Molecular Recognition

Assembling Dimeric π Stacks on Gold Surfaces by Using Three-Dimensional Lock-and-Key Receptors**

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The study reported herein details a method to generate through self-assembly the shortest of π stacks, only two molecules high, which are covalently attached to gold substrates. A rigid, surface-bound molecular receptor (Figure 1 a) is first formed through the simultaneous attachment of three surface-active groups to a metal. These receptors bind molecules that have a complementary π surface and hydrogen-bonding pattern to form dimeric π stacks. A lynch pin for success in a number of emerging materials, such as organic field-effect transistors,[1] molecular rectifiers,[2,3] and single-molecule electronics[4] is controlling and manipulating the contacts between aromatic molecules and metal surfaces.[5,6] Ultimate success in these materials will require the development of self-assembly processes that operate at molecular length scales as a means of gaining interfacial control and programmed complexity. Herein, we demonstrate that highly functionalized molecules (**1b**; Figure 1 a) can be programmed through steric interactions to present three thiols on one face of an aromatic ring that bind strongly to gold substrates. These surface structures have a C_3-symmetric, hydrogen-bonding receptor site (Figure 1 c,d) nested at their base that directs the recognition and assembly of cofacially stacked π surfaces (Figure 1 b).

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The hexasubstituted aromatic (**1a**) was employed because it was recently shown to stack in bulk through a synergy between hydrogen bonds and π-stacking interactions to form infinite columns.[7] In addition, the optical properties of **1a** indicate this class of molecules has promise as a one-dimensional electronic material.[8] High-coverage monolayers of **1b**[9] were formed from solution by simultaneous deprotection of the acetate protecting group and deposition onto gold films.[10] The surface conformation of **1b** was analyzed by surface spectroscopy[5,11–13] and scanning tunneling microscopy (STM).[14]

The analysis of the monolayer shows that all three of the sulfur atoms are simultaneously attached (as depicted in Figure 1 b–d). Infrared reflection absorption spectroscopy[15] measurements from the monolayer show the presence of diagnostic signals for the core functional groups of **1b** including the alkane side chains and the amides[16] and the complete loss of the acetate protecting group. The advancing (75°) and receding (65°) contact angles for a water droplet on these films are consistent with a surface that presents both alkyl and carbonyl groups (Figure 1 c).[13] X-ray photoelectron spectroscopy (XPS; Figure 2 b), probing the S_{2p} core electrons, reveals that all of the sulfur atoms are bound to gold[18] precluding the formation of disulfides and free thiols.[12c,13,17] The thickness of the layer measured by ellipsometry[18] is 1.3 nm, in good agreement with the calculated thickness of approximately 1.2 nm (Figure 1 c) with the 10-carbon substituent on the alkyne side chains extending upward.

This surface conformation can be imaged directly using STM for samples of **1b** prepared on atomically flat gold samples,[19] shown in Figure 2 a. The samples show high coverage of molecular-scale disks with no apparent order of these disks within the plane. Analysis of these images reveals that the smallest detectible features have a height of approximately 1.2 nm and a width of about 3 nm. These values are consistent with the dimensions of the molecule when bound to the surface (Figure 1 b–d). Note that the gold layer is apparently stabilized by the threefold symmetric thiols. The characteristic pitting and restructuring observed with relatively simple alkane thiols is absent in these samples.[5] This effect is probably a result of the extremely low mobility of both the surface-bound molecules and the top layer of gold as a result of this multipoint attachment.

Because the tethers on the amide side chains are very short and the central core is sterically congested, the amount of conformational flexibility imparted to these molecules is minimal. Early studies on this core structure, revealed that the amide is twisted out of the aromatic ring-plane by the neighboring alkyne substituents at roughly a 45° angle.[7] Simple conformational analysis[20] of the 2-thiolamidoethane side chain of **1b** reveals that this subunit should have a *trans* arrangement of its sulfur and nitrogen atoms. Moreover, the amide N–H unit and the amide carbonyl group should be exclusively antiparallel to each other. Given these constraints, there is only one torsional degree of freedom (between the amide nitrogen atom and the first methylene unit) that determines whether the carbonyl or the N–H group is on the same face as the sulfur atom. From these models, it is not possible to produce a monolayer that presents its N–H groups

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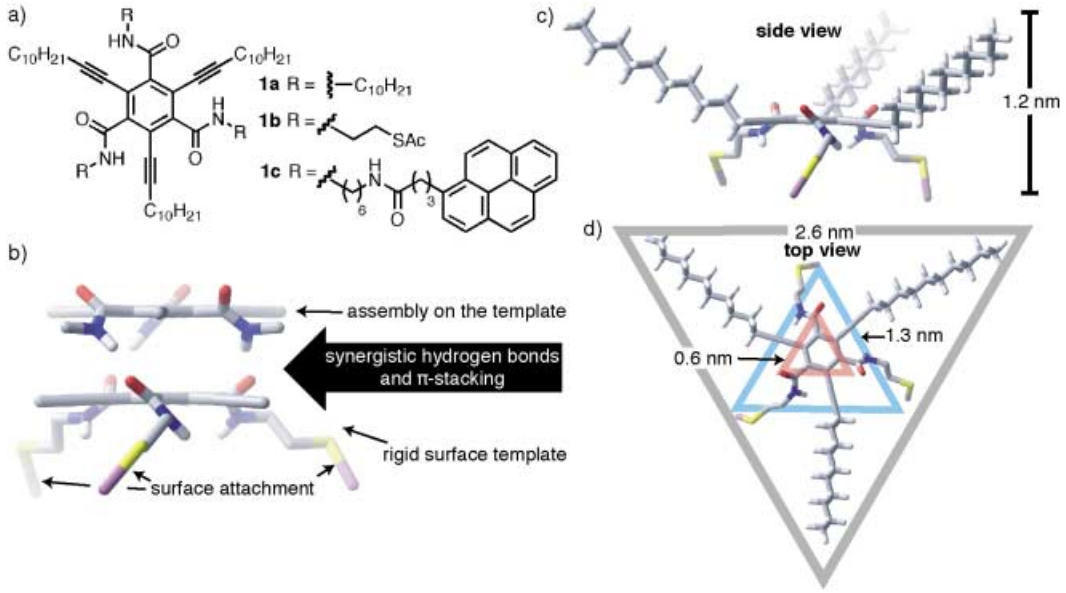

Figure 1. a) Crowded aromatics with both amide and alkyne substituents. b) Molecular model[20] of a dimer stack of **1b** (red = oxygen, gray = carbon, blue = nitrogen, yellow = sulfur, purple = gold surface atom). The hydrogen atoms and the substituents on the alkynes have been removed for clarity. c) Side-view of the model when bound to surface showing the nested receptor site. d) Top view showing three vertical levels of information written into the molecular substructure. The lower level (blue triangle) defines the surface attachment that positions the amide carbonyls away from the surface (red triangle) into a C_3-symmetric hydrogen-bonding site. The gray triangle defines the hydrocarbon chains.

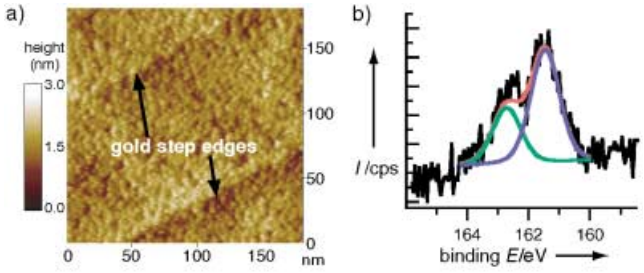

Figure 2. a) STM image (150 pA, 500 mV) of **1b** on gold revealing molecular-scale disks attached to a gold surface; b) Sulfur XPS spectrum of **1b** on gold shows the characteristic 2:1 ratio at 161.5 eV and 163 eV for sulfur atoms bound to gold. The the red, blue, and green lines are curves fits to the data (black line).

away from the surface (i.e., opposite of the arrangement in Figure 1b–d) because of the intervention of the carbonyl group and the restrictive triple attachment. Therefore, the films must form a template that has three hydrogen-bond acceptor carbonyl groups at the surface (as in Figure 1).

Once bound to the surface, a receptor forms as shown in Figure 1c. The groups defining this structure are depicted in Figure 1d with three vertical levels of equilateral triangles about the central aromatic ring. The vertices of the blue triangle (1.3 nm apart) define the surface attachment of the three thiols to the metal holding the aromatic ring approximately 0.5 nm from the gold surface. The red triangle (side 0.6 nm) is defined by the threefold symmetric arrangement of amide carbonyl groups that act as hydrogen-bond acceptors. The large grey triangle (side 2.6 nm) is defined by the hydrocarbon side chains providing a second C_3-symmetric mode of discrimination for guest binding. In concert, this orchestrated functionality provides a 3D receptor whose π surface is close to its van der Waals radii from the gold surface. This surface conformation is similar to the one deduced for the bulk material **1a**.[7] This situation implies that there is little reorganization penalty for molecules to associate with these receptors. To create a sensitive reporter molecule for binding to these surface receptors, a fluorescent analog, **1c**, was synthesized[7] that carries three pyrene chromophores on alkyl tethers.[21] **1c** was found to self-associate in bulk into 1D nanostructures similar to what was observed for **1a**.[7]

When the films of **1b** were placed into solutions containing **1c**,[22] then removed, rinsed, and dried, ellipsometry detected only a 0.5 nm increase in the layer thickness. This value is consistent with the measured value from molecular models, such as the one in Figure 1b, for the addition of a single layer of molecules. Fluorescence spectroscopy shows pyrene emission that is characteristic of the isolated pyrene molecules lacking any detectible excimer emission (Figure 3a).[21] Moreover, the fluorescence intensity is consistent with an incremental increase in the layer thickness. STM images of these samples (Figure 3b) reveal a largely complete second layer of molecules (measured to be ca. 0.6 nm above the monolayer) associated with the original monolayer. Given the uniform height of this second layer it must be tightly bound. It is intriguing that the rinsed films show either monolayer or bilayer and no higher stacks. The noncovalent association with this first additional layer could be higher due to the increased rigidification of the molecules upon binding to the metal. In addition, stacks higher than dimers could be disfavored by dipole–dipole repulsions between adjacent columns.

To test if the surface receptors were selective for particular a size, shape, and hydrogen-bonding pattern, **2**

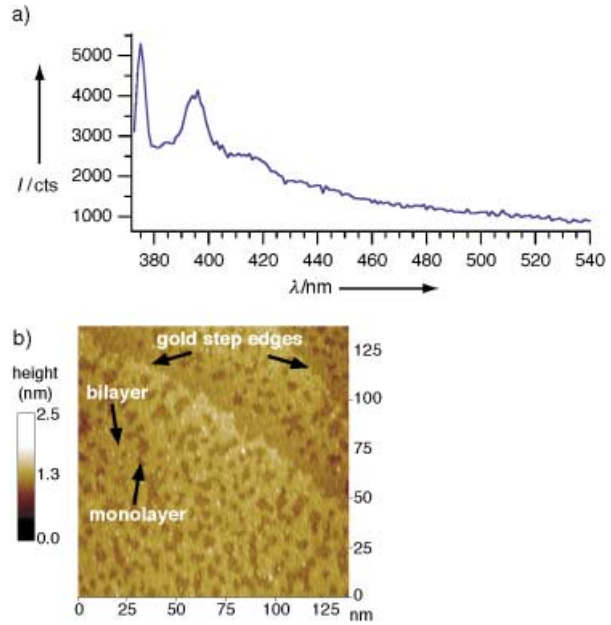

Figure 3. a) Fluorescence (excitation 355 nm) from a monolayer film of **1b** associated with fluorescent probe **1c** showing isolated pyrene emission. b) STM image (150 pA, 500 mV) of a similar sample showing incomplete bilayer coverage.

(Figure 4) was synthesized. It lacks the threefold symmetry of the alkyne and amide side chains of **1a–c**. The choice of the dansyl fluorophore for **2** was critical because its excitation wavelength is very close to that of pyrene but its fluorescence emission is red-shifted to about 485 nm. Therefore, the mixture on a surface is easily deduced from the emission spectrum. As above, monolayers of **1b** were immersed in an equimolar mixture of **1c** and **2**. After removal and rinsing, the resulting fluorescence spectrum (Figure 4b) is essentially indistinguishable from the one in Figure 3a for **1b** and **1c** (that lacked the dansyl chromophore). As an additional control experiment, the monolayers of **1b** were incubated in solutions of **2**, removed and rinsed. These surfaces showed

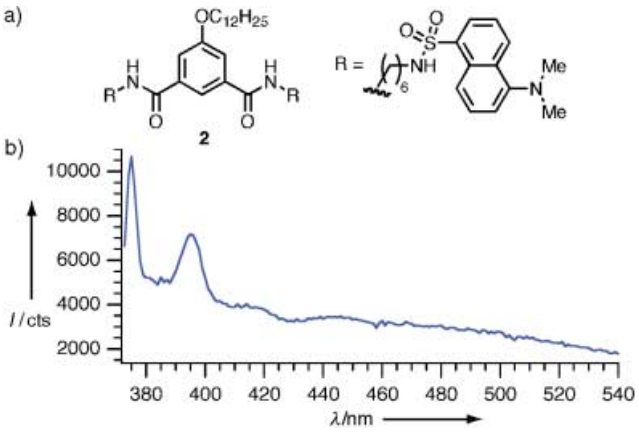

Figure 4. a) Molecule **2** is used to test for selectivity in competition experiments with **1c** for binding to monolayers of **1b**. b) Fluorescence spectrum (excitation: 355 nm) from a monolayer of **1b** after immersion in a equimolar (0.1 mM) mixture of **1c** and **2**.

only a very small amount of dansyl emission. If the fluorophores are switched, that is, putting the dansyl fluorophore on the C_3-symmetric core and the pyrene on the bis(amide) core, the surface shows exclusively emission from the dansyl fluorophore. Therefore, these surface-bound molecules are able to select from solution between two different molecules based on a complementary structure.

In conclusion, a new concept is advanced for creating surface-bound molecular sockets capable of directing the assembly of aromatic molecules at very short length scales. One aspect that is critical for success is the use of preorganization where the molecule's bulk conformation is similar to its surface-bound structure. The simultaneous binding of three thiols creates a rigid surface structure holding its π face close to the metal substrate. Steric interactions in both the crowded aromatic core and the short surface-active tethers of these highly functionalized monolayers direct the hydrogen-bonding and hydrophobic functional groups upwards. The C_3-symmetric receptor site is capable of discriminating between different aromatic molecules from solution. For traditional π surfaces[23] this type of selection is not likely to occur because of the weak interactions between aromatic molecules.[24] The dimeric stacks formed here provide an unprecedented model system to study electrical conductivity of π stacks on metallic surfaces. In addition, the surface template should have a dipole moment that increases as the molecules stack through head-to-tail hydrogen bonds.[25] These dipolar dimers could show rectification of electrical current[2] and have properties that are a consequence of their polar order.[26]

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[20] Molecular modeling was performed with MacroModel v7.0 and the Amber* force field [F. Mohamadi, N. G. J. Richards, W. C. Guida, R. Liskamp, M. Lipton, C. Caufield, G. Chang, T. Hendrickson, W. C. Still, *J. Comput. Chem.* **1990**, *11*, 440 – 467]. The gold atoms were added after minimization and the Au–S bond length was estimated to be 0.24 nm.

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