

Direct Identification of Conformational Isomers of Adsorbed Oligothiophene on Cu(100)

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A direct conformational analysis using scanning tunneling microscopy (STM) has been performed for individual adsorbed α -octithiophene molecules on Cu(100). *s*-cis and *s*-trans conformational isomers are induced by the rotational flexibility of individual thiophene rings. By adding bulky N-silyl substituents to octithiophene, we successfully identify the *s*-cis and *s*-trans conformational isomers using STM. The obtained relative abundances of the *s*-cis and *s*-trans conformations are analyzed using *ab initio* molecular orbital calculations.

Organic thin films of π -conjugated molecules have attracted great interest due to their promising potential for electronics and electro-optic devices.¹ α -Oligothiophene is one of the most extensively studied π -conjugated molecules because of its characteristic electronic and optical properties.^{2–10} It has been well-known that the electronic properties of α -oligothiophenes are governed by intramolecular π -conjugation, which depends on the torsion angle between neighboring thiophenes.^{11–13} Nevertheless, the rotational flexibility of the thiophene–thiophene single bonds induces two conformational forms, *s*-cis and *s*-trans, in which the energy difference has been calculated as only about 0.5 kcal/mol with the *s*-trans conformer as the most stable.¹⁴ Whereas the *s*-cis conformer has been observed for bithiophene in the gas phase,^{15,16} all *s*-trans conformations have been exclusively observed in the crystal phase of many α -oligothiophenes,^{17,18} which should be due to the packing effects. Although the computational conformational analysis of α -oligothiophenes has been studied extensively,^{14,19,20} the experimental investigation has been limited so far.

In this paper, we report a direct conformational analysis of individual α -oligothiophene molecules on Cu(100) using low-temperature scanning tunneling microscopy (STM). To investigate the conformational properties of α -oligothiophene, we use a N-silyl substituted octithiophene (8T-Si), which is designed for the single molecular devices,^{21,22} as shown in Figure 1a. The π -conjugated backbone with about 3 nm in length is protected by the four bulky N-silyl substituents. Since the N-silyl groups are substituted to two adjacent thiophenes, the steric hindrance between them should fix into the *s*-trans conformation at C₄–C₅ and C_{4'}–C_{5'} bonds. Nevertheless, the rotational flexibility remains at the central C₁–C_{1'} bond of the octithiophene, causing the *cis*–*trans* isomerization. Parts b and c of Figure 1 show the *s*-trans and *s*-cis conformations of 8T-Si,

respectively, obtained by the AM1 semiempirical molecular orbital calculations,²³ in which the isomerization is induced by the rotation of the central C₁–C_{1'} bond. Although the characteristic assembling nature of various oligothiophene derivatives has been investigated by STM,^{24–26} it has been difficult to identify *s*-cis and *s*-trans isomers because orientations of individual thiophene rings cannot be resolved in the STM images. In this study, the conformational isomers should be distinguished from the different relative positions of the bulky N-silyl groups.

All experiments were performed in an ultrahigh-vacuum (UHV) system (base pressure less than 1×10^{-9} Pa) with a low-temperature scanning tunneling microscope.^{27–30} We used a single-crystal Cu(100) surface as a substrate, which was prepared by repeated cycles of Ar⁺ sputtering and annealing. The 8T-Si molecules were thermally evaporated at 588 K from a carefully outgassed Knudsen cell in an UHV. Although the relatively higher temperature was necessary for the deposition due to the large size of 8T-Si (C₈₀Si₁₆N₈S₈H₁₃₈; *M* = 1915), we confirmed that the molecules were successfully evaporated without decomposition. This thermal stability should result from the bulky N-silyl groups protecting the central octithiophene against any chemical reactions.^{21,22} The substrate was kept at room temperature during the molecular deposition, and was subsequently transformed to the low-temperature STM stage. All STM images were acquired in a constant current mode of 5.0 pA at 63 K.

Figure 2a shows a STM image of 8T-Si adsorbed on the Cu-(100) surface. Whereas a few molecules are observed on a terrace, most of the molecules are preferentially adsorbed at step edges. This result indicates that the large 8T-Si molecules can be diffused freely over the terraces at room temperature. As the coverage is increased, the molecules are aggregated on the terrace but do not show a strong tendency to order on the Cu(100) surface (as shown in the upper part of Figure 2a). Figure

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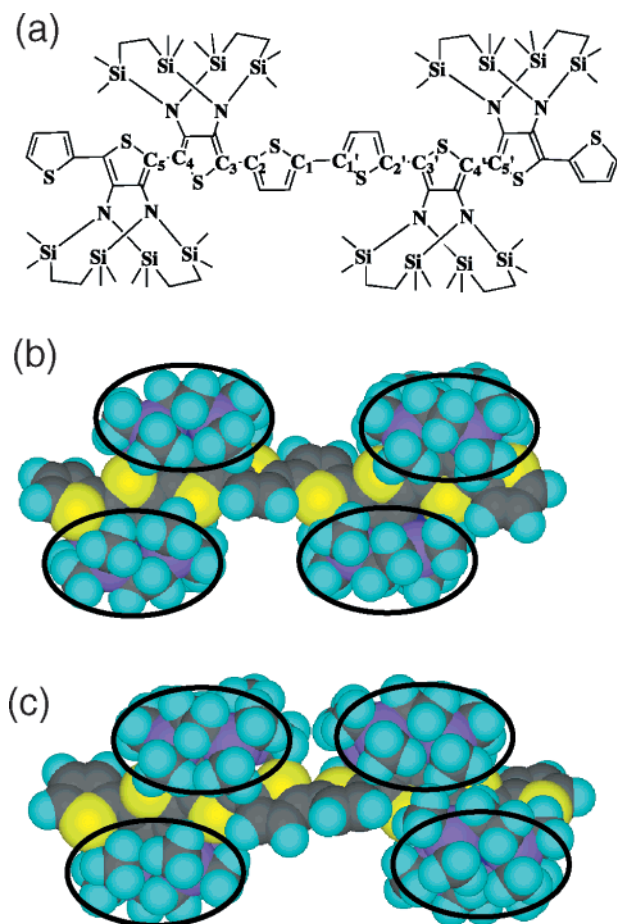


Figure 1. (a) Chemical structure of 8T-Si, in which four bulky N-silyl groups are substituted to the central octithiophene. Optimized structures of (b) *s*-trans 8T-Si and (c) *s*-cis 8T-Si, which are obtained by the AM1 semiempirical molecular orbital calculations. In these structures, the positions of the N-silyl groups are highlighted by ovals.

2b shows the typical STM image of isolated 8T-Si molecules on a terrace, which consist of two paired bright protrusions on the surface. From the molecular dimensions, each of the protrusions should correspond to the bulky N-silyl substituents, as shown in the high-resolution STM image of Figure 2c. The apparent height of about 6.0 Å in the STM image is slightly lower than the ideal dimension (about 7.7 Å) of the N-silyl substituent, which should be associated with the insulating nature of the substituents. The conformations can be identified from the relative positions of the bulky N-silyl groups, as indicated by ovals in Figure 2c. We identify the upper molecule as the *s*-cis conformation and the lower molecule as the *s*-trans one, which agree well with the calculated models of Figure 1. Figure 3 shows isolated 8T-Si molecules adsorbed at step edges. Although adjacent two N-silyl groups appear as only one protrusion in the STM image, the *s*-cis and *s*-trans conformations can also be distinguished from asymmetric structures of the two elliptical protrusions. As indicated by arrows in Figure 3, the trans conformer is additionally classified into two enantiomeric forms, which is characterized as prochirality induced by the adsorption to the surface. In addition, the *s*-cis molecules are frequently observed on the surface, even though the *s*-trans conformation is more stable. We derive the relative abundances to be 52.56 and 47.44 for *s*-trans and *s*-cis conformations, respectively, from a total of 780 molecules, which are independent of the adsorption sites (terraces or steps). During the STM imaging, we do not observe spontaneous conformational changes,³¹ which should result from stronger van der Waals

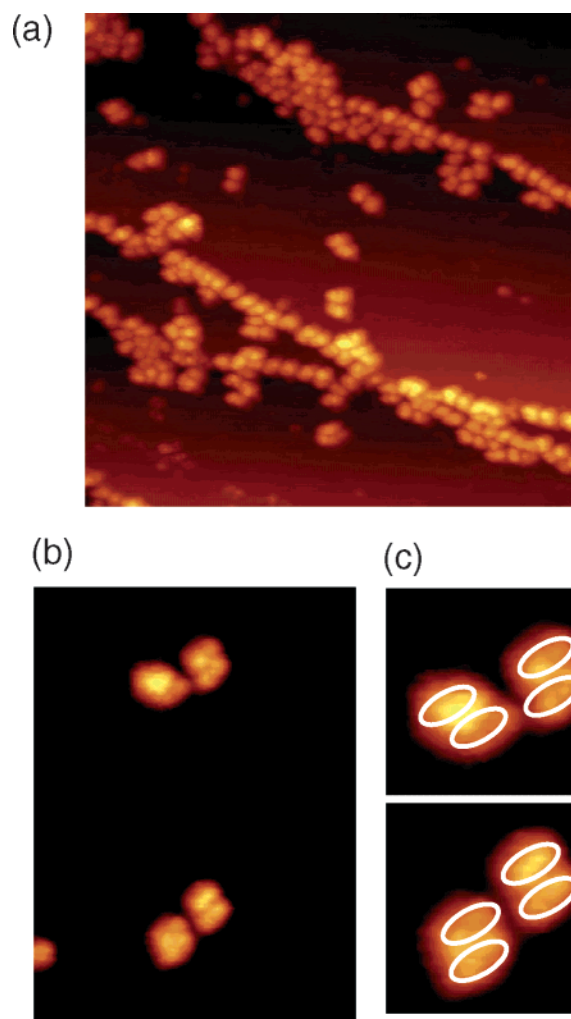


Figure 2. (a) STM image (52 nm × 52 nm, $V_s = -2.5$ V) at 63 K of adsorbed 8T-Si molecules on Cu(100). (b) Enlarged STM image (15 nm × 11 nm, $V_s = -2.7$ V) at 63 K of isolated 8T-Si on a terrace. (c) High-resolution STM images at 63 K of isolated 8T-Si, in which *s*-trans and *s*-cis conformations are clearly identified as the upper and lower molecules, respectively, as indicated by ovals.

interactions between surface and large N-silyl substituents, preventing rotational switching of adsorbed 8T-Si. This implies that the metastable *s*-cis molecules are originated by thermal excitation during the deposition at 588 K, and the metastable conformation is frozen by adsorption on the surface. For α -bithiophene (2T), the energy difference between the *s*-cis and *s*-trans conformations has been calculated to be about 0.5 kcal/mol with the *ab initio* methods,¹⁴ which is almost identical to the experimentally obtained value in the gas phase.^{15,16} When the entropies of the two conformations are assumed to be equal, the energy difference predicts the relative abundances of 61.00 and 39.00 for the *s*-trans and *s*-cis forms, respectively, at an evaporation temperature of 588 K. The calculated values are in disagreement with the present experimental values (52.56:47.44), and consequently, the large population of the *s*-cis conformer cannot be explained by the simple rotation of the central C₁–C_{1'} bond.

The contradictory results should be caused by additional conformational variations of 8T-Si, such as rotational flexibility at C₂–C₃ and C_{2'}–C_{3'} bonds. To understand the conformations of 8T-Si in more detail, we consider all of the possible conformations for N-silyl substituted α -quaterthiophene (4T-Si) which corresponds to the central region of 8T-Si. Although a total of 16 conformations is expected by the rotational

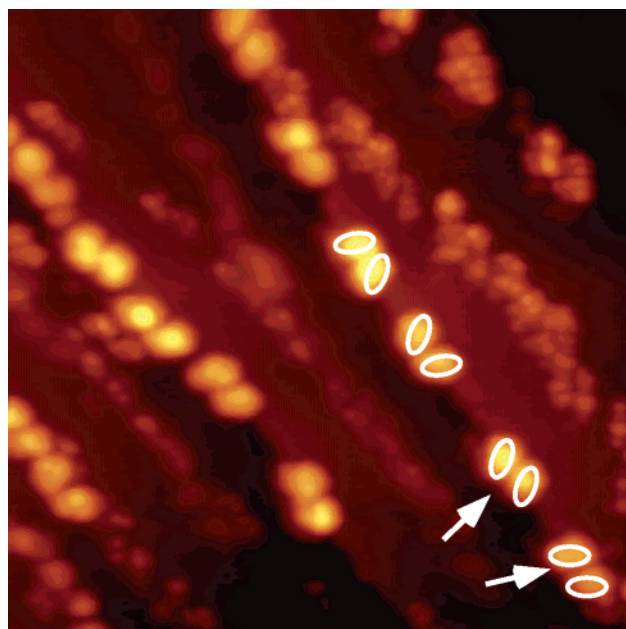


Figure 3. STM image ($28\text{ nm} \times 28\text{ nm}$, $V_s = -2.7\text{ V}$) at 63 K of 8T-Si molecules adsorbed at step edges. In the STM image, all of the N-silyl groups cannot be resolved, but the adjacent two N-silyl groups appear as only one elliptical protrusion. Nevertheless, the *s*-cis–*s*-trans conformations can be identified from the STM image. Furthermore, the *s*-trans molecules are additionally classified into two enantiomeric forms, as indicated by arrows, which cannot be superimposed on the surface.

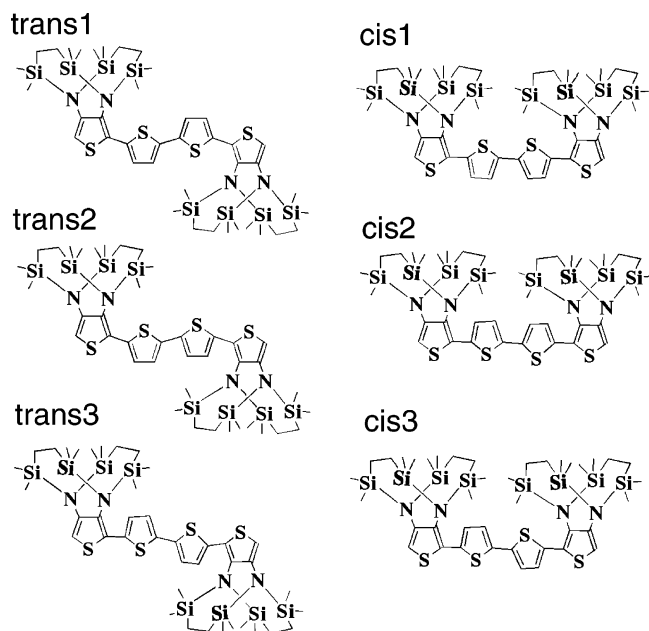


Figure 4. Six possible conformations of 4T-Si, formed by the rotations of individual thiophene rings. The macroscopic trans–cis conformations are characterized from the relative positions of the N-silyl groups.

configurations of the individual thiophene rings, the symmetry transformation results in reduction into only six configurations, as shown in Figure 4. For each conformation, the optimized structure was obtained from the *ab initio* Hartree–Fock calculations with the 6-31G* basis set, and then, the higher level calculations based on the density functional theory (B3LYP) with the 6-311G** basis set were performed to obtain the total energy.²³ These levels of theory have been considered as the most efficient procedure to study oligothiophenes.¹⁴ The obtained energy differences with respect to the ground state all-

TABLE 1: Relative Energy, Degree of Conformational Degeneracy, and Relative Abundances for Each of the Conformations, Obtained by the *ab Initio* Calculations

conformation	relative energy (kcal/mol)	degree of conformational degeneracy	relative abundance at 588 K (%)
trans1	0	2	26.43
trans2	1.33	4	16.07
trans3	1.23	2	8.79
cis1	0.64	2	14.90
cis2	2.11	2	4.00
cis3	0.64	4	29.81

trans conformation are given in Table 1. It is apparent that the total energy is almost proportional to the number of the local cis configurations, suggesting that the steric hindrance between bulky N-silyl groups should be negligible for 4T-Si. Furthermore, the energy barrier for the thiophene-ring rotation of 2T has been estimated as about 1–2 kcal/mol,¹⁴ which is comparable to the thermal energy at an evaporation temperature of 588 K. Thus, the conformational equilibrium of 8T-Si should be achieved during evaporation, although the all-*s*-trans conformation is expected to be dominantly formed in the solid state (before the evaporation).³² By taking account of the degree of conformational degeneracy, we also evaluate the relative conformational abundances at 588 K from the calculated energy, as listed in Table 1. Nevertheless, we are unable to distinguish all the conformations from the STM images, but only the two *macroscopic* cis–trans conformations which are classified by the relative positions of the N-silyl groups. In Figure 4, the left-side three conformers correspond to the macroscopic trans conformations of 8T-Si, whereas the right-side three, to the macroscopic cis conformations. From the classification of the macroscopic conformations, the evaluated relative abundances were obtained to be 51.29 and 48.71 for the trans and cis conformations at 588 K, respectively, in good agreement with the experimental values (52.56:47.44). Thus, the obtained cis–trans isomerization of 8T-Si should be induced by the thermal excitation during the evaporation at 588 K, and each of the high-temperature equilibrium conformations should be frozen by adsorption on the surface. The temperature dependent experiments are expected to further clarify the conformational nature. However, the calculated relative abundances are almost identical in a temperature range of 500–650 K, in which the evaporation of 8T-Si occurs. In addition, although the influence of the substrate surfaces is usually important for molecular assembly, the substrate should play a minor role in this study because the large N-silyl substituents prevent the thiophene-ring rotations on the surface.

In summary, we have directly investigated the *s*-cis and *s*-trans conformations of adsorbed 8T-Si on Cu(100) using low-temperature STM. Although we are unable to distinguish all the conformations of 8T-Si, the macroscopic conformations were identified from the relative positions of bulky N-silyl substituents. By comparing with the *ab initio* calculations, we found that the metastable *s*-cis conformations were induced by the thermal excitation during the evaporation at 588 K. Since similar isomeric variations are expected for many oligomers, the STM investigation provides a unique opportunity for the direct conformational analysis.

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