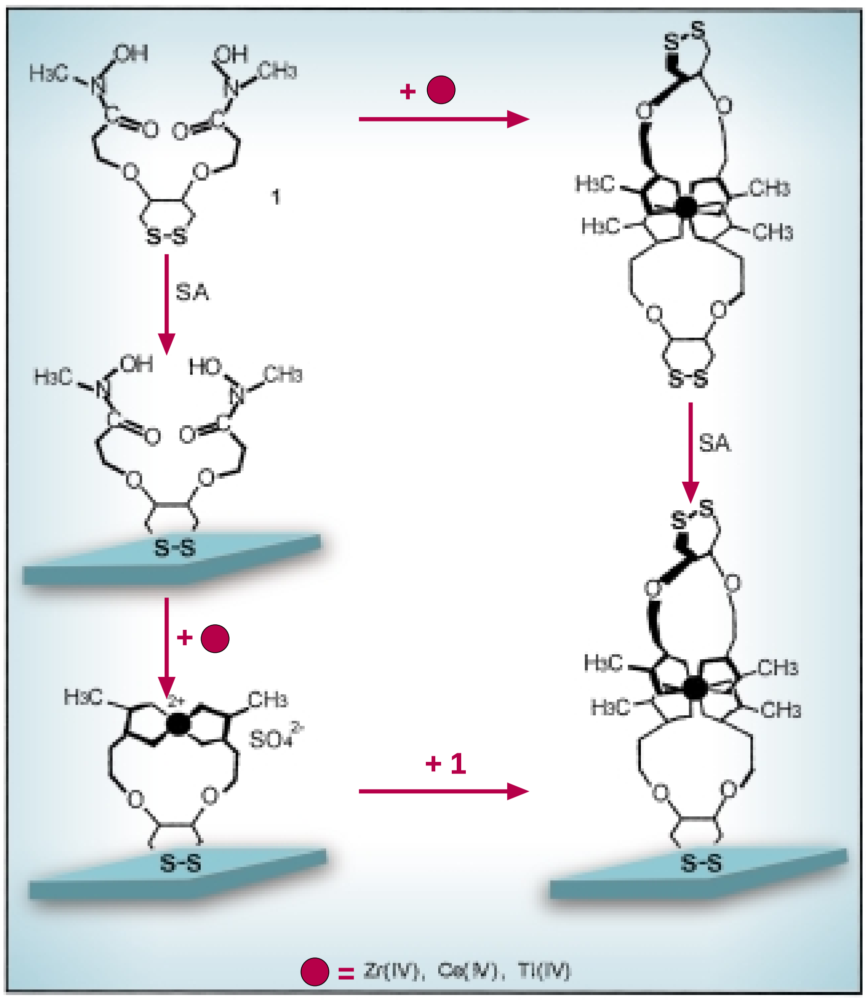
RESEARCH NOTES: New Routes to Self-Assembling Monolayers and Bilayers

As miniaturization proceeds apace, the construction and properties of uniform thin layers of molecules — only one (monolayers) or two molecules (bilayers) thick — assumes ever greater importance. Unlike nanostructures painstakingly built only one atom or molecule at a time, even relatively large electrically conducting surfaces can be readily coated with ultra-thin layers of special organic materials, which can be induced to assemble themselves into appropriate structures.

Prof. Israel Rubinstein of the Weizmann Institute and his colleagues have taken two great steps towards making such "macroscopic nanotechnologies" practical. First, although the surface of pure gold is theoretically hydrophillic and able to attract and bind molecules with charged polar groups, in practice these useful properties emerge only after extraordinarily careful and tedious cleaning to remove a tightly adsorbed 0.6 nanometer (nm, 10^{-9}m) or more layer of organic environmental contaminants. In contrast, the Israeli team has developed a relatively simple, inexpensive, highly reproducible method to prepare gold surfaces for monolayer deposition.

They first expose the gold surface to ultraviolet light, which converts oxygen (O_2) molecules in the nearby air into highly reactive ozone (O_3) molecules. The ozone oxidizes nearby organic contaminants into volatile products such as carbon dioxide and water. Then the surface is immersed in pure ethanol, which converts the gold oxide on the surface to pure gold. This procedure readily removed a subborn $C_{18}SH$ monolayer in a model test experiment.



Israeli researchers have found two useful new ways to assemble molecular bilayers held together by metal ions.

Self-assembling monolayers of alkythiol molecules, whose polar (hydrophillic) sulfur-containing head-groups bind to gold and whose long, fatty (hydrophobic) tails jut out from the gold surface, have been particularly well studied. The investigators applied an external voltage to help control the self-assembly of such alkythiol monolayers to their specially prepared gold surfaces in ethanol solution. Since the growing monolayer blocks electron transfer, the process could be monitored electrically in real time. The applied voltage speeded up assembly and, through a variety of effects, introduced considerable control over the simple and mixed monolayers formed.

The researchers also constructed more complicated bilayer structures, in which the two layers are held together by coordination bonds to a metal ion sandwiched in between them. They created these self-assemblying structures two different ways (see figure). In their step-wise procedure, a cyclical disulfide group anchors the first layer to the gold surface, then a metal (e.g., cerium) ion and a second layer are added. Both symmetric and asymmetric bilayers can be formed by this versatile method. In their quicker one-step method, the bilayer "building blocks" are prefabricated first, which allows full characterization of the metal complex before assembly. These "prefab" bilayer components are then anchored into place. A wide variety of versatile complex and, hopefully, useful new nanomaterials, including multilayers, should be formed by simple extensions of these techniques; and the Israeli researchers are avidly pursuing these and related avenues of research.