

 SELF-ASSEMBLED MONOLAYERS

A not-so-strong bond



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Self-assembled monolayers (SAMs) of organic molecules provide inexpensive and versatile surface coatings for applications ranging from biology to electrochemistry. When the substrate is a noble metal, thiol (–SH) moieties are commonly used as end groups because of the strong affinity of sulfur with metals. Conventional wisdom describes the thiol moieties as chemisorbed to planar gold surfaces, with the loss of hydrogen during the formation of the bond. Writing in *Nature Chemistry*, Latha Venkataraman and colleagues now reveal that in gold–thiol SAMs, the gold–sulfur coupling unexpectedly has a physisorbed character.

The nature of the gold–thiol bond influences the properties of SAMs, such as the interfacial electronic coupling and stability. Surface-sensitive probes cannot determine the nature of the bond, or follow the fate of the hydrogen atom

attached to the sulfur. By contrast, because the gold–thiol electronic coupling strongly depends on whether the bond has a physisorbed or chemisorbed character, single-molecule conductance measurements directly probe the nature of the bond. Moreover, the devices used to study single-molecule conductance, scanning tunnelling microscopy (STM) break junctions, provide insight on the properties of a single molecule, unlike characterization techniques, such as surface voltammetry or X-ray photoelectron spectroscopy, that can only examine several molecules at a time.

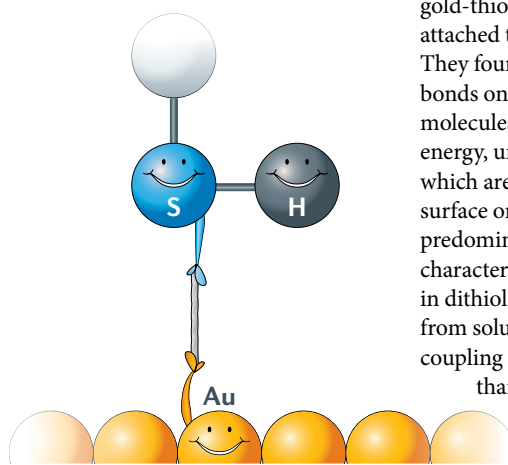
Venkataraman and colleagues combined single-molecule junction conductance measurements and density functional theory calculations to investigate the bonding, studying junctions formed by molecules comprising thiol, thioether (–SMe) and pre-formed gold–thiolate (–SAuR) linkers attached to a Au(111) surface. They found that chemisorbed bonds only form when an excess of molecules are present around high-energy, uncoordinated gold atoms, which are rare on the planar Au(111) surface on which the bonding predominantly has physisorbed character. “Critically, we show that in dithiol-based SAMs formed from solution, the gold–sulfur coupling has a physisorbed rather than chemisorbed character, in stark contrast to the accepted view,” comments Venkataraman.

Because computational studies of gold–thiol SAMs can only characterize the interaction of a single thiol-functionalized molecule with the surface, they don’t capture intermolecular effects. “Our work suggests that these effects may be important, and that constraints relating to the protonation state of the thiol or to the atomic structure of the underlying gold surface should be applied with care,” explains Michael Inkpen, first author of the study. “Because thiols and disulfides produce SAMs with very similar properties, proposed mechanisms should account for these different molecular precursors.”

Other factors — including surface reconstructions, the length of the sulfur substituent, pressure and temperature — may influence the formation mechanism of SAMs and the nature of the molecule–substrate bonding, thus requiring further study. These measurements may help to identify new linker groups and preparation methods that will facilitate the production of more stable SAMs with increased electronic transparency and stability.

“We are interested in continuing to use the STM break junction for the characterization of surface-bound molecular assemblies,” says Venkataraman. This method will be useful for studying the properties of different molecule–substrate contacts, the outcome of chemical reactions at the surface and the effects of different preparation conditions and post-assembly treatments on the SAMs.

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Credit: Lauren Robinson/Springer Nature Limited

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