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Supramolecular Assembly on Surfaces: Manipulating Conductance in Noncovalently Modified Mesoscale Structures

Grace M. Credo,[†] Andrew K. Boal,[‡] Kanad Das,[‡] Trent H. Galow,[‡] Vincent M. Rotello,*[,‡] Daniel L. Feldheim,*[,†] and Christopher B. Gorman*[,†]

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695, and Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

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Metal−molecule−metal junctions have been used to elucidate single-molecule properties in organic monolayers that are applicable in molecular electronics. For example, pore-based sandwich structures,[1,2] mechanical break junctions,[3] and Hg drop electrode top contacts[4,5] have been used to characterize the current−voltage properties of organic monolayers. Studies have also employed scanning tunneling microscopy (STM)[6,7] and conducting atomic force microscopy (cAFM)[8] to probe the current−voltage properties of molecular junctions with more limited contact areas. In particular, reports of STM studies on redox-active molecular monolayers have described the use of electroactive moieties in molecular junctions to facilitate nonlinear current−voltage behavior.[9] In a recent example, the nonlinear current−voltage phenomenon of negative differential resistance (NDR) was observed in an electroactive, ferrocene-terminated self-assembled monolayer (SAM).[7] The identification of nonlinear current−voltage properties such as NDR for individual molecules expands the potential applicability of molecule-scale components from use as conductive wires to multistate molecular switches.[2,5,10]

Chemical self-assembly is an attractive method for reversibly constructing well-defined supramolecular systems with properties defined by their molecular components.[11] In particular, hydrogen bonding is a familiar construction motif in natural systems and has been used to assemble functional nanostructures, such as metal nanoparticle-based networks.[12] Applying these concepts, noncovalent self-assembly provides a potential method to install and subsequently remove electroactive functionality in molecular electronics systems. To explore this possibility, we patterned a footprint region for molecular assembly on a surface featuring a recognition-element-terminated thiol. We then used moieties featuring complementary recognition to tune the current−voltage properties of the patterned region. In this work, we used an STM tip to pattern and probe molecular assemblies and independently verified the hydrogen bond-mediated assembly process using bulk electrochemical and spectroscopic techniques.

In our experiments, the initial "binder" molecule, diacyl 2,6-diaminopyridine decanethiolate (DAP, Figure 1A) was inserted into a background monolayer of decanethiolate on Au(111) using replacement lithography. As described in previous work,[7,13] the desorption of the initial alkylthiolate SAM was induced by elevated tip bias voltages, and adsorption of the replacement thiolate from solution was conducted in a low dielectric solvent, such as dodecane. Electroactive functionalization of the monolayer was then achieved through binding of the complementary ferrocene-terminated uracil (Fc−uracil) to DAP (Figure 1B) by incubation of the sample in a Fc−uracil solution. Replacement of the electroactive Fc−uracil by a nonelectroactive dodecyl uracil (Figure 1C) "eraser" was effected by the exposure of the replacement region to a solution of dodecyl uracil.

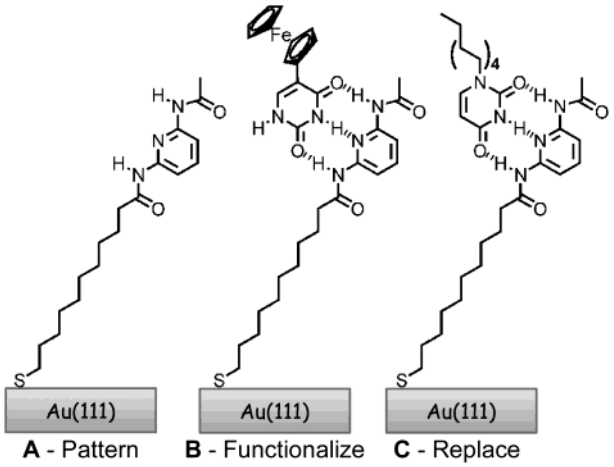

Figure 1. Formation of molecular assemblies. (A) Diacyl 2,6-diaminopyridine decanethiolate (DAP) "binder." (B) Recognition of complementary electroactive ferrocene-uracil. (C) Recognition of complementary nonelectroactive dodecyl uracil "eraser."

Selections from a more extensive series of low-current STM (Digital Instruments E, Pt:Ir tips) images of noncovalent assembly on an initial mesostructure are shown in Figure 2 (see Supporting Information for more images). In the first row, the DAP replacement region (300 nm)^2 was imaged at several bias voltages (Figure 2A−C), as indicated. The current-dependent apparent height contrast in the same area after binding of the Fc−uracil increases at much lower bias voltages (0.3−1 V) relative to the DAP region alone (Figure 2D−F). The significant increase in apparent height contrast in the STM images is attributed to the electroactive Fc−uracil/DAP assembly (Figure 1B). This is consistent with STM imaging of patterned Fc-terminated alkylthiolates observed previously.[7,13,14] STM images of the same region after exposure to dodecyl uracil (Figure 2G−I) indicated replacement of the electroactive Fc−uracil with the nonelectroactive dodecyl uracil as evidenced by the significant decrease in current-dependent apparent height contrast when compared to the DAP−uracil−Fc assembly region (Figure 2D−F). In Figure 2, the STM contrast in current−voltage properties among the different mesostructures becomes evident at bias voltages around 0.5 V (Figure 2B,E,H).

Recognition between the host−guest systems used in this study was further verified on nonpatterned assemblies by X-ray photoelectron spectroscopy (XPS, Figure 3A−C) and cyclic voltammetry

* To whom correspondence should be addressed. E-mail: chris_gorman@ncsu.edu; dan_feldheim@ncsu.edu; rotello@chem.umass.edu.
[†] North Carolina State University, Raleigh.
[‡] University of Massachusetts, Amherst.

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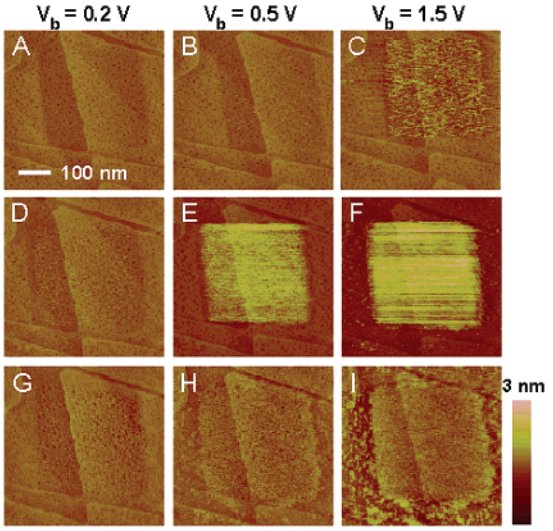

Figure 2. Low-current STM images of noncovalent assembly on a mesostructure footprint at several bias voltages (V_b), as labeled above. (A−C): Initial DAP replacement region inserted into a surrounding decanethiolate monolayer. (D−F): After binding of complementary electroactive Fc−uracil. (G−I): After binding of complementary dodecyl uracil. Setpoint current for all images was 10 pA.

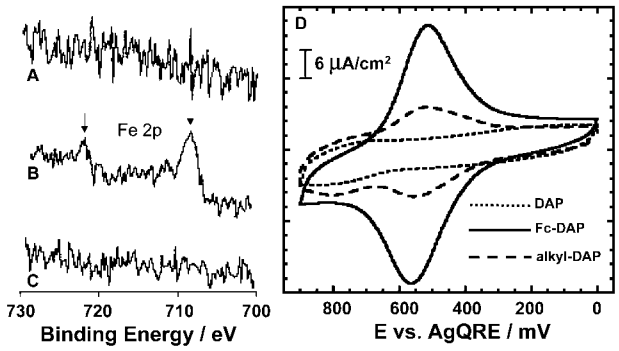

Figure 3. Bulk characterization of molecular assembly formation. XPS of (A) DAP monolayer, (B) Fc−uracil on DAP (708 and 722 eV peaks from Fe 2p), (C) iodo-labeled dodecyl uracil on DAP (iodine Auger peak at 733 eV, not shown) and (D) cyclic voltammograms (0.1 M TBAP in acetonitrile, Ag quasi-reference electrode, Pt counter, 100 mV/s, fourth cycle) of assembly.

(CV, Figure 3D). The peaks in Figure 3B at 708 and 722 eV are attributed to Fe (2p), confirming the presence of Fc−uracil on the surface. This peak disappeared with the replacement of Fc−uracil with iodo-labeled dodecyl uracil, concurrent with the appearance of the iodine Auger peak at 733 eV. Likewise, CV measurements indicated the binding of Fc−uracil to a DAP monolayer ($\Gamma = 5.3 \times 10^{-10}$ mol/cm^2) and its subsequent replacement by dodecyl uracil (Figure 3D). Further discussion of DAP monolayer coverage and Fc−uracil binding is included in the Supporting Information section. The contrast in electrochemical current−voltage properties near 0.5 V in Figure 3D correlates with what was observed in Figure 2.

In summary, we have used complementary hydrogen bonding molecules to control the noncovalent self-assembly and electronic properties of a chemically well-defined surface mesostructure. Specifically, we have demonstrated the use of hydrogen bonding to add and remove electroactive functionality in a mesoscale molecular assembly. In future studies, noncovalent interactions on a patterned surface can be used to construct increasingly complicated mesostructures with tunable current−voltage properties.

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Supporting Information Available: Additional data (STM images and image analysis, XPS, CV), chemical syntheses, detailed experimental procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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