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$Mo_6S_{9-x}I_x$ Nanowire Recognitive Molecular-Scale Connectivity

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ABSTRACT

We report on a new highly reproducible route to recognitive self-assembly of molecular-scale circuits using sulfur-terminated subnanometer diameter $Mo_6S_{9-x}I_x$ (MoSIx) molecular nanowires. We demonstrate solution-processed attachment of MoSIx connecting leads to gold nanoparticles (GNPs). We also show that naked nanowires have the potential to bind thiolated proteins such as green fluorescent protein directly, thus providing a universal construct to which almost any protein could be attached. We further demonstrate three-terminal branched circuits with GNPs, opening a self-assembly route to multiscale complex molecular-scale architectures at the single-molecule level.

An outstanding challenge in molecular electronics is to connect diverse molecular entities together into large-scale functional molecular circuits. The connectors between elements need to be able to self-assemble following well-defined routes and form reliable electrical contacts between them. To reproducibly self-assemble a complex circuit based on single molecules, it is essential that the connectors which join them have recognitive ability. They should be connectable to diverse entitites, such as gold metal surfaces[1] (for connections to outside world) and biomolecules (for nanosensors, nanoelectrodes, molecular switches), and, most importantly, they must allow branching. The connectors should also be available with predetermined diameter and length. They should also have covalent bonding to ensure reproducible transport and contact properties.

DNA-like molecules have specific molecular-scale recognition and can be used very effectively in molecular scaffold fabrication.[2] Very complex shapes have recently been demonstrated,[3] but unfortunately metal-coated DNA which is electrically conducting is much too thick to connect to individual molecules. Thinner coated DNA lacks electronic connectivity[4] and is not suitable for connecting molecular electronics elements. Some varieties of carbon nanotubes (CNTs) are conducting, and connectivity at their ends can be achieved by attachment of connecting groups.[5] Unfortunately manufacturing CNTs with predetermined properties is impossible at present, and the functionalized ends are typically not conducting,[6] limiting their usefulness as molecular connectors. Individual CNTs can be soldered in an electron microscope,[7] but the contact is not covalent and cannot be self-assembled.

The molecular-level connector kit which we propose here is based on $Mo_6S_{9-x}I_x$ (MoSIx) molecular wires (MWs). The

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material is relatively easily synthesized[8] and isolated. Just as importantly, single 0.9 nm diameter MWs are reproducibly obtained with lengths up to $l = 100$ μm by debundling. Different diameter[9] multiple-strand bundles can also be controllably obtained, ranging from $d = 1.6$ nm to >1000 nm (as measured by atomic force microscopy (AFM)). The length of MoSIx bundles can either be controlled in the synthesis process (for long bundles) and/or be shortened by subsequent ultrasonic treatment.

Measurements of the single-bundle longitudinal conductivity σ_L have shown metallic behavior in the ohmic regime, with resistivities[10,11] $\sigma_L > 500$ S/m, and ubiquitously linear $I-V$ characteristics also for thin bundles. Lithographic or dielectrophoretic contacts have both been shown to give similar contact impedances using different contact metals,[10] with current densities in excess of $J_c > 10^4$ A/cm^2.

Crucially, for use as molecular connectors, the MWs have S atoms at the ends, allowing covalent bonds to be formed to gold surfaces or to thiol groups on larger molecules which are commonly used for connecting molecules to contacts.[12] The latter allows recognitive self-assembly which is site specific and is defined by the thiol position on the molecule. The presence of S−H bonds on $Mo_6S_3I_6$ MWs was determined by Ellman's reagent, whereby S−H containing thyroglobulin protein was used as a positive control and stefin B protein (which does not contain any S−H groups) as a negative control. Details on preparation and Ellman's test are given in the Supporting Information.

Before self-assembly, $Mo_6S_3I_6$ nanowires (as supplied by Mo6 doo) were first annealed at 750 °C in a sulfur atmosphere. Subsequently they were ultrasonically debundled in isopropyl alcohol (IPA) to the desired average diameter according to the empirical formula[9] $d = 75C^{1/2}$, where C is the concentration in mg/mL. The GNP (British Biocell International) were first diluted 500 times in H_2O or IPA and then mixed with the nanowire dispersion in proportion of 1(nanowires):3(GNP). Drops of the solution are then dried and analyzed on a mica surface with a DI Dimension 3100 atomic force microscope in tapping mode. A systematic investigation by AFM reveals a large number of GNPs attached to the ends of MoSIx nanowires, such as the tadpole-like structure shown in Figure 1a. Measurements of height profiles along the MW in Figure 1b show the nanowire height as $h = 0.8 \pm 0.2$ nm and GNP size of 5.3 ± 0.5 nm. We obtain attachment yields of over 50% in water and 10% in IPA (measured by counting the ends of 21 MWs with and without GNPs attached). In comparison, very few (<5%) GNPs have been observed attached to the sides of MoSIx MWs. Control experiments with silver nanoparticles showed no attached particles.

Multiple connections to a single GNP have also been obtained. Two MWs attached to a single GNP are commonly observed (see examples shown in the Supporting Information). The emerging connectivity protocol for self-assembly of larger circuits involves sequential concatenation of individual components: with a yield y_i for each step i, the maximum final yield is approximately equal to the product of all the $Y = \Pi y_i$. Reaction temperature, choice of solvent, and concentration appear as the main control parameters controlling the yield. In Figure 2c we show a large branched circuit containing a number of GNP-MW connections. An expanded image of *three* thin MoSIx bundles connected to one GNP is shown in Figure 1d. The angle between the bundles is 120 ± 5°, and the diameters of the three connecting MWs are $d = 1.2$, 1.5, and 2 nm as shown in the profile measurements in Figure 1e.

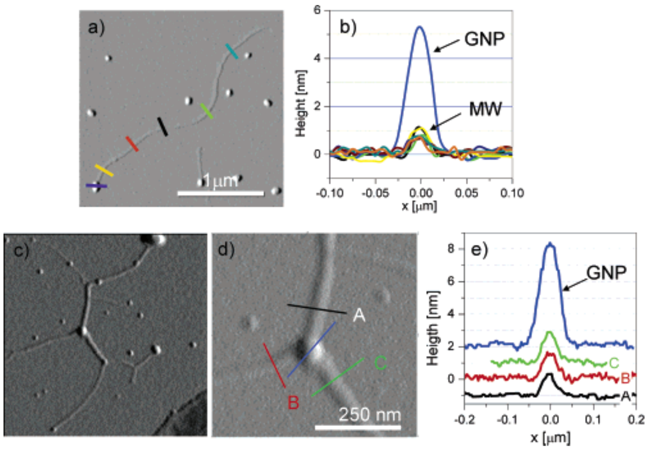

Figure 1. (a) An AFM tapping mode image of a single MoSIx molecular wire attached to a GNP. (b) From the height profiles, the GNP diameter is 5.2 ± 0.2 nm, and the MoSIx MW at multiple points along its length gives a height of 0.8 ± 0.1 nm. (The cross sections are color coded.) (c) A multiply connected object which contains two examples of a GNP attached to three MWs. (d) Three nanowires connected to a GNP from (c). (e) The height profiles A, B, and C show that the MW bundle diameters are 1.2, 1.3, and 1.4 nm, respectively. The height of the gold particle is 6 nm. (The height profile traces are displaced vertically for clarity.) All images were obtained on a mica surface in tapping mode.

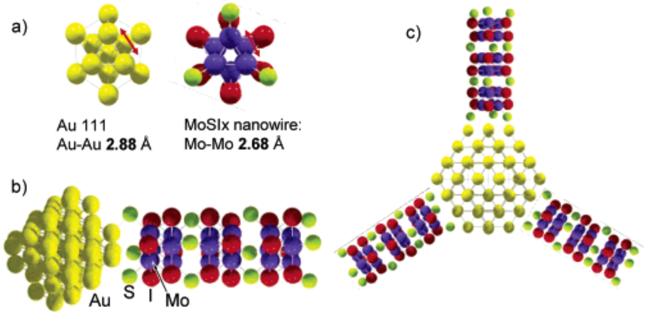

Figure 2. (a) The end-on view of the atomic arrangements of a MoSIx nanowire and a (111) GNP surface. The Au−Au atoms and Mo−Mo distances are indicated (with the red arrows). (b) A schematic structure of a possible GNP connection to a MoSIx molecular wire. (c) A schematic picture of a possible arrangement of three (single) MoSIx molecular wires attached to one GNP with a 120° geometry such as is observed in Figure 1.

Next, we discuss the possible geometry of the bonding between MoSIx MWs and GNPs. Connections to gold surfaces may be expected to have more than one covalent bond per MW. The Au atoms on [111] GNP faces are triangularly arranged, with Au−Au spacing of $d_{Au-Au} = 2.85$ Å. d_{Au-Au} is very close to the Mo−Mo distance $d_{Mo-Mo} = 2.68$ Å of Mo atoms at the ends of $Mo_6S_3I_6$ nanowire (Figure 2a). This suggests that the terminal S atoms on the MW ends

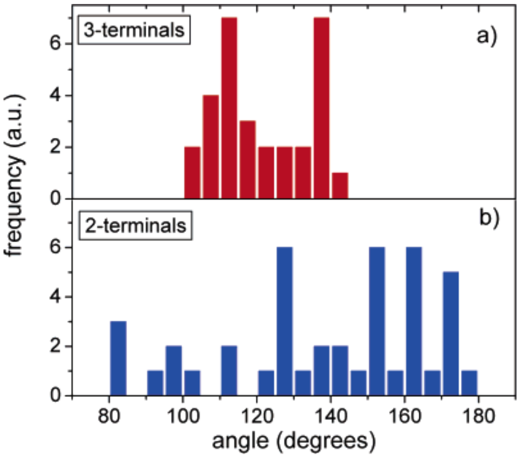

Figure 3. The frequency of occurrences of different angles between MoSIx nanowires (a) for two and (b) for three NW terminals connected to an individual GNP, respectively.

may readily form three bonds between the Mo atoms in the MW and the Au atoms on the GNP [111] faces as shown schematically in Figure 2b. In general, the shape and structure of small GNPs may strongly vary,[13] but GNPs with a cubic structure have two [111] faces at the corners of a truncated cube, whose normals are projected onto a plane at 120° to each other and a third face at 120° is a [100] face, forming a triangular arrangement shown schematically in Figure 2c. Larger circuits, with five MWs and two GNPs with the same 120° connectivity pattern have also been observed (such as in Figure 3c, additional examples are shown in the Supporting Information), suggesting that a favored geometry involves regular GNP structured nanoparticles. In Figure 3 we show the statistical distribution of angles which have been observed. We see that with three MWs connected to a GNP, the angle between them is centered around 120° and distributed between 100° and 145°. With two MWs connected to a GNP, the angles are much more widely distributed, ranging from 80° to 180°, larger angles (>120°) occurring more often than smaller ones (<120°). The substrate has been found to be important for orienting the MWs, and the 120° geometry in Figure 2 may be facilitated by the preferential alignment of MWs by the mica substrate. However, from the statistics in Figure 3, the fact that for the two-terminal GNPs the angles are rather spread, while for three-terminal GNPs they are not, supports the assumption that the 120° geometry is inherent to the connectivity of the GNP wires and not due to the mica substrate.

In Figure 4 we show two examples of MoSIx MW bundle connections to mutant green fluorescent protein (GFP) molecules. In order to allow S−S bonding, thiol-containing cysteine residue was inserted at the N-terminus of the GFP sequence (details of the cloning and gene expression and the preparation procedure are given in Supporting Information). The resultant GFP−Cys was mixed in water with MoSIx nanowires and deposited on a mica surface. The MoSIx−GFP self-assembly has a high yield of 90 ± 10%. In the first example shown in Figure 4, a 2.4 nm diameter MoSIx bundle is attached to a GFP−Cys aggregate with a diameter approximately 5 nm. In the second example, a GFP−Cys aggregate (10−13 nm height) is attached to two nanowires, each approximately 2.5 nm in diamater. Just as with GNPs, we do not observe GFP attached to the sides of nanowires, only at the ends, where S atoms are available for bonding on the MoSIx nanowires. Similar connections have been obtained also with other proteins containing thiol groups such as thyroglobulin (a further example is shown in the Supporting Information), thus demonstrating that the vast functional variability of biological macromolecules is ready for use at the single nanoparticle level.

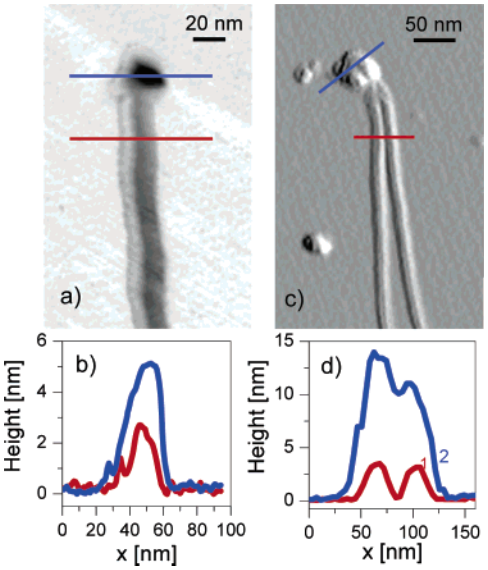

Figure 4. (a) A single MoSIx 2.4 nm diameter bundle attached to a GFP−Cys mutant protein containing thiols (left). (c) A GFP−Cys aggregate connected to two MoSIx nanowire bundles (right). The height profiles (b) and (d) corresponding to (a) and (c), respectively, are shown color coded. Both images are recorded in tapping mode.

We have demonstrated two possible routes for the construction of larger functional circuits using MoSIx MWs: via GNPs and by direct connection to thiolated biomolecules. The two approaches may lead to different possible applications. The use of GNPs offers the possibility of branching and construction of larger circuits. Directly connected functional biomolecules on the other hand can be used for sensor applications. In sensors and in larger circuits, it may be useful to electrically insulate the leads. Immobilization of nonconducting proteins on the surface of MoSIx nanowire bundles, such as has been recently demonstrated,[14] may be used for this purpose, leaving electrical contact only at the functionalized ends. In many nanoelectrode applications it is important that the connector has mechanical stability, for which thicker MW bundles can be chosen. All the MoSIx nanowire connections shown here appear to be inherently stable in air and compatible with Si-based technology. The branching demonstrated in Figure 1 is quite unique, and with optimized yields, improved self-assembly protocols, and control of MW size it is expected that rapid steps toward bottom-up system integration on the subnanometer scale can be realistically expected.

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Supporting Information Available: A description of methods for preparation of proteins and further examples of self-assembled conjugates. This material is available free of charge via the Internet at http://pubs.acs.org.

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