CORROLES

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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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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	C_6F_5 C_6F_5 C_6F_5 H H C_6F_5	5,10,15- tris(pentafluorophenyl)corrole
Cl-2	C_6F_5 N H C_6F_5 C_6F_5 SO_2CI	2,17-bis(chlorosulfonato)-5,10,15- tris(pentafluorophenyl)corrole
2	C_6F_5 C_6F_5 H C_6F_5	2,17-bis(sulfonato)-5,10,15- tris(pentafluorophenyl)corrole
1-Ga	C_6F_5 C_6F	5,10,15- tris(pentafluorophenyl)corrolato- gallium(III) monopyridine

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Abbreviation	Structure	Name
2-Ga	C_6F_5 C_6F	2,17-bis(sulfonato)-5,10,15- tris(pentafluorophenyl)corrolato- gallium(III) monopyridine
1-Sn	C_6F_5 C_6F_5 C_6F_5 C_6F_5	5,10,15- tris(pentafluorophenyl)corrolato- tin(IV) chloride
2-Sn	C_6F_5 C_6F	2,17-bis(sulfonato)-5,10,15- tris(pentafluorophenyl)corrolato- tin(IV) hydroxide
2-Mn	C_6F_5 C_6F_5 C_6F_5 N N C_6F_5 SO_3H	2,17-bis(sulfonato)-5,10,15- tris(pentafluorophenyl)corrolato- manganese(III)
1-In	$\begin{bmatrix} C_6F_5 \\ N C_1 N \\ I N \\ C_6F_5 \\ N N \\ N $	5,10,15- tris(pentafluorophenyl)corrolato- indium(III) chloride anion