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## Memorandum

To: Lauren Eppensteimer
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From: Lawrence A. Bottomley
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Re: UNCF-Merck Undergraduate Science Research Scholarship Report

The purpose of this memorandum is to document the achievements of **Miss Iquo Ekama Onofiok**, during her tenure as an *UNCF-Merck Undergraduate Science Research Scholarship* recipient. She has completed her studies at Georgia Tech, earning a B.S. degree in chemistry in May, 2004.

Her research productivity during the period of her scholarship was outstanding - on par with advanced graduate students in my group. She synthesized, purified and completely characterized two metalloporphyrin-based anti-microbial compounds for covalent attachment to nylon fabrics. Upon excitation with ultraviolet light, these compounds activate singlet oxygen. Microbes on the fabric are subsequently destroyed by this active oxygen species. During the latter nine months, she has focused on the synthesis and characterization of a series of alkoxy-substituted tetraphenylporphyrins that display unusual discotic and nematic phase liquid crystalline behavior. She has discovered a unique synthetic pathway to these materials and characterized their ordered assembly materials using differential scanning calorimetry, polarized light microscopy and scanning tunneling microscopy. She has presented her findings at the Southeastern Regional Meeting of the American Chemical Society as well as at the Electrochemical Society meeting (a copy of the abstract is attached). Ekama's research productivity is truly outstanding especially when one takes into consideration that she is already working independently on this project. This is a remarkable accomplishment for a third year undergraduate student.

She spent a summer at Merck on a summer internship in partial fulfillment of the requirements for her UNCF Fellowship. There she worked with an organic chemist attempting to improve the synthesis of a lead compound undergoing clinical trials. Ekama discovered a synthetic route to an important intermediate in this sequence. Her product was essentially one enantiomer, improving the overall yield of the clinically active enantiomer and reducing the number of synthetic steps to the ultimate product by

two. In short, Ekama has enjoyed remarkable success in research both at Georgia Tech and at Merck.

Ekama is motivated, intelligent, articulate, hard-working, interactive, and personable. She is well liked by her colleagues. She enjoys science, takes pride in her work, and already displays the qualities that will propel her to a leadership position. Her scientific presentations are lucid, logical and laden with content. She is poised, polished and very professional in her delivery.

I *enthusiastically* and *whole-heartedly* supported Ekama's application for medical school. She was accepted into several prestigious medical schools (including Stanford). She enrolled in the M.D.-Ph.D. program in the fall of 2005 at the University of California, Davis and is making excellent progress there. She intends to pursue a career in medical research. The quality of the medical program coupled with the research training available at UC Davis matches well with her career aspirations.

Ekama ranks among the very best undergraduates with whom I have been associated over the past twenty years. I am confident that she will become one of the very best medical researchers of her generation.

*Abstract of presentation at*
*The Electrochemical Society Meeting*
*Presentation #963*
*Quebec City, Quebec*
*May 18, 2005*

# Preparation and Properties of Mono-, Di-, Tri-, and Tetra-Octyloxyphenyl-substituted Porphyrins

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The goal of this research is the synthesis and characterization of a series of alkoxy-substituted tetraphenylporphyrins that display unusual discotic and nematic phase liquid crystalline behavior. We report herein, the synthesis and characterization of a set of substituted tetraphenylporphyrin derivatives with substituents that should promote a nematic/smectic phase transition near room temperature. Since alkyl-substituted tetraphenylporphyrins are known to be discotic phase materials, the hypothesis to be tested is whether the liquid crystalline temperature range can be significantly expanded by coupling functionality known to assemble into a nematic phase onto the alkyl chains.

A series of octyloxyphenyl-substituted porphyrins were synthesized using two different methods. Tetra(octyloxyphenyl-substituted) porphyrin was prepared from the corresponding octyloxybenzaldehyde and pyrrole using Lindsay's method. Sequentially substituted derivatives were prepared by reaction of tetra(4-hydroxyphenyl)porphyrin with 1-bromooctane. Chromatographic separation on silica gel provided pure fractions of the mono-, di-, and tri-substituted porphyrins, including the two isomers of the di-substituted product. All compounds were characterized by proton nmr spectroscopy, mass spectrometry, and electrochemistry. Ordered assemblies of these materials were characterized using differential scanning calorimetry, polarized light microscopy and scanning tunneling microscopy (STM). High-resolution images revealed uniform lamellar assemblies of porphyrins arranged side by side with interdigitated alkyl chains.

A series mono-, di-, tri-, and tetra-substituted octyloxy-cyanobiphenyl porphyrins were also synthesized by two different methods. Synthesis was accomplished by a modified Adler method: first synthesizing the aldehyde-terminated precursors containing the substituent groups, and, then fusing them together with pyrrole into a porphyrin. The reaction was accomplished successfully producing a mixture of six porphyrins with varying numbers of both substituents, but all porphyrins products being tetra-substituted. Purification and separation of the porphyrins was accomplished using column chromatography on aluminum oxide and silica gel, respectively. According to the FAB-

MS, the separation of the two di-octyloxycyanobiphenyl isomers substituted with two of each substituent was not achieved. Separation of all other non-isomeric porphyrins was successful. The synthesis of these isomeric porphyrins was achieved by reaction of each di(4-hydroxyphenyl, 4-octyloxyphenyl)porphyrin isomer with 1-bromo-8-(4-cyanobiphenyl)octane.

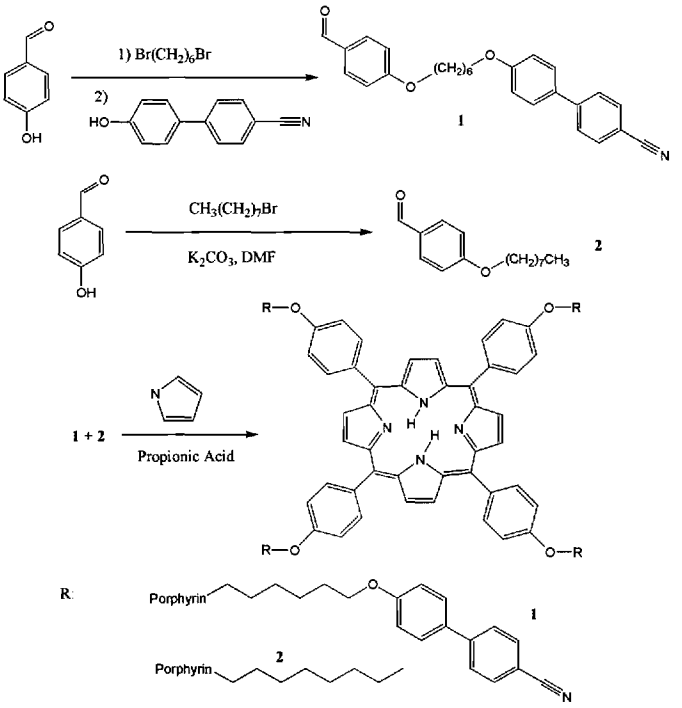


**Figure 1.** Synthetic scheme for the synthesis of a series of para-substituted tetraphenyl porphyrins with octyloxy-cyanobiphenyl substituents to promote discotic and nematic phase behavior near ambient temperature.