Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information for: Self-Assembled Monolayers of Terminal Acetylenes as Replacements for Thiols in Tunneling Junctions

Davide Fracasso and Ryan C. Chiechi*

Stratingh Institute for Chemistry and Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

E-mail: r.c.chiechi@rug.nl

Sample Preparation

The Au and Ag substrates used in this work are made by mechanical template stripping (mTS), which is described in detail elsewhere.[1] In our case, we deposited 200 nm of Au (or Ag) (99.99%) by thermal vacuum deposition onto a 3" n-type technical grade silicon wafer (with no-adhesion layer). Using UV-curable Optical Adhesive (OA) Norland 61, we glued 1 cm^2 glass chips on the metal surfaces. The mTS procedure provides ultra flat smooth surfaces, which allows the self-assembly process to achieve higher yields of working junctions. All samples were made by incubation of freshly cleaved Au (or Ag) slides in 10 mM solution in ethanol at room temperature under a nitrogen atmosphere for $\sim$ 20h. All molecules used in this work: 1-Hexyne, 1-Octyne, 1-Decyne, and 1-Dodecyne were purchased and used as receive from Sigma Aldrich.

---

*To whom correspondence should be addressed

Conductivity Measurements

Data were acquired in a home-built setup that is described in detail elsewhere.[2] Each SAM was measured by placing a tip of EGaIn in contact and acquiring at least ∼500 scans across ∼ 3 substrates for an average of 6 scans per junction. For longer and more stable SAMs we record up to ∼3500 scans. Traces in which the instrument reached compliance were considered shorts and were discarded (they reflect only the compliance limit of the instrument and have no physical meaning). Histograms of the values of J at each value of V were fit to Gaussian distributions. Table 2 is a summary of the number of traces and the percentage of junctions that shorted for each SAM. We calculated this percentage from the number of junctions that shorted during a measurement, however, since we collected an average of five scans per junction, these yields can be described as the percentage of junctions that shorted within approximately five scans.

Attenuated Total Reflectance (ATR)

IR spectra were recorded using a Nexus FT-IR with ATR configuration, DTGS KBr detector with the liquid suspended on diamond crystal. A drop of neat alkynes was analyzed using this instrumentation.

ATR FT-IR with variable angle horizontal.

IR spectra were recorded using Bruker VeeMax, PMA MCT detector. Incident angle of the IR beam was set to 60°, resolution of 9 mm^{-1}. The full spectra recorded is shown in Figure S3. The stretching region for C-H (2800-3000 cm^{-1}) is also reported in the main text. We used a ATRMax II Variable Horizontal ATR Accessory from Pike Technologies with Germaniun crystal.

Surface Enhanced Raman Scattering (SERS)

Gold beads were used as working electrodes for SERS measurements. The gold beads were prepared from 0.5 mm 99.999% Au wire (Schöne Edelmetall B.V), which was melted in a H_2 gas flame to form a bead with a diameter of 2-3 mm. The freshly prepared beads were cleaned chemically and electrochemically. Roughening of the gold bead electrode was performed according to the procedure described by Tian et al.[3] SERS active surfaces were obtained after 9 cycles and the measured electrochemically active surface area did not change significantly with further cycling. Immediately after cleaning, the substrates were immersed into a solution of the compound for subsequent monolayer formation. λ_{exc} 785 was used for SER measurement.

X-ray Photoelectron Spectroscopy (XPS)

XPS was performed using a Surface Science SSX-100 ESCA instrument with a monochromatic Al K_α X-ray source ($h\nu$ = 1486.6 eV). The pressure in the measurement chamber was below 1×10^{-9} mbar during data acquisition. The electron take-off angle with respect to the surface normal was 37°. XPS spectra were analyzed using the least-squares curve fitting program Winspec. Deconvolution of the spectra included a Shirley baseline subtraction and fitting with a minimum number of peaks consistent with the structure of the molecules on a surface, taking into account the experimental resolution. The profile of the peaks was taken as a convolution of Gaussian and Lorentzian functions. Binding energies are reported ± 0.1 eV and referenced to the Au $4f_{7/2}$ photoemission peak originating from the substrate, centered at a binding energy of 84 eV. The uncertainty in the peak intensity determination is 2% for carbon. All measurements were carried out on freshly prepared samples; on each surface 4 points were measured to check for reproducibility.

In XPS, the same element in different chemical environments shows up as different spectral contributions; this spectroscopy can therefore be employed to confirm the formation of dodecyne SAMs on Au by analyzing the C 1s core level region of the XPS spectra shown in Figure S5. The contributions of sp, sp^2, and sp^3 hybridized carbon species can be identified as indicated in Figure S5 and their relative amounts deduced as reported by Hu et al. sp bound carbon appears at a binding energy of 283.7 eV and amounts to 4.3% of the total C 1s intensity, sp^2 hybridized carbon (which is also present in the bare Au and likely arises from unreacted alkenes int optical adhesive) is responsible for the peak at 284.5 eV which contributes with 49.7% to the C 1s signal and the *sp*^{3} species is identified at 285.5 eV making up 20.9% of the total C 1s intensity. The spectral contributions at 286.4 eV (12.1% of the total carbon intensity), 288.6 eV (6.7%), and 289.6 eV (4.9%) are assigned to C−O, C=O, and COOH as indicated in Figure S5, while the small peak at 291.5 eV (1.4%) is the shake-up peak corresponding to $\pi \rightarrow \pi^*$ transitions concomitant with the photoemission process. The relative amount of sp and *sp*^{3} hybridized carbon and occurrence of the shake-up peak confirm the presence of dodecyne self assembled monolayer on the surface.

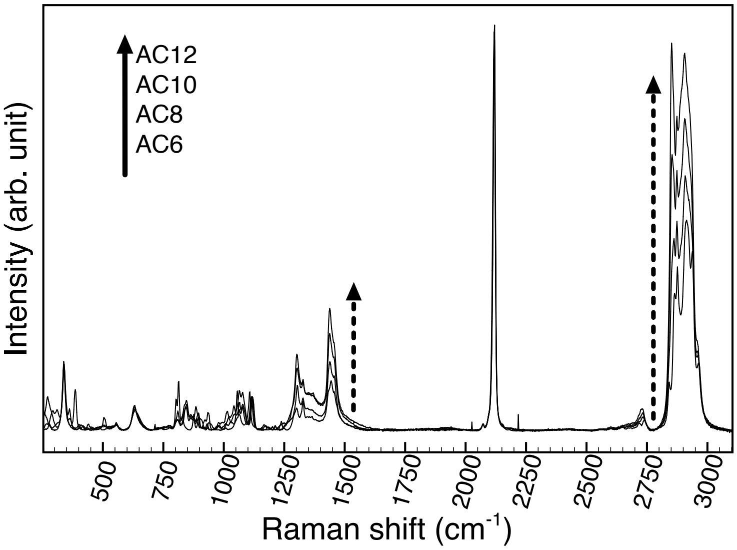

Figure S1: Ordinary Raman spectra of 1-Hexyne (AC6), 1-Octyne (AC8), 1-Decyne (AC10), 1-Dodecyne (AC12) obtained by droping the neat compounds on Au substrates.

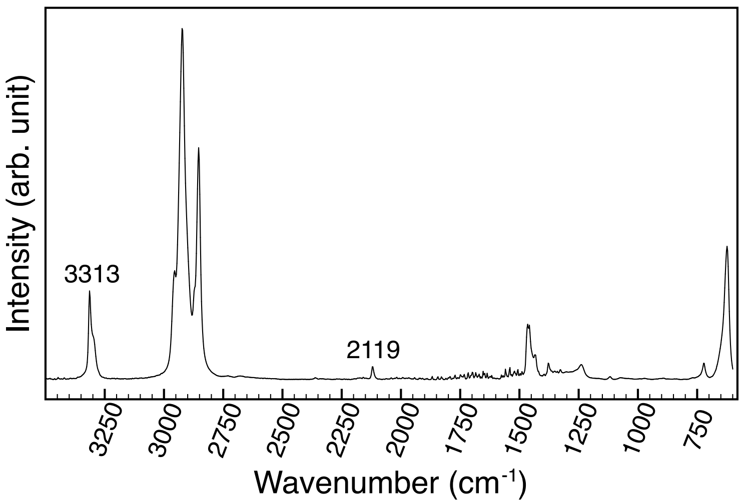

Figure S2: FTIR spectra of 1-Dodecyne with Attenuated total reflectance (ATR)

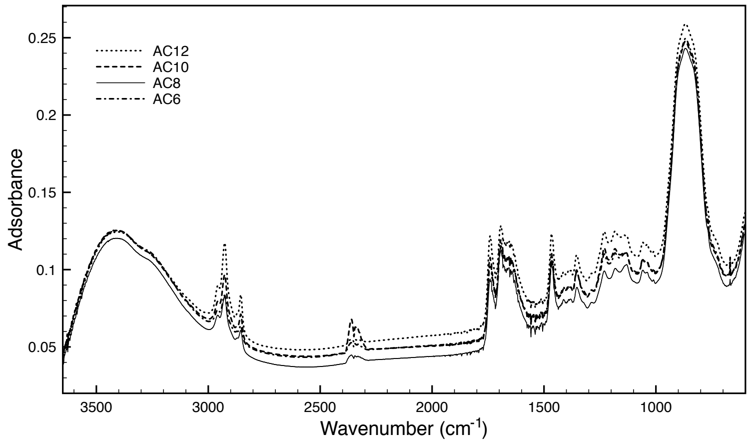

Figure S3: ATR FT-IR recorded spectra for the molecules studied in this work. The represented spectra are without baseline correction.

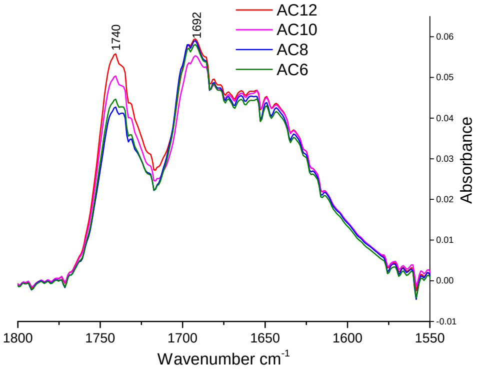

Figure S4: ATR FT-IR spectra showing two modes at 1740 and 1692 cm^{-1}.

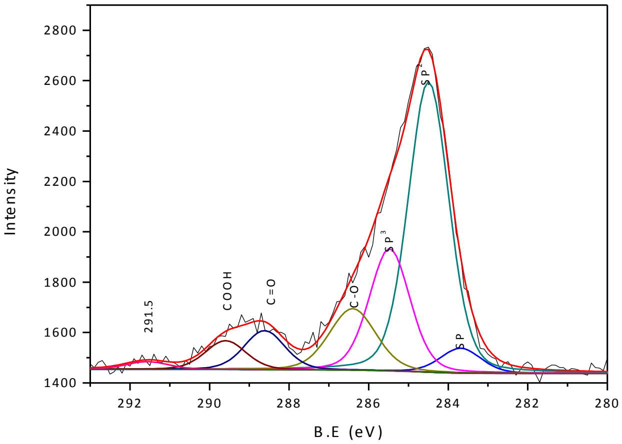

Figure S5: XPS spectra for AC12 SAMs on Au.^{TS}

References

(1) Weiss, E. A.; Kaufman, G. K.; Kriebel, J. K.; Li, Z.; Schalek, R.; Whitesides, G. M. *Langmuir* **2007**, *23*, 9686–9694.

(2) Fracasso, D.; Valkenier, H.; Hummelen, J. C.; Solomon, G. C.; Chiechi, R. *J. Am. Chem. Soc.* **2011**, *133*, 9556–9563.

(3) Tian, Z.-Q.; Ren, B.; Wu, D.-Y. *J. Phys. Chem. B* **2002**, *106*, 9463–9483.