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Bifunctional, Conjugated Oligomers for Orthogonal Self-Assembly: Selectivity Varies from Planar Substrates to Nanoparticles

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Orthogonal self-assembly, first illustrated by Wrighton and Whitesides, describes a way to selectively bind different kinds of molecules to different regions on a chemically heterogeneous substrate.[1] The key to this differential binding is elucidating which types of linking groups (e.g., headgroups) on a molecule will bind to one surface while avoiding (or eventually becoming displaced from) a different surface. Despite the obvious usefulness of this idea in nanometer-scale construction, only a few reports[2,3] provide synthetic aspects relevant to orthogonal self-assembly. Little information is available as to which chemical functional groups can be employed in the presence of others (e.g., the relative tolerance of one chemical functional group for another). Moreover, the relative affinity of a given substrate for one functional group over another is not well understood in the general case.

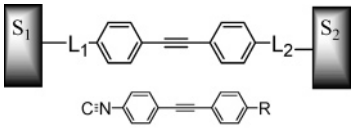
A simple extension of the orthogonal self-assembly concept is to employ molecules that contain terminal groups with different functionalities (e.g., Figure 1). This type of orthogonal self-assembly could then be useful in the installation of molecules into metallic junctions where the molecule in question should only be inserted "one way". In this case, the two junctions and the chemistries used to bind to them should not be the same.

While there are several reports describing the synthesis of molecular wires designed to bridge between two metallic contacts, all of these molecules have the same functional group at each terminus.[4] The other alternative, covalent attachment at only one of the two contacts and only mechanical interaction at the other, leaves unclear the nature of the second interaction[5] and generally leads to high contact resistances.[6] To install molecules between metallic contacts with a directional sense using orthogonal self-assembly, different functional groups at each terminus are required. The synthesis and assembly of such molecules will also assist in more fully answering the questions posed above about tolerance and selectivity.

In this communication, we report the synthesis of molecule **1a** in which thioacetate and isonitrile groups are placed at the two ends. Furthermore, experiments are presented to indicate qualitatively the relative affinity of these groups for gold and platinum substrates and nanoparticles.

The synthesis of molecule **1a** with thioacetate and isonitrile groups was achieved by palladium-catalyzed coupling of *p*-iodophenyl thioacetate with *p*-formamido phenyl acetylene (see Supporting Information). It was determined that the thioacetate group was tolerant of phosgene-mediated dehydration of the formamide to the isonitrile,[7] and the desired molecule (**1a**) was obtained in 88% yield after purification.

It has previously been indicated[1,2] that thiols bind selectively to gold over platinum and isonitriles bind selectively to platinum over gold. These conclusions were drawn from the competition of two types molecules for a given type of surface. To examine this competition in a bifunctional oligomer, two types of experiments were performed. First, molecule **1a** was incubated with both Au and Pt



1a R = $SC(O)CH_3$
1b R =H

Figure 1. (Top) Schematic of bifunctional, orthogonal self-assembly where Ln refers to a chemical functional group and Sn refers to a substrate to which it preferentially binds. (Bottom) Structures of the molecules used in this study.

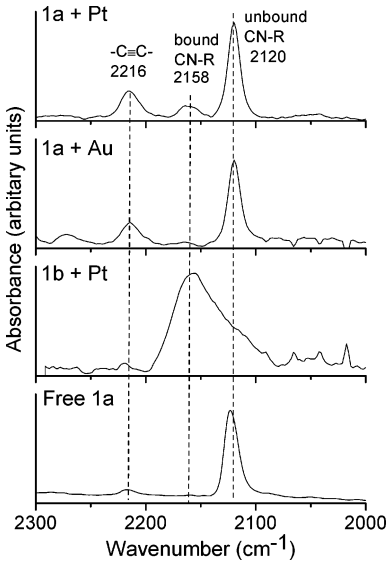


Figure 2. Grazing angle IR spectra of **1a** (after deprotection) and **1b** incubated with gold and platinum substrates.

substrates following the protocol for in situ deprotection reported previously.[8] Ellipsometric thicknesses of 13.8 ± 3.7 Å (on Au) and 14.1 ± 5.1 Å (on Pt) indicated that monolayers of these molecules formed on each substrate (given an estimated molecular length of 14 Å from AM1-level geometry optimization). These monolayers were further evaluated using grazing angle infrared reflectance spectroscopy (Figure 2). An enhanced acetylene stretch at ca. 2216 cm^{-1} was observed in these monolayers and in spectra subsequently taken on nanoparticles. More importantly, the isonitrile stretch of the molecule on both gold and platinum indicated mostly unbound isonitrile, suggesting that these molecules were bound via the thiol groups. On the basis of previous work,[9] a ca. 50−70 cm^{-1} shift upon binding of an isonitrile to platinum was expected. As a control, a monolayer of molecule **1b** was formed on Pt. This molecule lacks a thiol, and the monolayer composed of it showed a broad stretch centered around 2158 cm^{-1} corresponding mostly to bound isonitrile. Thus, it is concluded that isonitrile binding to Pt occurs, but not under the competing influence of a thiol group.

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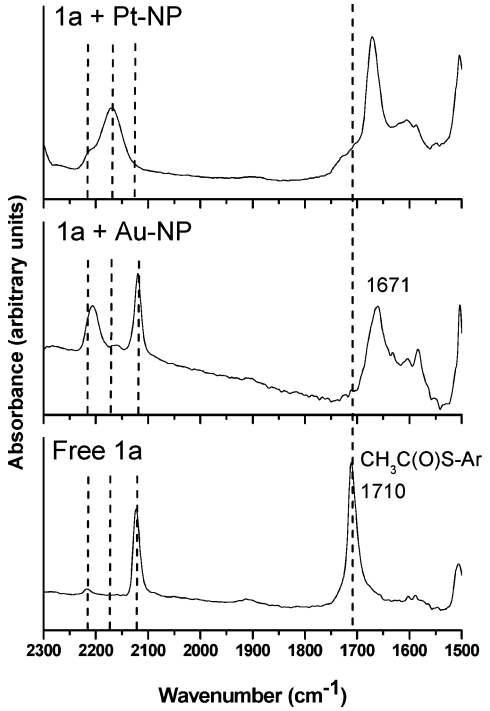

Figure 3. Transmission IR spectra of **1a** after deprotection and incubation with hexanethiol-capped gold and platinum nanoparticles.

In a second set of experiments, molecule **1a** was incubated with hexanethiol-capped Au nanoparticles (Au-NP)[10] and hexanethiol-capped Pt nanoparticles (Pt-NP)[11] also after in situ deprotection of the aromatic thioacetate group.[9] The results of binding were evaluated using transmission infrared spectroscopy of a sample after evaporation of the solution onto a KBr plate (Figure 3). The carbonyl peak observed in the spectrum of free **1a** at 1711 cm^{-1} was shifted to a lower wavenumber, consistent with deprotection to form free acetic acid and thiol. Figure 3 shows that, when the molecule was incubated with Au-NP, no change in the position of the isonitrile stretch was observed. This is consistent with a lack of binding between isonitrile and gold. In contrast, when the molecule was incubated with Pt-NP, the shift in isonitrile stretch expected upon binding was observed.

The results of these two experiments (e.g., binding to a nominally bare substrate versus binding to a nanoparticle where the molecule may have to displace hexanethiol or insert into a defect site in the thiol coating) are quite different. Further, the apparent selectivities for binding in these cases do not follow those observed by Wrighton and Whitesides[1] in which separate, thiol-containing and isonitrile-containing molecules competed for a bare metal substrate. Thus, these results indicate a new dimension when thinking about orthogonal self-assembly and indicate the relative selectivity in two cases for the archetypal thiol/isonitrile on Au/Pt interactions.

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Supporting Information Available: Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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