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 1a) 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 1a) 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 C3-symmetric, hydrogen-bonding receptor site (Figure 1c,d) nested at their base that directs the recognition and assembly of cofacially stacked π surfaces (Figure 1b).

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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 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 C3-symmetric hydrogen-bonding site. The gray triangle defines the hydrocarbon chains.

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. 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 that carries three pyrene chromophores on alkyl tethers. 1c was found to self-associate in bulk into 1D nanostructures similar to what was observed for 1a.

When the films of 1b were placed into solutions containing 1c, 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). 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. 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 film of 1b after immersion in an equimolar (0.1 mM) mixture of 1c and 2.

(For 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 only a very small amount of dansyl emission. If the fluorophores are switched, that is, putting the dansyl fluorophore on the C3-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 pre-organization 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 C3-symmetric receptor site is capable of discriminating between different aromatic molecules from solution. For traditional π surfaces 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[26] and have properties that are a consequence of their polar order.[26]

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[9] The synthesis of 1b and 1c was performed as outlined for 1a[7] and will be reported elsewhere.


[15] Experimental details for similar IR measurements have been reported elsewhere.[6b]

[16] The IR spectrum from monolayers of 1b contains signals for the alkyl groups (ca. 2960 cm⁻¹/C₀) and for the amide I (1665 cm⁻¹/C₀) and amide II (1555 cm⁻¹/C₀) transitions.


[18] Experimental details for similar ellipsometry measurements have been reported elsewhere.[6b] The XPS spectrum shows the 2:1 doublet at 162 eV characteristic of a Au–S bond.[12c]

[19] STM measurements were carried out with a Nanoscope E (Digital Instruments, Santa Barbara, CA) at room temperature in air. STM tips were prepared from cutting Pt–Ir wire. Gold substrates were purchased from Molecular Imaging and annealed with a hydrogen flame prior to use.

[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.


[22] 1b was incubated overnight in a solution of 1c in CH₂Cl₂, (0.1 m).


