## **Supplementary Information**

# Towards molecular electronic devices based on 'all-carbon' wires

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## 1. X-ray photoelectron spectroscopy (XPS) measurements.

X-ray photoelectron spectroscopy (XPS) spectra were acquired on a Kratos AXIS ultra DLD spectrometer with a monochromatic Al K $\alpha$  X-ray source (1486.6 eV) using a pass energy of 20 eV. The photoelectron take off angle was 90° with respect to the sample plane. To provide a precise energy calibration, the XPS binding energies were referenced to the C1s peak at 284.6 eV. Figure S1a, S1b and S1c show XPS scans of the Si2s region for the powder of 1, an Au|C<sub>8</sub>SiMe<sub>3</sub> film and an Au|C<sub>8</sub>H film; respectively. As it can be observed, a peak at 152.85 eV corresponding to the free TMS group is

obtained for the powder (Figure S1a), the same peak is observed for an Au|C<sub>8</sub>SiMe<sub>3</sub> film revealing that the desilylation has not been completed (Figure S1b). Nevertheless, after immersing the modified surface in a 0.05 M TBAF solution in THF at room temperature for 30 min no peak was observed in the Si2s region which demonstrates that the distal trimethylsilyl (TMS) groups on the monolayer modified electrode are cleaved to give an Au|C<sub>8</sub>H film (Figure S1c).



Figure S1. (a) XPS spectra of Si2s region for the powder of 1, (b) for an  $Au|C_8SiMe_3$  film and (c) for an  $Au|C_8H$  film.

#### 2. Thickness of the Au|C<sub>8</sub>H film.

The thickness of an Au|C<sub>8</sub>H film, Figure S2a, was obtained by using the atomic force microscopy (AFM) scratching technique. This method consists in ploughing the organic film with the AFM tip in contact mode and then imaging the scratched area (500x125 nm<sup>2</sup>) to get the depth profile, Figure S2b. The data collected and plotted in the depth histogram to obtain information about the thickness of the monolayer of **1** correspond to the white dashed box depicted in Figure S2b, which is spread over equivalent areas of a bare Au(111) terrace and adjacent monolayer of **1** on Au(111). By subtracting the height of the bare gold substrate (revealed after removing the organic film) from that of the surrounding monolayer, the thickness of the film was obtained.<sup>1</sup> Accordingly, a representative cross section together with a detailed statistical analysis of the depth distributions corresponding to the organic layer and the bare Au(111) terrace surfaces are depicted in Figure S2d, respectively. Both contributions are fitted separately to Gaussian functions whose maximum difference allows an accurate estimation of the layer thickness, i.e.  $1.0 \pm 0.2$  nm.



Figure S2. (a)  $1.0x1.0 \ \mu\text{m}^2$  AFM image showing the topography of an Au|C<sub>8</sub>H monolayer film; (b)  $3.0x3.0 \ \mu\text{m}^2$  AFM image showing a  $1.5x0.5 \ \mu\text{m}^2$  scratch made in a smooth Au(111) terrace covered by the organic layer; (c) a representative cross-section profile across the scratch; and (d) a depth profile histogram corresponding to the dashed

white-boxed 400x300 nm<sup>2</sup> area, exhibiting the height value distributions related to bare gold, blue line, and an Au|C<sub>8</sub>H film, red line. From the height difference between the two maximums of the Gaussian fits, the thickness of the Au|C<sub>8</sub>H film, i.e.  $1.0 \pm 0.2$  nm, is obtained.

#### 3. Fabrication of an Au|C<sub>6</sub>C<sub>2</sub>(H)N<sub>3</sub>CH<sub>2</sub>Fc film by click chemistry.

After the incubation of an  $Au|C_8H$  film in a solution of (azidomethyl)ferrocene to incorporate a ferrocene derivative via copper catalyzed azide-alkyne (CuCAA) click reaction, the classical two-peaked quasi-reversible electrochemical response corresponding to oxidation/reduction of chemisorbed ferrocene active redox groups was obtained. Cyclic voltammograms registered under these conditions at different scan rates are shown in Figure S4a.



Figure S3. (a) Cyclic voltammograms recorded for an Au|C<sub>6</sub>C<sub>2</sub>(H)N<sub>3</sub>CH<sub>2</sub>Fc film in HMIm-PF6 ionic liquid at several scan rates ranging from 0.01 to 0.8 V·s<sup>-1</sup>. (b) Plot of  $E_P$  vs. log v for determining the  $k_{ET}$  at higher scan rates.

The standard heterogeneous electron transfer rate constant,  $k_{ET}$ , between the chemisorbed ferrocene groups and the underlying Au(111) electrode has been assessed by the Laviron analysis, Figure S4b. The resulting  $k_{ET}$  was  $3.21 \pm 0.11$  s<sup>-1</sup>.

## 4. Quartz Crystal Microbalance (QCM) measurements.

Quartz crystal microbalance (QCM) measurements were carried out using a Stanford Research System instrument, with a frequency counter with 0.1 Hz resolution, and employing AT-cut,  $\alpha$ -quartz crystals with a resonant frequency of 5 MHz having circular gold electrodes patterned on both sides. The variation in the resonator frequency before and after an incubation process is directly related to the mass

incorporated on the QCM substrate by means of the Sauerbrey equation<sup>2</sup> which establishes that:

$$\Delta f = -\frac{2 \cdot f_0^2 \cdot \Delta m}{A \cdot \rho_q^{1/2} \cdot \mu_q^{1/2}} \tag{1}$$

where  $f_0$  is the fundamental resonant frequency of 5 MHz,  $\Delta m(g)$  is the mass change, A is the electrode area,  $\rho_q$  is the density of the quartz (2.65 g·cm<sup>-3</sup>), and  $\mu_q$  is the shear module (2.95·10<sup>11</sup> dyn·cm<sup>-2</sup>).

## Determination of the surface coverage of Au|C<sub>8</sub>SiMe<sub>3</sub>.

A QCM resonator was incubated in a  $10^{-3}$  M solution of 1 in THF in which equimolar of TBAF in THF was added (5 µL solution of 1 M TBAF in THF) at room temperature for 10 min. Afterwards, the electrode was rinsed copiously by THF to remove the physisorbed species, and then dried under nitrogen flow. The variation of the resonant frequency of the substrate before and after incubation was determined to be 6 Hz. Using equation (1) and considering the frequency variation before and after deposition a surface coverage of the organic monolayer of  $3.13 \times 10^{-10}$  mol·cm<sup>-2</sup> is obtained once the formation of the Au|C8SiMe<sub>3</sub> film was carried out.

## Incorporation of GNPs to an Au|C<sub>8</sub>H film.



Figure S4. Amount of gold deposited onto an  $Au|C_8H$  film immersed in a dispersion of GNPs as a function of the incubation time.

#### 5. RMS measurements

Root Mean Squared (RMS) values were obtained for the bare Au(111) electrode, Figure S5a, an Au|C<sub>8</sub>H film, Figure S5b, and an Au|C<sub>8</sub>|GNP film, Figure S5c. In each case the RMS measurements were conducted over areas of 300x300 nm<sup>2</sup> of the AFM images corresponding to one-single smooth terrace of the underlying Au(111) surface (to rule out the influence of gold steps and grain boundaries), averaged over at least 30 AFM images extracted from different zones in each sample and also from distinct but equivalent samples.



Figure S5. 1.0x1.0  $\mu$ m<sup>2</sup> AFM images showing the topography of (a) the bare Au(111) electrode, (b) an Au|C<sub>8</sub>H film and (c) an Au|C<sub>8</sub>|GNP film. The average RMS values obtained for the afore-mentioned electrodes are depicted in the AFM images.

## 6. Diameter and height of the GNPs

Diameters and heights of GNPs have been obtained by using height profiles across AFM images, Figure S6a and S6b, over more than 100 individual particles. The statistical analysis of the data extracted from AFM images allows us to conclude that these GNPs exhibit an average diameter of around 24 nm (corrected by the tip convolution<sup>3</sup>) and an average height of ca. 7 nm. Histograms showing the height and diameter value distributions are depicted in Figures S6c and d, respectively.



Figure S6. (a)  $1.0x1.0 \ \mu\text{m}^2$  AFM image of an Au|C<sub>8</sub>|GNP film. (b) Representative cross section and analysis profile illustrating the dimensions of the measured GNPs. Histograms showing the particle diameter (corrected by the tip convolution), red line, and height distributions, blue line, corresponding to 100 GNPs from different AFM images, (c) and (d), respectively. Averaged NPs diameter and height values are depicted in their respective graphs.

## 7. Gold nanoparticles surface coverage

A bearing analysis of the AFM images was made in order to calculate the gold nanoparticles surface coverage on an Au|C<sub>8</sub>|GNP film. In a bearing analysis, the depths of all pixels of the image with respect to a reference point, i.e., the highest pixel are analyzed. This kind of analysis renders an accurate estimation of the percentage of area covered by features, i.e. surface coverage, at every pixel depth. The statistical analysis of coverage data recorded over 300x300 nm<sup>2</sup> areas from 30 different but equivalent AFM images rendered an average GNP-coverage of  $39 \pm 2$  %, Figure S7.



Figure S7. (a) 500x500 nm<sup>2</sup> AFM image of an Au|C<sub>8</sub>|GNP film with the mask in blue unveiling nanoparticle-free areas. (b) Depth histogram showing the distribution of height data at different depth referred to a reference point, i.e. the highest pixel (black line). The blue line (bearing analysis) indicates the relative projected area covered at each depth value depicted as a blue mask in the topographic image. The small peak in the histogram marked with a red-dashed vertical line is attributed to the nanoparticlefree molecule-modified substrate while the green line accounts for the selected height threshold corresponding to the lowest maximum peak associated with the height of the measured GNPs. (c) Histogram showing the average percentage of GNP-covered substrate area obtained for fifty equivalent but different 500x500 nm<sup>2</sup> AFM images.

### 8. Conducting-AFM measurements



Figure S8. A log-log plot to show the presence of a single power regime in the load force region explored in this work.



Figure S9. Representative *I-V* curves obtained by positioning the c-AFM tip on top of GNPs when a set-point force of 12 (black), 15 (red) and 18 nN (blue) was applied. The shape of these curves with a linear section only at low bias voltages and increasingly curved gradients at higher bias are characteristic of metal-molecule-metal junctions and rule out the presence of short-circuits.



Figure S10. Representative *I-V* curves obtained by positioning the c-AFM tip on regions of the Au|C<sub>8</sub>|GNP film not covered by GNPs when a set-point force of 2.5 (black), 8.5 (red) and 11 nN (blue) was applied. The shape of these curves with a linear section only at relatively low bias voltages and increasing curve gradients at higher bias are characteristics of metal-molecule-metal junctions and rule out the presence of short-circuits. Damage to the film is produced when higher set-point forces are applied.



Figure S11. (a) 4.0x4.0  $\mu$ m<sup>2</sup> AFM image of an Au|C<sub>8</sub>H film showing the scratch made by ploughing the organic film with the AFM tip in contact mode. (b) Current image of (a) where only high current is observed in the scratched area revealing the absence of short-circuits in the Au|C<sub>8</sub>H film.



Figure S12. A Fowler-Nordheim plot for the average *I-V* curve showed in Figure 6b, where two distinct regimes (I and II) are evident and the transition voltage is marked.

#### 10. References

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