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# Controlling the interparticle distance in a 2D molecule–nanoparticle network

C M Guédon<sup>1</sup>, J Zonneveld<sup>1</sup>, H Valkenier<sup>2,3</sup>, J C Hummelen<sup>2,3</sup> and S J van der Molen<sup>1</sup>

<sup>1</sup> Kamerlingh Onnes Laboratorium, Leiden University, PO Box 9504, 2300 RA Leiden, The Netherlands

<sup>2</sup> Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

<sup>3</sup> Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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## Abstract

Mechanically controllable break junctions allow for an impressive level of control over the distance between two electrodes, but lack stability at room temperature. On the other hand, two-dimensional (2D) networks of nanoparticles bridged by molecules form a stable device structure for investigating molecular conductance properties. Here, we combine both techniques to create a robust platform for molecular charge transport with control over the inter-electrode distance on the picometer scale. The resistance change due to bending of our structures is dependent on the molecular species present between the nanoparticles.

 Online supplementary data available from [stacks.iop.org/Nano/22/125205/mmedia](http://stacks.iop.org/Nano/22/125205/mmedia)

(Some figures in this article are in colour only in the electronic version)

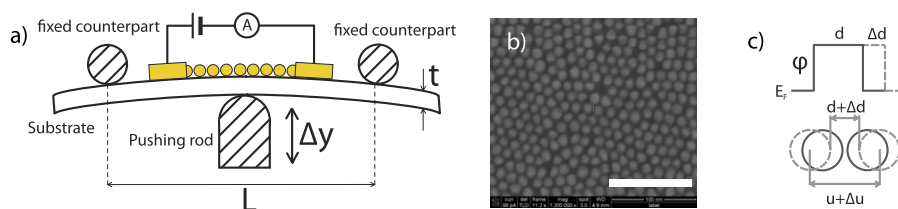
Research in molecular electronics is strongly inspired by the possibility to encode a well-defined functionality, such as switchability, into a single molecule [1, 2]. On the road towards nanoscale functional devices, various fundamental questions arise. Many of these have to do with the details of the connection between a molecule and two electrodes. For example, the distance between the electrodes defines if and how a molecule can be connected between two metals. Moreover, a molecule that exhibits a significant length change upon switching is likely to lose its functionality in a rigid junction. Interestingly, the inverse may also be true, a possible example being spin transition molecules [3]. Since the length of such a molecule is larger in its high-spin than in its low-spin state, straining it may actually induce a spin transition.

Here, we aim for a stable molecular device structure which allows one to vary the inter-electrode distance on the sub-Ångstrom scale. For this, we combine two techniques which have proven their use in molecular transport studies: mechanically controllable break junctions (MCBJs) [4, 5], and 2D nanoparticle–molecule networks [6–9]. MCBJs are widely used to study single molecule conductance and allow for tuning of the inter-electrode distance with great accuracy. However, they lack stability at room temperature. Devices based on molecule–nanoparticle networks, on the

other hand, offer great stability even at 293 K. One reason for this is that a nanoparticle–molecule–nanoparticle junction has a tiny mechanical loop. The other reason is that a conductance measurement forms a statistical average over a full array. Hence, fluctuations (molecular bond breaking and re-attachment) on the single junction level average out.

Here, we combine the advantages of both techniques to create a 2D molecule–nanoparticle network in which the interparticle distance can be varied.

We start with the synthesis of gold nanoparticles (NPs) following the Slot and Geuze method [10]. In this way we obtain NPs that are  $10 \pm 1$  nm in diameter and charge stabilized in water. Next a solvent exchange step is performed (water to ethanol) to self-assemble alkanethiols, in this case octanethiols, on the NPs to prevent aggregation. After another solvent exchange step (ethanol to chloroform) the NPs are self-assembled into a 2D network on a convex air–water interface due to the evaporation of the solvent. This is followed by a microcontact printing step, i.e. the network is transferred from the water surface to the substrate using a polydimethylsiloxane (PDMS) stamp. Note that the self-assembled alkanethiols define the initial interparticle distance [7]. As a bendable substrate, we use phosphor–bronze which needs to be electronically isolated from the NPs.



**Figure 1.** (a) Schematic cross-section of the measurement setup. By bending a phosphor–bronze substrate in a three-point geometry, a 2D nanoparticle–molecule network is stretched. (b) Scanning electron micrograph of an octanemonothiol protected gold NP network; the scale bar shown is 100 nm. (c) Schematic view of the tunnel barrier when the distance between the surface of two nanoparticles is increased from  $d$  to  $d + \Delta d$ . We define  $u$  as the distance between the centers of the nanoparticles. Note that  $\Delta u = \Delta d$ . The height of the energy barrier equals  $\phi$ .

The insulating layer applied will also need to transmit the substrate deformation and to offer good adhesion to the NP network. We tested four different materials (PMMA, N-1410, SU-8 and poly-imide) spin coated on our substrates. Poly-imide, already used for MCBJ substrates [4, 11], shows the best adhesion properties for the NPs. Finally gold contacts are deposited by shadow mask evaporation, the electrodes being 160  $\mu\text{m}$  apart (more details on the device are given in the supplementary information, SI, available at [stacks.iop.org/Nano/22/125205/mmedia](http://stacks.iop.org/Nano/22/125205/mmedia)). In this way, a network is created in which a unit junction comprises two nanoparticles separated by a tunnel barrier that consists of two monolayers of alkanemonothiol. From here it is also possible to create a 2D network of metal–molecule–metal junctions using a place exchange step [6–9]. This results in the formation of one or a few molecular junctions as discussed below (see also SI available at [stacks.iop.org/Nano/22/125205/mmedia](http://stacks.iop.org/Nano/22/125205/mmedia)). Interestingly, the network's sheet resistance can be directly related to the average resistance of a single junction [7] (SI available at [stacks.iop.org/Nano/22/125205/mmedia](http://stacks.iop.org/Nano/22/125205/mmedia)).

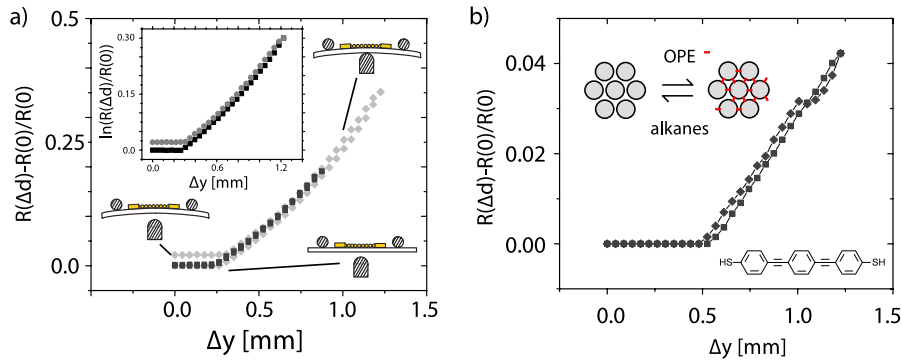
For our experiments, we mount a substrate onto an MCBJ setup, as illustrated in figure 1(a). A pushing rod, capable of bending the substrate in a three-point geometry, is driven by a motor that can be operated continuously or stepwise. The network on the substrate is connected via spring-loaded contacts to an  $IV$ -converter and a data acquisition card. A bias voltage of 2 V is typically applied to the network, resulting in a voltage drop of a few mV for each junction. The resistance is recorded while bending. All the measurements are done at room temperature and in a low vacuum chamber at a pressure of about  $10^{-3}$  mbar.

Let us first anticipate what happens when we bend a network with alkanemonothiol only, i.e. without dithiolated molecular bridges. When displacing the pushing rod by a distance  $\Delta y$ , as shown in figure 1(a), the upper surface of the phosphor–bronze substrate is elongated. Its deformation is transmitted by the poly-imide layer to the NP network (figure 1(b)), resulting in lateral strain on the network. To get a picture of the resulting resistance behavior of our structure, we note that a unit junction formed by two NPs is basically a tunnel junction. Its barrier height,  $\phi$ , is defined by the work function of gold covered by alkanemonothiol. The barrier width is the distance  $d$  between the edge of two NPs as shown in figure 1(c). For reasons that will become clear later, we also define  $u$ , the distance between the centers of

the two nanospheres. The junction resistance can be written in the form:  $R \propto e^{2\kappa d}$  where  $\kappa = \frac{1}{\hbar}\sqrt{2m\phi}$  with  $m$  the electron mass and  $\hbar$  the reduced Planck constant. The change in resistance when elongating the junction with  $\Delta d$  is thus expected to follow:  $\ln(R(\Delta d)/R(0)) = 2\kappa \Delta d$ , where  $R(0) \equiv R(\Delta d = 0)$ . In the linear regime we can simplify this relation to:  $(R(\Delta d) - R(0))/R(0) = 2\kappa \Delta d$ . Hence, we can accurately monitor the displacement between the nanoparticles by measuring the network's resistance response.

In a typical experiment the substrate is bent back and forth by moving the pushing rod in steps of  $\Delta y = 0.043$  mm. After each step the resistance change is probed. Figure 2(a) shows the result for a sample with octanemonothiol tunnel junctions with an initial resistance of 176 M $\Omega$ . The data are plotted both linearly, showing  $(R(\Delta d) - R(0))/R(0)$  versus  $\Delta y$ , and semi-logarithmically, displaying  $\ln(R(\Delta d)/R(0))$  (see inset). Two experiments are shown; in the first case (black squares) the sample was bent less than in the second case (gray diamonds, also later in time). Figure 2(a) exhibits a plateau for small displacements. This has a trivial reason, as it corresponds to the situation where the pushing rod is not yet touching the substrate (see right bottom cartoon in figure 2(a)). Once the substrate is actually bent, however, the resistance increases significantly, as anticipated above. For larger displacements, the curves deviate from linearity as indeed expected. Upon plotting  $R(\Delta d)/R(0)$  semi-logarithmically, the curves become straighter. However a small deviation at high  $\Delta y$  is still present, probably due to plastic deformation (see below). As also can be seen on the other measurements in the supporting information (available at [stacks.iop.org/Nano/22/125205/mmedia](http://stacks.iop.org/Nano/22/125205/mmedia)) we remain generally within the linear regime. The relative change in resistance  $(R(\Delta d) - R(0))/R(0)$  per mm pushing rod displacement for this sample is found to be  $0.34 \pm 0.02$  mm $^{-1}$  (from the black squares). We investigated five such samples and  $(R(\Delta d) - R(0))/R(0)$  varied from 0.20 to 0.36 per mm pushing rod displacement, with an average of 0.30 mm $^{-1}$  (see SI available at [stacks.iop.org/Nano/22/125205/mmedia](http://stacks.iop.org/Nano/22/125205/mmedia)).

Let us now have a closer look at figure 2(a) and focus on the second experiment shown (gray diamonds) where the substrate is bent further than before, i.e. to  $\Delta y = 1.25$  mm. In this case, the retracting trace does not come back to its original value. In fact, the plateau for small  $\Delta y$ , discussed above, is located at a higher resistance value and spans to higher  $\Delta y$  than before. This discrepancy is related to plastic deformation, i.e. permanent bending of the substrate as



**Figure 2.** (a) Relative resistance change as a function of pushing rod displacement,  $\Delta y$ . A schematic view of the substrate is shown next to the curve to illustrate: (i) the plateau for low displacements before the pushing rod touches the substrate, (ii) the case when the substrate is fully bent, and (iii) hysteresis due to plastic deformation of the substrate. In the inset the same data are plotted in a semi-logarithmic way. (b) Relative resistance change as a function of pushing rod displacement for a network with OPE3 bridges. The pushing trace is represented by squares and the backward trace features diamonds. In the upper inset the molecular exchange reaction is schematically depicted and in the lower inset the chemical structure of OPE3 is shown. Note the kink in the back trace around 1 mm, which is due to slipping of the driving motor.

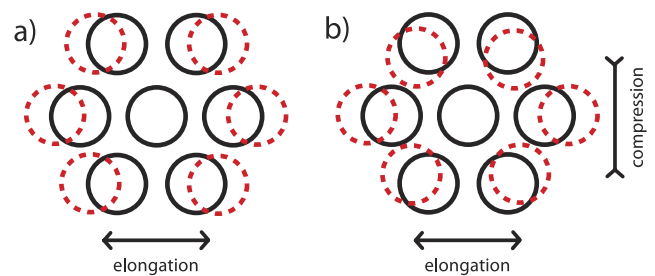
indicated in the left cartoon in figure 2(a). Hence, the pushing rod needs to move further up, to larger  $\Delta y$ , before additional bending is possible. All these observations demonstrate that the resistance change is due to network elongation, which itself results from deformation of the substrate. Hence, our device opens the road towards a strain sensor (or bending sensor) based on tunneling transport. In addition, we can deduce that the networks are more or less homogeneously deformed, i.e. deformation does not lead to fractures in the structure. Indeed, if fractures were formed, they would lead to large tunnel gaps and resistance increases much beyond our expectation (see below). Furthermore, scanning electron microscopy (SEM) characterization after the bending experiment shows no evidence of fracture formation. We note that similar networks have been shown to be elastically deformable, with a Young's modulus of several GPa [12].

Let us now have a more quantitative look at the deformation of the NP network and the resulting resistance changes. For this, we can rely on previous deformation calculations performed for MCBJs [4, 11]. When displacing the pushing rod by a distance  $\Delta y$ , the network will elongate by a distance  $\Delta U$ , measured from electrode to electrode, as given by:

$$\Delta U = \frac{6tU\Delta y}{L^2}\zeta. \quad (1)$$

Here  $L$  is the distance between the two fixed counterparts (20 mm in our case),  $t$  the thickness of the substrate (3 mm), and  $U$  the distance between the two evaporated electrodes (see figure 1) [4].

The correction factor  $\zeta$  has been introduced by Vrouwe *et al* to compensate for device-specific features such as undercut as well as stacking order of the different materials used [11]. In the ideal case where the deformation of the substrate is exactly transferred to the structure on top of it (MCBJ or network)  $\zeta = 1$ . In the case of lithographically defined MCBJs the undercut amplifies the deformation of the substrate which results in  $\zeta > 1$  [11].



**Figure 3.** Schematic view of a basic lattice unit unstretched (black lines) and stretched (red dotted lines). In (a) the deformation is unidirectional as the NPs are well attached to the substrate. (b) As a consequence of the loosely attached NPs to the substrate the Poisson effect induces a compression in the direction perpendicular to the deformation.

The conductance through an NP network can be described from a simple unit cell as shown in figure 3 (see also SI available at [stacks.iop.org/Nano/22/125205/mmedia](http://stacks.iop.org/Nano/22/125205/mmedia)). Such a unit cell may be deformed in two ways. On the one hand, we consider the case where the NPs are well attached to the underlying layer. Then, the network will be deformed uniaxially as shown schematically in figure 3(a). On the other hand in figure 3(b) we show the case where the NPs are loosely connected to the substrate. Then the network, when elongated in one direction, will be compressed in the perpendicular direction to keep its total surface constant; the so-called Poisson effect. Let us define  $N = U/u$  as the average number of nanoparticles between the electrodes in the  $\hat{x}$  (or  $\hat{u}$ ) direction. Consequently, for a network lattice direction lined up with the  $\hat{x}$  direction  $\Delta U = N\Delta u = N\Delta d$  (see figures 1(c) and 3). We can also calculate the length changes of the junctions in the other lattice directions, for both 2D models, using simple trigonometry. With this we can obtain values for  $2\kappa$  from our measurements for both 2D models. Let us first assume ideal transfer of deformation, i.e.  $\zeta = 1$ . The apparent  $2\kappa$  values thus obtained for our experiment are  $0.15 \text{ \AA}^{-1}$  for well attached NPs and  $0.21 \text{ \AA}^{-1}$  for loosely

connected NPs. These should be compared to a  $2\kappa$  value of  $0.87 \text{ \AA}^{-1}$  as experimentally found for alkanemonthiols in similar junctions [13]. We relate the discrepancy to the incomplete translation of the substrate elongation to the network, i.e. to  $\zeta$  being smaller than unity. Demanding that  $2\kappa = 0.87 \text{ \AA}^{-1}$  for our junctions as well, we find  $\zeta = 0.18$  for uniaxially deformed networks and  $\zeta = 0.24$  for Poisson deformed networks (full Poisson effect). There are several factors that may lead to a value  $\zeta < 1$ . Possibly, the polyimide layer takes up part of the deformation (unlike in MCBJs there are no undercuts in our networks). However, our 2D NP array is also not perfect. It consists of many 2D grains with a distribution of lattice directions. We tested our 2D models for unit cells with different orientations, but found only small variations in  $\zeta$  (up to 15%). However, the grain boundaries may take up some of the strain. We note nevertheless that it is unlikely that the grain boundaries incorporate all elongation, since then a gap much larger than  $\Delta d$  would open. That would induce much larger resistance changes than we observe, due to the exponential nature of tunneling.

The typical distance change  $\Delta d$ , derived from the above, is tens of picometers. This is enough to induce a transition in a spin transition molecule [14]. Therefore, figure 2 demonstrates a stable platform in which the distance between adjacent nanoparticles can be controlled on a very small scale. We note that the experiments were reproduced on the time scale of days.

As we have seen that an NP network can be controllably stretched, we can insert conjugated molecular bridges into it and study the response to deformation. For this, we choose acetyl protected dithiolated oligo-phenylene ethynylene (OPE) molecules with three phenyl rings, i.e. OPE3. These are conjugated rod-like molecules (see lower inset of figure 2(b)) that have been studied by several groups [7, 15]. The alkanemonthiol-protected gold NP networks are immersed in a 0.5 mM OPE3 solution, deprotected by triethylamine in tetrahydrofuran (THF), for 24 h [16]. This allows the dithiolated OPE3 molecules to form bridges between two neighboring NPs, as indicated in the inset of figure 2(b) [7, 8]. After this procedure, the resistance of the network in figure 2 has dropped to 34 M $\Omega$ , as compared to 175 M $\Omega$  for the original alkanemonthiol network. The resistance change due to molecular exchange is considerably lower than found by Liao *et al* [7], but close to the values found by the same group in [8]. This discrepancy is probably due to an incomplete exchange reaction in our case. Nevertheless, the resistance change is large enough to conclude that transport is dominated by the OPE molecules.

Figure 2(b) shows a bending experiment for an OPE-substituted sample, similar to the one in figure 2(a). We find that the network's resistance responds linearly to changes in  $\Delta y$  in the regime probed. The absolute resistance changes found are much smaller than for the alkanemonthiol networks. Moreover, also the relative resistance change  $(R(\Delta d) - R(0))/R(0)$  has dropped significantly, from  $0.34 \pm 0.02 \text{ mm}^{-1}$  for the initial network to  $0.06 \pm 0.01 \text{ mm}^{-1}$  for the OPE-bridged sample. Since, apart from molecular bridging, the network itself is unchanged, we expect that  $\Delta U/\Delta y$  and thus  $\Delta d/\Delta y$  have the same values as for the

original alkanemonthiol network (see equation (1)). Hence, it is reasonable to state that the quantity  $(\Delta R/R)/(\Delta d/d)$ , i.e. the resistance response to strain, has dropped by a factor  $0.34/0.06$ . In other words, the insertion of OPE bridges has significantly changed the properties of our junctions, both in absolute resistance and in strain sensitivity. It is tempting to relate  $(R(\Delta d) - R(0))/R(0)$  to the exponential factor  $2\kappa$ , or more exactly, to the quantity  $\beta$  for the OPE series. This  $\beta$ -value is defined as the decay factor of conductance with molecular length  $L$ , for a series of oligomers [13, 17, 18]. However, we do not view this as the correct interpretation, since the OPEs are quite rigid rods compared to the relatively soft gold particles. It is more likely that the position of the molecule–Au connection changes upon straining the junction. For example, if the Au–thiol bond is initially near a step edge on the gold nanoparticle, it may jump over this edge to the upper gold layer upon pulling. Recently, Martin *et al* argued that the latter configuration yields a higher resistance value [19].<sup>4</sup> We anticipate, however, that the situation will be very different for less rigid molecules. Spin transition molecules [14] in particular are good candidates for future experiments, as they can be switched from a low-spin to a high-spin state when stretched [3]. Such measurements may be supported by surface enhanced Raman spectroscopy (SERS) studies, which would allow one to follow molecular vibrations as the junctions are strained.

In summary, we present a new method to statistically study molecular transport as a function of inter-electrode distance. Our platform combines the stability of 2D-molecular networks with the control of mechanically controllable break junctions with a maximal variation of around 50 pm per junction. We demonstrate that both the absolute and relative resistance response depend on the molecular species present in the junctions. Hence, this study paves the road towards future experiments on strain-sensitive molecules.

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## References

- [1] Metzger R M 2008 *J. Mater. Chem.* **18** 4364–96
- [2] van der Molen S J and Liljeroth P 2010 *J. Phys.: Condens. Matter* **22** 133001
- [3] Parks J J *et al* 2010 *Science* **328** 1370–3
- [4] Agrait N, Yeyati A L and van Ruitenbeek J M 2003 *Phys. Rep.* **377** 81–279
- [5] Smit R H M, Noat Y, Untiedt C, Lang N D, van Hemert M C and van Ruitenbeek J M 2002 *Nature* **419** 906–9
- [6] Andres R P, Bielefeld J D, Henderson J I, Janes D B, Kolagunta V R, Kubiak C P, Mahoney W J and Osifchin R G 1996 *Science* **273** 1690–3

<sup>4</sup> We note that the change of  $(R(\Delta d) - R(0))/R(0)$  upon straining should then be seen as a statistical effect, i.e. as a result of shifting distributions in molecular anchoring.

- [7] Liao J H, Bernard L, Langer M, Schönenberger C and Calame M 2006 *Adv. Mater.* **18** 2803
- [8] Bernard L, Kamdzhilov Y, Calame M, van der Molen S J, Liao J and Schönenberger C 2007 *J. Phys. Chem. C* **111** 18445
- [9] van der Molen S J, Liao J H, Kudernac T, Agustsson J S, Bernard L, Calame M, van Wees B J, Feringa B L and Schönenberger C 2009 *Nano Lett.* **9** 76–80
- [10] Slot J and Geuze H 1985 *Eur. J. Cell Biol.* **38** 87–93
- [11] Vrouwe S A G, van der Giessen E, van der Molen S J, Dulic D, Trouwborst M L and van Wees B J 2005 *Phys. Rev. B* **71** 035313
- [12] Mueggenburg K E, Lin X M, Goldsmith R H and Jaeger H M 2007 *Nat. Mater.* **6** 656–60
- [13] Akkerman H B and de Boer B 2008 *J. Phys.: Condens. Matter* **20** 013001
- [14] Chandrasekar R, Schramm F, Fuhr O and Ruben M 2008 *Eur. J. Inorg. Chem.* 2649–53
- [15] Xiao X Y, Nagahara L A, Rawlett A M and Tao N J 2005 *J. Am. Chem. Soc.* **127** 9235–40
- [16] Valkenier H, Huisman P A, van Hal E H, de Leeuw D M, Chiechi R C and Hummelen J C 2011 *J. Am. Chem. Soc.* at press
- [17] Tao N J 2006 *Nat. Nanotechnol.* **1** 173–81
- [18] Huisman E H, Guedon C M, van Wees B J and van der Molen S J 2009 *Nano Lett.* **9** 3909–13
- [19] Martin S, Grace I, Bryce M R, Wang C S, Jitchati R, Batsanov A S, Higgins S J, Lambert C J and Nichols R J 2010 *J. Am. Chem. Soc.* **132** 9157–64