Chemistry at Interfaces

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Interfacial Systems Chemistry: Towards the Remote Control of Surface Properties

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Controlling the functionality of exposed surfaces is a key prerequisite for manipulating the properties of objects. This statement is true even more for nanoparticles, where the relative importance of atoms or molecular subunits exposed at the surface is much greater than for macroparticles. The tailoring of interface-controlled phenomena requires not only the fabrication of such surfaces with predefined static properties, for advanced applications it is also desirable to devise a remote control, such that surface properties can be adjusted by an external stimulus. The complex molecular architecture required to achieve this goal is an instructive example of the topics addressed in the emerging field of interfacial systems chemistry.

In the context of cells, nature addresses this requirement by providing dedicated membrane proteins with properties tailored to various purposes. In many cases the properties of the end of transmembrane proteins protruding from the outer surfaces are not fixed but can be controlled and modified from within the cell.

When the desired static functionality of a surface can be realized by appropriate organic molecules, the most convenient way to render a particular property to a substrate is by grafting these target molecules to a surface. Presently, the most important approaches for such a functionalization of interfaces are the thiolate-based self-assembly on gold substrates[1,2] and the silane-based approach suitable for hydroxylated insulator or semiconductor surfaces.[3,4] Both approaches rely on monomers of the type A-L-F, where A acts as an anchor forming a covalent bond to the substrate, L is a linker, and F is the target moiety exhibiting the desired functionality. In principle this is a rather straightforward and flexible strategy for the fabrication self-assembled monolayers (SAMs). Numerous molecules have been synthesized and shown to yield molecular thin layers exposing organic surfaces with the desired composition.[1,2] The most important anchoring mechanisms are the formation of thiolate (that is, S-Au) and siloxane (i.e. Si-O-X) bonds using thiols or silanes (chloro-, ethoxy-, or methoxysilanes), respectively.[5]

When analyzing in more detail the chemical and physicochemical properties of these thin organic layers formed by grafting monomers on substrates, one realizes that quite often the actual functionality of the SAM formed does not correspond to that expected based on the behavior of the target molecule F in solution. An instructive example of this pronounced difference between actual and predicted surface properties is the chemical activity of thioacetates. Whereas in solution thioacetates can be readily cleaved to yield free SH groups, exposed organic surfaces with SAMs composed of thioacetates are rather unreactive towards the basic solutions used for the cleavage in solution.[6] The reason for these unexpected and so far unpredictable deviations from the normal properties of functional units is steric effects, which arise from the dense, two-dimensional packing of the target molecules F.

As the reactivity of molecular units exposed at a surface can deviate strongly from that in solution, one can expect that also the dynamic properties needed for the remote control of surface properties, for example, the switching of a molecule between different conformations, are severely affected when these units are incorporated in a SAM. Azobenzene is a prototype molecule that can be switched between two conformations by visible and ultraviolet light, and can thus—in principle—be used for controlling certain surface properties, for example, work function, wettability, and chemical reactivity. Following the strategy outlined above this would simply require linking azobenzene at the α position to an anchor A and attaching another functional unit at the ω position.

The goal of fabricating such a “smart” surface, which can be switched by an external stimulus, has challenged surface chemists for quite some time. Azobenzene switching is effective in solution, but apparently the transition from *trans* to *cis* requires a certain amount of free space. This restriction is already apparent when one compares the properties of azobenzene in solution and to those in the bulk. Whereas in solution the molecule can be switched readily from *trans* to *cis*, in the condensed form typically no switching can be induced, even after prolonged irradiation times.

The same steric hindrance is observed in the application of SAMs to functionalize interfaces as described above. Although in a few cases a complete switching of azobenzene-based thiolate SAMs could be achieved,[7] in many other cases the switching was found to be hindered by steric constraints:

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within an ordered two-dimensional array the packing is simply too dense to allow for the transition from the *cis* to the *trans* state.[8]

Interestingly, in a few cases an incomplete switching of azobenzene-based SAMs has been reported, which has been attributed to the increased free space around a minority species,[9] thiolate molecules adsorbed at substrate defects, steps, vacancies, or close to contaminations. Within the perfectly packed, two-dimensional packed arrays, however, the same limitations as in the three-dimensional bulk apply. As a result, only a fraction of the surface functionalities can be switched.

A number of approaches have been proposed to surmount this problem. The most obvious is to dilute the functionalized thiolates in a matrix of nonfunctionalized thiolates and thus provide sufficient space for the switching between the different azobenzene conformers. This approach, however, suffers from a number of drawbacks, one of which is the phase separation typically observed when thiolate-based SAMs are prepared from a mixture of two different thiols. Only recently have strategies been proposed to overcome this problem,[10] and the use of bulkier thiolates has been investigated. A typical approach is to use spacers with larger cross-section, thus increasing the "footprint" and consequently the area available per single azobenzene unit. A successful realization of this approach has, however, not yet been reported.

In a recent paper, Herges and co-workers[11] have proposed a somewhat different scheme, where the space required for the azobenzene unit to perform its function, namely to rotate the upward phenyl group from the *trans* position down to the *cis* position, is provided by using a novel type of anchor, namely a triacatriangulinium ion (TATA$^+$) and either an ethynyl or a phenyl unit as the linker to attach the target molecule, for example, azobenzene.

In this case the anchor does not bind to the substrate by forming a covalent bond as in the case of the gold thiolates or the siloxanes. Instead, a combination of van der Waals interactions, the typical strong attractive forces between planar molecular systems and a metal surface (which lead to a fairly strong binding of graphite segments to Au[12,13]), along with noncovalent interactions between the three nitrogen atoms and the Au substrate fix these "molecular platforms" to the substrate. That the sum of such interactions can become comparable in strength to that of thiolate bonds was demonstrated in a recent paper where two planar organic molecules, melamine and perylene tetracarboxydiimide (PTCDI), were adsorbed also on Au(111) and found to form a highly ordered, two-dimensional network.[14] Subsequent immersion into a solution of organothiols did not lead to a removal of the hydrogen-bonded network; instead only the bare parts of the Au substrate within the open melamine–PTCDI network were filled with thiolates.

The footprint of the TATA platforms employed by Baisch et al.[11] is rather sizeable, so that the azobenzene unit attached to the platform like a flag on a suitable linking "flagpole" unit has sufficient space for the *trans*-to-*cis* conformational change. As expected, the photosensitive molecule can be switched between its two conformations by illumination with visible and UV light.[11]

The fundamental aspects of this novel and very promising strategy are illustrated in Figure 1. The authors provide scanning tunneling microscopy (STM) data at molecular resolution which show that the TATA$^+$ ions form a well-defined network on the clean Au(111) substrate. The formation of such two-dimensional, supramolecular structures on metal surfaces by the adsorption of suitable organic ligands is an interesting topic in itself and has recently attracted a substantial amount of attention.[15] These superlattices already exhibit some functionality; for example, metal atoms can be incorporated by formation of coordinative carboxylate–metal bonds or by insertion into porphyrins,[16] and the subunits can be polymerized yielding covalently bonded two-dimensional nets.[17]

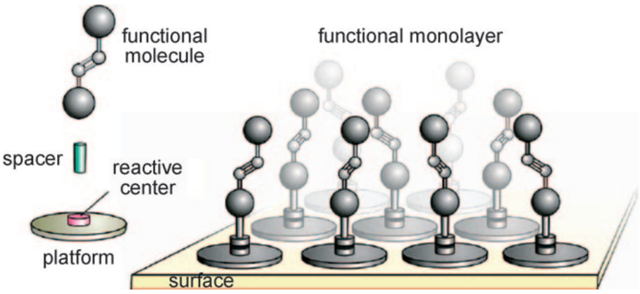

Figure 1. Representation of the platform approach employed by Baisch et al. The size of the platform determines the distance between the functional molecules, F, attached via the linker (or spacer) to the platforms, which are bound to the substrate surface. Reproduced from Ref. [11] with permission.

The approach taken by Herges and co-workers goes significantly beyond these previous results confined to two-dimensional networks. They attach a "flagpole" to the planar subunit, which allows the attachment of additional functional molecules and thus the introduction of a third dimension. This platform-based approach has much potential for other applications, for example, providing organic templates for the deposition of metal–organic frameworks on gold surfaces.[18,19] For such future applications it would be desirable to obtain more information on the particular type of anchoring of the TATA$^+$ carbocation on the Au substrate and in particular to obtain more information about the location of the BF_4^- counterion. In addition, experimental values for the binding energies are required, which might help to characterize in more detail the type of interaction between the TATA$^+$ cation and the gold substrate. For example, the STM data do not indicate whether the reconstruction of the gold surface is lifted by the adsorption of the molecules,[20] whether this rather complicated reconstruction of the substrate is preserved as in the case of hexa-*peri*-hexabenzocoronene (planar graphite segments) on the same substrate.[12,13] Finally, the STM data seem to indicate that the lateral order present in the TATA$^+$ monolayers is substantially inferior to that obtained with organothiols,[21] which form substantially stronger covalent bonds to the metal substrate.

In conclusion, the platform approach presented by Herges and co-workers has potential for the development of a flexible strategy for the functionalization of surfaces, in particular with regard to molecular functional units that require more free space than that available in two-dimensional ultrathin organic layers prepared by conventional means.

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[5] Presently, in the literature the term "SAM" is not used in a consistent way. For thiolate-based SAMs, the anchoring of the molecular constituents of the monolayer is sufficiently flexible to allow for the development of highly ordered films. For silane-based ultrathin organic layers on, for example, SiO_2, however, the binding of the monomers to the substrate is so strong that long-range order typically does not develop. As a result many authors refrain from using the term SAM for silane-based monolayers.

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