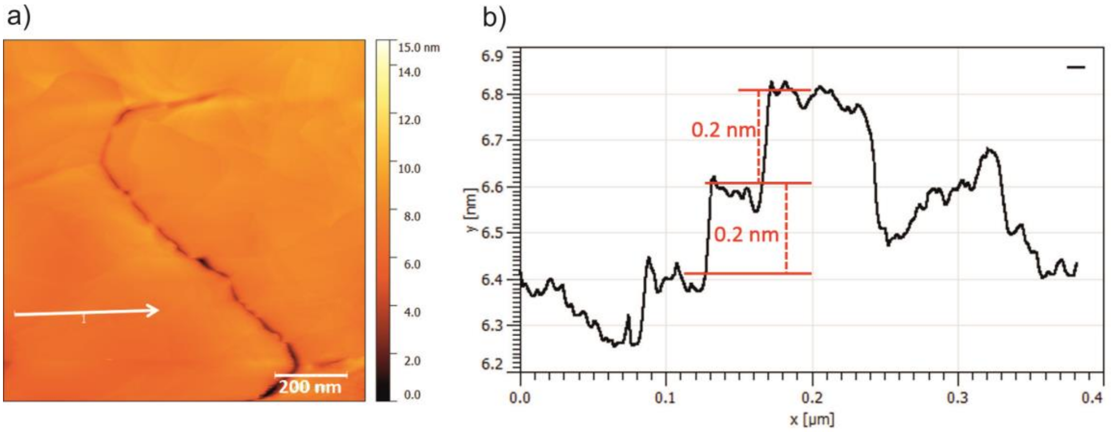
Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2016

Electronic Supplementary Information

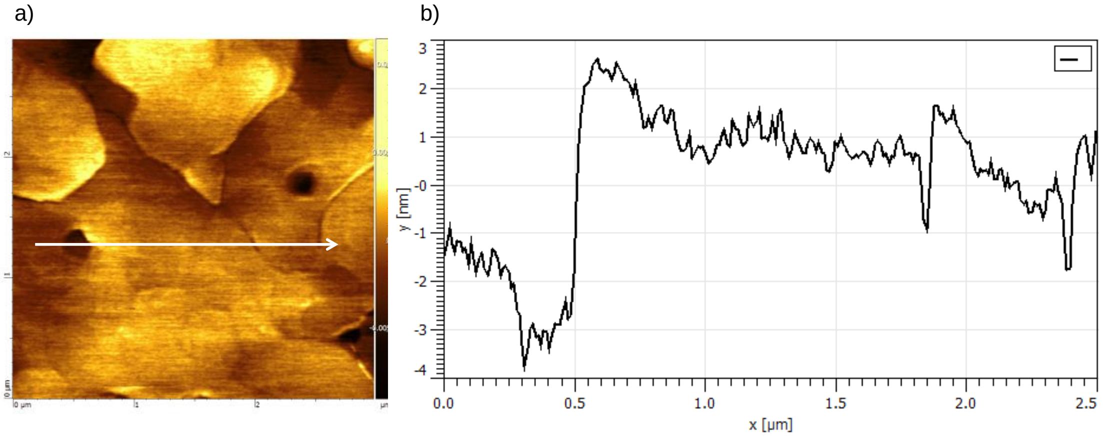
Strongly enhanced Raman scattering of Cu-phthalocyanine between graphene and Au (111)

Wan-Ing Lin,[a] Mohammad Fardin Gholami,[a] Paul Beyer,[a] Nikolai Severin,[a] Feng Shao,[b] Renato Zenobi,[b] and Jürgen P. Rabe[a,c]

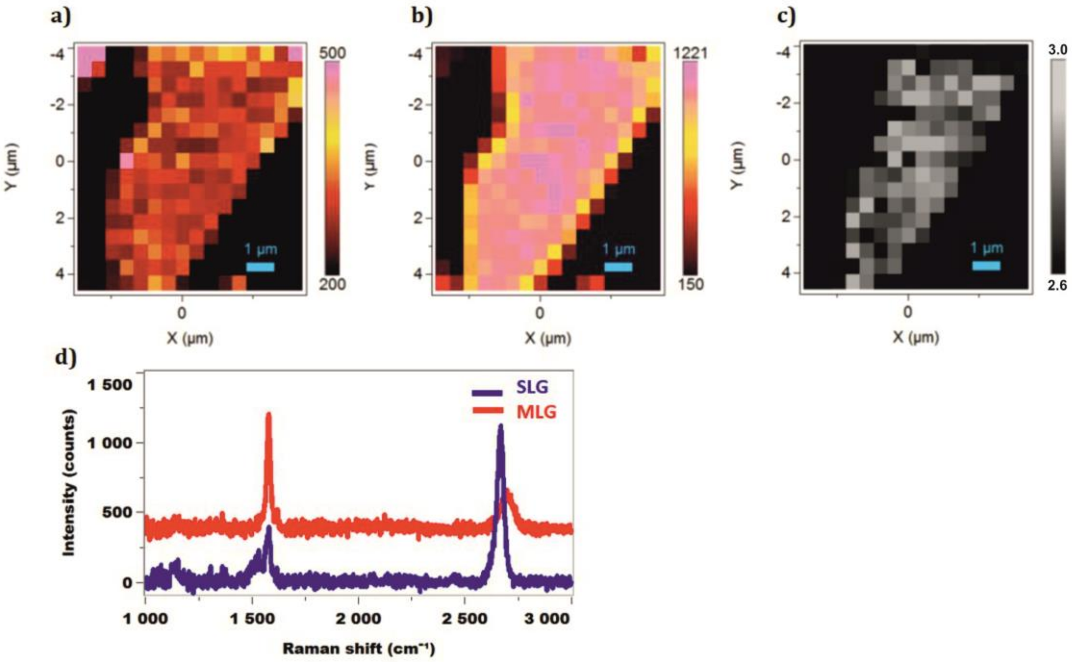
a. Department of Physics, Humboldt-Universität zu Berlin, 12489 Berlin, Germany
b. Department of Chemistry and Applied Biosciences, ETH Zurich, CH-8093 Zurich, Switzerland
c. IRIS Adlershof, Humboldt-Universität zu Berlin, 12489 Berlin, Germany



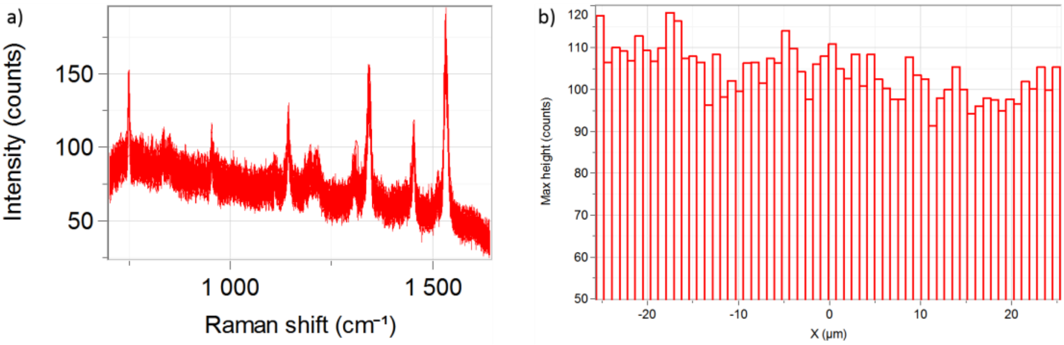
SI-Fig. 1 a) 1x1 µm² STM image of bare Au (111) surface. b) Cross-section profile indicated with arrow in a) showing the atomic steps of gold terrace.



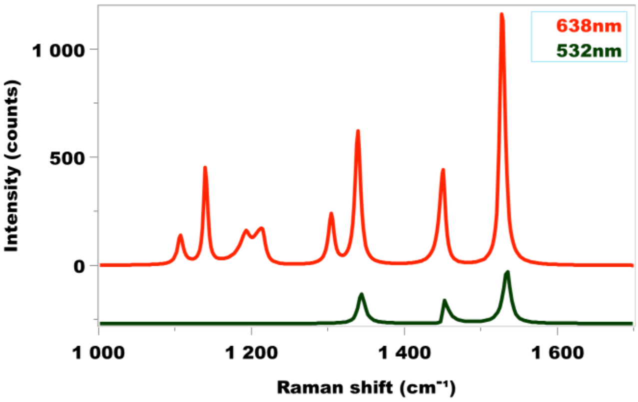
SI-Fig. 2 a) 3x3 µm² SFM image of bare Au(111) surface obtained in contact mode. b) Cross-section profile indicated with arrow in a) showing the flatness of the substrate.



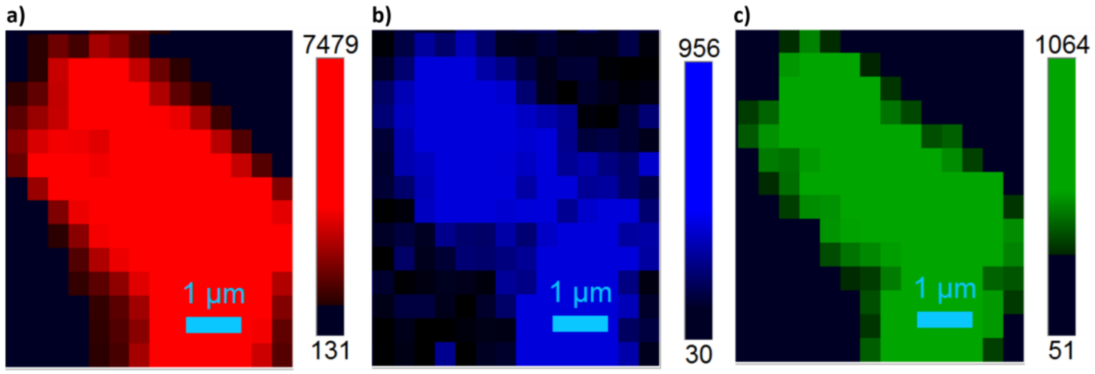
SI-Fig. 3 Raman spectroscopy of mechanically exfoliated single layer graphene on gold. Maps of integrated a) G-peak intensities, b) 2D-peak intensities, c) I_{2D}/I_G, and d) comparison of Raman spectra of single layer graphene (blue line) and multi-layered graphene (red line) illuminated by 532 nm light.



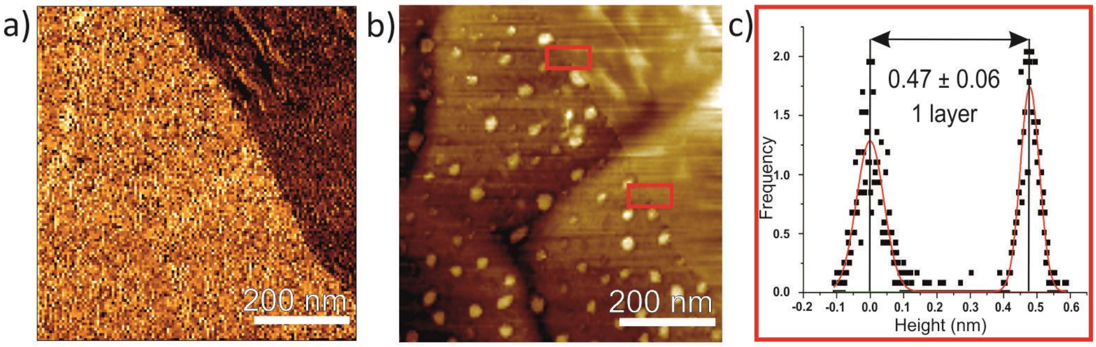
SI-Fig. 4 The signal homogeneity of CuPc coated on gold. a) The measured raw data (displayed in waterfall) over a 50 µm length scale with 60 spectra. A higher background at lower Raman frequencies is observed due to the gold substrate. b) The histogram of intensity counts of the peak at 1530 cm^{-1} yields an average value of 105 and a standard deviation of 6,13. (Peak was treated with background subtraction and single Lorentzian fitting). Illuminated with 638 nm light for 10 seconds.



SI-Fig. 5 Spectra of CuPc on gold were acquired by illuminating with laser light at different wavelengths (638nm and 532nm) as in Fig SI 3. Upon excitation with the 638 nm laser, the peak intensities are much stronger than for the 532nm laser excitation due to the resonance Raman effect. The fluorescence background from gold was subtracted to fit the baseline. The spectra shown were fitted.



SI-Fig. 6, Integrated intensity map of a) molecule distribution (red), b) the G band (blue) and the 2D band (green) of a SLG sheet, illuminated at 638nm for 30 seconds.

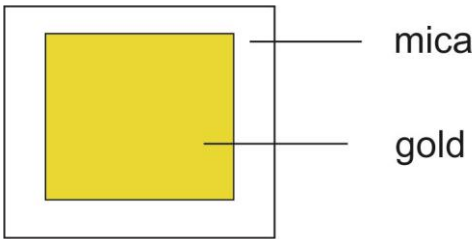


SI-Fig. 7 SFM-QI imaging. a) slope image at setpoint force of 1nN b) Height image at contact point. c) Histogram of the height distribution from the selected areas in b) marked in red. Discussion: Fig. a) With slope of force-distance-curve at a setpoint force of 1nN, it allows to distinguish the areas coated with graphene from uncoated areas. Fig. b) presents a height image at the contact point with the sample, showing a region of the gold, coated with CuPc and partially covered by a single layer graphene sheet. Upon fitting this to two Gaussians we obtained the histogram displayed in c), revealing a height difference of 0.47 ± 0.06 nm (error including standard deviation and instrument uncertainty in vertical piezo movement). The value is close to the interlayer distance of graphenes in graphite (0.34 nm). However, we do not exclude the unknown contribution of the interaction between graphene and substrate. We therefore attribute the corresponding area to a single layer of graphene. Note that there are also some particles appearing in the height images, which inevitably evolve from the ambient environment before or during the measurement. However, they do not influence our measurements significantly, since the Raman intensity counts of the CuPc coated on gold corresponding to our laser spot size show good homogeneity in SI-Fig. 4.

Experimental methods:

Materials

As a substrate, Au (111) with 200 nm thickness on mica (4x4 mm^2, #20020020) was purchased from Phasis, Geneva, Switzerland. The substrate is partially covered with gold (as SI-Fig. 8). The sample of Graphene-CuPc-gold was prepared on the substrate surface coated with gold, while the Graphene-CuPc-mica sample was prepared on the same substrates on mica. These allows the molecular film prepared at the same batch in vacuum evaporation. Graphene is produced from HOPG (obtained from Momentive Performance Materials Quartz, Inc. OH 44149, United States) by mechanical exfoliation with a contamination-free method[1]. CuPc was purchased from Sigma Aldrich with 99,95% purity. CuPc molecules were vacuum evaporated onto Au (111) and mica. In order to remove contaminations and promote the formation of large gold crystals on the surface, the substrates were flame annealed before introducing them into a vacuum chamber. Following this, a second annealing step (770 K, 1 h) was performed in vacuum before starting the film growth. Afterwards the molecules were thermal evaporated from a resistively heated quartz crucible at a rate of 0.9 nm·min^{-1} to obtain single monolayer films according to the methods[2,3]. The base pressure in the vacuum chamber during annealing and evaporation was $1 \cdot 10^{-8}$ mbar.



SI-Fig. 8 substrate structure of Au(111) on mica.

Setup

Raman measurements were carried out on a confocal Raman microscope (XploRA ONE™, Horiba Jobin Yvon, Paris, France) with a 633 nm laser for illumination and with a 1800 cm^{-1} grating. A 532nm laser was used for illumation coupled with a 2400 cm^{-1} grating to determine the single layer graphene peak position and FWHM, which yields 2 cm^{-1} uncertainties in measurement. A 100x objective lens (Mitutoyo, Japan) was used to focus the laser beam on the sample with a spot size 0,7 μm. The acquisition time was 30 s with a typical laser power of 2 mW at the sample stage. SFM images were acquired with an AIST-NT scanning probe microscope on a bare gold surface. A medium-soft silicon cantilever from Olympus with frequency ≅80kHz was used for Contact mode-SFM and images were recorded at 1 Hz. Later to establish a better understanding of the samples, samples were investigated using SFM imaging in quantitative imaging mode using Nanowizard III (JPK GmbH) operated with a 20x20 μm scanner. QI images were recorded at a typical rate of 5-17 min per image. Silicon tips on silicon nitride cantilevers with a tetrahedral base were used with a typical resonance frequency of 70 kHz and a spring constant of 1.7 N/m. The tips exhibited a typical apex radius of 7 nm with an upper limit of 10 nm, having a tip cone half angle of 18 degrees, as specified by the manufacturer (Olympus Corporation). Experiments were carried out under ambient conditions. Deflection sensitivity was calibrated by acquiring force-distance curves on a clean sapphire surface (Bruker). Cantilevers spring constants were calibrated using the thermal noise method.[4] Cantilevers were calibrated using spring constant and thermal noise calibration over a clean sapphire surface. QI images were made at approach and retraction speeds of 50-150 μm/s. Set points of 1 to 5 nN were used to image graphene over the gold surface coated with CuPc molecules. The SFM images were processed and analyzed with JPK supplied image-processing software.

Calculation of the enhancement factor

Here the assembled substrates effect (EF_1) was calculated by taking the intensity of CuPc sandwiched between GERS on the gold substrate and dividing by the intensity of CuPc deposited on mica. To compare solely the GERS effect (EF_2), we divide the intensity counts of individual molecule peaks of CuPc sandwiched between graphene and mica to the uncovered molecules on mica. Last, the GERS effect on gold (EF_3) was calculated by dividing the individual peak intensity of molecules under the graphene by the intensity of that peak of uncovered molecules on gold. EF_4 illustrates the substrate effect: enhanced signals from the gold substrate compared to that on mica. The spectra were treated with background subtraction and fitted to take the highest intensity.

References

1. B. Rezania, M. Dorn, N. Severin, and J. P. Rabe, *Journal of Colloid and Interface Science*, 2013. **407** 500-504.
2. J. Niederhausen, P. Amsalem, A. Wilke, R. Schlesinger, S. Winkler, A. Vollmer, J. P. Rabe, and N. Koch, *Physical Review B*, 2012. **86** 081411.
3. D.G. de Oteyza, A. El-Sayed, J.M. Garcia-Lastra, E. Goiri, T.N. Krauss, A. Turak, E. Barrena, H. Dosch, J. Zegenhagen, A. Rubio, Y. Wakayama, and J.E. Ortega, *Journal of Chemical Physics*, 2010. **133**. 214703
4. H.-J. Butt and M. Jaschke, *Nanotechnology*, 1995. **6** 1.