Supplementary Material (ESI) for PCCP

A molecular wire incorporating a robust hexanuclear platinum cluster.

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SUPPLEMENTARY INFORMATION

Experimental details for syntheses.

$[Pt_6(\mu\text{-}PBu^t_2)_4(CO)_4Cl_2]$ (**1**) was prepared as previously described.[1] 1,4-butanedithiol (Aldrich) was used as purchased. Solvents were dried by conventional methods and distilled under nitrogen prior to use. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer equipped with a UATR sampling accessory. NMR spectra were recorded on a Varian Gemini 200 BB instrument (200 MHz for ^{1}H) at room temperature (about 293 K); frequencies are referenced to the residual resonances of the deuterated solvent (^{1}H, ^{13}C), to 85% H_3PO_4 (^{31}P), and to H_2PtCl_6 (^{195}Pt). Materials and apparatus for electrochemistry have been previously described. [2]

*STM imaging of low-coverage monolayers of **3**.*

A flame–annealed gold–coated glass slide was dipped into a dilute (10^{-4} – 10^{-5} M) solution of **3** for one minute to allow the formation of a low coverage monolayer. We next employed the scanning tunnelling microscopy (STM) based I(s) technique of Haiss *et al*[3] to fabricate Au|**3**|Au molecular junctions and to measure their electrical properties. The STM was placed inside its environmental chamber and the system was purged with dry argon overnight in order to remove as much water and oxygen from the system as possible. The surface was imaged in order to find an area containing molecules (conditions of I_0 = 0.1 nA were used with bias voltages ranging between 0.2 and 1.2 V). Under these conditions wire formation was generally suppressed, although occasional molecular bridges were seen in images that looked like bright lines or streaks.

Once an area of molecules had been identified, the gold STM tip was brought to a fixed z distance using a set point current of 10-20 nA, above either a single molecule, or a cluster of molecules. The feedback loop was switched off, and the tip was withdrawn while maintaining a constant x–y position. A current–distance (*I(s)* where s = relative tip–sample distance) curve was collected. We typically observed current–distance behaviour characteristic of the formation

of molecular wires (see Figure 2a) with a plateau in the current (I_M) due to conductance through the fully–extended molecule in its lowest-energy conformation. As the tip was withdrawn further, the molecule detached at a distance characteristic of its length (tunnelling current therefore diminishing sharply), and this break-off distance was also measured. The experiment was repeated many times, and the results were analysed statistically by adding together all the data points for each I(s) curve collected that contained a plateau or plateaux – bare exponential and noisy scans were dismissed.

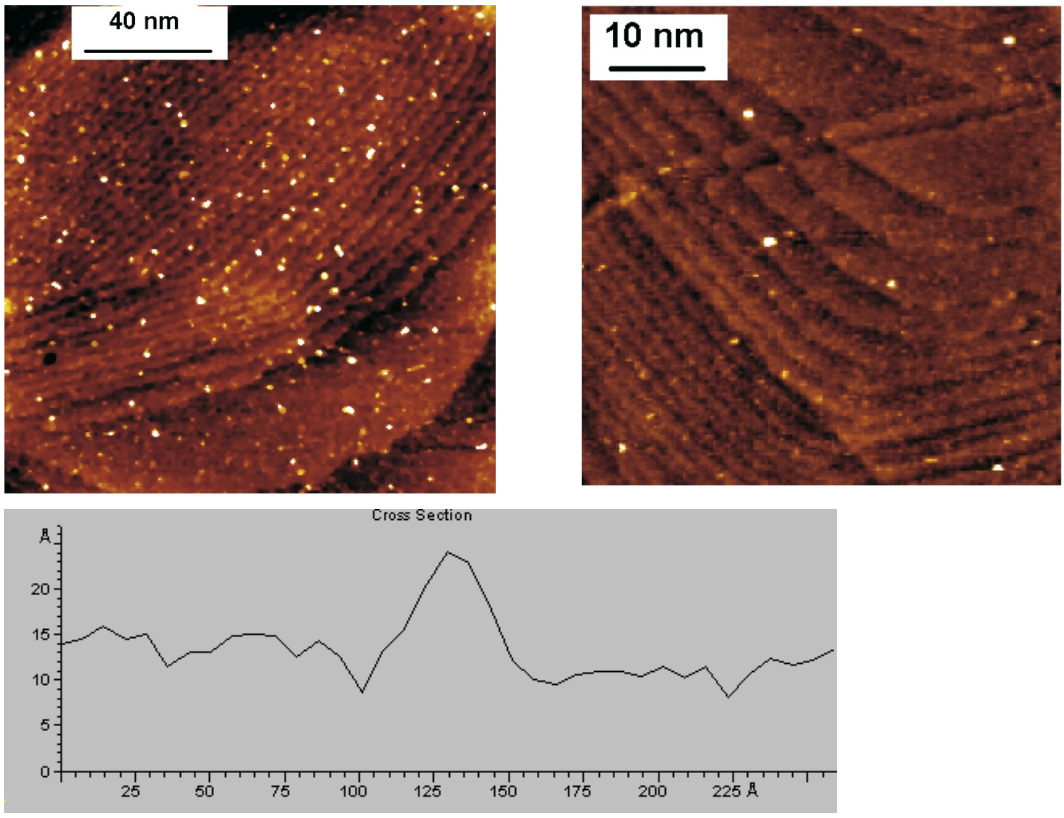

Figure S1. Images of low coverage monolayer of **3** on flame-annealed Au on glass slide (V_b = 1.2 V, I_0 = 100 pA, scan speed = 1 line/sec, no. points per line = 512, resolution = 0.4 nm). The images show an area of Au(III) terraces. Note that the molecules, seen here as bright dots, adsorb preferentially at step edges, hence the lines of dots seen in the left-hand upper image. Line scans across the bright dots (lower image) show that their height is consistent with intact **3**.

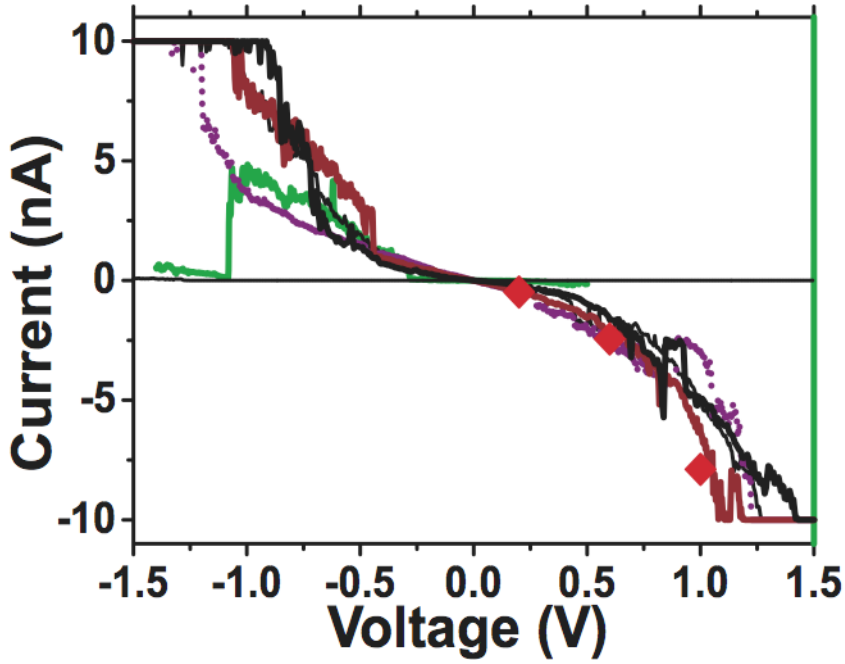

Figure S2. Additional representative experiments in which a Au tip is scanned between ±1.5 V while held above the surface of a monolayer of **3** on a Au substrate, and a molecule (or molecules) bridge the substrate and tip for the whole (or most) of the scan. Note that the Au|molecule|Au junctions are significantly more unstable at negative tip biases ('jumps' in current consistent with molecules attaching/detaching during the scans can be seen). The mean currents obtained from results of the multiple I(s) experiments at different tip potentials are shown as red diamonds.

References

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3. W. Haiss, H. van Zalinge, S. J. Higgins, D. Bethell, H. Höbenreich, D. J. Schiffrin and R. J. Nichols, *J. Am. Chem. Soc.*, 2003, **125**, 15294-15295.