Electronic Supplementary Information

Identification of vibrational signatures from short chains of interlinked molecule-nanoparticle junctions obtained by inelastic electron tunnelling spectroscopy

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Functionalisation of Au nanoparticles:

A solution of 1.90 mmol $HAuCl_4 \times 3H_2O$ and 1.90 mmol of the corresponding α,ω-*bis*(triphenylmethylthiol) alkane in 20 ml of THF was vigorously stirred at 25 °C until the solution starts to become clouded. To the resulting auburn solution triethylsilane (1.90 mmol) was added dropwise at 25 °C to form a purple solution immediately. After stirring for 18 hours at 25 °C the solution was filtered and ethanol (500 ml) was added to precipitate gold nanoparticles. The suspension was filtered and the precipitate was washed exhaustively with ethanol (3 × 300 ml) to remove unbound molecules. Benzene was added to solve the precipitate from the filter paper. After evaporation of the solvent the alkanedithiol-derivatised gold nanoparticles were obtained as red solid. Dissolving in toluene gave the gold nanoparticle solutions for trapping experiments.

Fabrication of ODT-AuNP network in nanoelectrode plateform:

Nanoelectrode platform with gap sizes of 20nm, were prepared by top-down approaches using combined techniques of electron-beam lithography and photography and ion beam milling[22]. A 100 nm wide and 2 μm long gold wire was patterned using a FEI XL30

Environmental Scanning Electron Microscope (ESEM) operated at an acceleration voltage of 30 kV. A double layer resist was used and consisted of a bottom layer of PMMA 495k A4 and a top layer of PMMA 950k A4 which resulted in an undercut structure that facilitated subsequent metallization and lift-off. Nanogaps 15-20nm wide, were cut in the EBL gold wire by usage of a 1 pA focused ion beam of Ga+ ions from a FEI Strata DB235 FIB/SEM at an acceleration voltage of 30 kV.

Dielectrophoretic trapping of these gold nanoparticles was carried out by the placement of a 10 µL drop of an AuNP solution on top of the nanoelectrode and application of an alternating voltage (AC) of 1.25 - 1.5 Vpeak-peak at 1 MHz frequency using a Tektronix AFG 3102 Function generator. The removal of protecting groups after trapping was carried out by placing sample in an acidic deprotection solution (5 mL trifluoroacetic acid, 5 mL dichloromethane and 0.5 mL triethylsilane) for 20 min to establish chemisorbed junctions at both ends of the 1,8-octanedithiols thereby creating an AuNP-molecule-AuNP network bonded to the gold nanoelectrodes.

Structural characterization:

Scanning electron microscopy has been carried out by using Zeiss LEO 1550. Scanning electron microscopy has been done to observe devices after all electrical and IETS measurements. Imaging has been done at 15kV. Transmission electron microscopy has been carried out to measure inter-AuNPs distances and agglomeration before and after removal of the protecting trityl groups from alkanedithiol in AuNP solutions. Transmission electron microscopy has been carried out using FEI Tecnai F30 ST at 300kV.

Electrical measurements:

Electrical characterization (DC) is carried out in ambient conditions in the same probe station using an Agilent B1500A semiconductor parameter analyzer. Electrical connections to the contact pads are made by usage of a Karl Suss probe station. The probe station is housed

in a shielded enclosure, i.e., a Faraday cage, in dark and this cage is placed on top of a stone table to reduce mechanical vibrations. Electrical characterization is performed by making positive and negative voltage sweeps and recording the corresponding currents. The IETS measurement had been carried out by inserting wire bonded sample on chip holder into a cylinder containing liquid helium by using dip stick. The IETS signal was recorded by using two lock-in amplifiers (Stanford research systems Model SR830 DSP) in parallel to the programmable DC source meter (Yokogawa 7651).