

SUPPORTING INFORMATION

Enhanced charge transport across molecule-nanoparticle-molecule sandwiches

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SECTION SI.1

Additional data for 1,8-Octanedithiol

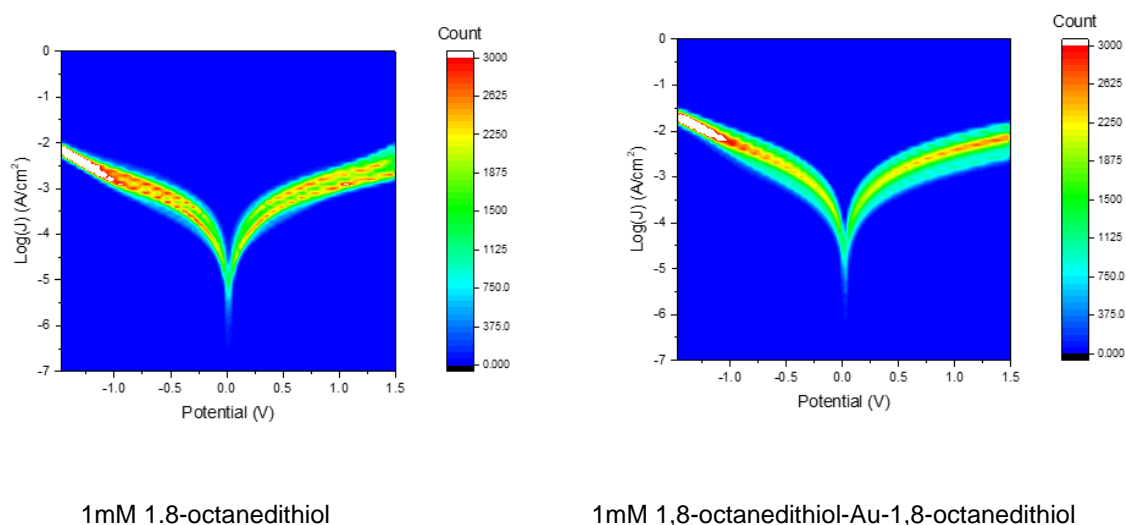


Figure S1: 2D map of current density vs bias voltage compiled from 1219 Au/1,5-pentanedithiol/Ga₂O₃/eGaIn junctions.

SECTION SI.2

Simple geometrical model for the Au-ML-GNP-ML devices showing enhanced electrical conductance

The influence of nanoparticles sitting non-symmetrically and non-uniformly in the junction with a combination of shorter and longer tunnelling bridges is modelled. A conventional circuit model is used consisting of tunnelling resistors (the alkanedithiol linkers, e.g. hexanedithiol) connecting the bottom gold electrode to the NPs and then hexanedithiol connecting to the top electrode (which for simplicity is also assumed as gold). With the NPs not perfectly and not uniformly aligned in the middle of a non-uniform dual SAM layer. This is modelled by very slightly shorter tunnelling distances counterbalanced by very slightly longer distances (the “shorter” effective tunnelling distances might result, for example, from more tilted alkanedithiol molecular bridges or gauche defects or other disorder). Because the tunnelling current is not linear in distance this means that they do not balance out and current enhancement results which is more as the NPs in the layer become more staggered and the effective tunnelling distances more heterogeneous. This staggering in effective tunnelling distances is mathematically modelled in a simple geometric way. In addition, for

straightforward modelling it is assumed that the NPs are metallically connected. A normal distribution of tunnelling gap distances is assumed together with the know exponential tunnelling decay:

$$R = R_0 \exp(-\beta x)$$

It is then assumed that the molecular bridges act as parallel tunnelling resistors on both sides of a nanoparticle (treated as a simple contact) with non-uniform parallel resistors, i.e.

$$\frac{1}{R_{sum}} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} \dots \dots \dots$$

This gives the following plot of effect of nanoparticle position variance (or rather variance in the tunnelling bridges effective tunnelling bridge length) on conductance enhancement:

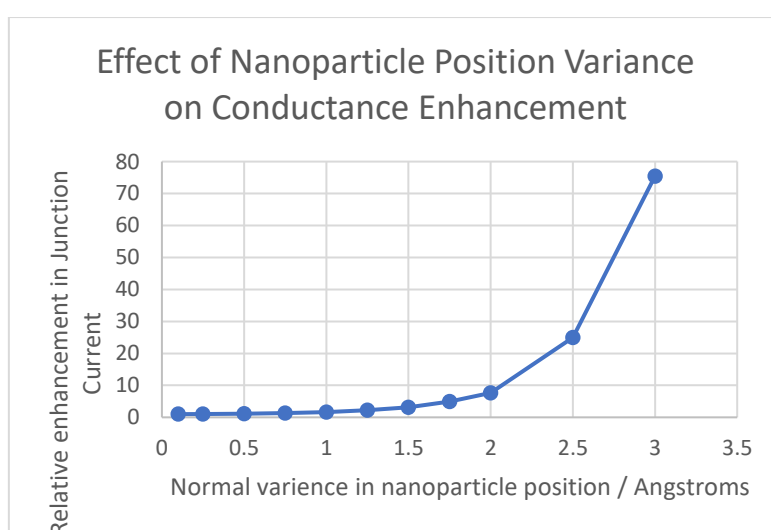


Figure S2 Effect of nanoparticle position variance on conductance enhancement (see text for model description). Modelled with hexanedithiol linkers for the double layer structure with variance in the nanoparticle position manifesting as a normal distribution of hexanedithiol tunnelling barrier distances.

This is a very simple toy model with large assumptions but shows that there only has to be a height variance of around 2 Angstroms, and a corresponding prevalence of short and long tunnelling distances to the connecting electrodes, to produce a current enhancement of a factor of 10, in line with the experimental observation for the devices formed with 1,6-hexanedithiol.

SECTION SI.3

Discussion of selected IR spectroscopic data from the literature for alkanethiol monolayer capped gold nanoparticles.

Infrared spectroscopy is useful technique for analyzing formation of self-assembled monolayers, whether at 2D planar surfaces (“2D SAMS”) or around nanoparticles (“3D SAMS”). However, care should be exercised in interpreting blue shifts in CH₂ stretching modes as related to an increasing gauge defect concentration in the polymethylene chains of 3D SAMs, since other factors may contribute, such as environment, packing, solvent ingress, ordering in the outer head group region or different phases on different faces of the nanocrystal. Nevertheless, IR spectroscopic analysis of the C-H stretching region of the

methylene backbone can be informative here, through analysis of the CH₂ symmetric and antisymmetric bands positions, which are well known for well-ordered “2D” SAMs on flat gold substrates. Shifts of these band positions for monolayer protected gold nanoparticles with alkanethiolate SAMs (“3D” SAMs) has been used to judge conformational order and packing of these SAMs and infer the possible presence of gauche defects.¹ For example, Hostetler et al. have contended that chains of the alkanethiol SAMs on Au nanoparticles longer than hexanethiol are highly ordered, while shorter ones display disordering.² For smaller monodisperse gold nanocrystals (Au₂₅) Antonello et al. found for alkanethiol lengths below decanethiol (C₁₀, n = 10), monolayer protected clusters exhibited more defects, with a progressive blue shift of the CH₂ stretching modes with decreasing n.³ Therefore, IR data in the literature does show evidence for a degree of disordering particularly for smaller chain length and cluster sizes, but chain ordering is dependent on other factors such as environment, compression of nanoparticle films and temperature.

References

1. Nieto-Ortega, B.; Burgi, T., Vibrational Properties of Thiolate-Protected Gold Nanoclusters. *Accounts of Chemical Research* **2018**, *51* (11), 2811-2819.
2. Hostetler, M. J.; Stokes, J. J.; Murray, R. W., Infrared spectroscopy of three-dimensional self-assembled monolayers: N-alkanethiolate monolayers on gold cluster compounds. *Langmuir* **1996**, *12* (15), 3604-3612.
3. Antonello, S.; Arrigoni, G.; Dainese, T.; De Nardi, M.; Parisio, G.; Perotti, L.; René, A.; Venzo, A.; Maran, F., Electron Transfer through 3D Monolayers on Au₂₅ Clusters. *ACS Nano* **2014**, *8* (3), 2788-2795.