Mo$_6$S$_3$I$_6$ molecular wires: from one-dimensional electron fluids to a self-organised critical self-assembled network

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Abstract. We have studied the charge transport through flexible Mo$_6$S$_3$I$_6$ molecular wires of different diameters and found that it is dominated by two main phenomena. Tunnelling from Fermi liquid electrodes into the Tomonaga-Luttinger liquid electron system of the one-dimensional wires determines the behaviour of about half the measured samples, while for the other half environmental Coulomb blockade arising from deformations or imperfections is the main mechanism. The unique S-bonding chemistry of Mo$_6$S$_3$I$_6$ wire ends and gold nanoparticles enables self-assembly of large molecular-scale inorganic networks. These show an intrinsic tendency to self-organize into a scale-invariant critical state as found also in biological neural networks.

1. Introduction

Progress in molecular electronics faces two major challenges: finding the adequate molecular building blocks and assembling them into functional structures. While big advances have been made in molecular transistors and switches, molecular connectors are still elusive. In this paper we report on the electronic transport properties of Mo$_6$S$_3$I$_6$ molecular wires (MoSI MWs) [1, 2] and show how they self-assemble into scale-invariant self-ordered critical networks upon co-dispersion with gold nanoparticles (GNPs).

2. Methods

MoSI MWs are prepared as described in [3], yielding stable dispersions containing MW bundles with diameters ranging from 1 to a few 100 nm. For transport measurements nickel electrodes were prepared by electron beam lithography. The MW bundles were deposited via dielectrophoresis - by placing a drop of solution over the electrodes and applying a 50 Hz AC electric field to the electrodes. The entire circuits were then annealed in vacuum at 700 °C for 1 h. AFM images of typical samples after annealing are shown in the insets of figures 1a and 2a.

For the network formation a dispersion in water was diluted and centrifuged to contain only thin bundles of 1-3 nm diameter. A GNP dispersion of 5 nm nominal diameter (British Biocell International) was added and the mixture was left to react and form a network for 3 days at 4 °C. Thus prepared samples are drop-cast onto muscovite mica and rapidly heat dried with a lamp. Mica was chosen since water has a low contact angle on the mica surface and during drying MWs and MW networks are deposited rather homogeneously, while on other surfaces they tend to form large
aggregates, which compromises the network analysis. Samples were also prepared on a holey carbon substrate for examination of the MoSI-GNP connections by HRTEM.

3. Charge transport
We measured the I/V characteristics of about 30 samples for different temperatures from 20 K to room temperature and find that about half the samples consistently display a behaviour as depicted in figure 1 as an example of this group, while the others behave as shown in figure 2. For both groups we examine whether their behaviour can be described by one of the nonlinear transport processes known from the literature on low-dimensional conductors: tunnelling from Fermi liquid contacts into a Tomonaga-Luttinger liquid (TLL) [4,5], environmental Coulomb blockade (ECB) [6], and variable range hopping (VRH) [7].

Figure 1. a) Normalized I-V characteristics at different temperatures. The current was arbitrarily normalized at 1 V for all curves. At 295 K, \(I_0=230\) nA. The inset shows a AFM topographic image of the annealed circuit.

b) A plot of \(I/T^{\alpha+1}\) vs \(eV/kT\), \(\alpha=2.3\). All curves collapse onto one (same colour code as a). The inset shows the zero-bias conductance (slope of \(I-V\) curve at low bias, \(V=\pm 20\) mV) as a function of temperature and a fit to \(T^\alpha\).

TLL behaviour has been invoked in describing the transport in circuits containing carbon nanotubes [8], conjugated polymers at high currents [9], and \(\text{Li}_2\text{Mo}_6\text{S}_6\) nanowires [10], the latter being close relatives of MoSI MWs. The characteristic temperature and field dependence of tunnelling into a TLL (see [4] for a detailed analytic description) makes the set of curves shown in figure 1a collapse onto one single curve when \(I/T^{\alpha+1}\) (with the exponent \(\alpha\) obtained from the power-law temperature dependence of the zero-field differential conductivity, see inset) is plotted against \(eV/kT\), as shown in figure 1b. Given the excellent agreement with TLL and the poor agreement with both ECB and VRH we conclude that in the first group of samples the current limiting step, which defines the \(T\)-dependent \(I/V\) behaviour, is tunnelling from metallic contacts into the one-dimensional electron liquid of the MWs. For increasing bundle diameters we find a linear increase of the conductance rather than the quadratic one we expect if all MWs in the bundle conducted. We therefore conclude that only the outermost MWs contribute to charge transport and there is no transversal conduction (e.g. inter-wire hopping) that would make the inner bundles available for transport.
ECB is observed if an element in a circuit acts as a quantum dot, which accepts electrons only at the expense of some electrostatic energy. This leads to a characteristic kink in the I/V curve (see figure 2a), which translates a crossover between two regimes for the differential conductance around the kink (right panel). The second group of samples shows a behaviour that is dominated by ECB (while neither TLL nor VRH can describe the data). From the position of the kink we can estimate the capacity of the quantum dot, which for the sample shown in figure 2 is $C = e/2V \sim 5 \times 10^{-19}$ F. This is about 10% of the capacity of the whole bundle between the two contacts [11], indicating that only a segment of the bundle forms the quantum dot. This segmentation can either arise from strong bending, or from stacking faults during the growth, as seen in the HRTEM image in figure 2b.

![Figure 2](image)

**Figure 2.** a) Normalized $I$-$V$ at different temperatures. The current was arbitrarily normalized at 1 V for all curves. The dashed line is the tangent to the low temperature curve. The inset shows an AFM topographic image of the annealed circuit and slope of the $I$-$V$ curve at low bias, $V = \pm 20$ mV as a function of temperature and a fit to $T^\alpha$, $\alpha = 3.5$. At 295 K, $I_0 = 620$ nA.

b) The derivatives $dI/dV$ obtained from the normalized $I$-$V$ data. The derivative at low V increases as T increases from 18 to 300 K. The inset shows a high-resolution transmission electron microscope image of a MW bundle with a diameter of 124 nm. The defects in the structure are clearly visible as streaks across the wire which may cause the formation of a quantum dot. The vertical line marks the $I=0$ intercepts from the tangent in a).

We conclude that the MoSi MWs in a bundle are channels of TLL conductors. Only a fraction of the channels (probably the MWs on the surface) contribute to the conduction mechanism. In one group of bundles tunnelling from the Fermi liquid electrodes into the TLL is the rate-limiting step and therefore dominates the electronic transport properties. In the other group there are breaks in the conducting channels, which modify the TLL behaviour through ECB.

4. Network formation

The self-assembly of MW-GNP networks proceeds in a solution that contains approximately 1 thin NW bundle and 1 GNP per 10-100 $\mu$m$^3$ of water. The GNPs are more mobile and first attach to the molecular wire ends or defects, after which they act as anchoring spots for other wires and a three-dimensional (3D) network is formed. After deposition on the substrate, the water evaporates and the 3D network formed of flexible MWs collapses into a 2D shape that can be imaged with an AFM (see figure 3a). Many MWs are bent between vertices, with the convexity preferentially pointing towards the lower right corner. This indicates that bending is caused by a directed flow as the water droplet
shrinks while the GNPs anchor on the surface. The anchoring also prevents orientation of the MWs along the three mica axes, as is observed for isolated bundles without GNPs. Once the solvent is removed, the MWs themselves also stick strongly to the substrate.

**Figure 3.** a) The raw AFM topographical image of a large self-assembled network on mica. The GNPs have a height of 5 nm and are connected with nanowires whose height ranges from 0.9 to 2.5 nm. The small dots believed to be individual MoSI clusters have a height of 1.4 nm and are not of interest here. b) A computer generated network based on the data shown in panel a is used for further analysis of the network properties. Line colours signify length of each segment and vary from light green (short) to blue (long). Vertexes with particles are marked with black dots. c) High-resolution transmission electron microscopy images of a GNP connected to a break in the MoSI bundle.

For statistical analysis the topographical AFM image was transformed into a mathematical graph, recording the vertex coordinates and connections between them (figure 3b). The graph consists of more than 2000 vertices and approximately 4000 edges connecting them across an area of 10 × 10 μm². Slightly less than half of these vertices contain a GNP, the others arise simply from branched bundles and from crossing of MWs as the 3D network formed in solution collapses into 2D.

From the analysis of the mathematical graph we extract the distribution of edge lengths (see figure 4b). While individual bundles show a log-normal distribution function (see figure 4a), the edge lengths in the graph follow a power law $P(x) \sim x^{-\alpha}$ with $\alpha \approx -2.3 \pm 0.1$ for most of the measured length range, from 100 to around 3000 nm. The cut-off below 100 nm is a result of the finite lateral resolution of the AFM tip. Although we cannot measure the original 3D network properties in solution, we expect it to
exhibit a similar power-law length distribution, while the exponent $\alpha$ may be different from what we obtain in 2D.

**Figure 4.** a) The length distribution of individual nanowires in an isopropanol solution can be described with log-normal distribution. b) The length distribution of MW segments in the analyzed network with fitted power-law tail: $P(x) \sim x^\alpha$, $\alpha = -2.3 \pm 0.1$. The colour of the dots in the graph corresponds to the colour coding of the graph edges in figure 3b.

Since the AFM lateral resolution is limited to $>20$ nm, edge lengths significantly below 100 nm are not accurate. However, by closely examining smaller sections of the network we observed that some of the thicker bundles in the network are actually composed of numerous thinner wires forming an intricate web of their own [12]. Although the AFM resolution precludes mapping of these features, they suggest that shorter edges are much more frequent than they appear in our statistics and the observed power-law dependence may continue well below 100 nm.

The power-law behaviour of the edge lengths indicates that the network is scale-invariant over a large range. Such self-organized critical behaviour occurs in neural networks [13] and leads to the functionality of brains [14]. Neurons operate via electrical signals (action potentials) propagating through the network, where the vertices (the somas) act as nonlinear elements that process the signals, while the axons transmit the signals. A superficial analogy suggests that the GNPs might act as nonlinear elements (or be replaced other nanoparticles or molecules which do), while the MWs can transmit the electrical signals between them. However, the MoSI-GNP circuits are much smaller than biological neural networks, and charge transport is much faster since it is governed by Coulomb blockade at the nodes rather than the action of chemical neurotransmitters on neuron receptor sites. The faster charge transport and the shorter signal paths make the MoSI-GNP (or MoSI combined with other active nodes) networks potentially much faster than biological networks of equivalent complexity.

**5. Conclusions**

The present experiments show that non-linear low-dimensional transport dominates the behaviour of MoSI MWs and bundles formed from them. The TLL model with its distinctive data collapse of the I-V characteristics at different temperatures holds well for a significant proportion of the thin wire circuits. Another subset of thin wires shows clear signatures of the kinked I-V curves predicted by
ECB. Discontinuities in the wires either as a result of bending, and/or structural stacking faults within the wire are believed to cause the formation of quantum dots, which lead to the occurrence of ECB behaviour. MoSI MWs can be dispersed to thin enough bundles to allow covalent S bonding of their ends to individual molecules [15], so for the construction of molecular scale circuits, where thin and relatively short wires are of interest, they may potentially revolutionize molecular electronics. Our analysis of the first self-assembled inorganic conducting network shows that the system is in a self-ordered critical state. Such systems are amenable to sophisticated data processing, not least in the human brain. The MoSI-GNP networks are much smaller than typical neural networks, which bears the scope for low energy consumption and fast electronic processing speeds. The unique chemical connectivity enables to use a wide variety of nonlinear vertex elements with different functionalities.

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