

Electronic Supporting Information

Site-Selective Functionalization of in-plane Nanoelectrode-Antennas

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Site-Selective Desorption of C-PEG from Optical Nanoantennas

In the main text we use Kelvin Probe Force Microscopy (KPFM) to verify the site-selective desorption of octadecanethiol (C18-SH) from an optical nanoantenna with a gap of 30 nm (see figure 2). In the following, the direct removal of C-PEG from one antenna arm is demonstrated. As the distance between the antenna electrodes is smaller than the optical resolution in PL measurements, we again employ KPFM. Figure S1a displays a KPFM image of a nanoantenna, after the C-PEG SAM was desorbed from the left electrode (see main text for experimental details). An uncorrected contrast of 16 mV is measured between the two arms (see figure S1b), signaling that the antenna is site-selectively functionalized with C-PEG. This value is lower than the surface potential (SP) contrast for an antenna which is partially covered with C18-SH (cf. figure 2e in the main text). We attribute this to a reduced SAM density for C-PEG molecules. As a consequence, the SAM molecules have an unfavorable orientation on the surface. The work function change is determined by the dipole moment perpendicular to the surface, and thus a SAM with strong dipole moment but tilted orientation induces only a

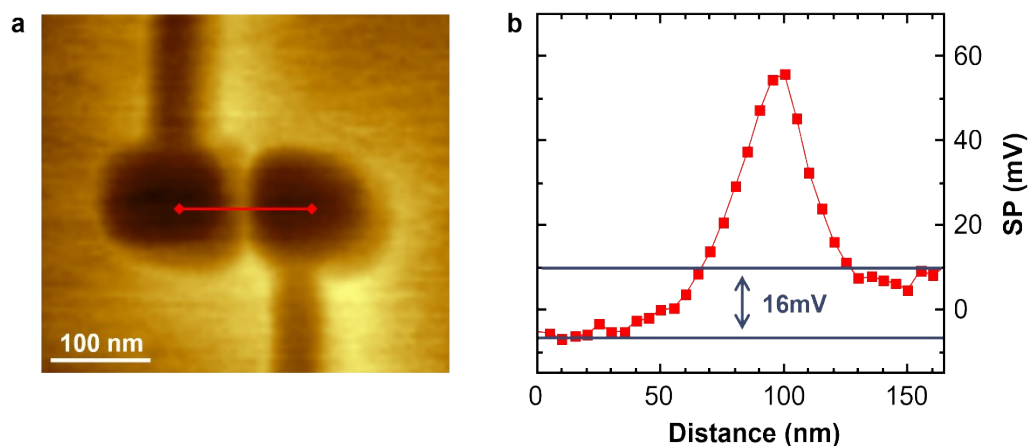


Figure S1: Site-selective functionalization of optical antennas with C-PEG. **a)** KPFM image of an optical antenna after C-PEG is directly desorbed from the left antenna arm. **b)** Cross-section along the red line in **a)** showing a measured and uncorrected surface potential difference of 16 mV between the two antenna arms. The peak arises due to a different surface potential of the glass in the antenna gap.

small contrast in KPFM measurements.¹

KPFM Correction

KPFM measurements strongly underestimate the SP contrast due to the long range of electrostatic forces and the large tip diameter (50 nm). We therefore correct KPFM measurements by applying a voltage to the electrodes and gradually increasing the amplitude until the contrast disappears. In this chapter, our correction procedure is demonstrated for the example of microelectrodes with a spacing of 2 μm .

Figure S2a shows a KPFM image of an exemplary microelectrode structure at zero applied voltage. The bottom electrode is covered with C18-SH, while the top electrode was stripped. Next, the SP is measured along the white arrow for different voltages applied to the top electrode (see figure S2b). As expected, the SP changes at the top and remains constant at the bottom electrode (which is grounded). The gradual SP plane at the top electrode is attributed to a slightly inhomogeneous desorption of C18-SH. Nevertheless, we can extract the SP contrast between both electrodes and plot it as a function of applied voltage in figure S2c (error bars account for the gradual SP plane). It can be seen that we measure an uncorrected SP contrast of ~ 100 mV (at zero voltage), however, we need to apply 200 mV in order to equalize the potentials. A linear fit yields a slope of 0.49. Hence, a correction factor of 2 must be applied to our KPFM measurement and we obtain a true SP contrast of 200 mV induced by

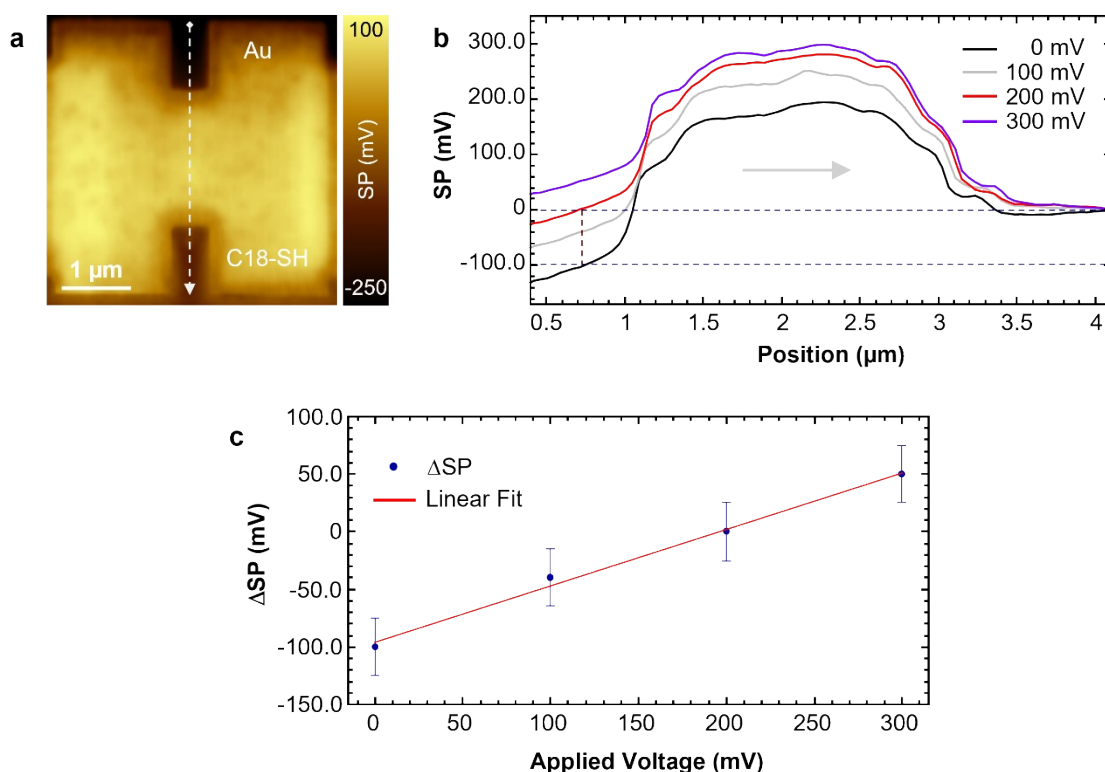


Figure S2: KPFM Correction. **a)** KPFM image of a set of microelectrodes (same structure as in figure 3d; main text) after desorption of C18-SH from the top electrode (no applied voltage). The surface coverage is denoted. **b)** Surface potential (SP) recorded along the white arrow in a) for different voltages. The voltage is applied to the top electrode, while the bottom electrode is grounded. All measurements are normalized to the bottom electrode (covered with C18-SH). The dashed lines help to extract the SP contrast between both electrodes (ΔSP). **c)** SP contrast between both electrodes as a function of applied voltage. The error bars originate from the SP plane at the top electrode (see b). A linear fit (red) yields a slope of 0.49, and thus a correction factor of ~ 2 must be introduced to obtain the true SP.

the site-selective functionalization with C18-SH. The deviation between measured and true SP is attributed to the long range of the measured electric forces. Not only the KPFM tip, but also the cantilever is probing the sample and collects SP signals from a larger area. Hence, the measured SP of a gold surface might be reduced by the signal simultaneously collected from a neighboring (not so distant) glass surface.

By applying the same correction procedure to the structure in figure 3e, we obtain a true SP contrast of 315 mV for C-PEG (between C-PEG covered gold (111) and bare gold (111)). Note, that C-PEG is hydrophilic, and thus a water layer might be accumulated on the C-PEG covered gold surface.

The measured SP contrast further decreases for nanoantennas with a gap size (30 nm) smaller than the KPFM tip diameter (50 nm; see figure 2 and S1). As stated in the main text, we see true SP contrasts of 200 mV (C18-SH) and 315 mV (C-PEG) as upper limits in our experiment (considering surface quality and water layers) – even for nanoantennas. We note, however, that smaller nanostructures suffer from rough surfaces leading to reduced SAM density, and thus smaller SP contrast.

Metal-Organic Nanoantennas with Symmetric Functionalization

This chapter demonstrates current-voltage characteristics of metal-organic nanoantennas with symmetric functionalization. Figure S3a depicts a schematic of the device. A nanoantenna is completely covered with C18-SH followed by evaporation of ZnPc. As shown in figure S3b, the IV-curves of such devices are symmetric. In contrast, the asymmetric current-voltage characteristics shown in figure 4 (main text) originate from site-selective functionalization with C18-SH.

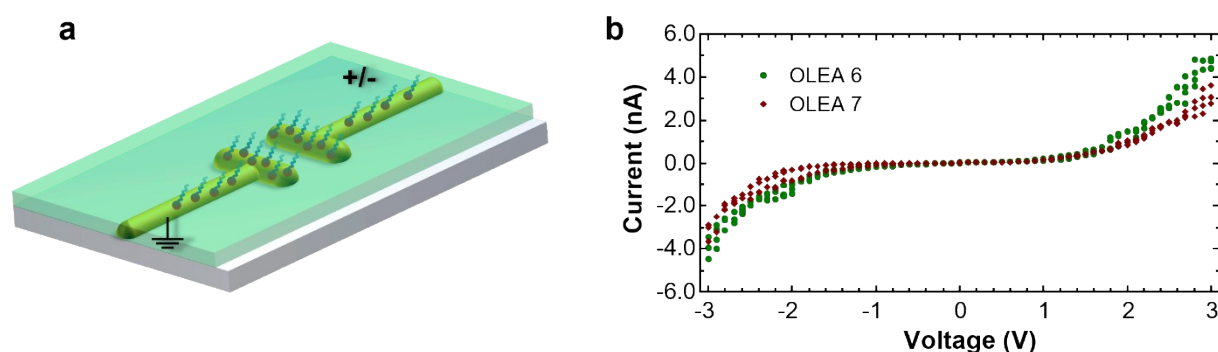


Figure S3: Current-voltage characteristic of devices with symmetric functionalization. a) Schematic of metal-organic nanoantenna completely covered with C18-SH. After SAM deposition, ZnPc (green) is evaporated. b) Current as a function of applied voltage for two different antennas (similar dimensions). Symmetric functionalization results in symmetric current-voltage characteristics.

References

- (1) R. W. Zehner, B. F. Parsons, R. P. Hsung, and L. R. Sita: Tuning the Work Function of Gold with Self-Assembled Monolayers Derived from X-[C₆H₄-CC-]_nC₆H₄-SH (n = 0, 1, 2; X = H, F, CH₃, CF₃, and OCH₃). *Langmuir* **15**, 1121, 1999.