

Supplementary Information for:

Oligothiophene Wires: Impact of Torsional Conformation on the Electronic Structure

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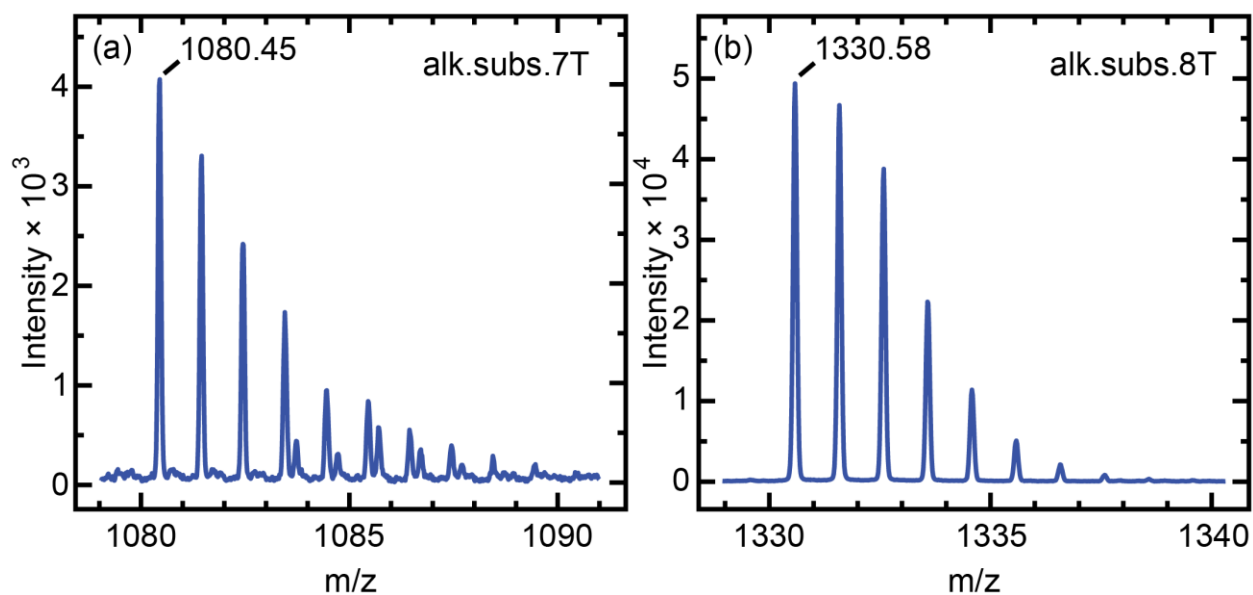


Figure S1. Sample characterization using nanoelectrospray ionization (nano-ESI) mass spectrometry [solution in THF, ESI voltage 1.4 kV]: (a) part of the spectra corresponding to alkyl-substituted 7T (calculated for $C_{64}H_{88}S_7$ 1080.49, found 1080.45), (b) part of the spectra corresponding to alkyl-substituted 8T (calculated for $C_{80}H_{114}S_8$ 1330.66, found 1330.58). The progression of peaks beyond the main m/z peak is the isotope series for each conformer.

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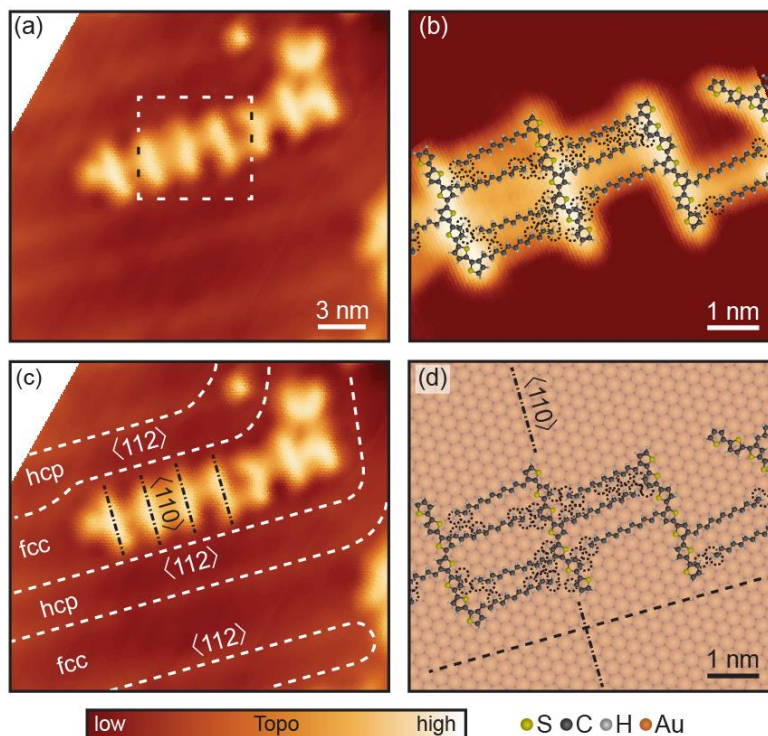


Figure S2. Adsorption of 7T molecules on Au(111). (a) STM image [set point 100 mV, 5 pA] of an aggregate of 7T molecules absorbed on the Au(111) surface. (b) Close-up STM topography of the region confined by the dotted rectangle in (a) with overlaid atomic models of 7T molecules showing that molecules attach to each other via alkyl substituents. The molecular models show that the thiophene rings comprising the DDQT backbones are nearly flat on the Au(111) surface, as determined from STM topography. (c) STM image from (a) with indicated molecular orientations and Au(111) crystallographic directions and highlighted surface reconstruction ridges. The oligothiophene backbones of 7T molecules are aligned along the $\langle 110 \rangle$ directions of the Au(111) surface, perpendicular to the straight sections of surface-reconstruction ridges, which run parallel to the $\langle 112 \rangle$ directions. (d) Model of 7T molecules from (b) matched to the Au(111) surface lattice. Au(111) crystallographic directions are indicated. 7T backbones are roughly aligned along the $\langle 110 \rangle$ direction. Dashed circles indicate the van der Waals radii of the hydrogen atoms.

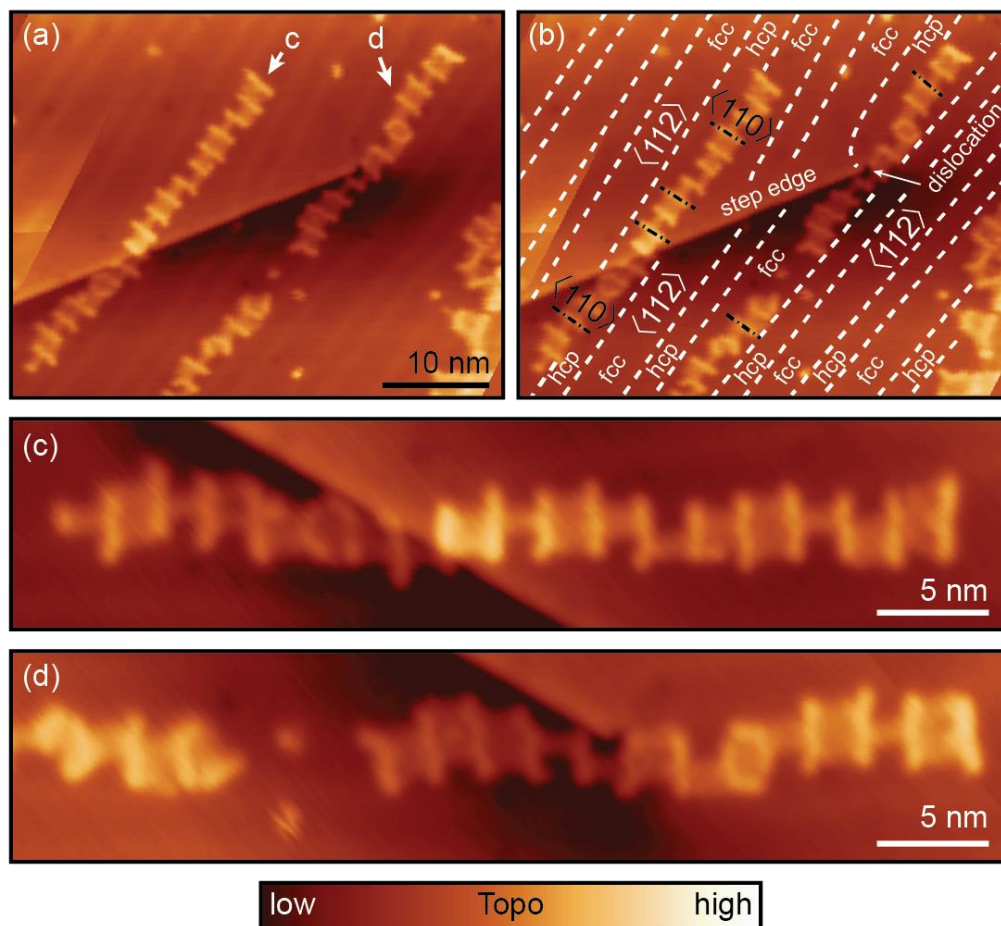


Figure S3. 7T molecular aggregates on Au(111).. (a) STM image [set point 100 mV, 5 pA] of an aggregate of 7T molecules absorbed on the Au(111) surface. (b) STM image in (a) with indicated molecular orientations and Au(111) crystallographic directions and highlighted surface-reconstruction ridges. The oligothiophene backbones of 7T molecules are preferentially adsorbed in fcc regions of the Au(111) surface reconstruction and aligned along the $\langle 110 \rangle$ directions of the Au(111) surface, perpendicular to the straight sections of surface reconstruction ridges, which run parallel to the $\langle 112 \rangle$ directions. (c) and (d) close-up STM topographies of molecular chains indicated in (a) showing chains extending over a Au(111) step.

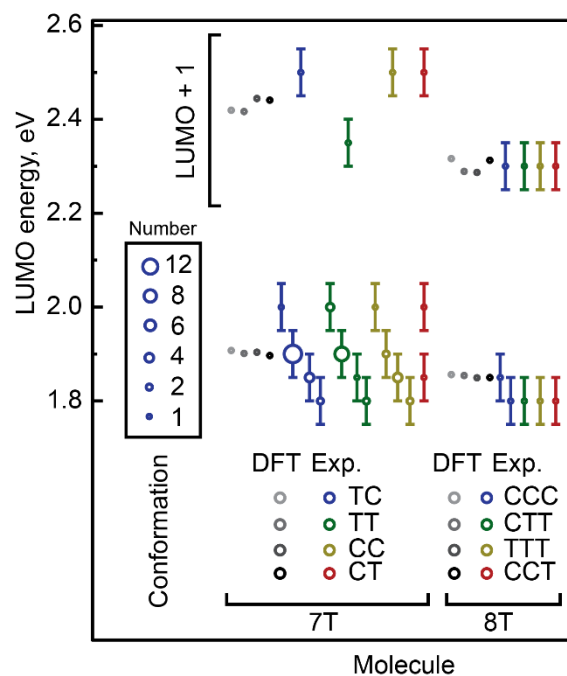


Figure S4. Distribution of LUMO and LUMO+1 energies of 7T and 8T acquired by STS. 5 8T molecules (2 CCC, 1 each of TTT, CCT and CTT) and 50 7T molecules (23 TC, 16 TT, 9 CC and 2 CT) were measured. Standard deviations for the 7T conformations are 0.031 eV (TC), 0.038 eV (TT), 0.051 eV (CC) and 0.117 eV (CT). DFT results are presented for comparison.

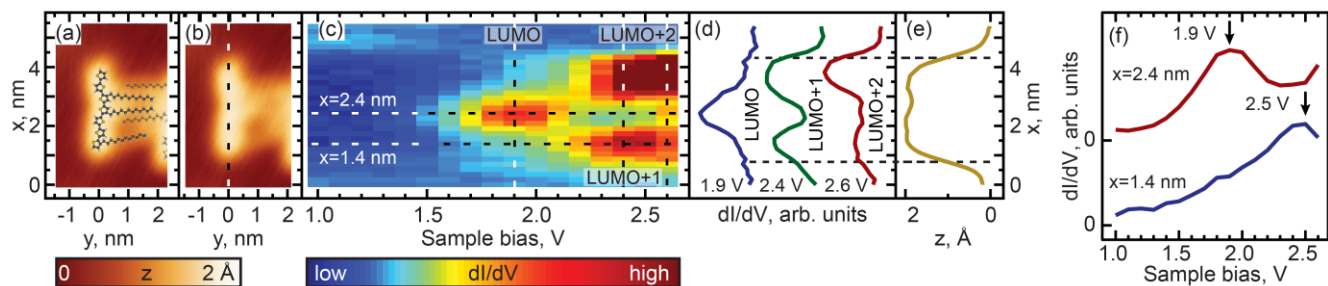


Figure S5. Same as Figure 3 for a CC conformer of 7T molecules. (a) STM image with an overlaid atomic model of the CCC-7T molecule. (b) STM image from (a) showing the path of mapping (dashed line). (c) DOS as a function of the bias voltage and position x along the path shown in (b). (d) LUMO, LUMO+1 and LUMO+2 DOS along the path shown in (b), obtained at voltages corresponding to the vertical dashed lines in (c). These voltages were chosen to maximize the contributions of the corresponding individual orbitals. Curves are shifted and normalized for clarity. (e) Backbone profile (z height vs. x coordinate) along the dashed line from (b). (f) Individual STS spectra from (c) measured at $x=2.1$ and 2.7 nm as indicated by horizontal lines in (c). Spectra are shifted for clarity. The LUMO state manifests itself as a peak at 1.85 V in the spectrum measured at $x=2.7$ nm, while LUMO+1 is observed as a peak at 2.3 V in the spectrum measured at $x=2.1$ nm. Only a shoulder of the LUMO+2 state is observed.

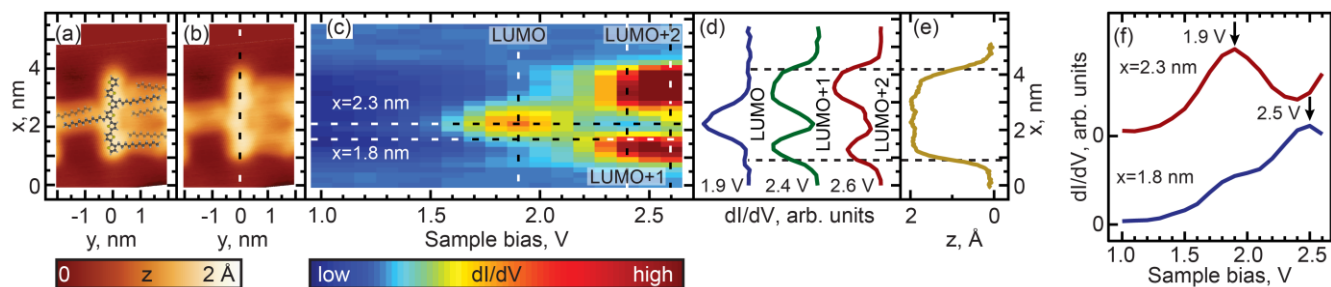


Figure S6. Same as Figure 3 for a TT conformer of 7T molecules.

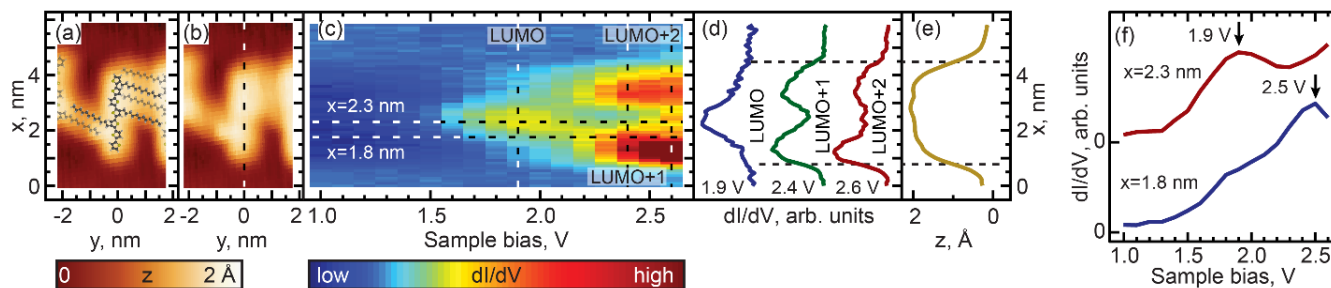


Figure S7. Same as Figure 3 for a TC conformer of 7T molecules.

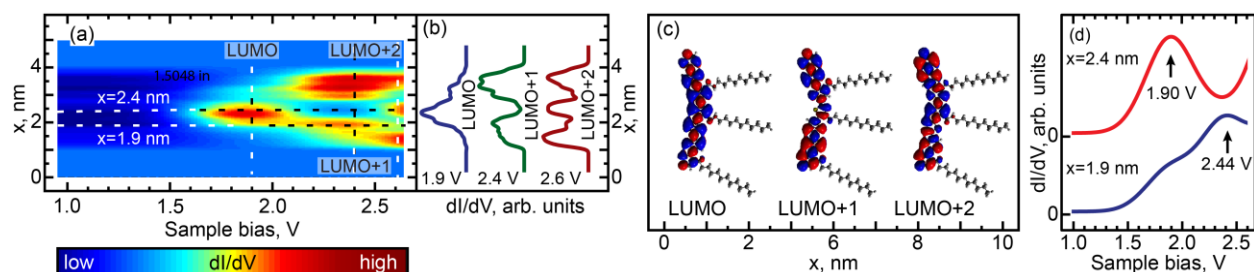


Figure S8. Calculated electronic DOS for a CC conformer of 7T molecules. (a) DOS (compare to Figure S3c) as a function of the bias voltage and position x along the path similar to that shown in Figure S3b. (b) LUMO, LUMO+1 and LUMO+2 DOS (compare to Figure S3d) along the same path as in (a), obtained at voltages corresponding to the vertical dashed lines in (a). These voltages were chosen to maximize the contributions of the corresponding individual orbitals. Curves are shifted and normalized for clarity. (c) Three-dimensional representations of DOS for LUMO, LUMO+1 and LUMO+2 showing the particle-in-a-box nature of these states. (d) Individual DOS spectra from (a) measured at spatial locations indicated by horizontal lines in (a). Spectra are shifted for clarity. The LUMO state manifests itself as a peak at 1.9 V (top curve), while LUMO+1 is observed as a peak at 2.3 V (bottom curve). Electronic structure calculations were performed with density functional theory (DFT) calculations using B3LYP/6-31G*.

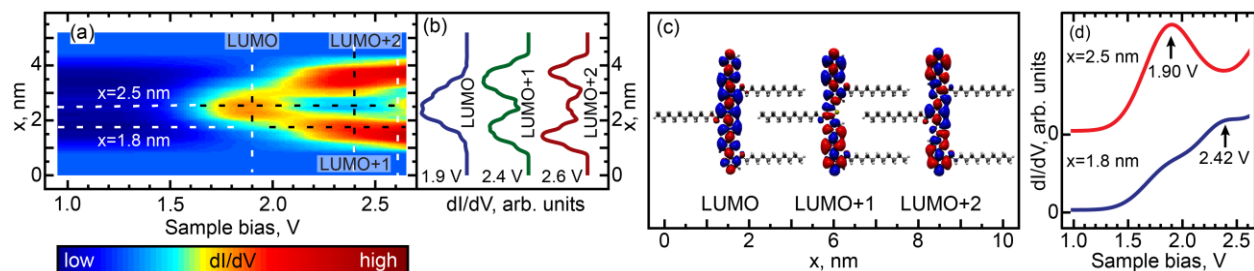


Figure S9. Same as Figure S6 for a TT conformer of 7T molecules.

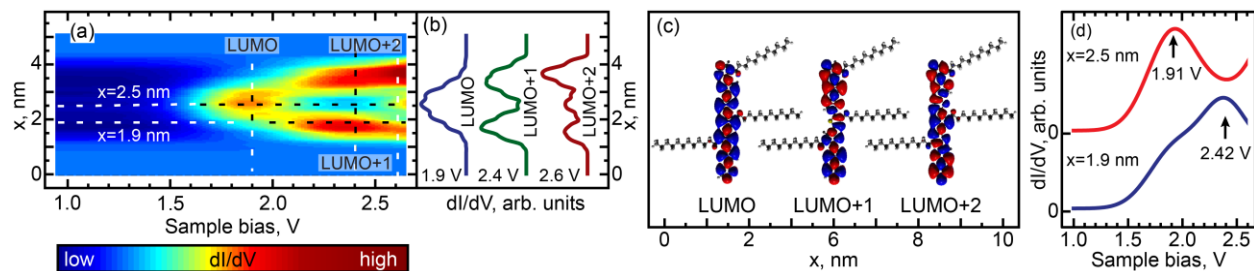


Figure S10. Same as Figure S6 for a TC conformer of 7T molecules.