

Adsorption-Induced Conformational Isomerization of Alkyl-Substituted Thiophene Oligomers on Au(111): Impact on the Interfacial Electronic Structure

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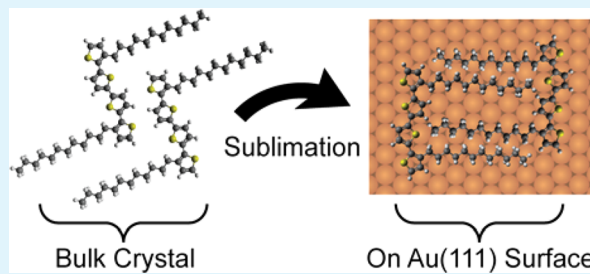
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Supporting Information

ABSTRACT: Alkyl-substituted quaterthiophenes on Au(111) form dimers linked by their alkyl substituents and, instead of adopting the trans conformation found in bulk oligothiophene crystals, assume cis conformations. Surprisingly, the impact of the conformation is not decisive in determining the lowest unoccupied molecular orbital energy. Scanning tunneling microscopy and spectroscopy of the adsorption geometries and electronic structures of alkyl-substituted quaterthiophenes show that the orbital energies vary substantially because of local variations in the Au(111) surface reactivity. These results demonstrate that interfacial oligothiophene conformations and electronic structures may differ substantially from those expected based on the band structures of bulk oligothiophene crystals.

KEYWORDS: adsorption configuration, quaterthiophene, oligothiophene, scanning tunneling spectroscopy, surface reconstruction, organic electronics



Operation of electronic devices based on organic semiconductors depends, to a great extent, on the properties of interfaces between the external electrical contacts and organic materials. The interface electronic structure is a particularly important element of the physical picture of electron transport and is often a result of substantial contact-induced rearrangement of the local electronic structures of the molecules and electrode surfaces.^{1,2} The conformational flexibility of many classes of organic semiconductors composed of conjugated polymers and oligomers presents an additional level of complexity: the sensitivity of the molecule–surface interaction to the molecular conformation in the interfacial layer^{3,4} can lead to pronounced inhomogeneities of electron-transport properties across the interface. These interfacial conformations are difficult to study using surface-averaged experimental techniques and also present an excessively large phase space of possible conformers for theoretical simulations.

An important example of organic semiconductors where interfacial conformational effects may be significant is the wide class of materials related to oligothiophenes. Recent work on alkyl-substituted oligothiophenes has demonstrated that judicious synthetic placement of alkyl substituents improves the molecular packing in the solid state, which enables better electronic coupling between individual molecules, resulting in

charge-carrier mobilities of up to $6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁵ A potential complication that may impact oligothiophene-based applications is that the relative flexibility of oligothiophene backbones has been found to lead to conformational polymorphism,^{6,7} resulting in variations of the electronic properties in the solid state.^{8,9} Similarly, the effects of conformational polymorphism specific to interfaces may be expected to affect the charge-transport properties in oligothiophene-based devices. This expectation is supported by several scanning tunneling microscopy (STM) studies, which demonstrated that substituted oligothiophenes can show conformational polymorphism,^{10–12} as well as diverse self-assembly regimes caused by the presence of substituent groups.^{13,14} However, while conformation-resolved scanning tunneling spectroscopy (STS) studies of substituted oligothiophenes adsorbed on graphite have been reported,¹³ the effects of conformational polymorphism on the interfacial electronic structure have not been investigated.

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Here we, for the first time, report a STS study of the electronic structures of substituted oligothiophenes adsorbed in different conformations on a model metal [Au(111)] substrate showing atomic-scale chemical interaction with adsorbed oligothiophenes. In our study, we used alkyl-substituted quaterthiophene (didodecylquaterthiophene, or DDQT in the following) containing a conjugated backbone composed of four thiophene rings and two alkyl chains attached to the backbone (see Figure 1 for models of the molecular structure). The

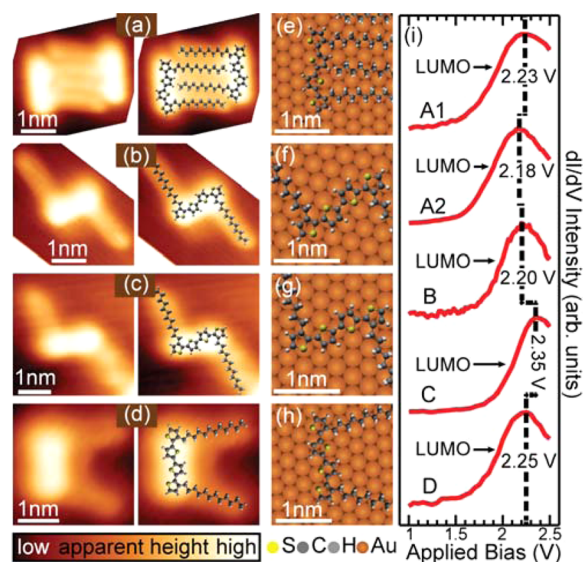


Figure 1. Adsorption configuration of DDQT molecules on Au(111). (a) STM image of two DDQT molecules in the cis conformation, forming a dimer with overlaid molecular structures. (b and c) STM images of DDQT molecules in the trans conformation, with overlaid molecular structures. (d) Same as parts b and c for an individual cis molecule. (e–h) Models of the DDQT backbone matched to the Au(111) surface lattice for adsorption configurations from parts a–d, respectively. (i) STS of the LUMO state corresponding to the two molecules from part a, curves A1 and A2, and molecules from parts b–d, curves B–D, respectively. STM imaging was carried out at a bias voltage of 100 mV and tunneling currents of 5–50 pA.

relatively short thiophene backbone of DDQT allows us to isolate the effects of short-range disorder on the electronic structure, with the backbone still being long enough for the quantum-confined frontier orbitals to be sufficiently close to the Fermi level of the Au substrate and accessible to STS.

We used a home-built cryogenic STM¹⁵ [see the Supporting Information (SI) for further details] to image DDQT molecules on the Au(111) surface in the regime of submonolayer molecular surface coverage, which revealed that the majority of molecules were self-assembled into pairs. The molecules in each pair were found to bind to each other by interdigitating substituent alkyl chains (Figure 1a). In these dimer-like structures, the molecules assumed the cis conformation, with both alkyl chains lying on the same side of the quaterthiophene backbone (Figure 1a). Individual molecules were observed less frequently and were primarily found in the trans conformation, with the alkyl chains lying on the opposite sides of the quaterthiophene backbone (Figure 1b,c). This trans-conformation morphology of the quaterthiophene backbone is close to that found in macroscopic crystals of unsubstituted quaterthiophenes¹⁶ and is also analogous to that found in DDQT crystals, where the terminal thiophenes are rotated by $\sim 12^\circ$ out of plane

with the rest of the backbone.¹⁷ The alkyl chains in the majority of DDQT molecules typically formed angles of $\sim 90^\circ$ with respect to the quaterthiophene backbone (Figure 1a–c). More rarely, individual cis conformers were also observed (Figure 1d) that showed varied angles between the substituent chains.

The observed tendency of DDQT molecules to form cis dimers suggests that at room temperature DDQT molecules are free to migrate on the Au(111) surface until they encounter other molecules [or Au(111) step edges]. Because very few DDQT monomers were found, dimerization driven by the DDQT alkyl chains must provide additional stabilization beyond the Au–thiophene interaction. Indeed, a substantial intermolecular “binding energy” originating from the interaction of alkyl chains can be expected based on the fact that the interaction energy of a pair of dodecane molecules is calculated to be in the range of 0.4–0.5 eV.¹⁸ The fact that dimers formed from cis conformers were primarily observed (very few trans–cis dimers and trans–trans dimers were observed) further suggests that in molecular aggregates torsional transformation of molecules between the cis and trans conformations, leading to minimization of the overall energy of molecular aggregates, must readily occur at room temperature. This scenario is supported by the fact that the terminal rings of oligothiophenes have a low energy barrier for rotation.¹⁹

Additional stabilization of cis conformers is provided by the enhanced electrostatic interaction of cis conformers (compared to trans conformers) with the substrate. This enhanced interaction arises from the nonzero molecular dipole moments (2.32 D for the cis conformer versus 0.06 D for the trans conformer; see Table S1 in the SI), which interact with image charges at the metal surface.²⁰

Further inspection of STM images shows that thiophene backbones of the majority of observed molecules can assume three distinct orientations on the Au(111) surface (Figure 2). Specifically, in reference to the herringbone $22 \times \sqrt{3}$ surface reconstruction features of Au(111), the backbones of all molecules were orthogonal to one of the three possible directions of the surface reconstruction herringbone ridges (these run along the three possible $\langle 112 \rangle$ directions; see Figure 2d–f). The observed preferential orientations of the DDQT backbones can be rationalized by analyzing the oligomer–surface interaction in terms of the sum of interactions of individual thiophene units with the Au(111) surface. Density functional theory (DFT) calculations predict that binding of individual thiophene molecules to Au(111) results in adsorption configurations, where the thiophene S atom binds directly on top of one of the surface Au atoms,²¹ with other adsorption sites being up to 40 meV higher in energy.²² The site-specific interaction is accompanied by a small charge transfer from the Au surface to the S atom, which acquires an extra 0.08 e for the perpendicular (with respect to the surface plane) orientation of the thiophene ring and 0.10 e for a nearly flat orientation, forming a small angle with respect to the Au(111) surface.²³ These differences in the strength of the interaction result in the nominally flat-lying orientation²¹ being ~ 40 meV more stable than the vertical orientation.²² These predictions for individual thiophene molecules are consistent with STM imaging of DDQT molecules, which shows molecular profile heights of ~ 2 Å, suggesting that the constituent thiophene rings are nearly flat on the Au(111) surface. [The flat adsorption geometry is also in accordance with previous results obtained for octithiophenes on Au(111) in the low-coverage regime.²⁴]

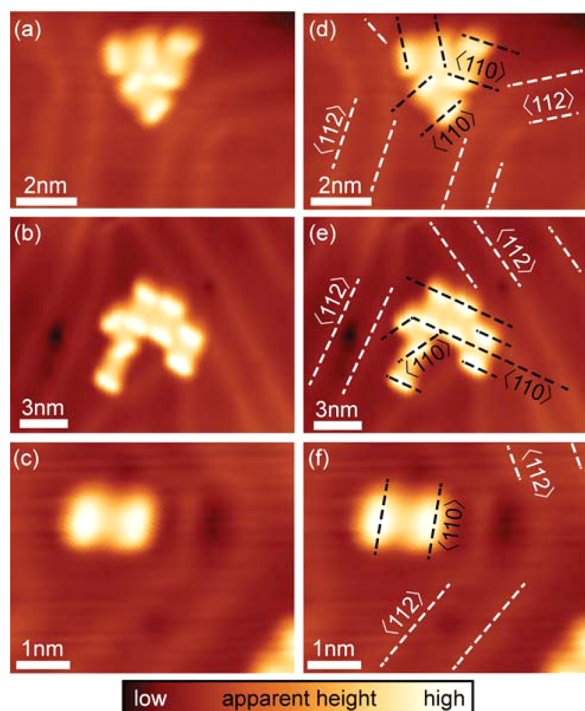


Figure 2. Registry of DDQT molecules with the underlying Au(111) surface. (a–c) STM images of DDQT molecules on the Au(111) substrate. (d–f) Same as parts a–c but showing the molecular orientations and Au(111) crystallographic directions. The quaterthiophene backbones of DDQT molecules aligned along one of three $\langle 110 \rangle$ directions of the Au(111) surface, perpendicular to the Au(111) surface reconstruction ridges aligned primarily along the $\langle 112 \rangle$ directions, as shown. STM imaging was carried out at bias voltages of 0.1–1.0 V and tunneling currents of 1–5 pA.

We expect that the site-specific interaction between the Au and S atoms described above should result in minimum-energy adsorption configurations of DDQT, where the oligothiophene backbone is oriented so as to allow the constituent S atoms to be in the direct vicinity of select Au atom top sites. To qualitatively evaluate the possible DDQT/Au(111) adsorption configurations, we will thus focus on the placement of the S atoms of the quaterthiophene backbone with respect to the Au(111) lattice. We first consider the two outermost S atoms because this pair (compared to other possible pairs of S atoms) may be more easily matched to the Au(111) lattice (because of the larger separation between these S atoms). In addition, the terminal thiophene rings are more torsionally flexible than the inner thiophene rings,¹⁹ which may allow the terminal S atoms to make better contact with the corresponding Au atoms. For the planar backbone structure of *cis*-quaterthiophene (*trans*-quaterthiophene) obtained using geometry optimization in the gas phase, the distance between the terminal S atoms is ~ 1.14 nm (1.19 nm), a very close match to 1.15 nm, which is equal to four Au lattice constants along the $\langle 110 \rangle$ direction. Observation of molecular orientations parallel to the $\langle 110 \rangle$ direction (Figure 2) is thus consistent with the expectation for the two terminal S atoms of every DDQT molecule to be located directly above individual Au atoms (Figure 1e–g). The question arises, however, of whether the geometries shown in Figure 1e–g are unique candidates for minimum-energy adsorption configurations based on our qualitative reasoning relying on the Au–S interaction. For example, by using the same reasoning, one can identify other backbone orientations in which two of the four S

atoms are located at two different Au top sites (Figure S1 in the SI). As Figure S1 in the SI shows, such orientations are different from that of Figure 1e in that the latter orientation is the only one in which all four S atoms are located in the direct vicinity of (different) Au top sites, which means that this orientation should be the most stable. A similar distinction exists for the *trans* versus *cis* conformers aligned along the $\langle 110 \rangle$ direction: the two inner S atoms of *trans* conformers are located near the Au 3-fold hollow sites and bridge sites, which makes the *trans* conformation less energetically favorable, consistent with the higher abundance of *cis* conformers in STM images. The predominance of the *cis* conformation may also be, in part, due to the better lattice-matching of the terminal S atoms for the *cis* conformation compared to the *trans* conformation (1.14 nm for *cis* versus 1.19 nm for *trans* matched to 1.15 nm corresponding to four Au lattice constants along the $\langle 110 \rangle$ direction).

We note that, despite the fact that intermolecular interaction via alkyl ligands is the main driving force for DDQT dimerization, this interaction does not noticeably affect the orientations of *cis* conformers. This suggests that the interaction of alkyl ligands has a relatively weak dependence on the orientation with respect to the Au(111) surface. This conclusion is supported by the fact that alkyl ligands in Figure 1 are aligned close to the $\langle 112 \rangle$ direction rather than the $\langle 110 \rangle$ direction, as observed for alkanes self-assembled on Au(111).²⁵

The presence of both *cis*- and *trans*-DDQT conformers in our STM images presents an opportunity to study the effects of torsional conformations on the oligothiophene electronic structure. To this end, we measured the local electronic structure of individual molecules by using STS. In STS, the local electronic density of states of individual molecules is quantified by measuring the derivative of the tunneling current as a function of the bias voltage (dI/dV) that serves as the energy scale (see the SI for further details).²⁶ STS spectra recorded on ~ 70 different DDQT conformers typically showed one well-resolved electronic state associated with the lowest unoccupied molecular orbital (LUMO) of DDQT, generally in the vicinity of 2.2 V (Figure 1i). Identification of molecular orbitals other than the LUMO is difficult because of the instability of DDQT ligand alkyl chains at higher voltages. This instability resulted in both motion and irreversible deformation of the alkyl chains (Figure S2 in the SI). At bias voltages comparable to that of the LUMO orbital, scission of the thiophene backbone was often observed (Figure S3 in the SI), limiting the molecular lifetime.

The obtained STS spectra (Figure 1i) allow us to make two unexpected observations. First, it is surprising that the LUMO energies for *trans* and *cis* conformations (measured using the same tip) can be very close (curves A2 and B in Figure 1i), despite the differences in their backbone structures. Indeed, DFT calculations for planar quaterthiophenes predict the *cis*-LUMO to be ~ 30 meV higher than the *trans*-LUMO (Figure S4 and Table S1 in the SI). Furthermore, molecules with nominally identical conformations (adsorption configurations) were found to have LUMO energies (measured using the same tip) differing by as much as 150 meV (for example, see curves A1 and A2 for the *cis* conformation and curves B and C for the *trans* conformation). These observations suggest that the energies of DDQT molecular orbitals are strongly affected by factors other than the apparent torsional conformation.

A possible explanation for the seemingly random variations of the observed LUMO energies is obtained through analysis of

the locations of individual molecules on the Au(111) surface. Indeed, the properties of the Au(111) surface are spatially modulated because of the presence of the herringbone $22 \times \sqrt{3}$ surface reconstruction, which leads to variations in coordination of the surface Au atoms. For example, recent DFT calculations of H and F atoms adsorbed on Au(111) show that these atoms are more stable in the face-centered-cubic (fcc) areas, compared to the hexagonal-close-packed (hcp) areas.²⁷ In accordance with these predictions, we find that DDQT molecules adsorb primarily in the fcc regions of Au(111) rather than the hcp areas (Figures 3a–c and S5 in the

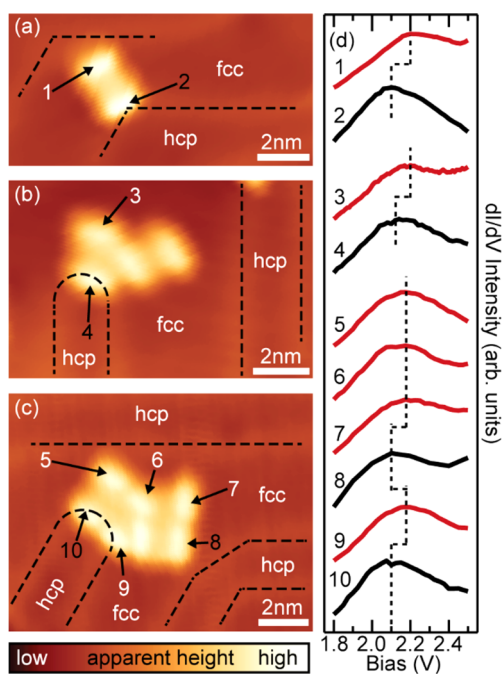


Figure 3. Correlation of the DDQT adsorption location with the LUMO peak energy. (a–c) STM topographies. Black dashed lines show the Au(111) reconstruction ridges. (d) STS spectra showing LUMO peaks for molecules in parts a–c. Each numbered spectrum corresponds to a molecule appearing with the same number in parts a–c. Molecules with black numbers in parts a–c are located closer to the reconstruction ridges than their neighbors. STS spectra of these molecules [black curves 2, 4, 8, and 10] in part d show LUMO peaks downshifted by ~ 100 mV in their respective groups of molecules (a–c). The proximity of the DDQT backbone to the reconstruction ridges thus reduces the LUMO energy. STM imaging was carried out at bias voltages of 0.3–1.0 V and a tunneling current of 5 pA.

SI). Further, similar preferential adsorption in the fcc areas was observed in STM studies of unsubstituted terthiophenes on Au(111).²⁸ In an analogous fashion, the spatially modulated coordination of the surface Au atoms can be expected to affect the Au–S interaction, and, consequently, the energies of DDQT electronic orbitals. In line with these general expectations, we find that, in our STS measurements, the LUMO energies of DDQT molecules are affected by the proximity to the hcp regions and reconstruction ridges. Specifically, as can be inferred from Figure 3, molecules located in the vicinity of the reconstruction ridges (molecules with black numbers in Figure 3a–c) exhibit LUMO peaks (black curves in Figure 3d) downshifted by up to ~ 100 mV compared to molecules located further from the reconstruction ridges. A statistical analysis of the LUMO energies determined from STS measurements for

68 molecules of both conformations (Figure S6 in the SI) shows variations of the LUMO energies with a standard deviation of ~ 80 meV, which is considerable compared to the ~ 30 meV energy difference between the *cis*- and *trans*-LUMO obtained in DFT calculations (Table S1 in the SI). Figure S6 in the SI shows that the average energy of the *cis*-LUMO is 50 ± 23 meV higher than that of the *trans*-LUMO, consistent with DFT calculations.

While spatial variations in the surface reactivity clearly have a substantial effect on the LUMO energies, other conformation-sensitive factors may also have significant contributions. Indeed, the varied matching of different conformers to the Au(111) lattice is likely to produce conformation-specific molecular structural relaxations and hybridization of molecular orbitals with the Au(111) states, which can both lead to conformation-specific orbital shifts.²⁹ For the same reasons, the overall Au–S interaction is likely to be different for the *cis* and *trans* conformers, resulting in different adsorption distances, which should, in addition to the factors noted above, affect the molecular orbital energies by altering the magnitude of image-potential screening.³⁰ Indeed, the adsorption distance of the *cis* conformers to the Au surface is likely smaller than that for the *trans* conformers because of the better match to the Au(111) lattice (Figure 1a–c) and the much larger dipole (2.32 D for *cis* versus 0.06 D for *trans*; Table S1 in the SI) interacting with its image in the Au surface.²⁰ The closer molecule–substrate distance, in turn, leads to a greater screening of the LUMO, which should result in a downshift of the orbital for the *cis* conformers.³⁰

Our findings highlight the complexity of physical and chemical interactions at the interfaces of metals and organic semiconductors. The atomic lattice of the Au(111) predominantly induces the *cis* conformation of oligothiophene molecules, which is very different from the *trans* conformation found in bulk crystals. One can thus generally expect that, in devices incorporating oligothiophene molecules and metal electrical contacts, the structure of the interfacial molecular layer may be entirely different from that of the molecular bulk of the device. The electronic structures of the molecules in the interfacial layer can be expected to display differences caused by local atomic-scale variations of the surface reactivity, which may be caused by either surface reconstruction or the presence of polycrystalline facets at metal contacts. While the current letter presents a direct visualization of this behavior, understanding the complex interplay between the conformational variability and local reactivity, as well as their impact on the interfacial electronic structure, will require further studies.

■ ASSOCIATED CONTENT

Supporting Information

Additional information and experimental data, including additional molecular adsorption models, STM images of DDQT alkyl side change manipulation, STM images of DDQT backbone scission, frontier orbitals calculated by DFT, and statistical distribution of observed LUMO energies. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03516.

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Notes

The authors declare no competing financial interest.

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