

Self-Assembly of Porphyrin Nanostructures

Casey Karler,[§] Leanne Alarid,[§] Kaifu Bian,[§] Hattie Schunk,[§] Brian Billstrand,[§] and Hongyou Fan^{†,§}

[†]*The University of New Mexico Center for Micro-Engineered Materials, Department of Chemical and Biological Engineering, Albuquerque, New Mexico 87133* and [§]*Sandia National Laboratories, Advanced Materials Laboratory, Albuquerque, New Mexico, 87106*

Abstract

Porphyrins are a class of optically active biomacromolecular compounds which play critical roles in biological energetic processes, including photosynthesis, and also serve as colorful pigments covering a wide range of the visible spectrum. In an effort to utilize these versatile porphyrins in advanced materials development, organized porphyrin nanostructures with photoactive properties have been obtained through a surfactant-assisted non-covalent self-assembly method (e.g., π - π interactions, metal-ligand coordination) through cooperative interactions of the porphyrin building blocks including zinc meso-tetra(4-pyridyl)porphine, tin meso-tetra(4-pyridyl)porphine, and meso-tetra(4-pyridyl)porphine. This method takes advantage of porphyrin insolubility when deprotonated in solution due to acid-base neutralization, thereby forcing them into surfactant micelles which stimulates self-assembly and eventually yields well-defined controllable external morphology. Electron microscopy characterization as well as X-ray diffraction confirmed controlled self-assembly of the macrocyclic building blocks into ordered nanostructures with controlled morphologies, such as nanorods, nanocubes, nanocylinders, nanooctahedron, nanowires and nanofibers. Investigation of variable parameters influencing the growth process showed that the final product morphology is determined by reaction conditions including pH, reaction time, injection speed, precursor concentrations, and surfactant types. Optical characterizations using UV-Vis spectroscopy and fluorescence imaging and spectroscopy show enhanced collective optical properties over the individual chromophores, favorable for exciton formation and transport. With active and responsive optical properties, these porphyrin nanostructures look to serve as promising components for a wide range of practical applications including sensing, optics, nanoelectronics, diagnostics, solar cells, photocatalysis, and pollutant photodegradation.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.