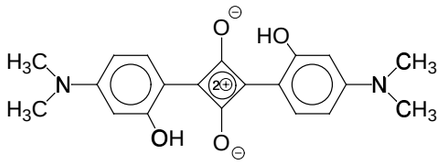
The Relationship Between Squaraine Dye Surface Morphology and Sensitization Behavior on SnS_2 Electrodes

Norihiko Takeda and B. A. Parkinson*

Department of Chemistry
Colorado State University
Fort Collins, CO 80523-1872

Bis(4-dimethylamino-2-di-hydroxyphenyl)squaraine, (1-1 OHSQ) and Bis(4-methyl-hexyl-amino-phenyl) squaraine, (1-6 SQ) dyes

Figure 1 Structure of 1-1 OHSQ



were deposited on van der Waals surfaces of SnS_2 single crystals by two methods, dipping in a dye solution and evaporation of dye solution. Dye morphologies and photosensitization properties on the same samples were studied with atomic force microscopy (AFM) and photoelectrochemical measurements. AFM experiments in air revealed two distinct morphologies of dye aggregates and photocurrent measurements on the same samples in aqueous electrolytes showed correspondingly different photocurrent spectra. Three-dimensional needle-shaped 1-1 OHSQ aggregates aligned along crystal directions and showed a broad excitation spectrum that extended into the near-IR region with a peak around 800 nm. In contrast, flat aggregates, presumably consisting of monolayers of 1-1 OHSQ molecules, had a sensitization maximum around 680 nm. Both peaks were red-shifted from absorption peak of 1-1 OHSQ in bulk dichloromethane solution. Spectral differences between these dye aggregates are discussed in terms of intermolecular interactions. (Figure 2)

The 1-6 SQ dye had a different shift of the adsorption max on the surface from the sensitization maximum measured on the same SnS_2 sample. Measurement of the absorbed light and the quantum yield for sensitization showed that the quantum yield per absorbed photon approached 100% in many cases. Photocurrent-voltage curves showed onsets of photocurrent well after the flatband potential and were less steep than theoretically predicted for a high photocurrent yield system**.**

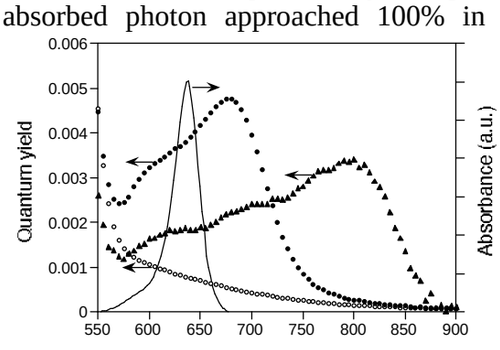


Figure 2. Photocurrent quantum yield action spectra measured at +0.7 V vs SCE bias in aqueous 1.0 mol L^{-1} LiCl electrolyte containing 10 mmol L^{-1} hydroquinone as a regenerator. Open circles, bare SnS_2; closed circles, 1-1 OHSQ on SnS_2 deposited by dipping for 12 min, closed triangles, ca. 1 ML equivalent amount of 1-1 OHSQ on SnS_2 deposited by dropping method. Quantum yields were calculated per incident photon flux. Absorption spectrum of 1-1 OHSQ in dichloromethane solution is shown for comparison.