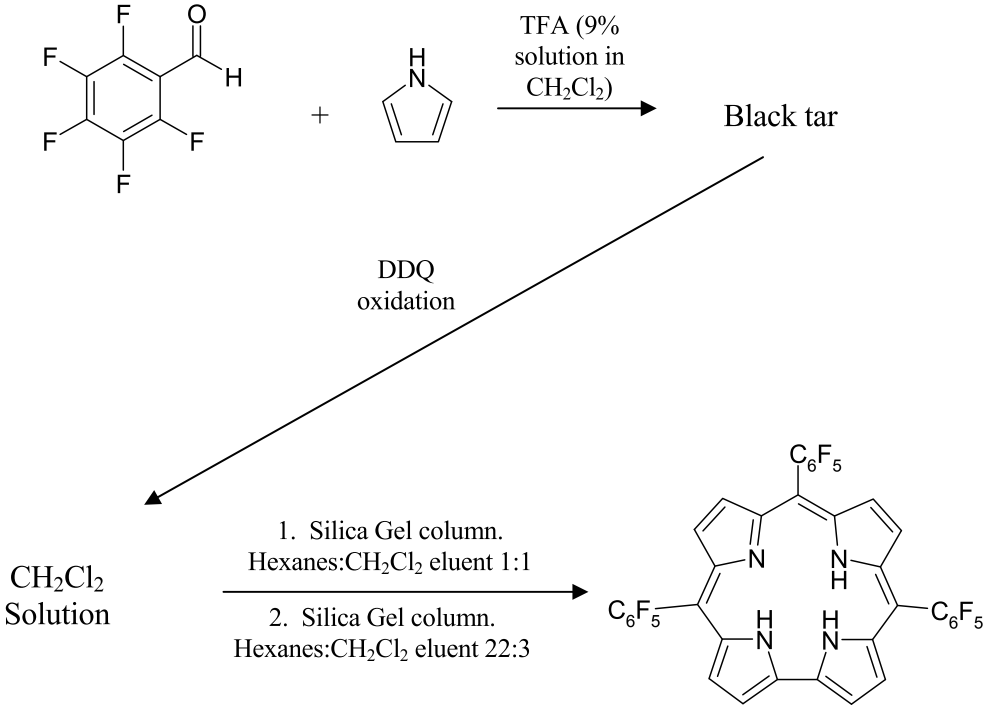
Figure 2.1. Structures of the two free-base corroles used in this study. a) 5,10,15-tris(pentafluorophenyl)corrole (**1**), and b) 2,17-bis(sulfonato)-5,10-15-tris(pentafluorophenyl)corrole (**2**).

of pyrrole with pentafluorobenzaldehyde, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-bezoquinone (DDQ) and column purification, as shown in scheme 2.1.

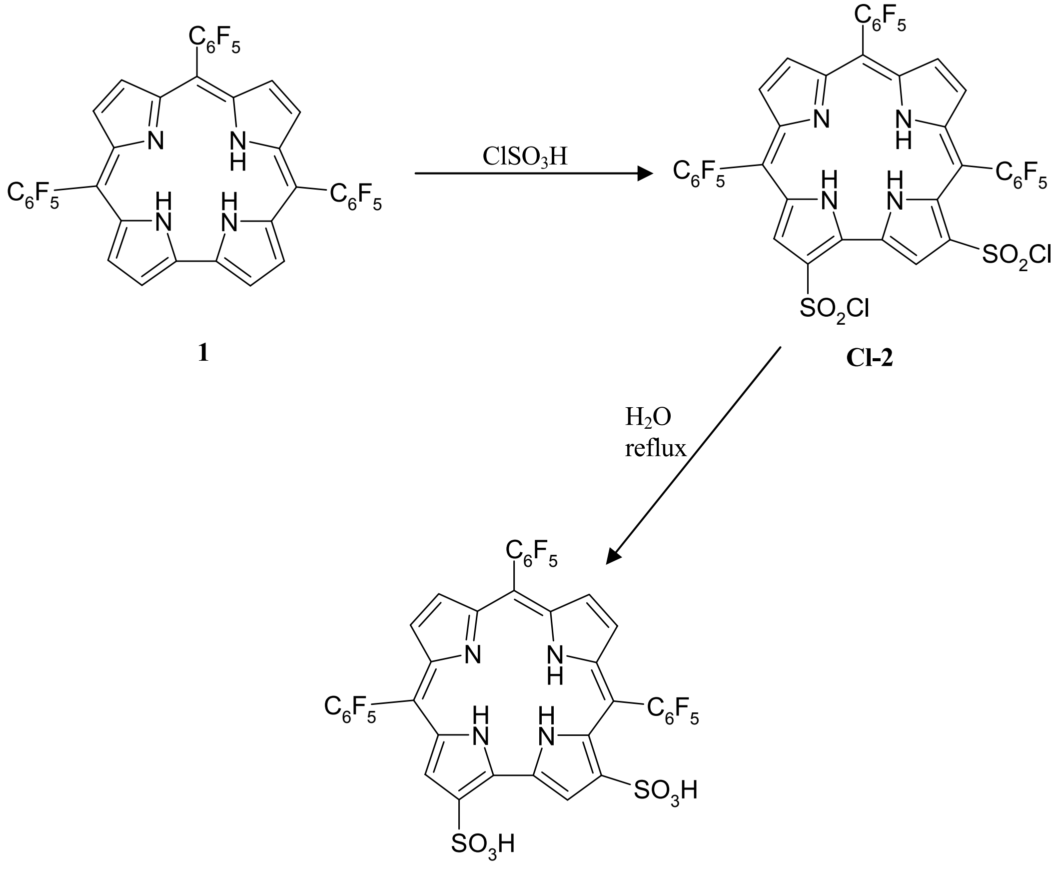
Once **1** has been made, chlorosulfonic acid can be used to substitute two of the β-hydrogens, and a subsequent hydrolysis step produces 2,17-bis(sulfonato)-5,10,15-tris(pentafluorophenyl)corrole (**2**) (see scheme 2.2).

The free-base corrole molecules **1** and **2** have shown themselves to be very versatile to metallation reactions. They are robust enough to survive reflux in high boiling solvents such as DMF, and the free-bases used here have shown no air-sensitivity. Indeed, the only factor requiring a metallation reaction to be performed under inert atmosphere is the stability of the starting metal salt. While it will be seen that the reactions with different metals vary somewhat in solvent and purification conditions, there are a great many similarities. For the most part the reactions described below involve refluxing the corrole free-base along with a metal salt (usually the chloride salt, as in the cases of gallium and tin corroles), followed by column purification, to provide the metallocorrole complex in high yield. Schemes 2.3 and 2.4 outline all the metallation reactions discussed below.

It has been seen that in considering a potential metallocorrole, size is an important factor. While the Ga(III) ion has been shown to form planar corroles[9], In(III) has shown itself to be too large to form a stable corrole complex, both in **1-In**, which decomposed on attempts at purification, and in the only previously known indium corrole, an octamethylcorrole-indium complex, also seen to decompose upon any attempts to purify the product[10].



Scheme 2.1. Current synthetic method used for **1**.

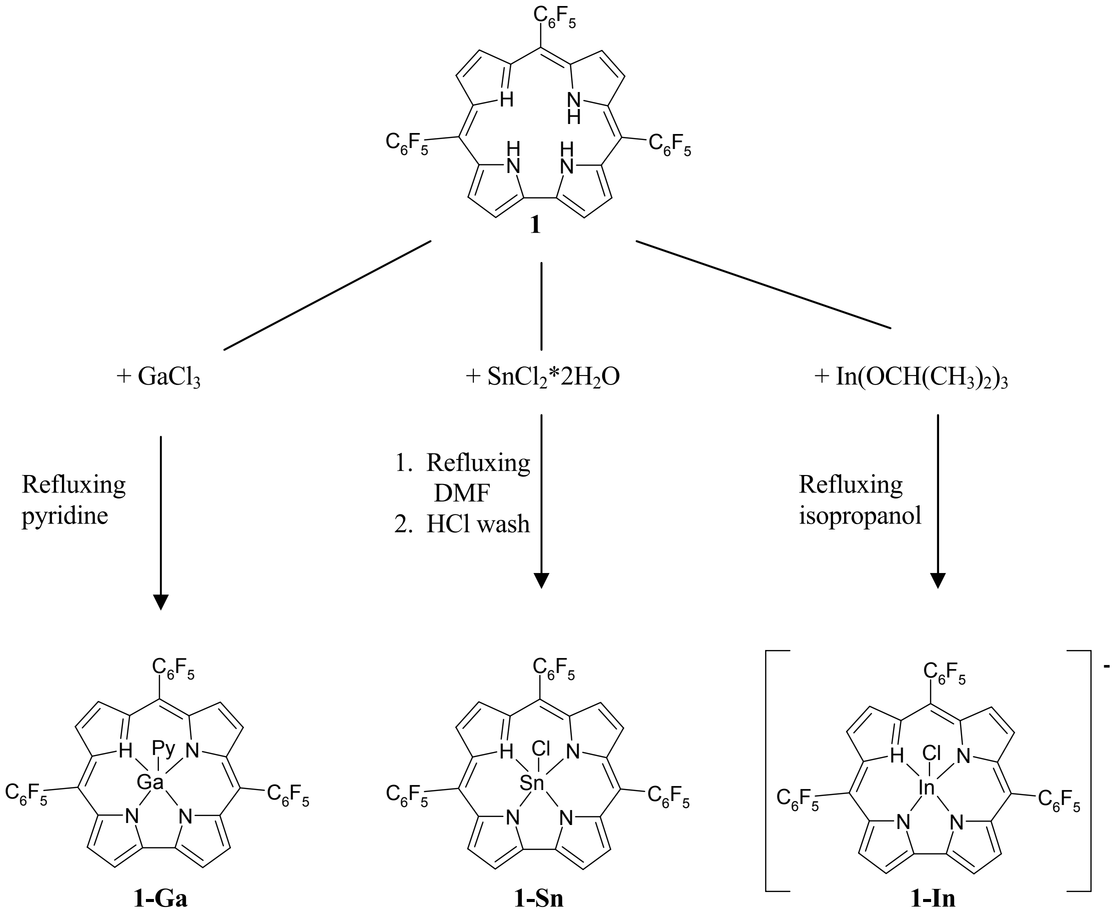


1

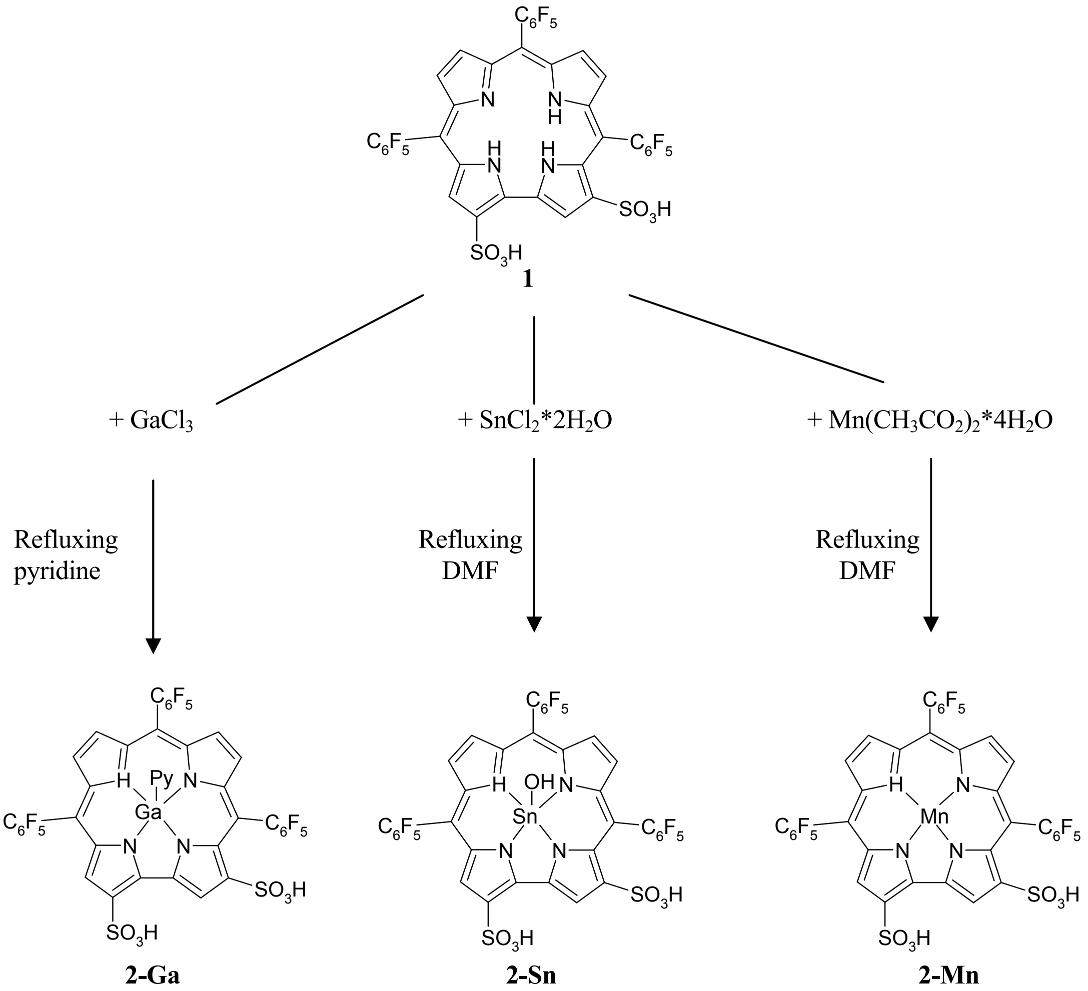
Cl-2

2

Scheme 2.2. Synthesis of **2**.



Scheme 2.3. Metallation reactions of **1**. Insertion of gallium requires column purification, **1-Sn** is purified through recrystallization, and no further purification was possible with the unstable **1-In** complex.



Scheme 2.4. Metallation reactions of **2**. All 3 metallocorroles are purified on a silica gel column.

pK_a of 2

With the synthesis of **2**, a water-soluble corrole, it becomes easier to talk about pK_as of the inner core protons. A core neutral corrole has three protons and one nonprotonated nitrogen atom. By contrast, a core neutral porphyrin has two protons and two nonprotonated nitrogen atoms. The absolute pK_as for protonation and deprotonation of **2** were measured two different ways.

In the first method, buffer solutions were made to cover a wide pH range. Solutions were made from these buffers at a constant concentration of **2**, and the absorption spectra were measured. It had previously been observed that the protonated and deprotonated forms of **1** showed characteristic changes in their absorption spectra[11]. The same effect is seen for **2**, and the spectra from this experiment show gradual transitions from protonated **2** ($\mathbf{2}^+$), to core neutral **2**, to deprotonated **2** ($\mathbf{2}^-$) as pH is increased. On the basis of these spectra, two rough pK_as can be assigned, at 2.5 and 5.2 for deprotonation of $\mathbf{2}^+$ and **2**, respectively (see figure 2.2).

These values were confirmed by a similar experiment monitoring pH effects on emission spectra of **2**. Again, previous work with **1** had shown a strong dependence of emission intensity on protonation state[8]. As with the previous experiment, buffers were prepared at varying pHs and were used to make solutions of constant concentration in **2**. Spectra were obtained by exciting the samples at 420 nm, a point where all species have similar absorption coefficients. The spectra again show two transition points, corresponding to deprotonation of **2+** and **2**, at pHs of 2.9 and 5.4, respectively. While this second value is

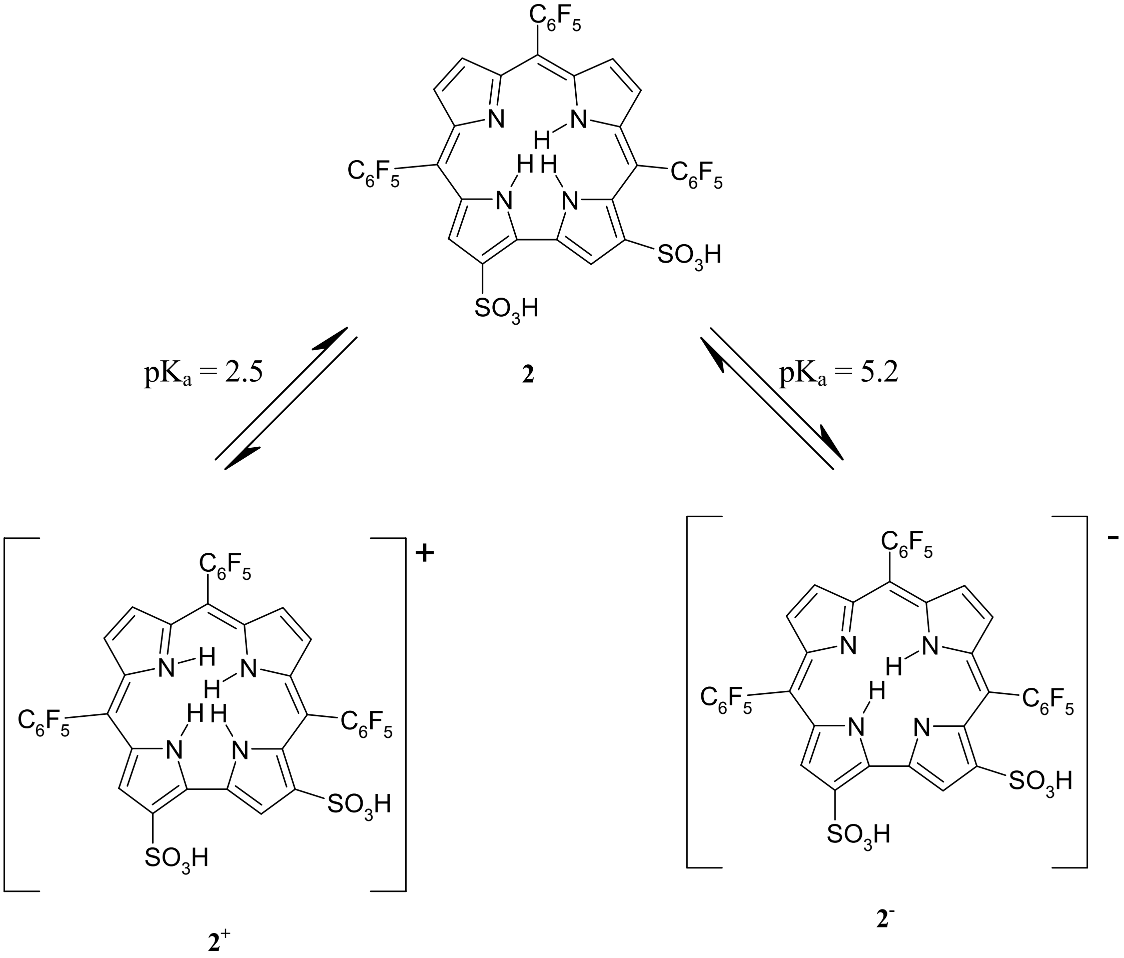


Figure 2.2. Protonation and deprotonation processes for **2**.

nearly identical to that from the first set of experiments, the first is farther off. However, given the lack of a perfect isobestic point for all the species, and given that the absorption change at 420 is greater at lower pH, greater error is expected in this number for the emission experiment. For this transition, the pK_a of 2.5 given by the first experiment is more reliable (see figures 2.3 and 2.4).

These pK_a values are especially interesting when compared to a representative water-soluble porphyrin, namely 5,10,15,20-tetra(*p*-sulfonatophenyl)porphyrin (**3**). The pK_a of this molecule is high enough that it can not be deprotonated in water. However, the value was measured in DMSO/water (4:1) and found to be 32.8[12]. The acidity constant for protonation of **3**, however, was found to be 4.8 (it should be noted that this is a double protonation event; the singly protonated form of **3** has not been observed)[13]. Upon inspection of these numbers, it becomes clear that the deprotonation equilibrium of corrole **2** is relatively closer to the protonation equilibrium of porphyrin **3** (the deprotonation equilibrium of $\mathbf{3}^{2+}$) than the deprotonation of **3**. This can be explained by considering the number of NH protons in each case rather than the formal charge. In both $\mathbf{2}^{-}$ and **3**, there are two NH protons in the core of the macrocycle. What can be gathered from the pK_a data, then, is that favorability of proton addition to either of these species is comparable, and core charge is not a large driving force for this reaction. Rather, sterics come into play. As seen in the crystal structure of **1** (figure 2.5)[14], the three protons of a core neutral corrole are in close proximity, and the macrocycle experiences some distortion to be able to fit all three. Indeed, one of the protons of **1** is 0.89 Å out of the mean plane of the four nitrogen atoms. Presumably there is a similar steric penalty for the protonation of **3**, and

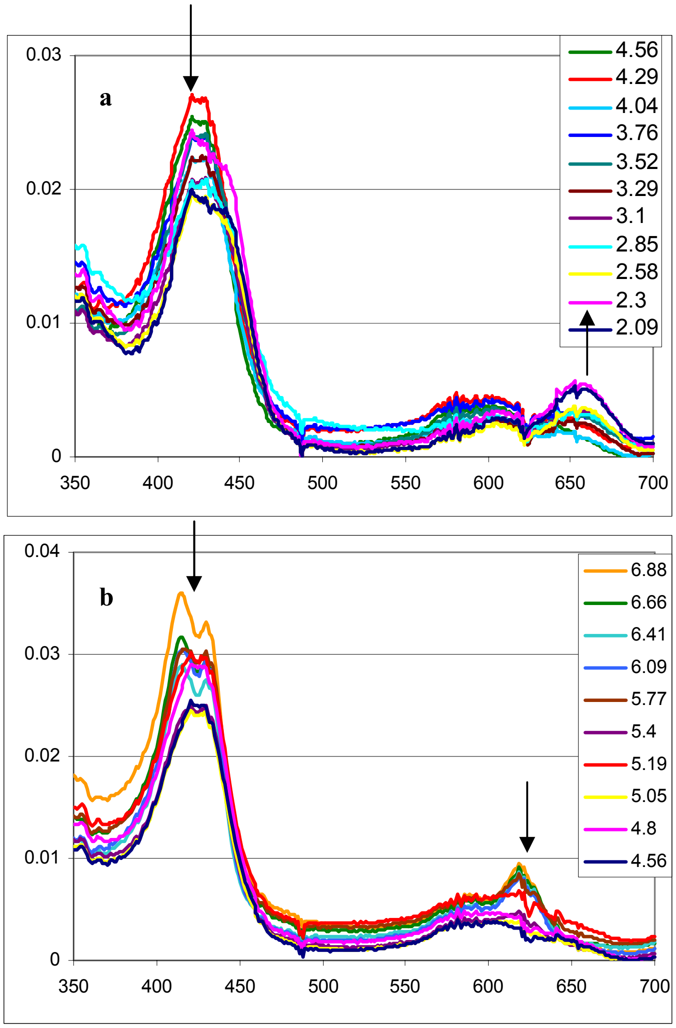


Figure 2.3. UV-vis spectra showing a) pH 4.56-2.09 (**2-2**$^{+}$) and b) pH 6.88-4.56 (**2**$^{-}$-**2**). General trends observed as pH is lowered have been noted.

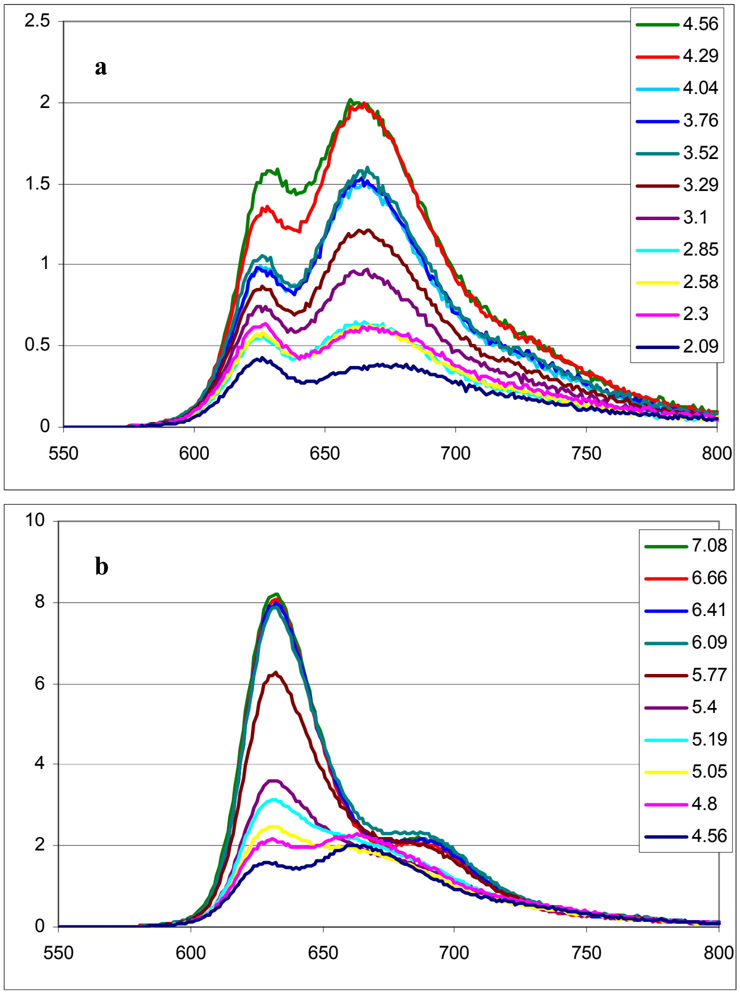


Figure 2.4. The pH-dependent fluorescence spectra: a) pH= 2.09 - 4.56. b) pH= 4.56-7.08. Note the different scales in (a) and (b).

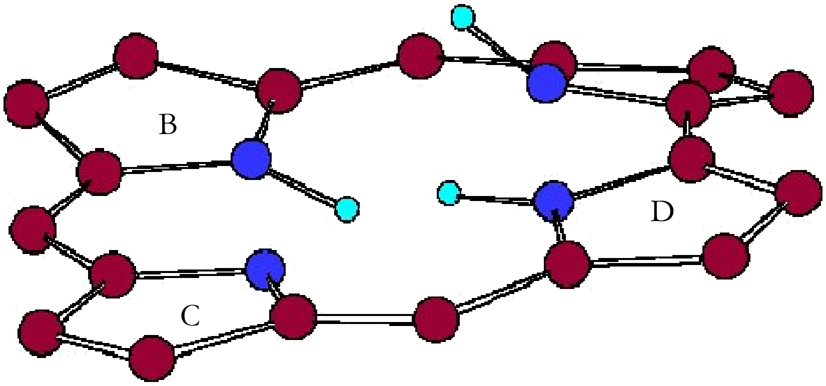


Figure 2.5. X-ray structure of **1**, with meso groups omitted for clarity. The protons on rings D, A, and B are -0.46, 0.89, and 0.1 Å out of the mean plane of the four nitrogens, respectively.

once either the corrole or porphyrin has three NH protons, there is no great steric inhibition to adding a fourth. This is evidenced by the small pH range in which **2** exists between $\mathbf{2}^-$ and $\mathbf{2}^+$, and the utter lack of a monoprotonated **3**, the molecule instead progressing directly to the diprotonated form.

Thus it can be seen that corroles are very versatile molecules, with interesting and useful spectroscopic properties. These properties will be discussed in greater detail in the following chapters.

Materials

All materials were purchased from Aldrich and used as received except where noted otherwise.

Pentafluorobenzaldehyde (98%, FW 196.07 g/mol, mp 20^o, bp 164-166^o, d 1.588 g/mL). Usually found as a solid except on particularly warm days. When solid, it was warmed to liquid with a heat gun prior to use. The liquid was then pipetted into a tared flask when measured by weight, or a particular volume was measured by syringe.

Pyrrole (98%, FW 67.09 g/mol, mp -23^o, bp 131^o, d 0.967 g/mL). While the bottle was stored in a refrigerator, the liquid did show evidence of photodecomposition products (the liquid was a dark yellow-brown). Prior to use the liquid was filtered through basic alumina to remove these excess products, affording a light yellow to colorless solution. The pyrrole was then pipetted into a tared flask to measure by weight, or a particular volume was measured by syringe.

Trifluoroacetic acid (TFA, 99%, FW 114.02 g/mol, mp -15.4^o, bp 72.4^o, d 1.480 g/mL).

Chlorosulfonic acid (99%, FW 116.52 g/mol, bp 151-152^o, d 1.753 g/mL).

2,3-Dichloro-5,6-dicyano-1,4-bezoquinone (DDQ, 98%, FW 227.01 g/mol, mp 213-216^o) was stored in a refrigerator.

Gallium(III) chloride (anhydrous beads, 99.99%, FW 176.08 g/mol, d 2.470 g/cm^3) was stored in a dry box.

Tin(II) chloride dihydrate (98+%, FW 225.63 g/mol, mp 37-38^o, d 2.710 g/cm^3) was purchased from Fischer Scientific.

Manganese(II) acetate tetrahydrate (99+%, FW 245.09 g/mol, d 1.589 g/cm^3).

Indium(III) chloride (anhydrous powder, 99.999%, FW 221.18 g/mol, d 3.460g/cm^3) was stored in a drybox.

Indium(III) isopropoxide (5 w/v% solution in isopropanol, 99.9+%, FW 292.09 g/mol, d 0.808 g/mL).

Aluminum oxide, activated basic (standard grade, ~150 mesh, 58Å).

Silica gel 60 (particle size 0.040-0.063 mm) was purchased from EMD Chemicals through the VWR stockroom.

Sand was purchased from EMD Chemicals through the VWR stockroom.

All solvents were purchased from EMD Chemicals through the VWR stockroom. Solvents used were generally Omnisolv® quality, though no particular purity was required, except where otherwise noted.

Detailed Syntheses

In the first of the three methods for synthesis of **1**, to 2.82 g (14.3 mmol) pentafluorobenzaldehyde were added first 10 mL dichloromethane (CH_2Cl_2) followed by 1 g (14.9 mmol) pyrrole. This mixture was then added to a 50 mL round bottom flask containing 3 g alumina. The mixture was stirred while heating to 60^o C in an oil bath, causing CH_2Cl_2 to boil off. Once the solvent had been evaporated, the solid was maintained at 60^o for four hours. After heating, CH_2Cl_2 was added to the flask to dissolve the black residue, and the liquid was filtered through a Büchner funnel to remove the alumina. To the liquid were added 1.5 g (6.6 mmol) DDQ, and the solution was stirred for one hour. After 1 hour, the mixture was checked by TLC (1:1 dichloromethane:hexanes eluent), and a purple band with strong fluorescence under long-wave UV light could be seen.

7 grams of silica gel were added to the flask, and the liquid was evaporated to afford the product mixture adsorbed onto the silica gel. A 2-inch inner diameter column (henceforth referred to as the large column) was packed to a height of ~7 inches with dry silica gel, followed by a ~0.5 inch layer of sand. The solid product adsorbed on silica gel was then scraped out of the flask and layered on top of the sand, followed by a second layer of sand. The column was then eluted with a 1:1 mixture of dichloromethane and hexanes. Progress

of the fluorescent corrole band could be monitored with UV light. Starting with the first colored fraction, all products were collected until the fluorescent band had completely eluted from the column. To the eluted products 2.5 g silica gel were added, and the solvents were evaporated. A 1-inch inner diameter column (henceforth referred to as the small column) was prepared in the same manner as the large column, with the adsorbed product layered between two sand fractions. The column was run with a 22:3 mixture of hexanes to CH_2Cl_2 and was monitored by UV light. The fluorescent corrole band was collected by itself.

Usually a third purification was performed by evaporating the solvent from the column eluent and by dissolving the residue in a minimum of dichloromethane and hexane (~3:1). The solution was then put in the freezer to induce crystallization. The crystals were collected in a Büchner funnel to provide extremely pure corrole. Normally 2-3 crops of crystals could be obtained from a single batch, providing ~150 mg (0.2 mmol, 5% yield) of 5,10,15-tris(pentafluorophenyl)corrole (**1**).

In the second, neat method, reaction between pentafluorobenzaldehyde and pyrrole was performed in six small vials with specially fitted stirrers. 0.45 g (2.3 mmol) pentafluorobenzaldehyde was added to each vial. While stirring, 150 μL (2.2 mmol) pyrrole were added. The reaction is exothermic, and some boiling could be seen initially. The mixture quickly turned black, and the viscosity increased to produce a tar. The vials were allowed to sit with no external heating for ~60 minutes. The tar in each vial was then dissolved in CH_2Cl_2, and all six solutions were combined in a single flask. 1.5 g (6.6

mmol) DDQ were again added, and the reaction and purification proceeded as above. This method afforded approximately the same yield as the original method. Both of these methods showed very little ability toward scaling up, with overall yield plummeting upon any attempt.

The third method for synthesis of free-base, and the one that is currently in use in the group, is a variation of the neat method. To a 250 mL round bottom flask were added, in order while stirring, 1.73 mL (14 mmol) pentafluorobenzaldehyde, 140 μL of a prepared TFA solution (0.5 mL TFA in 5 mL CH_2Cl_2, overall amount of TFA added was 0.17 mmol), and 1.46 mL (21 mmol) pyrrole. The mixture was allowed to react for 10 minutes, during which time the methylene chloride was evaporated by the exothermic reaction, leaving a black tar. The tar was then dissolved in ~100 mL CH_2Cl_2, and 3.8 g (16.7 mmol) DDQ were added. This solution was allowed to stir for 5 minutes, after which 7 grams of silica gel were added and purification proceeded as above. Attempts to scale up this reaction reduced overall yield and ran into great problems with the first column, in that the amount of tar produced was too great to readily adsorb on the silica gel. Adding more silica gel resulted in larger product bands on the column, and overall separation was greatly reduced. However, given the short amount of time needed to run the reaction by this method, two batches could be prepared at once and run through the large column separately. The two runs could then be combined and separated together on the second column (which, conveniently, was the longer of the two). This method afforded ~250-300 mg of product (3.3-4% yield). While this was a slight decrease in overall yield of the reaction from the first method, the cost is outweighed by the more than two-fold decrease in time necessary to obtain the same amount of corrole by the two methods. It should also be noted that these yields are those obtained by this researcher in this work. Reported yields for the first reaction are twice that obtained herein[11]. The reaction for the current method is shown in scheme 2.1.

2,17-bis(sulfonato)-5,10,15-tris(pentafluorophenyl)corrole (**2**) was prepared from **1** in the following manner[15]. 80 mg (0.1 mmol) of **1** were dissolved in ~2 mL chlorosulfonic acid, in a 50 mL round bottom flask, and the solution was stirred for 5-10 minutes at room temperature. The flask was then cooled in an ice bath, and ice chips were added directly to the solution to quench the acid. Care must be exercised at this point in the size of the chips added. A large chip would cause the solution to pop out of the flask. Once the reaction was quenched, as evidenced by no further gas evolution upon addition of more ice, the flask was filled with deionized water, and the liquid was poured into a 500 mL separatory funnel. The flask was then rinsed with CH_2Cl_2 to dissolve any residue left, and this was added to the funnel, along with ~20 mL more CH_2Cl_2. The funnel was shaken, and the two phases allowed to separate, followed by collection of the organic phase. The aqueous phase was washed with two more portions of methylene chloride, and these organic phases were combined with the previous one. The aqueous phase was then discarded, and the combined organic phases were washed three times with deionized water, with only the organic phase being kept between washings. Once washed, the solvent from the organic phase was evaporated, leaving a green residue, identified as a bis(chlorosulfonated) corrole (**Cl-2**). This solid could be scraped off the flask to afford a powder. The powder was added to a 250 mL round bottom flask along with ~150 mL deionized water, and the liquid was refluxed 12-16 hours, during which time the solution changed from colorless to a dark green, indicating presence of the water-soluble **2**. After evaporation of the water, ~65 mg of **2** could be recovered (0.068 mmol, 68% yield from **1**). This is a remarkable reaction in its specificity. With no control over the number of substituents introduced to the β positions of the ring, there are 140 possible substitution patterns that are possible, ranging from unsubstituted to octasubstituted. This reaction provided one main isomer, with less than 5% contamination of a symmetrically substituted bis(sulfonated) isomer (3,17-bis(sulfonato)-5,10,15-tris(pentafluorophenyl)corrole).

Metallocorroles

5,10,15-tris(pentafluorophenyl)corrolato-gallium(III) monopyridine (**1-Ga**) was prepared from **1** by refluxing the free-base with a large excess of gallium(III) chloride in pyridine for one hour under inert atmosphere. Care must be exercised as gallium(III) chloride is very air sensitive. While the reaction can be done open to air, overall yield is reduced, and a larger excess of metal salt is needed. After the reaction was complete, the solvent was evaporated, and the compound was purified by use of the small column procedure outlined above, using a mixture of hexanes, methylene chloride, and pyridine (100:30:0.5) as eluent, and collecting the fluorescent fraction. The reaction provided **1-Ga** in overall ~80% yield.

2,17-bis(sulfonato)-5,10,15-tris(pentafluorophenyl)corrolato-gallium(III) monopyridine, **2-Ga**, was prepared in the same manner as **1-Ga**, starting from **2** and with the use of methanol:pyridine (19:1) as eluent for the column purification.

The synthesis of 5,10,15-tris(pentafluorophenyl)corrolato-tin(IV) chloride, **1-Sn**, started with dissolving **1** in DMF, followed by addition of 10-fold excess tin(II) chloride dihydrate. The solution was refluxed for 30 minutes, followed by evaporation of the solvent. The residue was dissolved in CH_2Cl_2 and filtered, and the filtrate was washed with concentrated HCl. The desired compound could be recrystallized from a mixture of hexanes and dichloromethane, with an overall yield of ~85%.

As with the gallium reactions, the initial metallation step in the synthesis of 2,17-bis(sulfonato)-5,10,15-tris(pentafluorophenyl)corrolato-tin(IV) hydroxide, **2-Sn**, was the same as its nonsulfonated counterpart, refluxing **2** in DMF with an excess of metal salt for 30 minutes. However, **2-Sn** is a water-soluble complex; therefore washing with concentrated HCl was not feasible, as the compound partitioned itself between the two layers. While the crude reaction mixture showed evidence of the tin corrole chloride, the Cl^- ligand exchanged for a hydroxide ligand over time. The transformation could be hastened by running the compound through a silica gel column, providing **2-Sn** in 90% yield.

2,17-bis(sulfonato)-5,10,15-tris(pentafluorophenyl)corrolato-manganese(III), **2-Mn**, was prepared from **2** and manganese(II) acetate tetrahydrate. Equal masses of the two compounds (a four-fold excess of manganese salt) were dissolved in DMF and refluxed for 15-30 minutes. After reflux, the solvent was evaporated and the compound was purified by running it through a small column using ethanol as eluent, giving **2-Mn** in ~90% yield.

The final metallocorrole synthesis considered in this project was that of 5,10,15-tris(pentafluorophenyl)corrolato-indium(III) chloride anion, **1-In**. Initial work with this compound focused on the addition of **1** to indium(III) chloride in refluxing DMF under argon. The crude reaction mixture showed evidence of **1-In** after 5 minutes and no further reaction after 30 minutes. However, attempts to separate this product from the numerous byproducts proved unsuccessful. When the same reaction was repeated in pyridine, in an experiment analogous to the synthesis of **1-Ga**, similar results were observed, and again numerous byproducts were seen. However, when the reaction conditions were changed, a very clean synthesis of **1-In** was discovered. In this synthetic pathway, **1** was added to a five-fold excess of indium(III) isopropoxide (5 w/v% in 2-propanol; used as solvent). Initially the reaction was stirred at room temperature and monitored by UV-vis. Under these conditions, there was evidence of a corrole product growing in at 30 minutes. Complete reaction took 36 hours. In later experiments, the solution was heated to reflux, and overall reaction time was reduced to 1 hour. Mass spectra of the crude reaction mixture revealed it to be very clean, with **1-In** the only corrole species evidenced. Note that this is without the deliberate addition of any chloride containing species, and the product was only observed as a monoanion. However, any attempts to perform further experiments with the compound, or even to store it for a period of time, showed it to decompose back to **1** and an unidentified indium salt (likely $In(OH)_3$).

^{1}H NMR Data[8, 11, 15, 16]

1 ($CDCl_3$) - δ = 9.10 (doublet, J = 4.4 Hz, 2H), 8.75 (doublet, J = 4.4 Hz, 2H), 8.57 (doublet, J = 4.4 Hz, 4H), -2.25 (broad singlet, 3H).

2 (CD_3OD) - δ = 9.68 (broad singlet, 1H), 9.14 (doublet, J = 4.8 Hz, 1H), 8.98 (doublet, J = 4.8 Hz, 1H), 8.90 (broad singlet, 1H), 8.86 (doublet, J = 4.8 Hz, 1H), 8.84 (doublet, J = 4.8 Hz, 1H).

Cl-2 ($CDCl_3$) - δ = 9.44 (singlet, 1H), 8.95 (singlet, 1H), 8.60 (doublet, J = 5.0 Hz, 1H), 8.50 (doublet, J = 5.0 Hz, 1H), 8.41 (doublet, J = 5.0 Hz, 1H), 8.18 (doublet, J = 5.0 Hz, 1H).

1-Ga (C_6D_6) - δ = 9.20 (doublet, J = 4.1 Hz, 2H), 8.88 (doublet, J = 4.4 Hz, 2H), 8.74 (doublet, J = 4.0 Hz, 2H), 8.66 (doublet, J = 4.6 Hz, 2H), 4.89 (triplet, J = 7.9 Hz, 1H), 4.32 (unresolved triplet, 2H), 2.84 (unresolved doublet, 2H).

2-Ga (CD_3OD) - δ = 9.77 (singlet, 1H), 8.77 (singlet, 1H), 8.70 (doublet, J = 4.8 Hz, 1H), 8.57 (doublet, J = 4.8 Hz, 1H), 8.48 (triplet, J = 4.3 Hz, 2H), 8.27 (broad singlet, 2H), 7.71 (unresolved triplet, 1H), 7.30 (broad singlet, 2H).

1-Sn ($CDCl_3$) - δ = 9.4 (doublet, J = 4.3 Hz, 2H), 9.0 (doublet, J = 4.9 Hz, 2H), 8.9 (multiplet, 4H).

2-Sn (CD_3OD) - δ =10.04 (s, 1H), 9.04 (doublet, J = 4.8 Hz, 1H), 8.96 (singlet, 1H), 8.94 (doublet, J = 5.2 Hz, 1H), 8.84 (doublet, J = 4.3 Hz, 2H).

Mass Spectral Data

The mass spectrum for **2-Ga** was obtained from MALDI-TOF experiments. Other mass spectra were obtained by electrospray ionization. Species represented by each peak are given, where M is the parent molecule as shown in schemes 2.3 and 2.4. Percentages given are relative peak intensities. See figures 2.6-2.11 for actual versus predicted spectra.

1 – m/z = 797.1 $[M+H]^+$, 795.1 $[M-H]^-$

2 – m/z = 954.8 $[M-H]^-$

1-Ga – m/z = 941.7 $[M+H]^+$

2-Ga – m/z = 1021.9 $[M-C_5H_5N]^+$

1-Sn – m/z = 913.1 $[M-Cl]^-$ (23.6%), 1001.0 $[M+3(H_2O)-H]^-$ (100.0%)

2-Sn – m/z = 1026.9 $[M-OH+Cl-SO_3H]^-$ (100.0%), 1106.8 $[M-OH+Cl-H]^-$ (60.8%)

2-Mn – m/z = 1006.8 $[M-H]^-$ (35.4%), 1029.0 $[M-2H+Na]^-$ (100.0%)

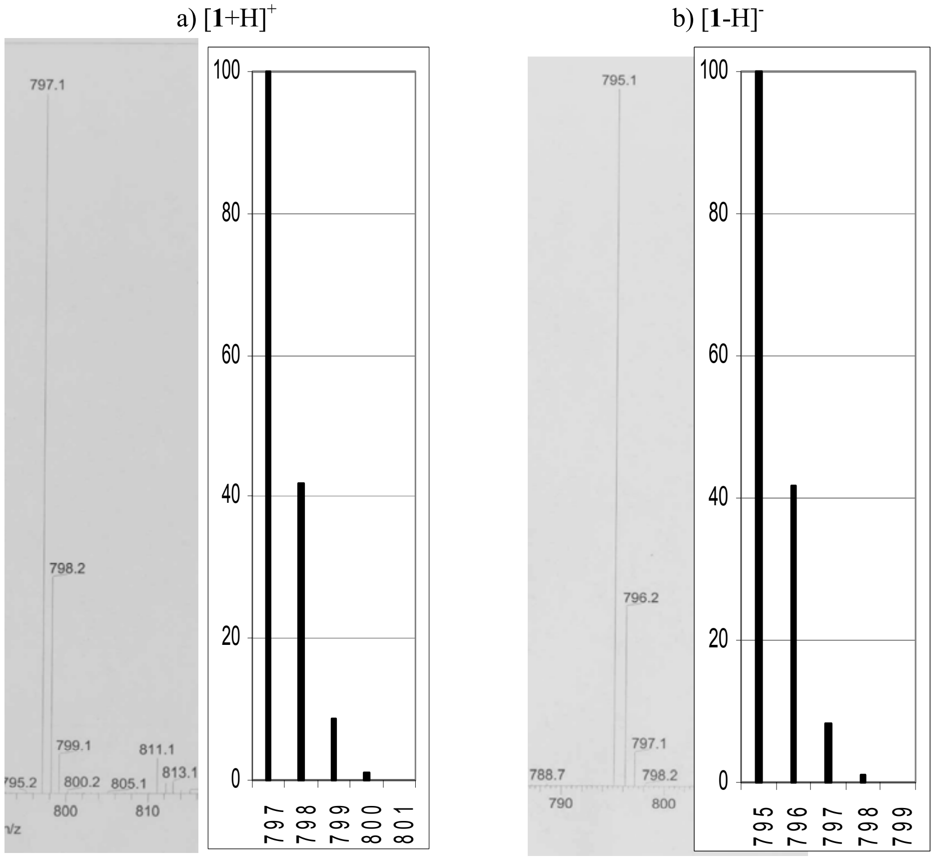


Figure 2.6. Actual (left) versus predicted (right) mass spectra for a) $[\mathbf{1}+\mathrm{H}]^+$ and b) $[\mathbf{1}-\mathrm{H}]^-$.

[**2**-H]$^-$

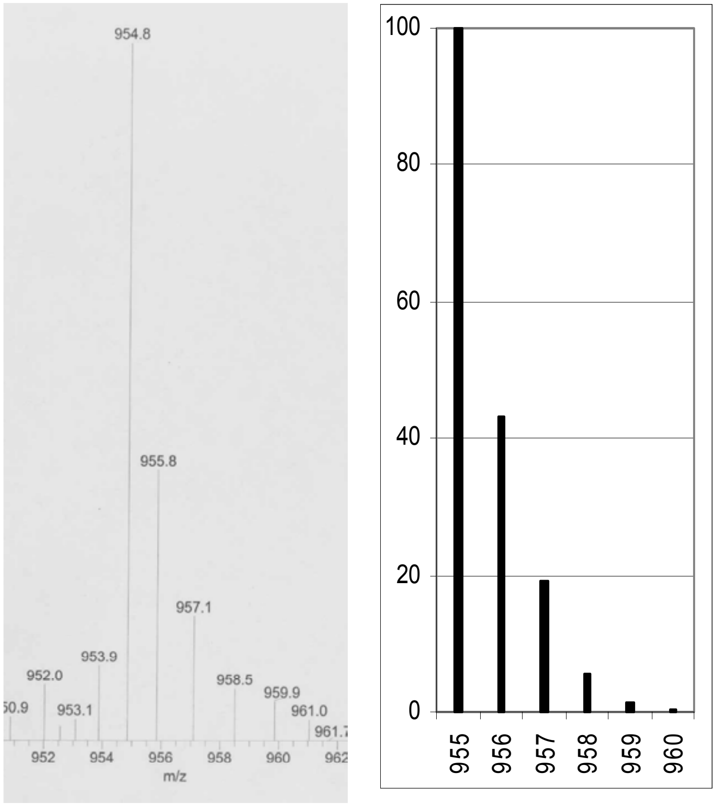
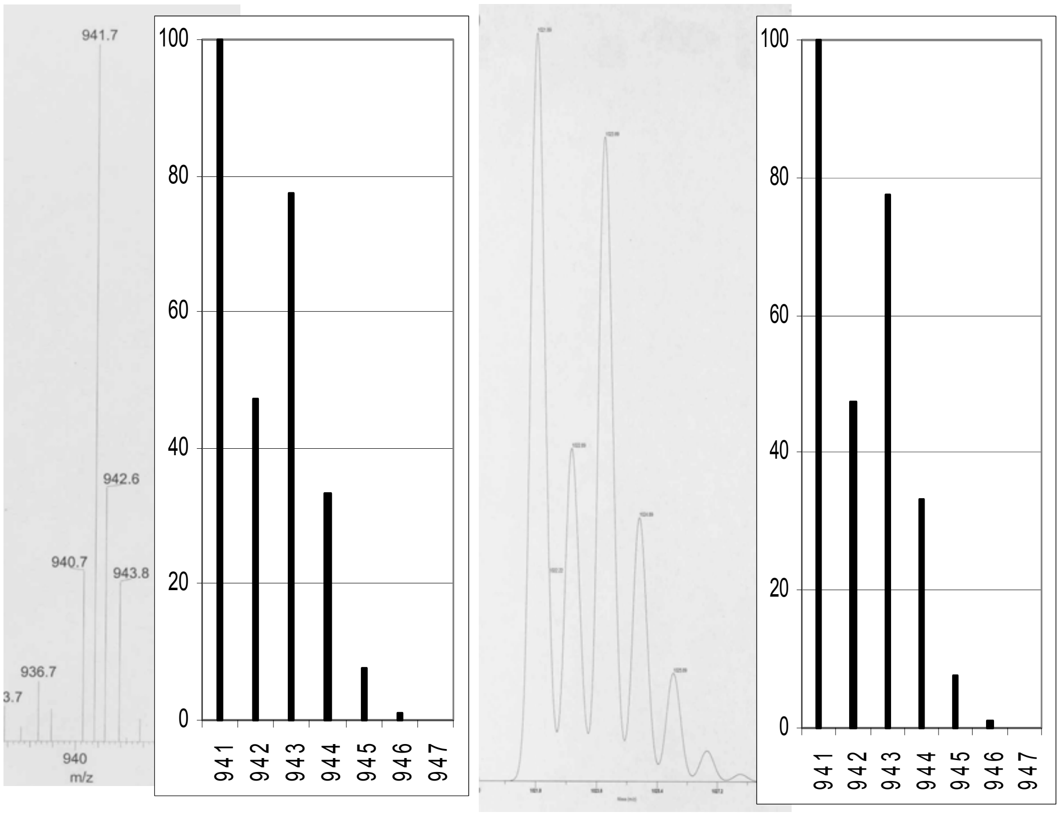


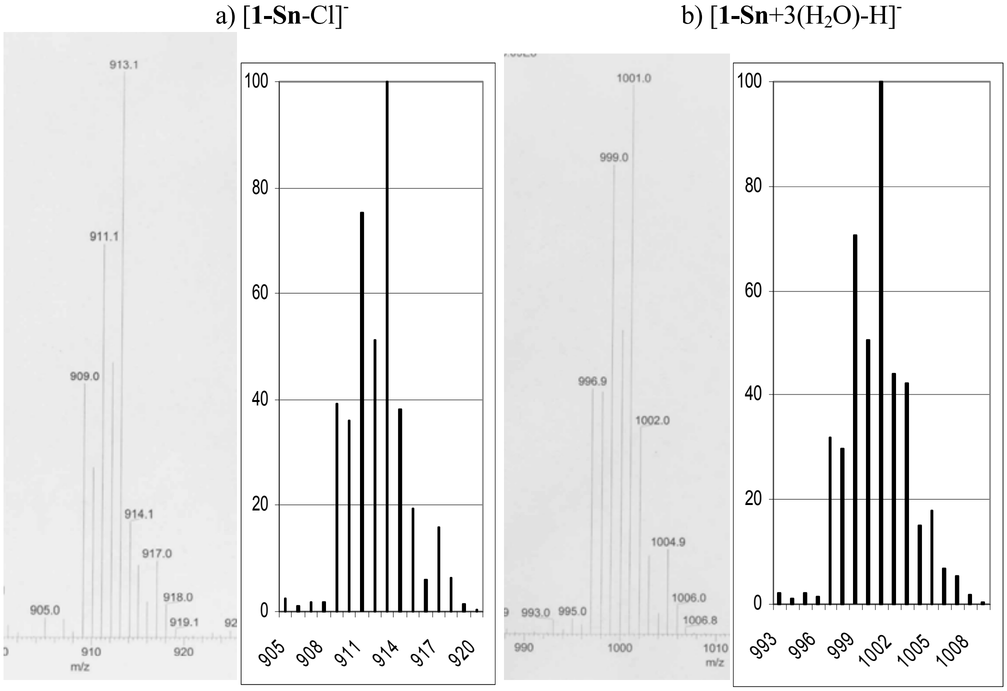
Figure 2.7. Actual (left) versus predicted (right) mass spectra for [**2**-H]$^-$.



a) [**1-Ga**+H]$^+$

b) [**2-Ga**-C_5H_5N]$^+$

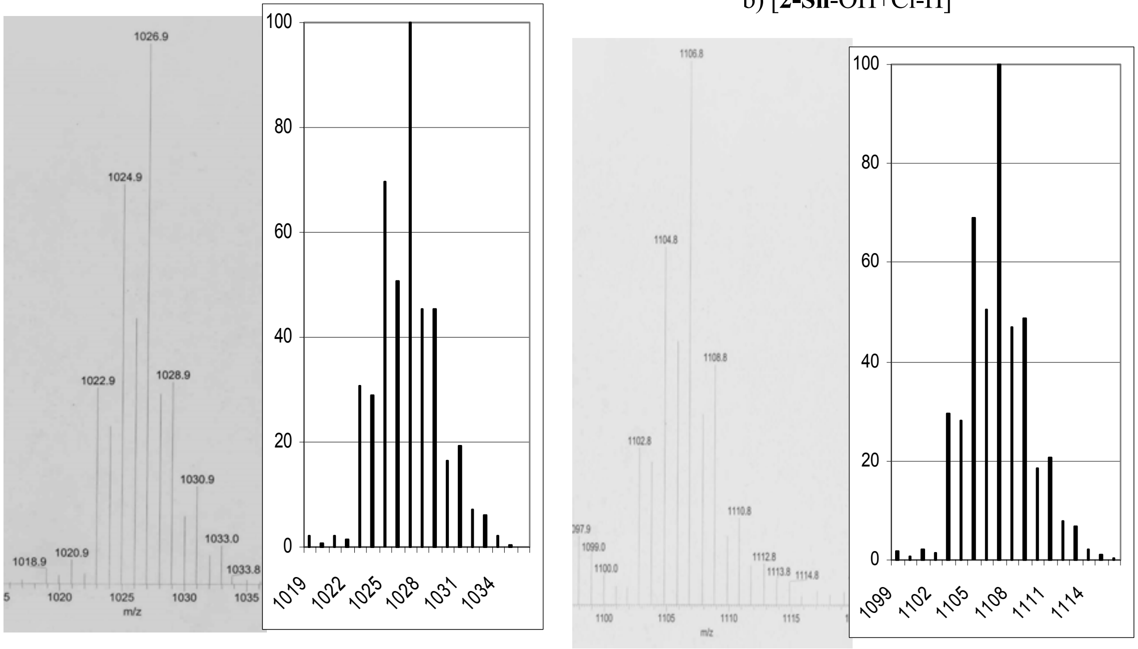
Figure 2.8. Actual (left) versus predicted (right) mass spectra for a) [**1-Ga**+H]$^+$ and b) [**2-Ga**-C_5H_5N]$^+$.



a) [**1-Sn**-Cl]$^-$

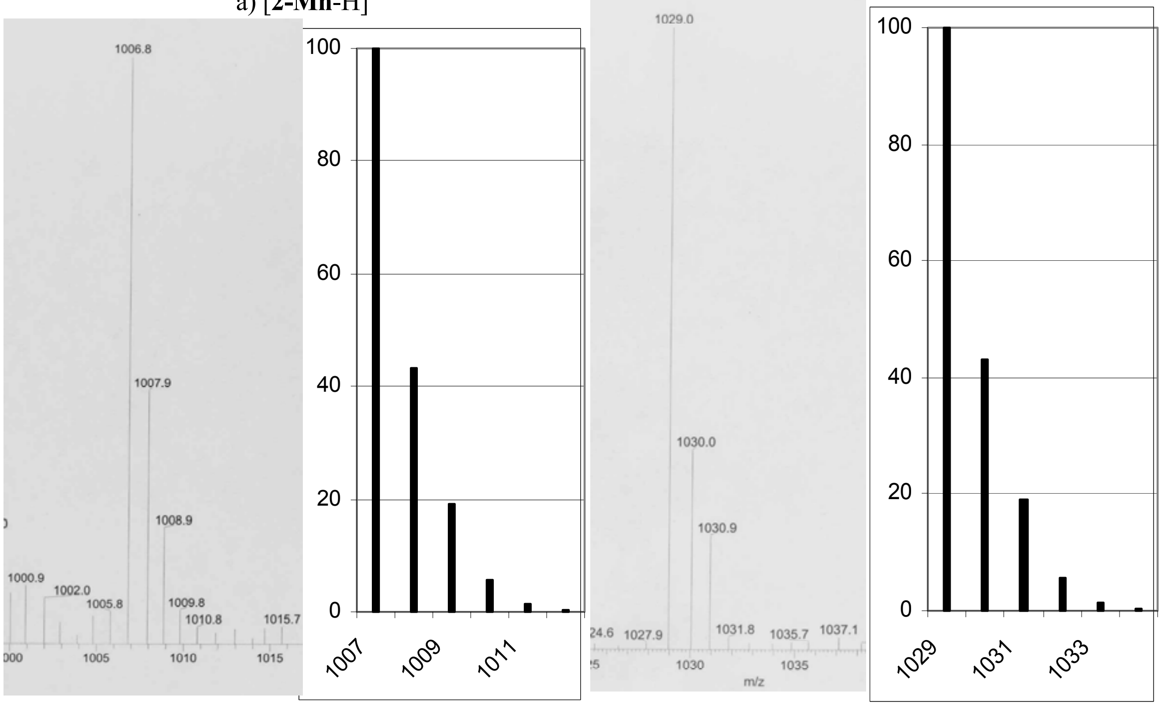
b) [**1-Sn**+3(H_2O)-H]$^-$

Figure 2.9. Actual (left) versus predicted (right) mass spectra for a) [**1-Sn**-Cl]$^-$ and b) [**1-Sn**+3(H_2O)-H]$^-$.


a) [**2-Sn**-OH+Cl-SO$_3$H]$^-$

b) [**2-Sn**-OH+Cl-H]$^-$

Figure 2.10. Actual (left) versus predicted (right) mass spectra for a) [**2-Sn**-OH+Cl-S$_2$O$_3$H]$^-$ and b) [**2-Sn**-OH+Cl-H]$^-$.



a) [**2-Mn**-H]$^-$

b) [**2-Mn**-2H+Na]$^-$

Figure 2.11. Actual (left) versus predicted (right) mass spectra for a) [**2-Mn**-H]$^-$ and b) [**2-Mn**-2H+Na]$^-$.