

## Supporting Information

### Supramolecular Structures and Chirality in Dithiocarbamate Self-Assembled Monolayers on Au(111)

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## Experimental

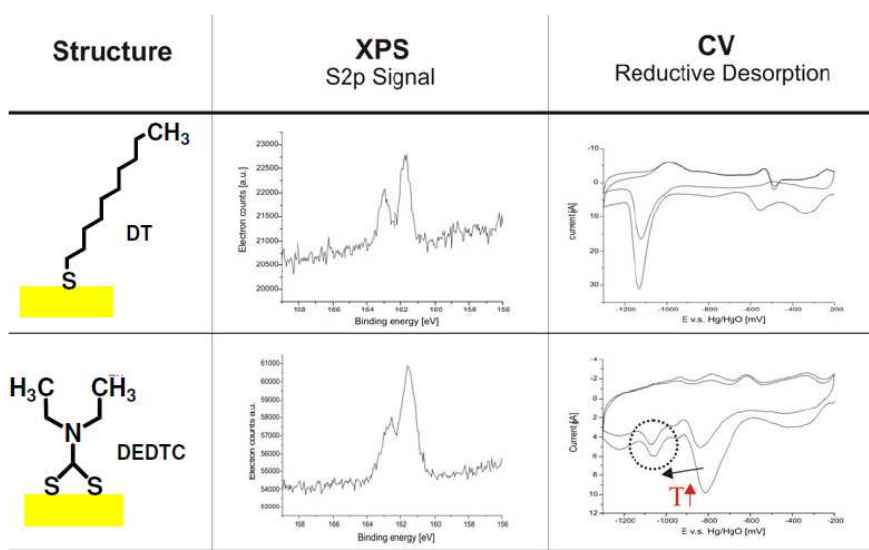
All glass-wares were cleaned by piranha solution before use. SAMs of sodium N,N-diethyldithiocarbamate·3H<sub>2</sub>O (DEDTC) (~99%) and decanethiol (DT) (~95%) (Sigma-Aldrich) were prepared by the immersion of freshly prepared Au(111) substrates into 1 mmol solution of each compound in ethanol (Fluka, p.a. quality) at room temperature for more than 12h. After immersion, the samples were thoroughly rinsed with ethanol, blown dry by N<sub>2</sub> gas and kept in Ar filled container before analysis. The XPS spectra were recorded with ESCALAB 220i XL (VG Scientific) photoelectron spectrometer. The samples were exposed to monochromatic Al K $\alpha$ -radiation (1486.6 eV) and the spectra were recorded in constant analyzer energy (CAE) mode with analyzer pass energy of 20 eV. The sulfur content was determined relative to a full monolayer of DT by normalization of the S2p counts by the counts of the Au4f photoelectrons. Electrochemical (CV) experiments were performed using a BAS 100a Electrochemical Analyzer with a home built electrochemical cell. As reference electrode Hg<sup>+</sup>/HgO (OH<sup>-</sup>) system was chosen. Freshly evaporated gold film on mica were punched into identical round pieces ( $\varnothing$  8mm) and mounted on a dedicated, gold plated clamp after preparation. All electrochemical experiments were performed in de-aerated 0.5M KOH in aqueous solution. The surface density of molecules was determined from the desorption charge. STM experiments were performed using a Nanoscope III Multimode low current STM and an Omicron UHV-AFM/STM. All measurements were performed with self-cut Pt/Ir (80/20) tips. Imaging conditions for the different molecular systems: DEDTC/Au, 70 pA, 500 mV (Omicron) and 1 pA, 200 mV (Multimode); and DT/Au, 2 pA, 100 mV (Multimode).

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Contact angles of water were measured in the dynamic ( $\theta_d$ ) and static ( $\theta_s$ ) mode on a Krüss surface science system at ambient temperature and humidity conditions.

### XPS and CV

Figure SI1 shows molecular schemes for DEDTC and DT; S2p XPS spectra and CV diagrams recorded on DEDTC/Au and DT/Au. XPS data clearly reveals presence of one sulfur species for each of these systems and CV indicates reductive desorption waves indicating the chemisorption of the investigated molecules. For DEDTC/Au, CV detects a second species at lower desorption potential (circle), which we attribute to bound inter-domain species of DEDTC. Increasing the temperature leads to a stronger pronunciation of this signal thereby supporting the presented model of SMAs. The comparison of the XPS sulfur content to the reductive desorption current measured by CV, shows a good agreement: for DEDTC  $0.9 \pm 0.2$  e / molecule. In the desorption process, one molecule captures one electron, and thus the molecular surface coverage determined by XPS and CV agree within negligible errors.



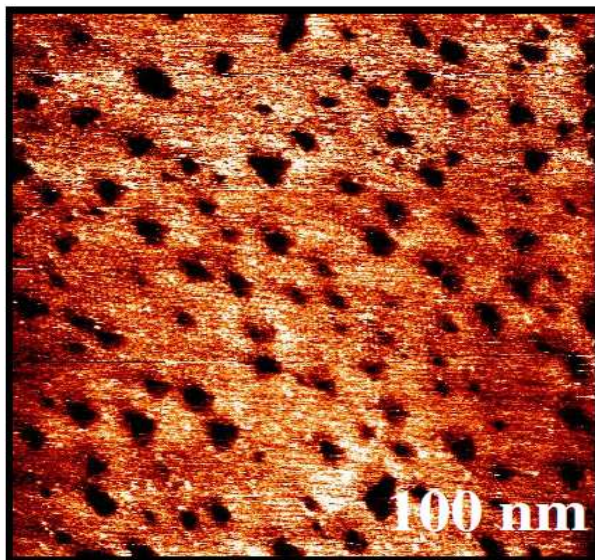
**Figure SI1.** S 2p XPS spectra and CV characteristics of DT/Au and DEDTC/Au.

### STM

Figure SI2 presents STM images of DEDTC/Au on a large scale on which FT-image was taken. The assignment of lobes imaged by STM to corresponding molecular features and structures closely relates to the question of the exact imaging mechanism of molecularly resolved STM pictures. Despite of the manifold of available STM investigations on thiol compounds the STM contrast mechanism remains under discussion. Different mechanisms for the major contribution to the tunneling current have been proposed so far: a) tunneling into

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the density of states of gold, which is modified by the ad-molecules on the surface, (1) b) tunneling into the sulfur gold bond, (2) and c) tunneling directly into the molecular back bone of the ad-molecules. (3) The possibility to differentiate between different sized thiols in STM data (decanethiol and dodecanethiol), (4) or from thiols bearing different tail groups (hydroxyl and methyl), (5) indicates that the tunneling mechanism also includes the entire molecular entity. This is probably due to the fact that both S atoms form a conjugated electronic structure in combination with the C and N atom of the DTC binding group (6).



**Figure SI2.** Large area (100 nm x 100 nm) STM image taken on DEDTC/Au.

Further, the STM data were taken under ambient conditions. Long *n*-alkanethiols form a perfect hydrophobic layer with a measured contact angle of water  $\theta_d$ :  $98^\circ \pm 2^\circ$  and  $\theta_s$ :  $94^\circ \pm 2^\circ$  for DT/Au, which usually leads to very nice high resolution images. In contrast, the DEDTC/Au has much smaller contact angles of water  $\theta_d$ :  $57^\circ \pm 2^\circ$ ,  $\theta_s$ :  $56^\circ \pm 2^\circ$ , which raises the possibility of additional adsorbates e.g. H<sub>2</sub>O molecules.

## References

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