Self-Assembled Monolayers Stabilized by Three-Dimensional Networks of Hydrogen Bonds

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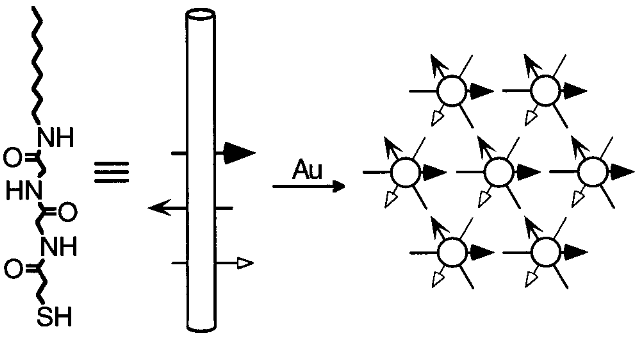
Self-assembled monolayers (SAMs) formed from thiols on coinage metals have been widely studied for over a decade,[1] yet reports of *ordered* SAMs with internal substitutions are rare.[2] An understanding of how internal functionalities can stabilize SAMs through cross-linking interactions would immediately impact the design of new materials with enhanced stability, including chemically tailored surfaces, sensors, and molecular photoresists.[3] One approach to stabilizing SAMs is the incorporation of internal hydrogen bonding cross-links, mimicking fibrous protein aggregates such as silk and collagen.[4] Such assemblies would also have fundamental importance as spectroscopic models of peptide tertiary structures,[5a] spacers for electron-transfer studies,[5b] and functional mimics of protein aggregates such as amyloid plaques.[5c] Toward this end, we and others have investigated the structures of thiol-based SAMs containing single internal amide groups.[2d−f] In addition, recent reports describe non-cross-linked α-helical polypeptide SAMs,[6a−d] disordered oligopeptide SAMs,[6e] and oriented proteins adsorbed to SAMs.[6f−h] However, structurally well-characterized SAMs stabilized by extensive and ordered hydrogen bonding interactions are heretofore unknown.

Here we report a SAM (**1**/Au) that is stabilized by three layers of internal hydrogen bonds, resulting in a network of lateral cross-links within the film (Figure 1). This structure is supported by independent lines of evidence from external reflective infrared spectroscopy (FTIR-ERS) and X-ray photoelectron spectroscopy (XPS). Further, thermal desorption studies of **1**/Au demonstrate improved stability compared to SAMs formed from octadecanethiol (ODT/Au),[7] as expected for the replacement of hydrophobic interactions with hydrogen bonds.[8]



1 **1, side view** **1/Au, top view**

Figure 1. Formation and structure of **1**/Au. The fully extended conformer of **1** (left) is depicted as a cylinder (center) with arrows defining axes along which hydrogen bonds can form. Upon self-assembly on gold (right), the peptide domain of each precursor becomes conformationally locked as a ternary (3_1) helix with the screw axis oriented normal to the substrate. Each amide is rotated about that axis by 120° with respect to neighboring amides. The precursors thus associate as in polyglycine II, forming extensive and ordered intermolecular hydrogen bonds within the SAM.

The amide region of a well-ordered SAM derived from **1** could assume one of three structures, based on the known and hypothesized hydrogen bonding motifs of polyglycine.[9] In a structure reminiscent of polyglycine II (PGII),[10] the amide region of each molecule assumes a 3_1 helical structure, forming a network of hydrogen bonds within the film (Figure 1). In another structure, the SAM comprises rows of β-sheets as in antiparallel polyglycine I (AP-PGI).[10] A third form, with chains oriented in the same N→C direction, is based on the putative parallel polyglycine I (P-PGI), which has not been observed in the bulk.[10]

The peptide chains in **1**/Au are parallel and ordered, consistent with PGII-like and P-PGI-like structures, as determined by XPS[11a] and contact angle goniometry. All the sulfur headgroups are chemisorbed to gold, as indicated in XPS by a 1.2 eV decrease in the binding energy of the S (2p) doublet upon adsorption.[1c−e,2d,11b] The constituent elements are present in the proportions expected for the anisotropically adsorbed precursor **1** and exhibit the expected angle dependency.[11b] The high advancing contact angle (113 ± 2°, water) is consistent with a well-ordered methyl surface.[1d]

The signature frequencies and intensities of a PGII-like backbone conformation are revealed in the amide region in the FTIR-ERS[12a−c] of **1**/Au (Figure 2). The correlation of IR amide frequencies with polypeptide backbone conformations is well

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[7] ODT/Au is wellknown to form chemisorbed monolayers ~23 Å thick with close-packed, fully extended hydrocarbon chains tilted ~30° off surface normal.[1]

[8] Landin, J.; Pascher, I.; Cremer, D. *J. Phys. Chem. A* **1997**, *101*, 2996−3004 and references therein.

[9] Structures such as α, 3_{10}, ω, and π helices are precluded in **1**/Au, since the precursor **1** contains only three amide bonds.

[10] Krimm, S.; Bandekar, J. *Adv. Protein Chem.* **1986**, *38*, 181−364 and references therein.

[11] (a) XPS provides surface elemental analysis, chemical state information, and depth profiles. See: Briggs, D.; Riviere, J. C.; Hofmann, S.; Seah, M. P. In *Practical Surface Analysis by Auger X-ray Photoelectron Spectroscopy*; Briggs, D., Seah, M. P., Eds.; Wiley & Sons: Chichester, 1983; pp 87−216. (b) See Supporting Information.

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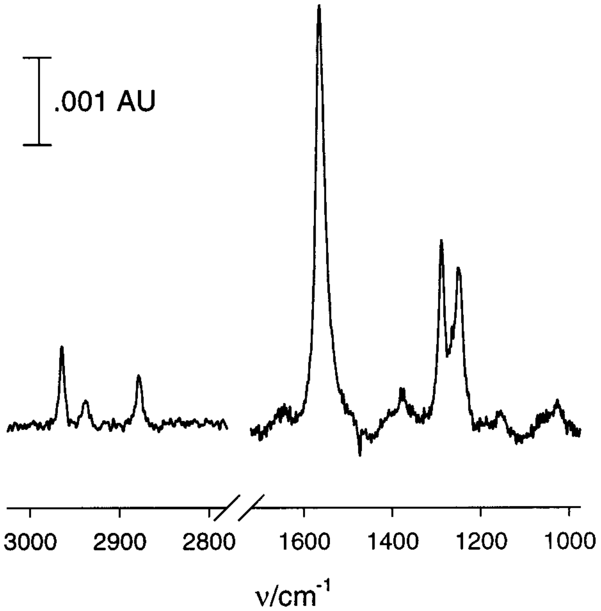

Figure 2. External reflective IR (FTIR-ERS) spectra of **1**/Au. Left: high-frequency region. Right: mid-frequency region. The amide III bands at 1380, 1283, and 1249 cm^{-1} are signatures of a PGII-like backbone conformation.

founded;[10] in particular, the amide III complex of bands is the vibrational feature most sensitive to conformation of the amino acid chain.[10,12d] In **1**/Au, the amide III frequencies (1380, 1283, and 1249 cm^{-1}) are identical to those in PGII,[10] whereas in P-PGI the amide III bands would be expected at 1410 and 1162 cm^{-1}.[12e] In addition, the intensities of these diagnostic peaks should be strong in the PGII structure due to inclination of the $C^{\alpha}H_2$ (wag) and $C^{\alpha}H_2$ (tw) dipoles toward the metal surface.[10,12b−c] The strong intensities at 1283 and 1249 cm^{-1} thus support the proposed structure.

A PGII-like network of amides in **1**/Au is further supported by the balance of the IR amide data. In the PGII-like SAM, the NH and CO bonds are oriented nearly parallel to the substrate plane, as evidenced by the strong intensity of amide II (1563 cm^{-1}) and the absence of amide A (~3300 cm^{-1}) and amide I (~1650 cm^{-1}).[12f] The high degree of association between amides results in a large constraint upon the NH (ipb) mode,[2e] indicated by the high frequency of amide II.[12g] Finally, uniformity of hydrogen bonding is demonstrated in the narrow bandwidth of amide II, reflecting a narrow dispersion of bonding states.[12h]

A PGII-like amide sublayer is also supported by the high-frequency CH region of the IR. In ODT/Au, mismatch between headgroup spacing and optimum hydrocarbon chain−chain distance is relieved by tilting of the hydrocarbon chains, demonstrated by characteristic relative intensities of CH_2(asm) at 2918 cm^{-1} and CH_2(sym) at 2850 cm^{-1}.[1a−c,2b−e,12c] Because the interchain distance in crystalline PGII is ~0.2 Å less than the headgroup spacing in ODT/Au,[1f−g,10] hydrocarbon chains templated on a PGII-like amide region should be constrained toward surface normal. Accordingly, in **1**/Au the hydrocarbon chains extend along the substrate normal with HCH bonds parallel to the substrate, as evidenced by the absence of CH_2(asm and sym) (Figure 2). The vertical orientation of the hydrocarbon chains, taken together with the strong interchain hydrogen bonding indicated by the amide II frequency, suggests that the interchain spacing is the same as in PGII. Thus, hydrogen bonding appears to dominate over templating of thiolates on the Au(111) lattice in determining the structure of the assembly,[1f−g] a point that will be addressed by X-ray diffraction.

Independent evidence supporting the PGII-like structure was obtained by measurement of the film thickness. **1**/Au was modeled with the amide region in PGI and PGII-like conformations.[11b] The helical form of **1** (PGII-like, $l = 23.3$ Å) is predicted to be significantly shorter than the rippled sheet chain (PGI-like, $l = 24.9$ Å), due to the twist of the amino acid residues. As determined by XPS,[11,13] the thickness of **1**/Au (23.2 ± 0.9 Å) is in agreement with the modeled PGII-like thickness and significantly less than the thickness of the model based on rippled sheet parameters.

Taken together, the observation of a full monolayer of chemisorbed thiol having the described orientation, order, and thickness provides compelling evidence that the amide region of **1**/Au comprises ternary (3_1) helices. In a functional demonstration that the three-dimensional network of hydrogen bonds stabilizes the SAM, we found that the onset of thermal desorption of **1**/Au in argon (175 °C) occurs at temperatures 125° higher than ODT/Au (as determined by XPS).[11b] Over the course of 80 min at 175 °C, nearly 50% of the ODT-derived SAM is desorbed, while only ~5% of the amide containing SAM is lost. The enhanced performance of **1**/Au is a striking demonstration of increased stabilization by hydrogen bonding. The greater stability of the hydrogen bonding network may be due to cooperative interactions reminiscent of those found in globular proteins.[14] The increased stability clearly demonstrates the potential of internally cross-linked SAMs for a wide range of surface modification applications where enhanced temperature tolerance is desired.[3]

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Supporting Information Available: Synthetic methods and characterization details with emphasis on XPS (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(12) (a) FTIR-ERS enables determination of molecular orientation because oscillator components parallel to the metal surface are not observed.[12b−c] Abbreviations: asm, asymmetric; sym, symmetric; str, stretch; ipb, in-plane bend; tw, twist. (b) Greenleer, R. G. *J. Chem. Phys.* **1966**, *44*, 310−316. (c) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 52−66. (d) In PGII, the amide III bands arise from $C^{\alpha}H_2$ (tw), $C^{\alpha}H_2$ (wag), NC^{α} (str), NH (ipb), and CN-(str), in descending order of contribution to the oscillator strength.[10] (e) P-PGI frequencies are as calculated by normal-mode analysis by which a wide range of polypeptide IR spectra has been accurately predicted.[10] (f) Amide II is due almost solely to NH (ipb), which oscillates perpendicular to the substrate in **1**/Au. Amide A arises primarily from NH (str) and amide I from CO (str), which are parallel to the substrate in **1**/Au. (g) Amide II appears at 1553 cm^{-1} for solid **1** (KBr) and 1515 cm^{-1} for **1** in dilute CCl_4. (h) Amide II has full widths at half-maxima of 24 cm^{-1} for **1**/Au, compared to 65 cm^{-1} for solid **1** (KBr).

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