

## Polymeric Porphyrins for Solar Photovoltaics and Solar Photochemistry

Carl C. Wamser,<sup>1</sup> Nicholas U. Day,<sup>1</sup> Chenyi Wang,<sup>1</sup> and Michael G. Walter<sup>2</sup><sup>1</sup>Department of Chemistry, Portland State University, Portland, OR 97207-0751<sup>2</sup>Department of Chemistry, University of North Carolina, Charlotte, Charlotte, NC 28223

We have been investigating conductive porphyrin polymers as the nanostructured base for novel inverse dye-sensitized solar cells. More recently, we have been investigating these materials as solar photocatalysts by incorporating within the porphyrin units pyridine groups and transition metals, notably Co and Fe, as catalytic sites.

Meso-tetra(4-aminophenyl)porphyrin (TAPP) undergoes oxidative electropolymerization to generate a thin electrode film of nanofibrous conductive polymer (poly-TAPP, Figure 1a). The individual porphyrin units are interconnected by linkers of phenazine/dihydrophenazine (Figure 1b), which are redox active and modulate the electronic conductivity. We have used poly-TAPP to construct an inverse DSSC by adding a surface layer of covalently bound complementary dye (TCPP) and filling the pores with an n-type semiconductor such as ZnO, TiO<sub>2</sub>, or PCBM. These act as solar cells with modest efficiency.[1]

When visualized as a solar photocatalyst, poly-TAPP offers the advantages of strong light absorption, high surface area, electronic conductivity, and the ability to tune photocatalytic properties by relatively straightforward modifications of the porphyrin units, either with substituents or metal ions. Cobalt porphyrins have been used as electrocatalysts for water reduction[2,3] as well as for CO<sub>2</sub> reduction[4]. In addition, there are recent reports of CO<sub>2</sub> photocatalytic reduction in aqueous solution using pyridine as the key redox-active species.[5] We are modifying poly-TAPP so that the surface porphyrin sites include pyridine units and/or cobalt metalloporphyrins. These materials will be investigated for photocatalytic efficacy for proton or CO<sub>2</sub> reduction.

[1] Walter, M. G.; Wamser, C. C. "Synthesis and Characterization of Electropolymerized Nanostructured Aminophenylporphyrin Films". *J. Phys. Chem. C*, 114, 7563-7574 (2010).

[2] Kellet, R. M.; Spiro, T. G. "Cobalt(I) Porphyrin Catalysis of Hydrogen Production from Water". *Inorg. Chem.*, 24, 2373-2377 (1985).

[3] Kellet, R. M.; Spiro, T. G. "Cobalt Porphyrin Electrode Films as H<sub>2</sub> Evolution Catalysts". *Inorg. Chem.* 24, 2378-2382 (1985).

[4] Morris, A. J.; Meyer, G. J.; Fujita, E. "Molecular Approaches to the Photocatalytic Reduction of Carbon Dioxide for Solar Fuels". *Accts. Chem. Res.*, 42, 1983-1994 (2009).

[5] Cole, E.; Lakkaraju, P. S.; Rampulla, D. M.; Morris, A. J.; Abelev, E.; Bocarsly, A. B. "Using a One-Electron Shuttle for the Multielectron Reduction of CO<sub>2</sub> to Methanol: Kinetic, Mechanistic, and Structural Insights". *J. Amer. Chem. Soc.*, 132, 11539-11551 (2010).

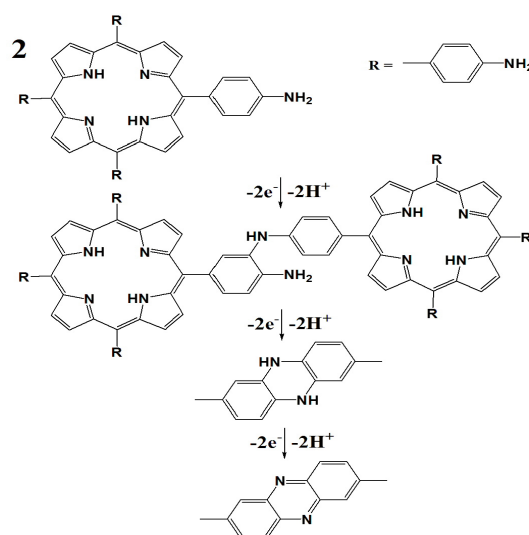
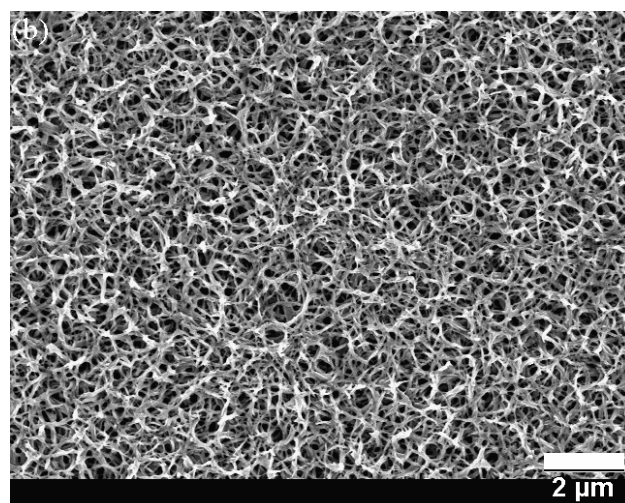


Figure 1. a) SEM of poly-TAPP generated by 15 cyclic voltammetric scans of 0.15 mM TAPP in CH<sub>2</sub>Cl<sub>2</sub> with 5% (v:v) pyridine between 0.0 - 1.0 V (vs. Ag/AgCl). b) Various forms of the linkers between TAPP units.