



Abstract MA2018-01 **972**



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Tetrapyrrolic Surface Coatings for Applications in Photoelectrosynthetic Fuel Production

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Abstract

Hybrid materials capable of linking light capture and conversion technologies with the ability to drive reductive chemical transformations are attractive as components in photoelectrosynthetic cells. [1] We have recently reported methods of applying molecular surface coatings composed of metalloporphyrin redox catalysts onto solid-state substrates that are either conductive or semi-conductive. [2-5] The metalloporphyrin catalysts used in this work are capable of activating electrochemical transformations including the conversion of protons to hydrogen and carbon dioxide to carbon monoxide. In one approach, metalloporphyrin precursors are prepared via a novel synthetic strategy to yield a macrocycle with a pendent 4-vinylphenyl surface attachment group at the beta-position of the porphyrin ring structure. [2] This modification allows use of a photo-induced immobilization chemistry to attach intact metalloporphyrins to a range of (semi)conducting surfaces. In addition, we have shown that initial application of thin-film polymer surface coatings can provide a molecular interface for assembling metalloporphyrin catalysts in a subsequent wet chemical treatment step. [3] In this presentation, spectroscopic characterization of these materials coupled with electrochemical analysis will be presented. These findings offer an improved understanding of the structure and function relationships governing this class of materials.

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2. D. Khusnutdinova, A. M. Beiler, B. L. Wadsworth, S. I. Jacob, G. F. Moore, *Chem. Sci.*, **8**, 253-259 (2017); **DOI:** 10.1039/c6sc02664h
3. A. M. Beiler, D. Khusnutdinova, B. L. Wadsworth, G. F. Moore, *Inorg. Chem.*, **56**, 12178 (2017); **DOI:** 10.1021/acs.inorgchem.7b01509
4. A. M. Beiler, D. Khusnutdinova, S. I. Jacob, G. F. Moore, *ACS Appl. Mater. Interfaces*, **8**, 10038-10043 (2016); **DOI:** 10.1021/acsami.6b01557
5. B. L. Wadsworth, A. M. Beiler, D. Khusnutdinova, S. I. Jacob, G. F. Moore, *ACS Catal.* **6**, 8048-8057 (2016); **DOI:** 10.1021/acscatal.6b02194

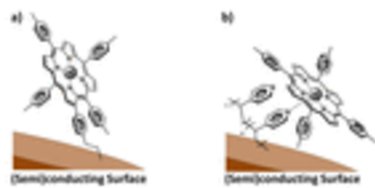


Figure 1. Depiction of metalloporphyrin catalysts grafted to a (semi)conducting surface using either a) a direct attachment strategy or b) application of an initial thin-film polymer surface coating.

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Figure 1

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