Using bacterial S-protein layers to probe accessibility of chemical end groups in self-assembled monolayers

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Bacterial S-protein layers are crystalline self-assembling systems with many applications in nanotechnology [1]. They have been used as templates for biomolecules and nanoparticles, with promising perspectives in the sensor technology [2]. On the other hand, self-assembled monolayers (SAMs) of thiol derivatives on metal surfaces (e.g., gold) of the form $SH-(CH_2)_n-X$ have been profusely studied due to their capability of tailoring surface properties, which are mainly determined by the chemistry of the end group, X [3]. Although the recrystallization of S-proteins is a phenomenon that takes places in a wide variety of non-biological substrates, the mechanism is not well understood. Using SAMs as substrates is a good strategy to investigate the forces involved in the formation of the protein layers and thus to understand the mechanism of recrystallization. A consequence of this will be the optimization of S-layer formation in order to get high quality, defect-free biogratings.

In this study we report the self-assembled recrystallization of S-proteins on SAMs of dialkyldisulfide derivatives. The dialkyldisulfide molecules used consist of two alkyl chains (branches) terminated in methyl and hydroxyl groups, and joined by a disulphur bond. The general form is $CH_3-(CH_2)_{11+m}-S-S-(CH_2)_{11}-OH$, with m = -6,-4,-2, 0, +2, +4 and +6. These molecules self-assemble on gold upon cleaving of the S-S bond, resulting in surfaces with methyl-terminated and OH-terminated branches, closely packed to each other. The parameter m defines the degree of protrusion of a branch with respect to the other: $m = 0$ means both branches have equal length, $m > 0$ means the CH3-terminated branches are exposed at the interfaces, meanwhile in the case of $m < 0$ the exposed branches are the OH-terminated (fig. 1). Disulfide SAMs have been previously characterized by contact angle, chemical force microscopy, X-ray photoelectron spectroscopy and Infrared spectroscopy [4].

The S-protein recrystallization has been used to probe the accessibility of the methyl and the hydroxyl end groups in the disulfide SAMs as a function of the chain length difference m. Atomic force microscopy and surface plasmon resonance have been used to monitor the recrystallization process of S-proteins onto these substrates and to characterize the resulting S-layers (thickness, unit cell parameters, crystal morphology, surface forces).

The results show that the S-layer morphology depend on m. A chain difference of 4 carbon atoms between the disulfide branches induces a change in the process of recrystallization, resulting in S-layers with different morphology and properties (fig. 2). The study shows that S-protein crystallization is sensitive to the accessibility of polar groups of the disulfide SAMs.

References:

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Figure 1

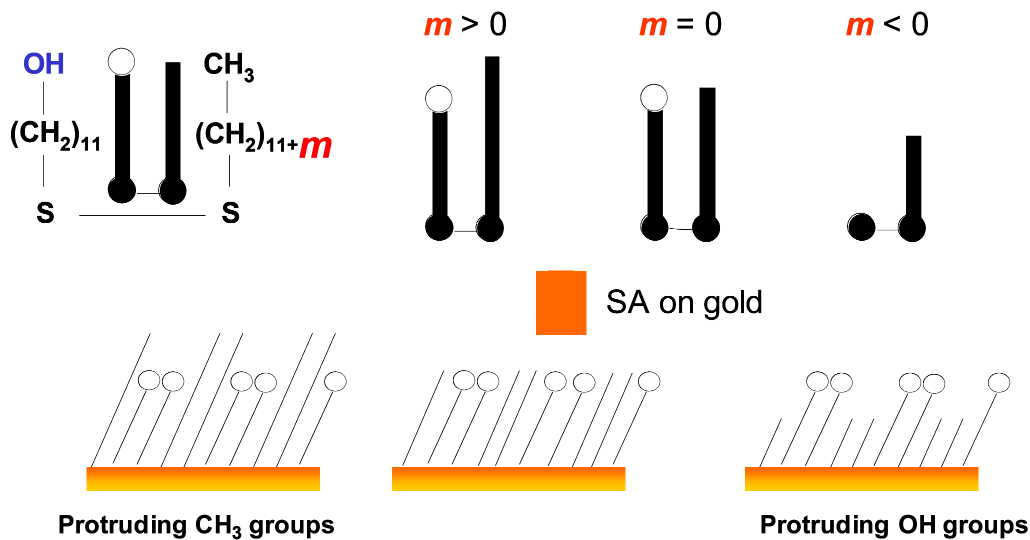

Figure 2