



Ordered structures of two sulfur containing donor molecules on the Au(111) surface

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ABSTRACT

We report experiments by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) on ordered structures of two sulfur-containing π -conjugated molecules on the Au(111)-surface, namely tetrabenzothianthrene (TBTA) and tetrathiotetracene (TTT). These molecules are candidates for donors in charge transfer salts. On Au(111) both molecules form long-range ordered structures that are commensurate to the top-most surface layer. For TBTA, the reconstruction of the Au(111) surface is maintained, whereas it is lifted by TTT. Both molecules lie flat on the surface. For TBTA, the structure indicates that the molecule is planarized upon adsorption.

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1. Introduction

In this paper we report the monolayer structures of two sulfur containing π -conjugated molecules, namely tetrabenzothianthrene (TBTA) and tetrathiotetracene (TTT), on the Au(111) surface. The structure formulae of both molecules are shown in Fig. 1. We note that TTT is often also named as tetrathianaphthacene (TTN) [1]. In general, these molecules are of interest as electron donating molecules due to the electron rich sulfur atoms in conductive organic solids. In this aspect TTT bears similarities to the smaller model molecule tetrathiafulvalene (TTF), which forms well investigated charge transfer crystals together with tetracyanoquinodimethane TCNQ [2]. The first synthesis of TBTA was reported in 1973 [3]; the synthesis of TTT already in 1948 [4]. To our knowledge there were no further studies on TBTA after 1973, whereas a number of investigations were performed on TTT. In 1965, Matsunga reported a high electric conductivity for compressed powder samples of pure TTT and of complexes of TTT with organic electron acceptor molecules [5]. These complexes were found to be semiconducting and showed a charge transfer from TTT to the acceptor species. In the following years, several further complexes of TTT were synthesized [6–8]; one of them showed even metallic conductivity down to 3.3 K [8]. Different radical cation salts of TTT have been reported more recently [9,10]. TTT is considered as a suitable donor material for organic electronics [1,11]. Furthermore, TTT-iodine complexes (TTT(I₃)) are interesting as active materials in thermoelectric generators [12]. Electrical properties

of vacuum deposited TTT films in pure and doped form have been investigated [13–15]. TTT films deposited on Au substrates were also studied by photoemission, but, to our knowledge, no structural or morphological details were obtained so far [1].

The investigation on thin films of charge transfer complexes of electron donating molecules on solid substrates [16] evidently motivates experiments on the adsorption and ordering behavior of the pure compounds on well-defined surfaces. In addition, such experiments yield information on molecule/surface interfaces that play a role in the form of electrical contacts in thin film devices. Sulfur containing larger π -conjugated molecules are principally good candidates for electron donors. Concerning their adsorption on surfaces there is the general question on the role of the sulfur atoms: do they participate in a delocalized bonding of the molecules via the π system, or do they form localized bonds to the surface, causing even disintegration from the molecule. One of the prominently studied classes of sulfur containing π -conjugated molecules are oligothiophenes. On Au(111), e.g., sexithiophene (6T) has been investigated in detail [17]. It was observed that the Au(111) reconstruction is partially lifted as a result of the chemical interaction with the molecules. Interestingly, this effect was encountered for TTT in the reported experiment, too.

Besides TTT monolayers, TBTA monolayers on Au(111) are reported in this paper. In this context we resume some information on the formerly unknown crystal structure of TBTA that will be relevant for our results further below. The crystal structure determination revealed that the TBTA molecule is folded; the folding line going through the two sulfur atoms (see Fig. 2). The dihedral angle between the two C₁₄H₈S₂ moieties amounts to 129.4° [18], which is close to that of the parent molecule of TBTA, namely thianthrene [19]. Therefore the sulfur

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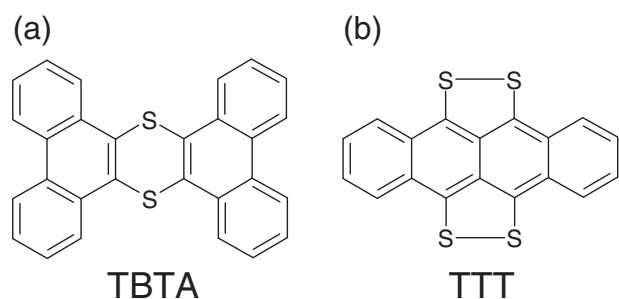


Fig. 1. Structure formulae of TBTA (a) and TTT (b).

lone pairs cannot contribute to the conjugated π -systems, and TBTA effectively exhibits two separated conjugated π -systems. In the crystal, a twofold axis runs through the molecule perpendicular to the $S \cdots S$ axis, giving the molecules crystallographic C_2 point symmetry, but the higher point symmetry C_{2v} is almost fulfilled. The molecules are stacked along the short crystallographic b axis, as illustrated in Fig. 2. Due to the folding of the molecules each individual stack is polar. The centrosymmetric crystal, however, is non-polar, since stacks with opposite polarity are present in equal amount. From its chemical structure we hence

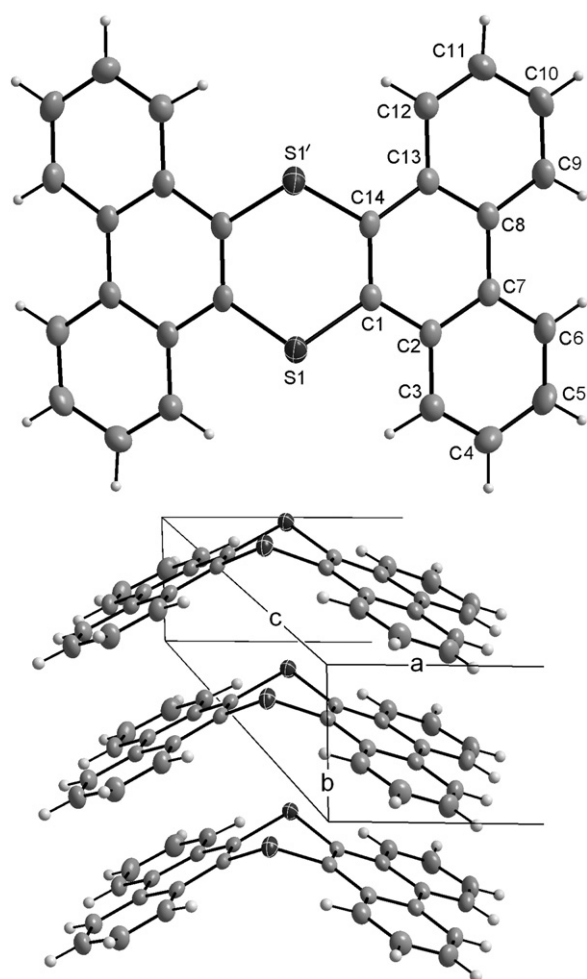


Fig. 2. Top: the molecule in the crystal structure of tetrabenzothianthrene (TBTA) in a view along the twofold symmetry axis. Thermal ellipsoids are scaled to include a probability density of 50%. Selected bond lengths/Å: S1–C1 1.774(2), S1'–C14 1.776(2), C1–C14 1.362(3), S1 \cdots S2' 3.113(1), C–C within aromatic rings 1.368(4)–1.450(3). Bottom: the stacking of the molecules along the crystallographic b axis.

expect a weaker electron donating character of TBTA compared to TTT, which is of planar molecular shape in the crystal [9]. However, adsorption on a surface might lead to a planarization of the TBTA molecule. Indeed, a planar configuration is known for the transition state of the inversion (“flipping”) of thianthrene [19]. The corresponding energy barrier is estimated at 26 kJ/mol (110 meV) for thianthrene dissolved in benzene [20]. From this small value we may expect that a planarization can be driven by the resulting increase in interaction energy of TBTA with a surface. Furthermore, a concomitant change in the donor strength of TBTA, namely an increase, can be envisaged, since for a planar TBTA, the sulfur lone pairs can contribute to the conjugated π -system, likewise as for the structurally related dibenzodioxine [21].

2. Experimental

The experiments were performed under ultra-high vacuum (UHV) conditions in two chambers. The first one was equipped with an instrument for performing spot profile analysis low energy electron diffraction (SPA-LEED) manufactured by Omicron NanoTechnology GmbH. The base pressure was 3×10^{-10} mbar. The Au(111) single-crystal sample could be heated by a tungsten filament via radiation up to 1000 K and cooled down to 90 K by liquid nitrogen. The SPA-LEED measurements on the organic monolayers were typically performed at electron energies of 41.5 eV or 56.5 eV with currents between 1 and 10 nA and at sample temperatures below 100 K. Degradation of the LEED patterns due to electron beam damage was not observed.

The second chamber contained a variable temperature STM (type RHK UHV 300) manufactured by RHK Technology equipped with a liquid helium cryostat. In addition, this chamber was fitted with an MCP LEED instrument from OCI. This was used to correlate the structural order of the samples investigated by STM with the structural order observed by SPA-LEED before. The STM measurements were either performed at room temperature (RT) or at a cryostat temperature of 16 K, measured by a silicon diode. All other temperatures were measured with a type K thermocouple. All reported STM images were recorded in constant current mode using Pt/Ir tips with a typical tunneling current I_t of 25 pA. Positive and negative bias voltages U_{bias} between 1.5 V and 2.5 V were applied to the sample.

The same Au(111) single-crystal was used subsequently for the experiments in both chambers. It was prepared by several cycles of Ar⁺-ion sputtering at 500–1000 eV for 30 min and annealing at 900–1000 K for 60 min. The effective transfer of the (0,0) spot measured by SPA-LEED exceeded 230 Å at an electron energy of 68.5 eV. For such a surface, the SPA-LEED images showed three orders of satellite spots around the (0,0)-spot which belong to the $22 \times \sqrt{3}$ reconstruction of the Au(111) surface, as reported for instance in [22]. The reconstruction results from a compression of the surface top layer in the $[111]$ direction [23]. Within the reconstruction domains, parallel *discommensuration lines* (DLs) in the $[\bar{1}\bar{1}2]$ direction are formed, two per $22 \times \sqrt{3}$ unit cell [24]. They separate regions with *fcc* and *hcp* stacking of the top layer. The DLs alter their direction by $\pm 120^\circ$ at the domain boundaries which separate parallel domains of the Au reconstruction of a striped shape (oriented in $[\bar{1}\bar{2}1]$ direction). This leads to the well-known *zig-zag* arrangement of the DLs. The positions where the DLs alter their direction are usually referred to as the “elbow” positions and mark the domain boundaries along the $[\bar{1}\bar{2}1]$ direction [25,26].

TBTA (416 amu) and TTT (352 amu) were both purified by gradient vacuum sublimation. This was done in order to remove traces of the solvents used in the synthesis and to test whether sublimation of the substances is possible without decomposition. For both molecules we obtained only one fraction of sublimed material and a black residue. TBTA is a pale yellow substance. Thin films of TTT have a green color, while thicker films and crystals of TTT have a black appearance.

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