

**Layer-by-Layer Fabrication of Porphyrin Multilayer Films via
Copper(I)-Catalyzed Azide-Alkyne Cycloaddition: Film Properties and
Applications in Dye-Sensitized Solar Cells**

by

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Abstract

Solar energy may be the only renewable source of energy available to the human race that could provide the energy we require while at the same time minimizing negative impacts on the planet and population. These characteristics may be instrumental in diminishing the potential for societal conflict. In order for photovoltaic devices to succeed on a global scale, research and development must lead to reduced costs and/or increased efficiency. Dye-Sensitized Solar Cells (DSSCs) are one class of next-generation photovoltaic technologies with the potential to realize these goals.

Herein, I describe efforts towards developing a new light harvesting array of chromophores assembled on oxide substrates using copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC or 'click' chemistry) that could prove useful in improving DSSC performance while maintaining low cost and simple fabrication. Specifically, molecular multilayers of porphyrin-based chromophores have been fabricated via sequential self-limiting CuAAC reactions to generate multilayered light harvesting films. Films of synthetic porphyrins, perylenes, and mixtures of the two are constructed in order to highlight the versatility of this molecular layer-by-layer (LbL) technique. Characterization in the form of electrochemical techniques, UV-Visible spectroscopy, infrared spectroscopy (IR), and water contact angle all indicate that the films are reacting as expected. Film thickness and morphology are investigated using X-ray reflectivity showing that film growth displays a high degree of linearity, while the roughness increases with thickness. Growth angles based on the porphyrin plane are estimated via a comparison of molecular models and experimentally determined thickness measurements. A more finite measurement of growth angle (and as a result the primary bonding mode) is determined by grazing angle IR spectroscopy. Blocking layer studies suggest that the films could be useful as a self-passivating layer in DSSCs to reduce recombination effects and improve DSSC device efficiency.

Porphyrin light harvesting films assembled on ITO show a cathodic photocurrent when assembled in a DSSC device. Cobalt^{2+/3+} and I/I₃⁻ redox mediators are commonly used in DSSCs as an electron shuttle. Experiments with cobalt^{2+/3+} redox mediators as well as I/I₃⁻ provide an initial benchmark for the performance of unoptimized solar cells with multilayered porphyrin sensitizer films. Devices operating with I/I₃⁻ show the

largest photocurrents, but low open circuit potentials. Devices using cobalt^{2+/3+} result in lower photocurrents but greater operating potentials than I⁻/I₃⁻. For all redox mediators tested, photocurrent increases with the addition of porphyrin layers beyond a monolayer. However, photocurrent reaches a maximum value at a point greater than one layer, after which it decreases. This demonstrates that multilayered porphyrin light harvesting films can be beneficial to improving DSSC performance but optimal film thickness (number of layers) is dependent on the redox mediator.

This facile and versatile technique for creating molecular multilayer films may have implications in light harvesting materials, sensors, and molecular electronics. It could be amenable to large scale roll-to-roll processing which would be advantageous for applications requiring large surface area depositions. In summary, these techniques allow for simple and rapid evaluation of numerous molecular components in light harvesting arrays that could lead to much needed breakthroughs in solar applications.