CORROLES

Thesis by

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My career at Caltech has, of course, been greatly influenced by the man who first called me to tell me I had gotten into Caltech, Harry Gray! Unfortunately I was on break and didn't get the call personally, but even over voice-mail Harry's enthusiasm for everything comes across loud and clear. Once in the presence of the man, it's difficult not to be excited about chemistry. His knack for explaining things so that they sound so simple, without making you feel stupid for not seeing it in the first place, is amazing and is what led to all the results presented here. I have learned a tremendous amount from you, and if I manage to retain only a fraction of it, I'll be set for life.

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Along these same lines, I must thank Dr. Atif Mahammed for his help along the way. When I was still struggling to make that second corrole he came to the States to show me how it was done.

Of course, getting to the first corrole was especially important, and for that I have to thank Dr. Alexandre Meier. From the first time I met with him to hear about the project he was extremely helpful and kind. His work in starting the corrole project in the group was amazing, and I am indebted to him for getting me started as well.

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As for the members of the group who didn't work directly on the project, the list of those who helped it along is still numerous. Dr. Jay Winkler provided much help in data interpretation and in teaching me to really think about all the factors in setting up an experiment so I only had to do it once. Dr. Steve Contakes provided the insight that finally led to a clean synthesis of indium corrole. Drs. Alex Dunn, Kristine Jensen, Judy Kim, Jenn Lee, and Randy Villahermosa, as well as Wendy Belliston Bittner, Brian Leigh, Melanie Pribisko, and Don all helped with the laser experiments and with trying to teach me how to run them myself, a skill I never quite picked up. Drs. Oliver Wenger and John Magyar provided the most non-laser related help. Over the years I had the opportunity to share space in Noyes with Gitrada Arjara, Wendy, Steve, Dr. Pierre Kennepohl, Bert Lai, Brian, Dr. Jeremiah Miller, Yen Ngyuen, Melanie, Crystal Shih, Karn, Don, Dr. Will Wehbi, and Keiko Yokoyama. All of them managed to make it one of the best places to work, full of laughter and fun, and just a great place to spend the days.

Of course, the influence of others is not limited strictly to those in the Gray group. As this is where I'm most likely to forget individual names, let me give blanket thanks to the Peters, Bercaw, Lewis, and Barton groups for help, resources, and equipment usage over the years. And specific thanks must go out to my committee members, Profs. Jackie Barton, Pat Collier, and Jack Richards for all their help along the way.

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As for those who helped keep me sane outside of research, foremost must be Andrew Waltman, my first roommate at Caltech, and later my Best Man. One of the greatest friends a guy could ask for. Rebecca Connor, Rachel Niemer, Brian and Amanda Sisk, Andrew Udit, and Lauren Webb all also fall into this category. Always there whenever needed for a laugh and a good time. Dr. Jeff Johnson, from fifty-page-long p-chem reports and studies on the physics of high-velocity water-balloon collisions with windows to emergency groomsman duty, you've always been a great friend and cohort. Shantanu

Sharma has been a wonderful friend and ally since he arrived at Caltech. Anytime I see a guy with three-inch-thick glasses, I'll think of you.

Ben Edelson, I didn't know you half as well as I would've liked, but still well enough to know Chemistry is worse off without you.

Dorothy Holm was one of the best neighbors I ever had, and I am happy for the chance to know her.

And of course, I could have never made it this far without my family. Mom, Dad, and Toni, thank you for the support, encouragement, and everything else you gave me along the way.

And lastly, partly because as an inorganic chemist I love symmetry, and partly just because I want to, I'll bring this back around to where it started. Susanna, thank you for putting up with me during the writing of the following 100+ pages. You deserve another degree just for that. Storm clouds may gather and stars may collide, but I'll love you until the end of time. Come what may, I will love you until my dying day.

ABSTRACT

Corroles, porphyrin analogues, are the center of a rapidly growing field of research. By virtue of a missing meso-carbon, corroles retain the aromaticity of porphyrins, but become tribasic ligands in place of the dibasic porphyrin. This thesis is a study of synthetic methods for corroles, as well as their photophysical properties and potential applications.

New synthetic methodologies for the free-base molecules have been used to obtain corroles with pentafluorophenyl meso substituents in both water-soluble and non-water-soluble forms. Closed-shell metallocorrole complexes have been synthesized by introducing Ga(III) and Sn(IV) ions into the macrocycle. Likewise, an open shell transition metal corrole utilizing Mn(III) has been made. Problems arising from making a third type of closed shell metallocorrole by introduction of In(III) are also discussed. Among other characterizations of these complexes, Gouterman's four-orbital model for porphyrins is reinterpreted under the reduced symmetry of the corrole macrocycle to explain the absorption and singlet emission spectra of the molecules. Evidence of a triplet excited state is also presented.

The application of corrole complexes to other aspects of chemistry is then examined in two different areas. The interactions of the water-soluble corroles with human serum albumin were investigated to assess their usefulness as diagnostic agents and drugs for cancer research. These highly colored compounds have also been introduced as the dye component of dye-sensitized solar cells, and various aspects of the cells, including overall efficiency, have been tested.

This thesis concludes with a summary of results obtained from collaborations on the interactions of corroles in cellular systems and synthetic attempts toward new types of water-soluble corroles, including an imidazole substituted chromium corrole and a sulfonated manganese nitrido corrole.

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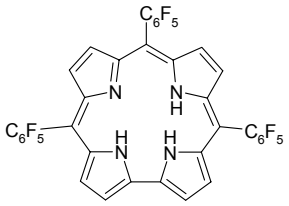
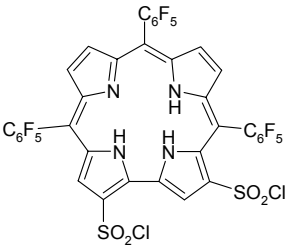
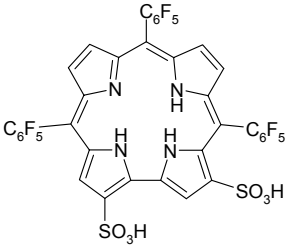
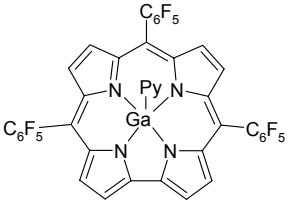
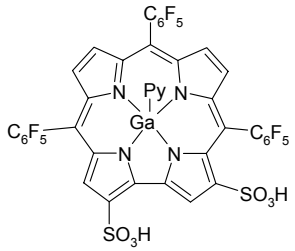
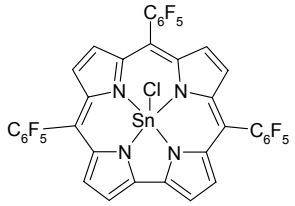
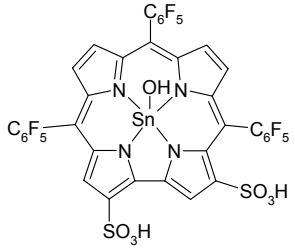
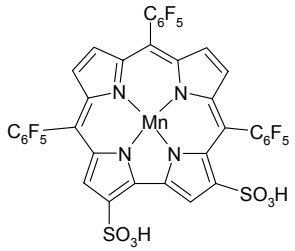
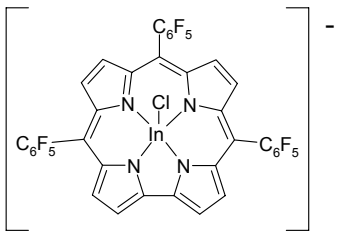
MOLECULE ABBREVIATIONS

Below is a list of the compounds synthesized in this work, along with their structures and the abbreviations used in the text.

Abbreviation	Structure	Name
1		5,10,15-tris(pentafluorophenyl)corrole
Cl-2		2,17-bis(chlorosulfonato)-5,10,15-tris(pentafluorophenyl)corrole
2		2,17-bis(sulfonato)-5,10,15-tris(pentafluorophenyl)corrole
1-Ga		5,10,15-tris(pentafluorophenyl)corrolato-gallium(III) monopyridine

Abbreviation	Structure	Name
2-Ga		2,17-bis(sulfonato)-5,10,15-tris(pentafluorophenyl)corrolato-gallium(III) monopyridine
1-Sn		5,10,15-tris(pentafluorophenyl)corrolato-tin(IV) chloride
2-Sn		2,17-bis(sulfonato)-5,10,15-tris(pentafluorophenyl)corrolato-tin(IV) hydroxide
2-Mn		2,17-bis(sulfonato)-5,10,15-tris(pentafluorophenyl)corrolato-manganese(III)
1-In		5,10,15-tris(pentafluorophenyl)corrolato-indium(III) chloride anion