A Non-Covalent Strategy for the Assembly of Supramolecular Photocurrent-Generating Systems

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Incorporation of molecular components for light harvesting and charge separation into artificial photosynthetic systems has encountered considerable hurdles. While many organic systems have been developed that exhibit reasonable light-harvesting efficiencies and much has been learned about the energy transfer, electron transfer, and charge separation processes that occur during photosynthesis, combining all of this knowledge to create a system that can efficiently convert photons to electrons remains an unfulfilled goal. Of primary concern is the creation of a highly organized supramolecular scaffold that optimizes light-harvesting efficiency and transfer rates, a need that is satisfied by the protein framework in natural photosynthetic systems.

In this communication, we describe preliminary studies that build on the results reported by several groups working in disparate fields.[1-14] Imahori et al.[1-3] have fabricated self-assembled monolayers (SAMs) on gold by depositing a covalently linked, multicomponent molecule containing alkanethiol, ferrocene, porphyrin, and C_{60} subunits. These SAMs have both light-harvesting and charge separation character as evidenced by the generation of current upon photoexcitation of the SAM in the presence of methyl viologen. Kimura and co-workers[7,8] also observed photocurrent generation following excitation of a SAM on gold that consists of an alkanethiol linked covalently to a helical peptide containing a carbazole group at the terminal residue. While the photocurrent-generating efficiency reported for these systems was promising, the synthetic effort involved in producing such multifunctional molecules was likely considerable.

In separate work, Mallouk,[9,10] Bard,[11,12] and others have studied the formation of multilayer, multicomponent thin films on gold via noncovalent interactions between sulfur-containing ligands and metal ions. In one study, Bard et al.[12] reported thin films produced by the repeated sequential deposition of mercaptoalkanoic acids and Cu(II) ions. The ability to construct multilayered thin films in this way suggested to us that it may be possible to noncovalently assemble complex systems such as those studied by Imahori and avoid the many complications commonly encountered in large molecule covalent synthesis.

To this end, we have fabricated two types of photocurrent-generating thin films on a gold surface as shown in Figure 1. SAM **I** consists of a pyrene chromophore coupled to a helical peptide that is attached to a gold surface[14] through an alkyl disulfide linker. SAM **I** is similar to systems reported previously by Kimura et al.[7,8] which exhibit photocurrent generation. SAM **I** served as a benchmark for films **II** and **III** (also shown in Figure 1), which are multilayered systems in which the light absorbing group (pyrene) is noncovalently coupled to a gold surface via metal–ligand complexation. These systems are noncovalently assembled by sequential deposition of three or more components. In film **II**, three components are used: decanethiol linked to a 4-pyridyl-2,6-dicarboxylic acid ligand; Cu(II) ions; and a pyridyl-2,6-dicarboxylic acid ligand linked at the 4-position through a methylenyloxy group
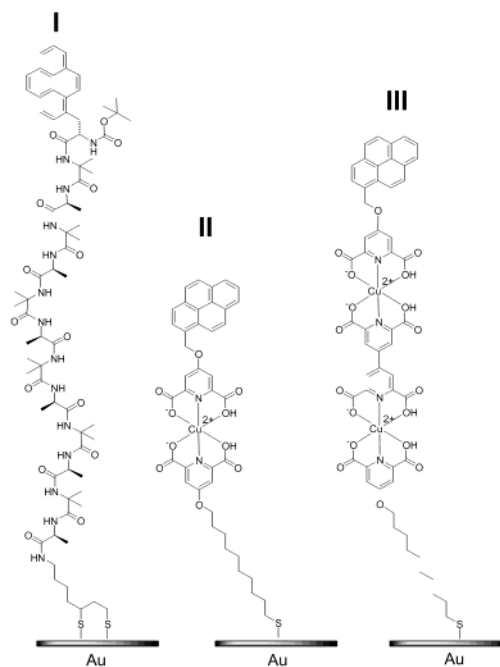

Figure 1. Structures of SAM **I**, and multilayered films **II** and **III**.

to the 1-pyrenyl chromophore. Film **III** possesses two additional noncovalently linked layers: a 4,4′-bipyridyl-2,2′6,6′-tetracarboxylic acid was deposited after Cu(II) followed by another layer of the same metal ion and finally the pyrene-containing ligand. Details of the synthesis of SAM **I**, and films **II** and **III**, and the method of deposition are provided in the Supporting Information.

Conductivity, impedance, contact angle, and IR experiments were carried out for SAM **I** and for films **II** and **III** (after the addition of each component). The conductivity (CV) results obtained for SAM **I** in an aqueous solution of $K_3[Fe(CN)_6]$ showed that following deposition of **I**, the conductivity is attenuated significantly as compared to bare gold at applied voltages in the range from −0.5 to 0.6 V versus SCE. This result as well as high impedance values indicate the formation of an ordered monolayer with few major defects, consistent with results obtained previously by Kimura et al.[7,8] for similar systems.

Conductivity and impedance values for **II** change as the individual components are deposited sequentially onto the gold surface. The CV of the bare gold surface shows the redox peaks of the ferricyanide,[8] whereas deposition of the pyridine-capped decanethiol again yields conductivity and impedance values (measured in the range from −0.5 to +0.6 V versus SCE) that suggest the formation of an ordered insulating monolayer. (We note that similar results were obtained when the ferricyanide was replaced with methyl viologen.) 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. There is also a
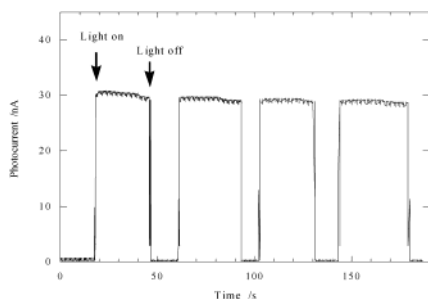
Figure 2. Photocurrent generated following exposure of **III** to ~0.1 mW at 350 nm at constant applied voltage = 0 V versus SCE. Photocurrent is expressed as nA/cm^2.

concomitant decrease in impedance. Deposition of the pyrene-containing ligand again results in attenuated conductivity and increased impedance. Similar conductivity and impedance behaviors were obtained for film **III** upon deposition of the second layer of Cu(II) ions and capping with the pyrene-containing ligand.

Contact angle measurements and IR spectra confirm that substantial changes in the surface occur following the addition of each layer. The changes in contact angles mirror the changes in hydrophobicity of each of the deposited components, while the IR measurements show conclusively the presence of each of the added layers. Conductivity, impedance contact angle, and IR data are available as Supporting Information.

The electrochemical changes that take place with the sequential exposure of the surface to each component in **II** and **III** indicate that in addition to a possible electronic role, the Cu(II) ion aids in organizing and stabilizing the film, probably by complexing with the pyridyl and bipyridyl ligands present (Figure 1). That deposition of the pyrene-containing ligand in **II** and **III**, as well as the bipyridyl ligand in **III**, results in significantly attenuated current values and enhanced impedance, indicates that the deposition of Cu(II) and subsequent addition of ligand results in a specific Cu(II)–ligand interaction rather than a nonspecific deposition. If the latter occurred, a significant amount of disorder in the film causing substantial defects and different CV behavior could be expected. One of us has shown previously that complexation of Cu(II) by 2,6-pyridinedicarboxylic acid groups results in the formation of stable complexes in which the metal ion is fully encapsulated between two of the ligands.[15]

Photoexcitation of SAM **I** and multilayered films **II** and **III** in the presence of methyl viologen by an unfocused, unfiltered, omnidirectional, 20 W, 350 nm Rayonet lamp (power incident on sample ~0.1 mW) causes generation of a cathodic photocurrent in the range 5–30 nA/cm^2 with **II** and **III** consistently exhibiting higher values than SAM **I** (5–10 nA/cm^2 for SAM **I**; 10–30 nA/cm^2 for **II** and **III**). Figure 2 shows the change in photocurrent for **III** as a result of alternately shuttering and unshuttering the light source. A photocurrent of 30 nA/cm^2 is comparable to, although somewhat smaller than that reported by Imahori and co-workers[7,8]

(~50–100 nA/cm^2) and represents a quantum efficiency of ~1%. In addition to enhanced current generation, **II** and **III** also appear to possess greater stability than SAM **I**. While repeated photoexcitation of SAM **I** eventually results in degradation of the film and loss of photocurrent after approximately 10 cycles, **II** and **III** did not show any decrease in current over several hours of alternating light/dark cycles.

We note that neither **II** nor **III** is an optimized system because there is a mismatch between the spectral output of the excitation lamp and the absorption spectrum of the pyrene chromophore. We are currently investigating other complexing ligands and metal ions as well as the effect that the distance of separation between pyrene and the gold surface has on the magnitude of the photocurrent. (The current systems range from 2 to 3 nm in distance between pyrene and the surface according to modeling studies.) Clearly, however, these preliminary results indicate that this noncovalent strategy is a potentially efficient and facile means by which to fabricate complex modular multicomponent supramolecular systems for device functions, including conversion of incident light to electric current.

Supporting Information Available: Synthetic details for SAM **I**, **II**, and **III**, methods and results for CV, impedance, IR, contact angle, photocurrent experiments, and preparation of SAMs and multilayered films (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Imahori, H.; Nishimura, Y.; Norieda, H.; Karita, H.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *Chem. Commun.* **2000**, 661–662.
(2) Imahori, H.; Norieda, H.; Nishimura, Y.; Yamazaki, I.; Higuchi, K.; Kato, N.; Motohiro, T.; Yamada, H.; Tamaki, K.; Arimura, M.; Sakata, Y. *J. Phys. Chem. B* **2000**, *104*, 1253–1260.
(3) Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukumuzi, S. *J. Am. Chem. Soc.* **2001**, *123*, 100–110.
(4) Uosaki, K.; Kondo, T.; Zhang, X.; Yanagida, M. *J. Am. Chem. Soc.* **1997**, *119*, 8367–8368.
(5) Kondo, T.; Ito, T.; Nomura, S.; Uosaki, K. *Thin Solid Films* **1996**, *284–285*, 652–655.
(6) Kondo, T.; Yanagida, M.; Nomura, S.; Ito, T.; Uosaki, K. *J. Electroanal. Chem.* **1997**, *438*, 121–126.
(7) Morita, T.; Kimura, S.; Kobayashi, S.; Imanishi, Y. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1535–1540.
(8) Morita, T.; Kimura, S.; Kobayashi, S.; Imanishi, Y. *J. Am. Chem. Soc.* **2000**, *122*, 2850–2859.
(9) Hong, H.-G.; Mallouk, T. E. *Langmuir* **1991**, *7*, 2362–2369.
(10) Yang, H. C.; Aoki, K.; Hong, H.-G.; Sackett, D. D.; Arendt, M. F.; Yau, S.-L.; Bell, C. M.; Mallouk, T. E. *J. Am. Chem. Soc.* **1993**, *115*, 11855–11862.
(11) Ogawa, S.; Hu, K.; Fan, F.-R. F.; Bard, A. J. *J. Phys. Chem. B* **1997**, *101*, 5707–5711.
(12) Brust, M.; Blass, P. M.; Bard, A. J. *Langmuir* **1997**, *13*, 5602–5607.
(13) Moore et al. have deposited helical peptides horizontally on gold surfaces. Strong, A. E.; Moore, B. D. *Chem. Commun.* **1998**, 473–474. Strong, A. E.; Moore, B. D. *J. Mater. Chem.* **1998**, *9*, 1097–1105.
(14) Fox et al. have investigated optical and electrochemical properties of SAMs in which pyrene chromophores are coupled to gold surfaces. Fox, M. A.; Whitesell, J. K.; McKerrow, A. J. *Langmuir* **1998**, *14*, 816–820. Reese, R. S.; Fox, M. A. *Can. J. Chem.* **1999**, *77*, 1077–1084.
(15) MacDonald, J. C.; Dorrestein, P. C.; Pilley, M. M.; Foote, M. M.; Lundburg, J. L.; Henning, R. W.; Schultz, A. J.; Manson, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 11692–11702.