

Non-Covalent Assembly of a Photoswitchable Surface

Christopher G. F. Cooper,* John C. MacDonald,* Ernesto Soto, and W. Grant McGimpsey*

Department of Chemistry and Biochemistry, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

Received October 25, 2003; E-mail: wgm@wpi.edu

We recently reported a noncovalent strategy for the fabrication of highly ordered thin films with the ability to generate electric current upon irradiation. In these systems, multiple layers of organic ligands are assembled by complexation with layers of transition-metal ions such as Cu(II).¹ Our intention in undertaking this multilayer approach is to show that the construction of complex, multicomponent supramolecular devices can be achieved noncovalently in considerably less time and with less effort than by covalent methods. To demonstrate its versatility, we have now applied this approach toward the construction of surfaces with photoswitchable wettability.

Control of surface wettability is currently of interest due to its importance in the fields of micro- and nanofluidics. Whitesides et al. and others have devoted considerable effort to the creation of multifunctional surfaces with variable wettability using microcontact printing techniques.^{2–5} More recently, several groups have shown that wettability can be controlled by externally applied stimuli such as light or an electric field.^{6–9} Building on these studies and our noncovalent method of assembly, we report a preliminary study in which the wettability of a multilayered surface capped with 2,2'-dipyridylethylene ligands can be switched permanently by photo-induced *cis*–*trans* isomerization.

For this work, we have assembled multilayered thin films **I** and **II**, as shown in Figure 1. Each film consists of a 2,2'-dipyridylethylene light absorbing group coupled to a gold surface via metal–ligand interactions. These films were fabricated by self-assembly of 4-[(10-mercaptodecyl)oxy]pyridine-2,6-dicarboxylic acid on a clean gold surface, followed by the deposition of Cu(II) ions (from CuBr₂) that complex with the pyridine headgroup of the previous layer, and finally, deposition of the 2,2'-dipyridylethylene ligand in either the *cis* (film **I**) or *trans* (film **II**) form, which serves to cap the Cu(II) ions.

Conductivity, impedance, contact angle, and grazing incidence IR experiments were carried out on films **I** and **II** after the addition of each layer and confirmed the ordered deposition of each component. Conductivity values (CV) for both **I** and **II** obtained in an aqueous solution of K₃[Fe(CN)₆] change as the individual components are deposited sequentially onto the gold surface. The CV of the bare gold surface shows the Fe³⁺/Fe²⁺ redox peaks for oxidation and reduction of ferricyanide,⁹ whereas deposition of the pyridine-capped decanethiol yields conductivity values (measured in the range –0.5 to +0.6 V versus SCE) that indicate the formation of an insulating monolayer with few defects. After the monolayer is exposed to a solution of Cu(II) ions, the CV of the film is nearly identical to that of bare gold with only a small decrease in peak current. This result indicates that the Cu(II) ions promote tunneling of electrons between the gold surface and the solution. Deposition of the dipyridylethylene ligands again results in attenuated conductivity consistent with formation of an insulating layer on the surface.

These results, in addition to impedance observations, are consistent with our previous studies of multilayered films. Contact

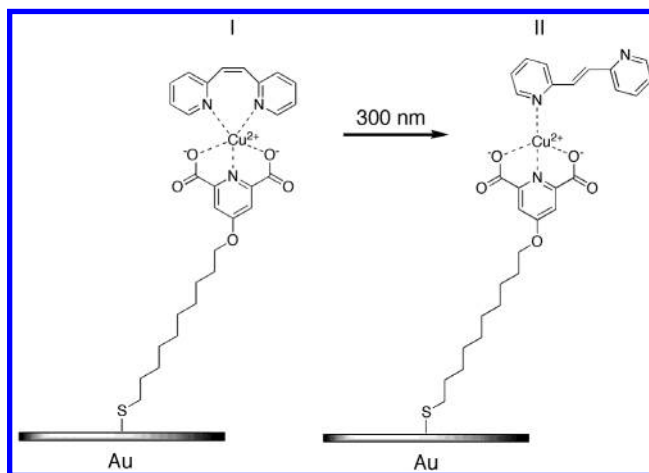


Figure 1. Structures of thin films **I** and **II**. **I** can be converted to **II** by irradiation with 300-nm light.

Table 1. Contact Angle Measurements for Films **I** and **II**

film	contact angle (deg)
gold	76 ± 1.0
film I	
component 1 (pyridyl-capped decanethiol)	76.0 ± 1.5
component 2 (Cu(II) ions)	58.0 ± 2.0
component 3 (<i>cis</i> -2,2'-dipyridylethylene)	76.5 ± 2.5
film II	
component 3 (<i>trans</i> -2,2'-dipyridylethylene)	63.5 ± 0.5
film I irradiated	57.0 ± 2.0
film II irradiated	64.0 ± 2.0

angle measurements shown in Table 1 and IR spectra (not shown) also confirm that substantial changes in the surface occur following addition of each layer. In particular, the IR measurements show conclusively the presence of each of the added layers. Conductivity, impedance, and IR data are available as Supporting Information.

Deposition of *cis*- and *trans*-dipyridylethylene leads to differences in the surface wettability with the *cis* isomer providing a more hydrophobic surface as determined from contact angle measurements. The difference in contact angle of ~13° between **I** and **II** is greater than that reported for a variety of photoisomerizable thin films that typically exhibit changes of ca. 9°. In addition, the CV results indicate that the *cis* capped surface is less conductive than the *trans* capped surface. Recalling that impedance measurements indicate well-ordered films in each case and that IR studies confirm the presence of the dipyridylethylene in each film, the difference in surface hydrophobicity can be attributed to differences in the electrostatics of the two surfaces that arise from different orientations of the two isomers. Molecular modeling by our group and previous studies by others involving nickel–dipyridylethylene complexes¹⁰ indicate that the *cis* isomer forms a symmetrical bidentate Cu(II) complex (Figure 1) that efficiently “caps” the metal ion, producing a hydrophobic packing arrangement on the surface. The *trans* isomer, however, is not able to form a stable bidentate

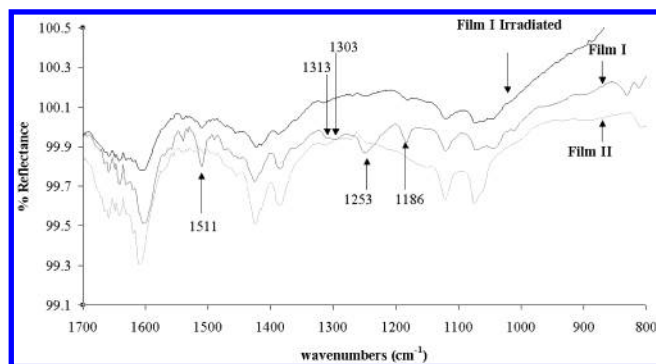


Figure 2. Grazing angle IR spectra of films **I**, **II**, and irradiated **I**.

complex because of its elongated structure. Although we have not yet determined the mode of binding, the *trans* isomer is likely monodentate, as shown in Figure 1. The structure shown in Figure 1 helps explain the enhanced wettability provided by this isomer because the Cu(II) ion in this case is not completely coordinated and, therefore, is free to complex with water. The uncoordinated pyridine ring also is free to bind water via hydrogen bonding at the ring nitrogen. Impedance measurements on **II** in fact show elevated capacitance values for the *trans* capped system, which indicates that diffusion occurs between the solution and the layer of metal ions. Further support for the binding arrangement described is provided by experiments carried out with *cis*- and *trans*-stilbene, which could not be deposited on the Cu(II) layer.

The contact angle, CV, impedance, and IR data also help to characterize the changes that occur following photoexcitation of the films. Exposure of **I** to 300 nm irradiation in chloroform¹¹ in the presence or absence of oxygen results in a substantial decrease in the contact angle, from 76.5° to 57°, a change that is consistent with *cis*–*trans* isomerization. We note that the contact angle obtained is somewhat smaller than that of unirradiated **II**. The smaller angle is likely a result of different packing arrangements in the films. Also, the conductivity of **I** increases following irradiation so as to be nearly identical to that of unirradiated **II**, while impedance measurements indicate that the irradiated film remains a well-ordered system. The clearest confirmation of isomerization of **I** is provided by IR measurements. Figure 2 shows the IR spectra of unirradiated **I** and **II** and **I** following irradiation. While the IR absorption bands that are normally used to distinguish between *cis*- and *trans*-dipyridylethylenes lie at frequencies lower than 1000 cm^{−1}, the sensitivity of our grazing incidence IR instrument is low in this region. There are several aromatic stretching frequencies that absorb above 1000 cm^{−1}, however, that are found in the spectrum of unirradiated **I** but are absent in the spectrum of **II**. In particular, **I** absorbs strongly at 1511 cm^{−1} and less intensely at 1313, 1303, 1253, and 1186 cm^{−1}, while **II** does not. Following irradiation of **I**, these bands are attenuated, and the spectrum of the irradiated film resembles closely that of **II**.

Previous studies on the solution photochemistry of 2,2′-dipyridylethylenes report quantum yields for *cis*–*trans* and *trans*–

cis photoisomerization equal to 0.84¹² and 0.12,¹³ respectively. Irradiation of **II**, however, does not yield any *cis* product as indicated by the lack of change in the CV, IR, and contact angle data. Failure of the *trans*-dipyridylethylene units to undergo photoisomerization to the *cis* isomers could be caused by ordered packing of the *trans*-dipyridylethylene in **II** that sterically inhibits the structural reorganization necessary for *trans*–*cis* isomerization to occur. The CV and impedance measurements of **II** indicate that the dipyridylethylene headgroups in fact are well-ordered in **II**. Another contributing factor could be that the solution photochemistry of *trans*-2,2′-dipyridylethylene differs from that of the Cu(II) complex on the surface.

The system described here demonstrates that noncovalent multilayer assembly provides a convenient means to fabricate highly ordered thin films with wettability that can be switched. Although the wettability of surfaces functionalized with dipyridylethylene is not reversible, this work provides proof-of-concept that chromophores with photoswitchable molecular structures can be attached noncovalently to surfaces, that noncovalent multilayer films terminated with such chromophores have well-ordered surface structures, that the wettability of such surfaces can be controlled photochemically, and that such multilayer thin films are stable before and after photoinduced changes in structure at the surface. We currently are using this methodology to incorporate photochromic molecules into similar noncovalent multilayer films to provide reversible switching of wettability. We expect that such systems will have broad application beyond wettability by providing new opportunities to control a variety of important surface-based processes such as metal-centered redox chemistry and heterogeneous catalysis.

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Supporting Information Available: Synthesis, film assembly methods, and characterization data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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