

PHOTOCURRENT GENERATION IN NON-COVALENTLY ASSEMBLED THIN FILMS

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Photocurrent-generating multilayered thin films were fabricated by non-covalent assembly based on metal ligand binding interactions. The films contain an underlying self-assembled monolayer (SAM) consisting of a decanethiol-linked covalently to an organic ligand (e.g., 4-hydroxy-2,6-dicarboxypyridine, 4-hydroxy-2,6-dicarboxybenzene, 4-hydroxy-pyridine or imidazole) as shown in Figure 1. Metal ions such as Cu(II), Co(II) and Fe(III) were deposited on the SAM forming a second layer. Deposition of subsequent layers was achieved by the incorporation of the appropriate organic ligand containing light absorbing pyrene chromophores (Figure 2). These multilayered films were characterized by contact angle measurements, quartz crystal gravimetry, ellipsometry, grazing incidence IR, cyclic voltammetry and impedance spectroscopy following deposition of each layer in the film. These measurements confirmed the formation of relatively well-ordered, stable layers. The films were incorporated into a three-electrode system in which the films on gold constituted the working electrode, the counter electrode was a platinum wire and the reference electrode was SCE. Photoexcitation at 350 nm, i.e., into the absorption band of the pyrene group, resulted in the generation of both cathodic and anodic photocurrent in the presence of methyl viologen, depending on the applied potential, and anodic current in the presence of the sacrificial electron donor, triethanolamine. The identity of the metal ions in the film had a significant effect on both the magnitude of the photocurrent and whether it was anodic or cathodic. For example, the magnitude of cathodic photocurrent generation at an applied potential of -0.2 V (vs. SCE) for films (as shown in Figure 2) with Cu(II) ions increases from 15 nA/cm² for a film with one layer of pyrene molecules to 65 nA/cm² after deposition of three layers of pyrene molecules.

Figures:

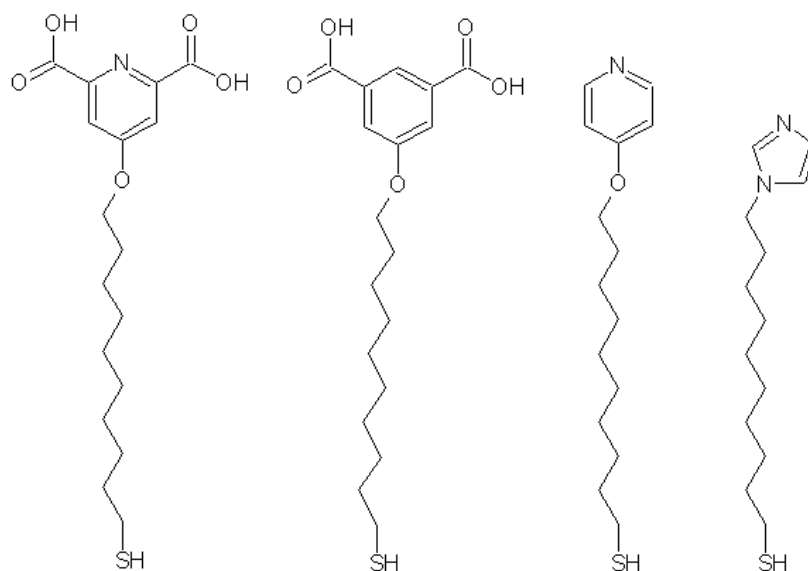


Figure 1. Structure of compounds used for preparation of underlying SAMs

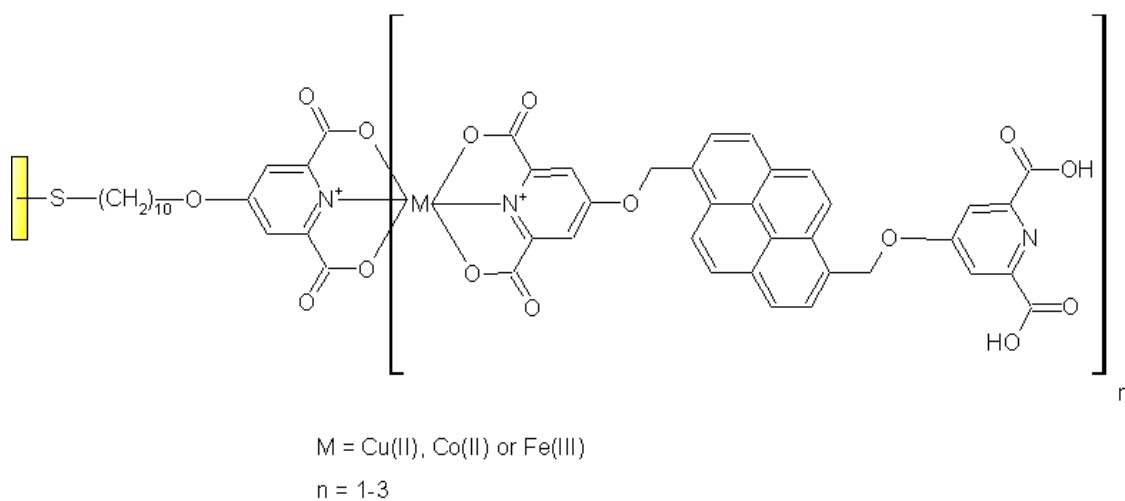


Figure 2. An example of multilayered thin films with 4-hydroxy-2,6-dicarboxypyridine ligands.