

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/40999997>

Direct Observation of Conformational Changes of β -Substituted Duodecithiophene on a Au(111)- $(\sqrt{3} \times 22)$ Substrate Using in Situ Electrochemical STM in 0.1 M HClO₄

ARTICLE *in* LANGMUIR · JANUARY 2010

Impact Factor: 4.46 · DOI: 10.1021/la902433j · Source: PubMed

CITATIONS

7

READS

43

5 AUTHORS, INCLUDING:



Bernard John Vallejos Tongol

University of Santo Tomas

11 PUBLICATIONS 71 CITATIONS

[SEE PROFILE](#)



Li Wang

Jiangxi Normal University

86 PUBLICATIONS 1,262 CITATIONS

[SEE PROFILE](#)



Shuehlin Yau

National Central University

93 PUBLICATIONS 1,885 CITATIONS

[SEE PROFILE](#)



Kingo Itaya

Tohoku University

246 PUBLICATIONS 8,379 CITATIONS

[SEE PROFILE](#)

Direct Observation of Conformational Changes of β -Substituted Duodecithiophene on a Au(111)-($\sqrt{3} \times 22$) Substrate Using in Situ Electrochemical STM in 0.1 M HClO₄

Bernard John V. Tongol,^{*,†,II} Li Wang,^{†,‡} Shueh-Lin Yau,^{*,‡,§,#} Tetsuo Otsubo,[§] and Kingo Itaya^{*,†,‡,§,¶}

[†]Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba-yama 04, Sendai 980-8579, Japan; [‡]Core Research Evolutional Science and Technology Organized by the Japan Science and Technology Agency (CREST-JST), Kawaguchi Center Building, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan; and [§]Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan.

^{II}Present address: Department of Chemistry, College of Science & Research Center for the Natural Sciences, University of Santo Tomas, Espana, 1015 Manila, Philippines.

[¶]Present address: College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China. [#]Present address: Department of Chemistry, National Central University, 300 Jongda Road, Jhongli, Taoyuan, Taiwan 320. ROC. [¶]Present address: WPI Advanced Institute for Materials Research (WPI-AIMR), Tohoku University.

Received July 7, 2009. Revised Manuscript Received September 29, 2009

The adsorption of hexahexylundecithiophene (12T) on a Au(111) electrode was investigated by using cyclic voltammetry (CV) and in situ electrochemical scanning tunneling microscopy (EC-STM) in 0.10 M HClO₄. Potential control at 0.20 V (vs RHE) revealed adlayer structures of mostly folded and rarely angular (oblique) and extended conformations on a reconstructed Au(111)-($\sqrt{3} \times 22$) surface. The angular and extended conformations predominate when the electrode potential is increased to 0.35 and 0.60 V. Folded structures are still evident, but dynamic STM studies showed unfolding of this conformation. With molecular STM imaging of 12T adlayers, we address the packing arrangement and conformational changes of 12T admolecules on the reconstructed Au(111) electrode surface.

Introduction

Parallel to the continuing development of research on polythiophenes (PT), we recently have witnessed a strong renewal of interest in oligothiophenes because of their application in electronic¹ and sensor devices.² At a more fundamental level, because of their simple and unequivocal structure, oligothiophenes constitute interesting simplified models for the study of the electro-polymerization mechanism of thiophene³ and the electronic and electrochemical properties of PT.⁴

Recent advances in the synthesis and processing of π -conjugated polymers and oligomers have produced various novel materials with fascinating physical properties. As the investigation of poly- and oligothiophenes becomes more detailed, the structure of these compounds in the solid state has become increasingly important for a more effective design. Their electronic

structure definitely depends on the degree of π conjugation, which is mainly governed by the backbone conformation.⁵ With respect to structure determinations in the solid state, however, because of their highly anisotropic shape and the resulting difficulties in crystallizing these compounds, X-ray structure determinations on oligothiophenes have become more prominent only recently.⁶ So far, the α -conjugated hexadodecylundecithiophene⁷ is the longest oligothiophene ever structurally characterized by X-ray analysis.⁵

Meanwhile, scanning tunneling microscopy (STM) represents an alternative or complementary method for the investigation of molecular arrangements of several β -alkylated oligothiophene^{6,7} and regiorandom and regioregular semiconducting poly(3-alkylthiophene) macromolecules on highly oriented pyrolytic graphite (HOPG) surfaces at the solid–liquid interfaces^{8,9} and in dry films.¹⁰ Moreover, STM provides information about intermolecular and interfacial interactions, which are important from the viewpoint of applying these materials in thin-film devices. Another strength of the STM technique lies in its capability to reveal local surface events, such as the transformation of ordered phases and the mobility of defects.¹¹ Complementary to the X-ray

*Corresponding authors. (B.J.V.T.) E-mail: bvtongol@mnl.ust.edu.ph. Tel/Fax: (63-2)7314031. (S.-L.Y.) E-mail: yau6017@ncu.edu.tw. Tel: 886-3-427957. Fax: 886-3-4227664. (K.I.) E-mail: itaya@atom.che.tohoku.ac.jp. Tel/Fax: 81-22-795-5868.

(1) *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, Germany, 1998.

(2) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93–116.

(3) (a) Roncali, J.; Garreau, R.; Garnier, F.; Lemaire, M. *Synth. Met.* **1986**, *15*, 323. (b) Zotti, G.; Schiavon, G. *Synth. Met.* **1990**, *39*, 183. (c) Roncali, J.; Giffard, M.; Jubault, M.; Gorgues, A. *J. Electroanal. Chem.* **1993**, *361*, 185. (d) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 430.

(4) (a) Cao, Y.; Guo, D.; Pang, M.; Qian, R. *Synth. Met.* **1987**, *18*, 189. (b) Jones, D.; Guerra, M.; Favaretto, L.; Modelli, A.; Fabrizio, M.; Distefano, G. *J. Phys. Chem.* **1990**, *94*, 5761. (c) Bauerle, P. *Adv. Mater.* **1992**, *4*, 102. (d) Guay, J.; Kasai, P.; Diaz, A.; Wu, R.; Tour, J.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 1097. (e) Hill, M. G.; Penneau, J. F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1106.

(5) Azumi, R.; Mena-Osteritz, E.; Boese, R.; Benet-Buchholtz, J.; Bauerle, P. *J. Mater. Chem.* **2006**, *16*, 728.

(6) Azumi, R.; Gotz, G.; Debaerdemaeker, T.; Bauerle, P. *Chem.—Eur. J.* **2000**, *6*, 735.

(7) Bauerle, P.; Fischer, T.; Bidlingmeier, B.; Stabel, A.; Rabe, J. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 303.

(8) Mena-Osteritz, E. *Adv. Mater.* **2002**, *14*, 609.

(9) Mena-Osteritz, E.; Meyer, A.; Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Meijer, E. W.; Bauerle, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 2679.

(10) Grevin, B.; Rannou, P.; Payerne, R.; Pron, A.; Travers, J. P. *J. Phys. Chem. Phys.* **2003**, *118*, 7097.

(11) Stabel, A.; Heinz, R.; De Schryver, F. C.; Rabe, J. P. *J. Phys. Chem.* **1995**, *99*, 505.

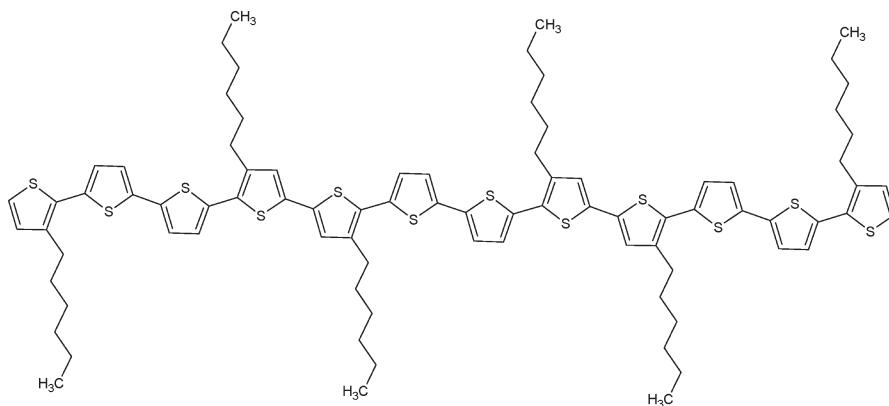


Figure 1. Chemical structure of hexahexylduodecithiophene (12T).

structural analysis of hexadodecylduodecithiophene in the 3D bulk material, the 2D molecular arrangement of the oligomer on HOPG was investigated by STM.^{5,7} A lamella-type ordering of molecularly resolved oligomers that exhibit an all anti conformation could be imaged over wide areas.

To our knowledge, only a few reports address the adsorption of poly/oligothiophenes on metal surfaces.¹² Wan's group^{12d} described the self-organization of two alkyl-substituted dual oligothiophenes on Au(111) using *in situ* EC-STM. Potential control at around 0.50 V revealed both linear and folded arrangements of 4T-tm-8T and 4T-tm-4T molecules on the Au(111) surface. The linear conformation is expected to adsorb on Au(111) with its thiophene ring parallel to the surface taking the most favorable geometry, whereas the folded conformation appears when some thiophene rings are forced to rotate.^{12d} Recently, we have reported the adlayer structures of a series of β -blocked long oligothiophenes on Au(111) by using electrochemical STM (EC-STM).^{12f} The results demonstrate the effect of the substrate on molecular adlayer formation. The importance of understanding the adlayer structures of oligothiophenes on metallic single-crystal electrodes (e.g., Au(111)) lies in providing fundamental information on the substrate–molecule interaction, which could be useful for the development of oligomer/polymer-modified electrodes and molecular devices. The use of well-defined surfaces such as the Au(111) single-crystal electrode would enable a detailed understanding of the mechanism involved at the electrode–electrolyte interface. Moreover, the ability to control the electrode potential using EC-STM would shed light not only on the electrochemical stability but also on the adlayer structures of oligothiophenes on Au(111) electrodes.^{12f}

The adsorption and crystallization of hexahexylduodecithiophene (12T) (Figure 1) on Au single-crystal surfaces have not been examined thus far. In this regard, this study is focused on electrochemical scanning tunneling microscopy (EC-STM) to investigate how 12T molecules are adsorbed on reconstructed Au(111)-($\sqrt{3} \times 22$) in 0.10 M HClO₄. We are able to acquire STM submolecular-resolution images to address the packing habit and conformational changes of 12T on a reconstructed Au(111)-($\sqrt{3} \times 22$) surface as a function of electrode potential.

(12) (a) Kaneto, K.; Harada, K.; Takashima, W.; Endo, K.; Rikukawa, M. *Jpn. J. Appl. Phys.* **1999**, *38*, L1062–L1065. (b) Kasai, H.; Tanaka, H.; Okada, S.; Oikawa, H.; Kawai, T.; Nakanishi, H. *Chem. Lett.* **2002**, 696–697. (c) Wang, L.; Yan, H.-J.; Wan, L.-J. *J. Nanosci. Nanotech.* **2007**, *7*, 3111. (d) Yang, Z.-Y.; Zhang, H.-M.; Li, S.-S.; Yan, H.-J.; Song, W.-G.; Wan, L.-J. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 3707. (e) Nishiyama, F.; Ogawa, K.; Tanaka, S.; Yokohama, T. *J. Phys. Chem. B* **2008**, *112*, 5272. (f) Tongol, B. J. V.; Wang, L.; Yau, S.-L.; Otsubo, T.; Itaya, K. *J. Phys. Chem. C* **2009**, *113*, 13819.

Experimental Section

Hexahexylduodecithiophene (12T) has been effectively synthesized as previously reported;¹³ the chemical structure is shown in Figure 1. Benzene (spectroscopy grade) was purchased from Kanto Chemical Co. The aqueous electrolyte solution was prepared with HClO₄ (Cica-Merck) and ultrapure water (Milli-Q SP-TOC, $\geq 18.2\text{ M}\Omega\text{ cm}$).

The Au(111) single-crystal electrode was prepared by the Clavilier method¹⁴ and was finally annealed in a hydrogen flame and quenched in ultrapure water saturated with hydrogen to obtain a reconstructed Au(111)-($\sqrt{3} \times 22$) surface¹⁵ before each experiment. The 12T adlayers were formed by immersing the Au(111) electrode into a 10 μM 12T benzene solution for about 10–60 s. The 12T-adsorbed Au(111) electrode was then rinsed with ultrapure water to prevent contamination, and it was transferred into an electrochemical cell for CV and STM measurements. STM observation was performed in HClO₄ solution under potential control. The potentials used were positioned in the double-layer region.

Cyclic voltammetry was carried out at 20 °C using a CHI 600 potentiostat with the hanging meniscus method in a three-compartment electrochemical cell in a N₂ atmosphere. Electrochemical STM measurements were performed on a Nanoscope E (Digital Instruments, Santa Barbara, CA) with tungsten tips etched in 1 M KOH. The tips were coated with nail polish beforehand to minimize the residual faradaic current. STM images were taken in constant-current mode and used with only flattened processing. All potentials are referenced to the reversible hydrogen electrode (RHE) in 0.10 M HClO₄.

Results and Discussion

As depicted in Figure 1, the structure of the hexyl-substituted duodecithiophene (12T) molecule is extended with alternating cis–trans (anti) thiophene units. According to molecular mechanics (MM2) calculations,¹⁶ 12T should be 4.7 nm long when extended. In comparison, the crystal structure of dodecyl-substituted duodecithiophene has a linear, relatively flat conformation as revealed by X-ray analysis.⁵ The thiophene units in this oligothiophene exhibit anti conformations except for the outermost

(13) Yamashiro, T.; Aso, Y.; Otsubo, T.; Tang, H.; Harima, Y.; Yamashita, K. *Chem. Lett.* **1999**, 443.

(14) Clavilier, J.; Faure, R.; Guinet, G.; Durand, R. *J. Electroanal. Chem.* **1980**, *107*, 205.

(15) Honbo, H.; Sugawara, S.; Itaya, K. *Anal. Chem.* **1990**, *62*, 2424.

(16) (a) The molecular models and parameters of 12T and its conformers were estimated using ChemSketch Freeware (version 8.17) and 3D Viewer (version 8.04) (Advanced Chemistry Development Inc., Toronto, Ontario M5H 3V9, Canada). (b) The steric energy of 12T and its conformers were calculated after energy minimization of the structures using CS Chem3D Pro (version 5.0) (CambridgeSoft Corp., Cambridge, MA). Chem 3D uses a modified version of Allinger's molecular mechanics (MM2) force field.

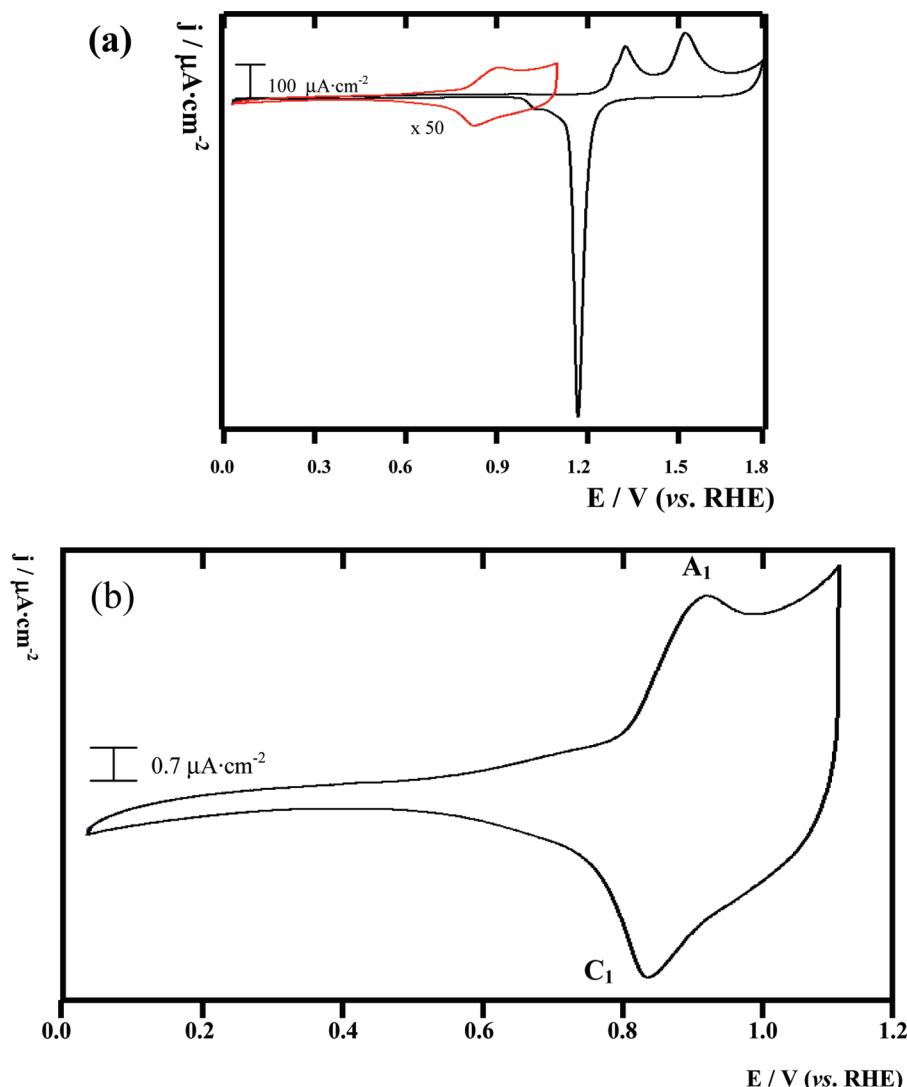


Figure 2. (a) Typical cyclic voltammograms (CV) of a bare Au(111) (black trace) and a 12T-modified Au(111) electrode (red trace) in 0.10 M HClO_4 electrolyte solution. The scan rate was 50 mV s⁻¹. The CV of the 12T adlayer was magnified 50 times vs the CV of bare Au(111). (b) Expanded CV of 12T-modified Au(111) from 0.0 to 1.2 V (vs RHE).

rings that display syn twisted conformations. Theoretical studies also support the fact that, depending on the substitution pattern of the oligothiophene backbone, the energy difference between syn and anti forms is rather small.¹⁷

Cyclic Voltammetry. Figure 2a presents typical cyclic voltammograms (CVs) recorded at a scan rate of 50 mV s⁻¹ after five scan cycles for a bare Au(111) (black trace) and a 12T-modified Au(111) electrode (red trace) in 0.10 M HClO_4 under a N_2 environment. The CV characteristic of bare Au(111) is identical to that reported for an electrochemically clean Au(111) electrode.¹⁵ The open-circuit potential (OCP) of the 12T-modified Au(111) electrode was around 0.60 V (vs RHE), and the potential scan was carried out in the negative direction with respect to the OCP. The 12T-coated Au(111) electrode produces a featureless profile from 0 to 0.50 V and an anodic peak (A_1) at 0.90 V in the positive sweep to 1.1 V (Figure 2b). The latter feature is attributable to the doping process, which results in the generation of

radical cations associated with charge-compensating anions along the oligomer matrix.¹⁸ On the reverse scan from 1.1 to 0 V, one peak (C_1) emerged at 0.82 V corresponding to the undoping process of the oligomer. The redox property of 12T-adlayers on Au(111) in 0.1 M HClO_4 is stable for repetitive scan cycles in a potential window from 0.0 to 1.1 V. These reversible redox features contain roughly 6.11 $\mu\text{C cm}^{-2}$ after correction for double-layer charging. The observed electrochemistry is mostly in accordance with the redox behavior of some β -substituted polythiophenes.¹⁹

During doping at 0.90 V, ClO_4^- inserts into the oligomer backbone, balancing the charges in the system. ClO_4^- exits the oligomer backbone during undoping at 0.82 V (Figure 2b). For the 12T-modified Au(111) electrode, it is assumed that three-electron oxidation is involved after full electrochemical doping of the 12T oligomer at 0.90 V (vs RHE). However, the three anodic peaks, indicative of a trication, are not well resolved from the CV

(17) (a) Distefano, G.; Dal Colle, M.; Jones, D.; Zambianchi, M.; Favaretto, L.; Modelli, A. *J. Phys. Chem.* **1993**, *97*, 3504. (b) Millefiori, S.; Alparone, A.; Millaflori, A. *Heterocyclic Chem.* **2000**, *37*, 847.

(18) (a) Roncali, J. *Chem. Rev.* **1992**, *92*, 711–738. (b) Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

(19) (a) Pern, F. J.; Frank, A. J. *J. Electrochem. Soc.* **1990**, *137*, 2769. (b) Tsai, E. W.; Basak, S.; Ruiz, J. P.; Reynolds, J. R.; Rajeshwar, K. *J. Electrochem. Soc.* **1989**, *136*, 3683. (c) Roncali, J.; Garreau, R.; Yassar, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *91*, 6706. (d) Meerholz, K.; Heinze, J. *Electrochim. Acta* **1996**, *41*, 1839–1854.

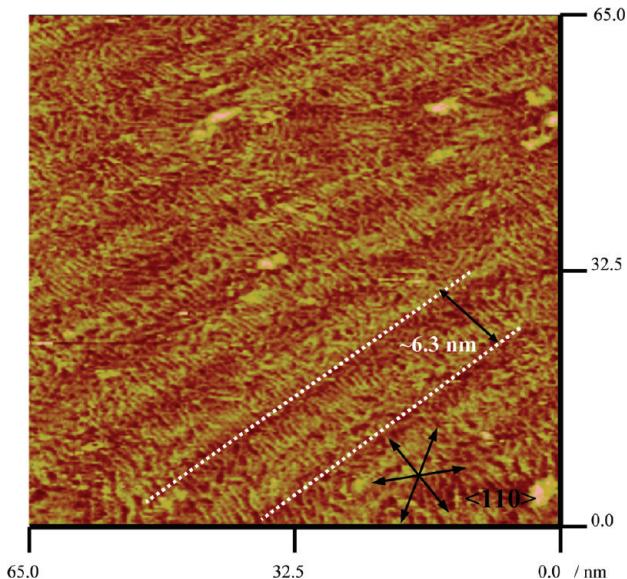


Figure 3. STM images of 12T admolecules in 0.1 M HClO_4 electrolyte at $E = 0.20$ V (vs RHE) revealing folded structures on $\text{Au}(111)-(\sqrt{3} \times 22)$ reconstructed surfaces. Tunneling parameters are as follows: $V_b = -100$ mV and $I_t = 1.0$ nA.

in Figure 2b, unlike those of 4T-modified and 8T-modified $\text{Au}(111)$ electrodes where one and two anodic peaks, indicative of a radical cation (polaron) and dication (bipolaron), respectively, have emerged from the CV profiles (Supporting Information). With increasing chain length of the oligomer, the potential difference between subsequent redox states decreases because the Coulombic repulsion between excess charges is reduced. At a certain length (12T in this case), the potential difference between two redox states vanishes.^{19d}

In Situ EC-STM. To study the adlayer structure of 12T on a $\text{Au}(111)$ electrode, *in situ* STM was performed in the present study. Figure 3 shows submolecular-resolution STM images of the 12T adlayer on a reconstructed $\text{Au}(111)-(\sqrt{3} \times 22)$ surface with an electrode potential held at 0.20 V in 0.10 M HClO_4 electrolyte. Apparently, the adsorption of 12T molecules did not lift the reconstruction at this potential because the herringbone²⁰ features were clearly discerned as zigzag patterns with elevated bright stripes, changing direction always by 120° . Interestingly, one domain structure appears to have folded conformations (i.e., $\sim 180^\circ$ folding of the oligomer backbone) (Figure 3) that are closely packed along the reconstruction rows. A $(\sqrt{3} \times 22)$ unit cell in a reconstructed $\text{Au}(111)$ substrate spans approximately 6.3 nm (indicated by a pair of dashed lines in Figure 3) along a horizontal covering the 0.5 fcc-bridge-hcp-bridge-0.5 fcc site.²¹ The pair of bridging regions contained within the $(\sqrt{3} \times 22)$ unit cell is manifested in the STM image as elevated pairs of parallel stripes. The adsorption behavior of the folded 12T conformation on the $\text{Au}(111)-(\sqrt{3} \times 22)$ surface will be addressed later in this article. The width of the intramolecular folded structure is about 1.0 nm as measured from the end-to-end distance of an isolated 12T molecule. Assuming the homogeneity of the compact structures and the ordered packing arrangement of the folded structures, the surface concentration was estimated and calculated to be 2.13×10^{-11} mol cm^{-2} . Considering the CV result discussed

previously, the charge passed in one branch of the redox peaks at 0.82 V was determined to be $6.11 \mu\text{C cm}^{-2}$; thus, the associated redox reactions should involve three electrons per 12T molecule or one electron per four thiophene monomers. This indicates a doping level of about 25% (i.e., the presence of one radical cation (polaron) per four thiophene units, which was initially assumed to be the principal carrier species).^{18a} There have already been many reports on charge carriers in conducting polythiophenes. However, the silent electron spin resonance (ESR) studies of conductive polythiophene films suggested spinless alternatives, such as dication (bipolaron),^{22a} π -stacked dimeric polarons (π dimer),^{22b} and two individual polarons on a single chain (chain dimer).^{22c}

Meanwhile, Figure 4 shows typical STM images of a 12T adlayer on $\text{Au}(111)$ acquired at 0.35 V in 0.10 M HClO_4 . Disordered domains were found on the atomically flat terrace, and individual molecules were recognized even over the large area of $100 \times 100 \text{ nm}^2$ (Figure 4a). Modulation is seen as rows on the surface as contrasted by the 12T admolecules. A careful inspection of the $\text{Au}(111)$ surface reveals that rows in Figure 4a are separated with a spacing ranging from 6 to 7 nm on the terrace (as indicated by a pair of white, dashed lines in Figure 4a), similar to Figure 3. A midscale ($50 \times 50 \text{ nm}^2$) STM image (Figure 4b), captured on another area, clearly shows not only an adlayer of disordered domains on the reconstructed surface but also admolecules of various conformations: folded, angular, and extended. Molecular models depicting these conformations of 12T are superimposed on the STM image (Figure 4b).

The following series of STM images in Figure 5 describes these conformational changes as a function of time and electrode potential. With an electrode potential initially held at 0.35 V, admolecular structures of mostly folded and rarely oblique (angular) conformations are clearly seen (enclosed in black, dashed boxes in Figure 5a). However, most of the folded structures are a bit tilted or slanted at the end with some molecules seeming to intertwine with one other. This is in contrast to Figure 3, where the folded structures appear to be ordered and closely packed with each other. After 5 min of imaging, most of the folded conformations open up or are transformed into angular or oblique conformations (enclosed in white, dashed boxes in Figure 5b). The STM image in Figure 5c captured after 9 min vividly demonstrates this conformational change as depicted by the 12T adlayer of a mostly extended conformation (indicated by white boxes in Figure 5c). The extended conformation has a chain length of 4.5 ± 0.2 nm, which agrees very well with theoretical calculations. The molecular dynamics of conformational changes is evident from this series of time-dependent STM images (Figure 5a–c). Apparently, folded structures are not stable as STM imaging progresses, as revealed by Figure 5a–c. They eventually “open up” to an extended structure that is a more stable conformation as revealed by theoretical calculations. At a later time, some structures in the adlayer became unclear (Figure 5d). The STM image of Figure 5d is hazy, and it was difficult for us to get a clear STM image using the same tunneling parameters. It was even more difficult to image when the electrode potential was increased gradually to 0.60 V (i.e., at the onset of oxidation of the 12T molecule) with the same tunneling parameters.

In an attempt to obtain better STM images, the tunneling parameters were modified by gradually changing the polarity of the bias voltage to obtain the STM images presented in

(20) Dakkouri, A. S.; Kolb, D. M. Reconstruction of Gold Surfaces. In *Interfacial Electrochemistry: Theory, Experiment, and Applications*; Wieckowski, A., Ed.; Marcel Dekker: New York, 1999; pp 151–173.

(21) Schneider, K. S.; Nicholson, K. T.; Fosnacht, D. R.; Orr, B. G.; Banaszak Holl, M. M. *Langmuir* **2002**, *18*, 8116.

(22) (a) Bredas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309. (b) Miller, L. L.; Mann, K. R. *Acc. Chem. Res.* **1996**, *29*, 417. (c) van Haare, J. A. E. H.; Havinga, E. E.; van Dongen, J. L. J.; Janssen, R. A. J.; Cornil, J.; Bredas, J.-L. *Chem.—Eur. J.* **1998**, *4*, 1509.

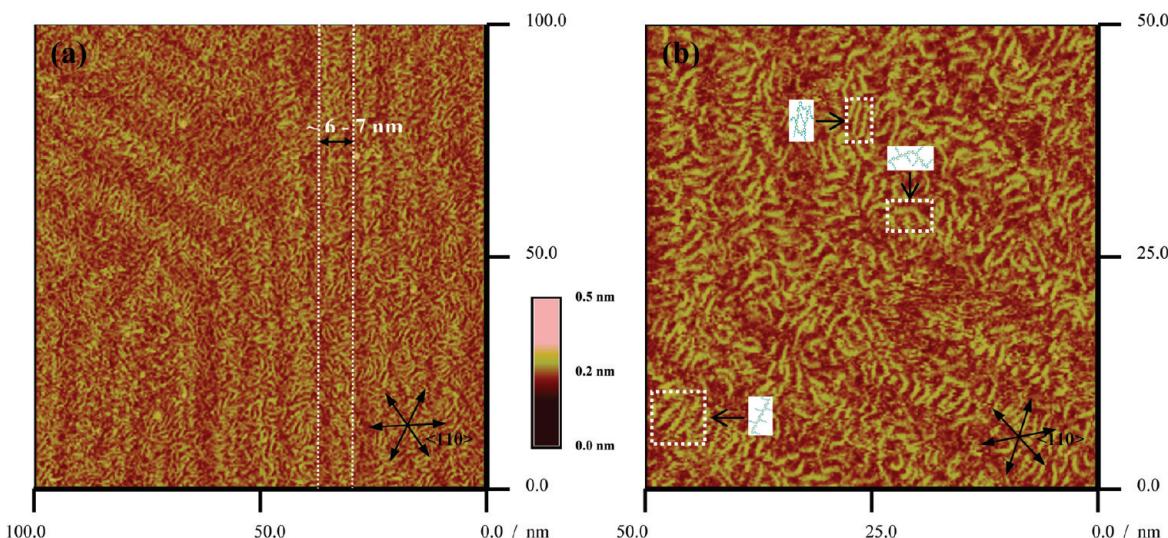


Figure 4. (a) Topographic view ($100 \times 100 \text{ nm}^2$) and (b) midscale STM image ($50 \times 50 \text{ nm}^2$) of 12T admolecules in 0.10 M HClO_4 electrolyte at $E = 0.35 \text{ V}$ (vs RHE) revealing oligothiophene structures of different conformations on a $\text{Au}(111)$ - $(\sqrt{3} \times 22)$ reconstructed surface. Tunneling parameters are as follows: $V_b = 70 \text{ mV}$ and $I_t = 150 \text{ pA}$ for both STM images.

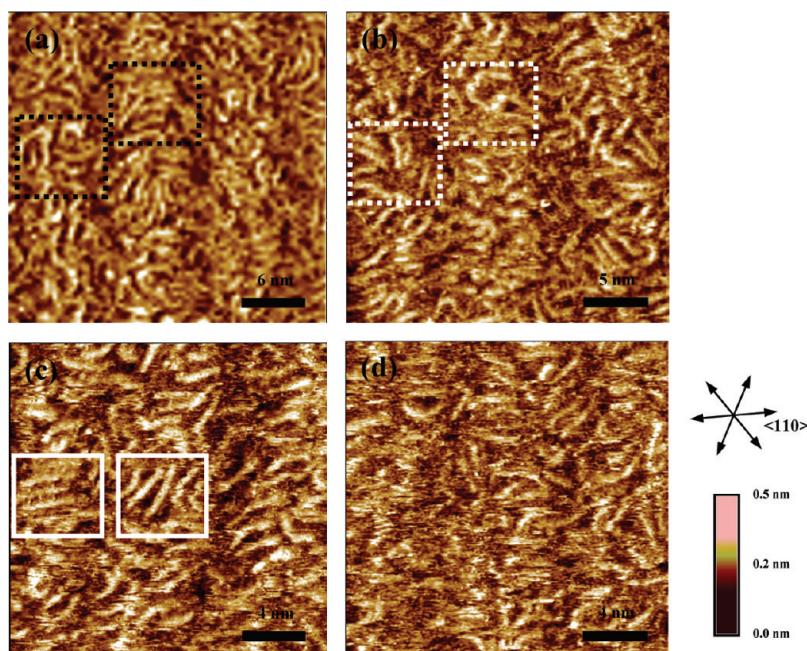


Figure 5. Dynamic STM images of a 12T-modified $\text{Au}(111)$ - $(\sqrt{3} \times 22)$ surface in 0.10 M HClO_4 electrolyte at $E = 0.35 \text{ V}$ (vs RHE) at/after (a) 0, (b) 5, (c) 9, and (d) 11 min revealing conformational changes in 12T adlayers at the electrode surface. Tunneling parameters are as follows: $V_b = 70 \text{ mV}$ and $I_t = 150 \text{ pA}$ for a–d.

Figure 6a–d. Figure 6a is a STM image taken after 25 min (relative to Figure 5a), with the electrode potential held at $E = 0.60 \text{ V}$ (vs RHE). The STM image is not clear, but after 1 min, the 12T adlayer of mostly angular and extended structures reappeared (Figure 6b). The STM image is stable for a few minutes as shown in Figure 6c,d with the same tunneling parameters. After 10 min, the STM image became hazy again. Increasing the potential to beyond 0.60 V caused a drastic restructuring of the 12T adlayer. Presumably, the adsorbed oligothiophenes are mobile and hence cannot be imaged by STM. Similar observations were seen on long oligothiophenes on $\text{Au}(111)$ at a higher electrode potential.^{12f} Potential control beyond 0.60 V could also result in the oxidative desorption of 12T molecules from the surface. However, a detailed mechanistic study of the dynamics of adsorption–desorption is difficult

to follow on the timescale of our STM analysis. Imaging was also difficult when the potential was switched back gradually to the double-layer potential of 0.35 V (vs RHE). The adlayer structures of mostly angular and extended conformations reappeared but are not stable on the surface. Thus, the electrode potential was carefully controlled all throughout the STM experiments.

We performed another STM experiment to check the stability of the adlayer structures. Potential control at 0.50 V (vs RHE) revealed adlayer structures of mostly extended conformation on the $\text{Au}(111)$ surface (Figure 7). There are some domains that have angular and oblique conformations, but similar to Figure 5, they would eventually unfold to extended conformations. Imaging beyond 0.50 V with the same tunneling parameters was done, but it resulted in STM images that are hazy.

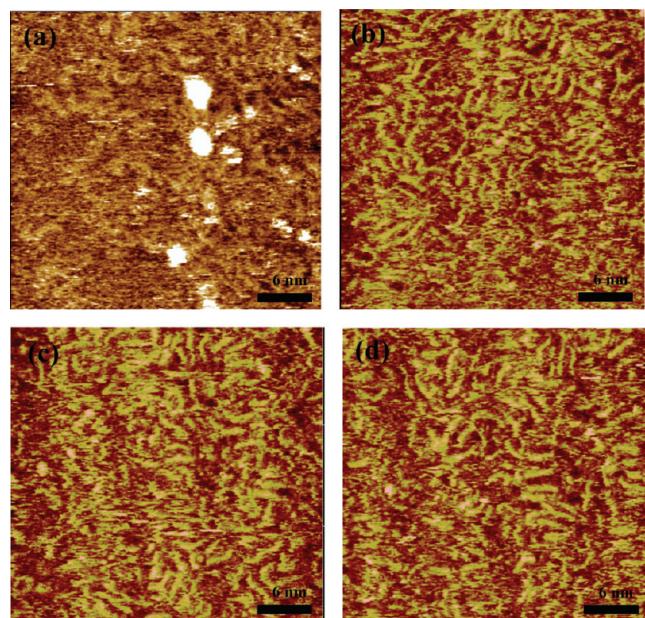


Figure 6. Dynamic STM images of a 12T-modified Au(111)-($\sqrt{3} \times 22$) surface in 0.10 M HClO₄ electrolyte at $E = 0.60$ V (vs RHE) after (a) 25, (b) 29, (c) 30, and (d) 31 min depicting the stability of 12T adlayers at the electrode surface. Tunneling parameters are as follows: (a) $V_b = -180$ mV and $I_t = 400$ pA and (b–d) $V_b = -180$ mV and $I_t = 100$ pA.

Molecular Mechanics Calculation. To visualize the structures observed in EC-STM, various conformations of 12T are illustrated in Figure 8 using molecular mechanics (MM2) calculations.¹⁶ The extended conformation of the 12T molecule is centrosymmetric, and the thiophene rings are denoted from A to F and from A' to F', respectively (Figure 8a). The duodecithiophene backbone has linear, relatively flat, and cis-trans (anti) conformations in the thiophene units. The alkyl side chains extend almost perpendicularly with respect to the thiophene backbone. The steric energy for the extended conformation after energy minimization is calculated to be 96.21 kcal mol⁻¹. On the other hand, the angular conformation of 12T is obtained by interannular rotation around single bonds in the F' thiophene unit in Figure 8a, resulting in three thiophene units in cis conformations (i.e., F, F', and E' in Figure 8b). The optimized structure is bent at an angle of 120° (Figure 8b). The steric energy for this conformation is computed to be 101.16 kcal mol⁻¹. Meanwhile, interannular rotation around single bonds in E and F' thiophene units in Figure 8a created five thiophene units in cis conformations (i.e., D, E, F, F', and E' in Figure 8c), which eventually fold to 180°, commonly called the hairpin fold^{8,9,12d} (Figure 8c) or simply folded structures in this article. The steric energy of this conformation after energy minimization is 94.84 kcal mol⁻¹. The steric energy values for the three conformers are not significantly different, which indicate that all conformers are possible and coexist on the surface.

However, when the 12T conformers were assembled individually and computations of the optimized structure were made

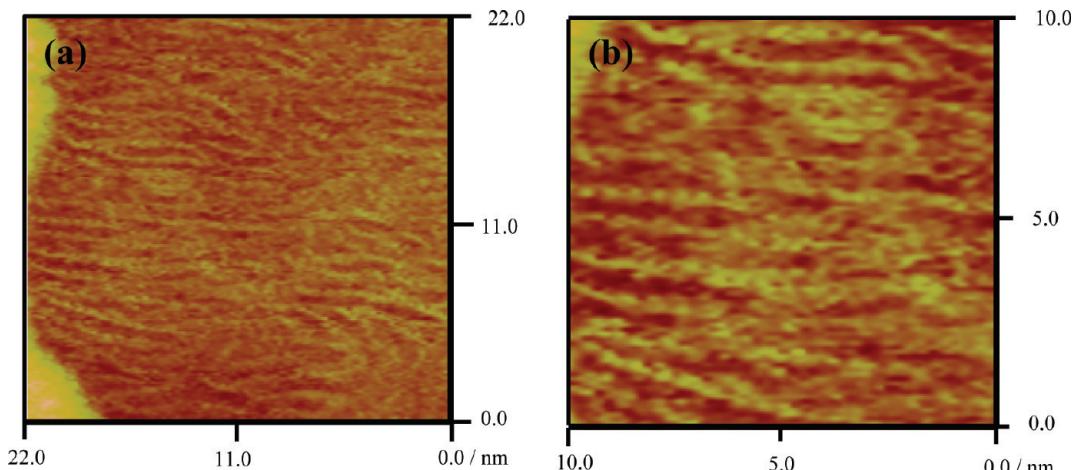


Figure 7. STM images of (a) 22 nm × 22 nm and (b) 10 nm × 10 nm 12T admolecules in 0.10 M HClO₄ electrolyte at $E = 0.50$ V (vs RHE) revealing extended structures on Au(111)-($\sqrt{3} \times 22$) reconstructed surfaces. Tunneling parameters are as follows: $V_b = -60$ mV and $I_t = 1.0$ nA.

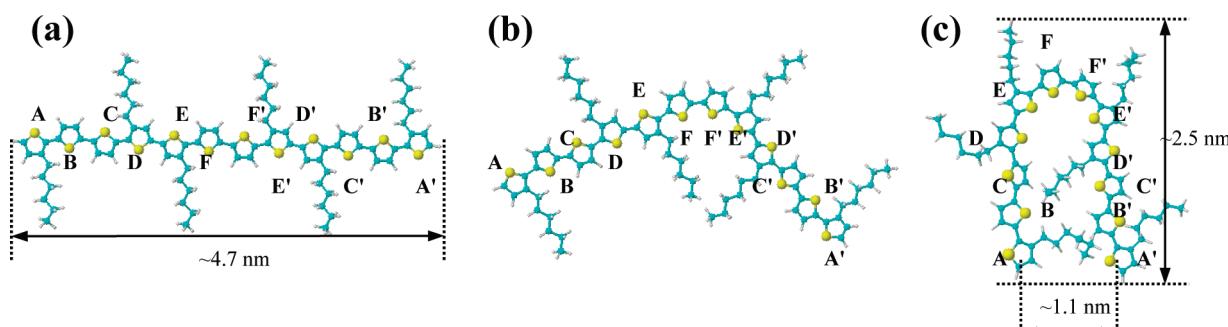


Figure 8. Molecular ball-and-stick models of 12T in various structural conformations: (a) extended, (b) angular (~120°), and (c) folded (~180°) structures.

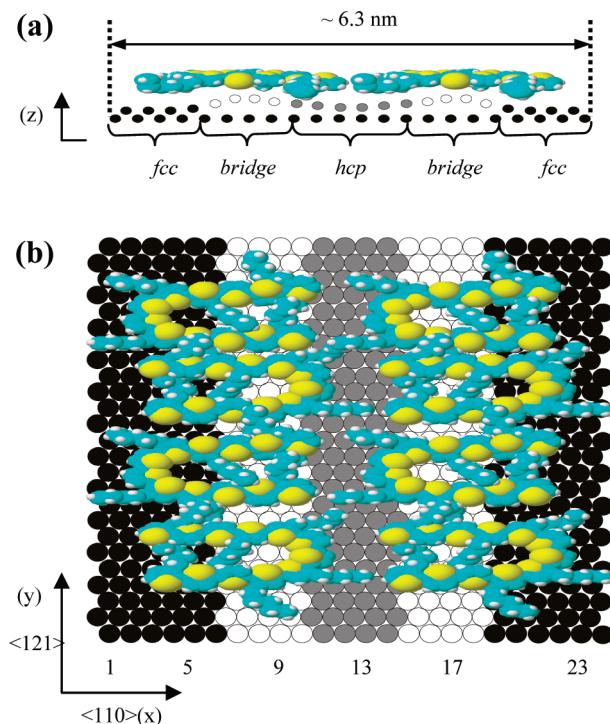


Figure 9. Proposed schematic model of the packing and stacking arrangement of 12T admolecules with a hairpin fold conformation as viewed from the (a) z axis and (b) x and y axes on a Au(111)- $(\sqrt{3} \times 22)$ reconstructed surface depicting the STM image in Figure 3. Gold atoms are color coded as follows: regions of ABC (face-centered-cubic (fcc)) and ABA (hexagonal-closed-packed (hcp)) stacking are black and gray, respectively, with transition (bridge) regions (between fcc and hcp) colored white. Molecular models of 12T molecules are those of space-filling models corresponding to the ball-and-stick structure in Figure 8c.

separately, a significant difference in the steric energy values was obtained. The steric energy values were 96.21, 182.55, and 191.84 kcal mol⁻¹ for extended, angular, and folded conformations, respectively. This would suggest an extended structure being the most stable and the folded structure being the least stable among the three conformations.

Other conformations (not shown in the Figure) could exist by rotation about inner interannular bonds, which creates more thiophene units in cis conformations on the backbone. This would have the effect of increasing the width in the intramolecular hairpin fold. Other possible conformations are a combination of hairpin and oblique structures, involving intramolecular folding at 180° and angular bending, which are slanted near the terminal thiophene units. The change in conformation is accompanied by an increase in steric energy, which is indicative of less-stable conformations.

STM Studies and Theoretical Calculations: A Correlation. In the case of 12T adsorption on reconstructed Au(111), the admolecules packed themselves in a folded conformation at a less positive potential of 0.20 V in 0.10 M HClO₄ (Figure 3). As schematically shown in Figure 8c, the dimensions of the fold are estimated from theoretical calculations to be 2.5 ± 0.1 nm in length (computed from the terminal hexyl carbon of thiophene E to the α terminal carbon of thiophene A) and 1.1 ± 0.1 nm in width (computed from the sulfur of thiophene A to the sulfur of thiophene A'). A $(\sqrt{3} \times 22)$ unit cell spans approximately 6.3 nm along a horizontal covering of the 0.5 fcc-bridge-hcp-bridge-0.5 fcc site.²¹ The pair of bridging regions contained within the $(\sqrt{3} \times 22)$ unit cell is manifested in STM images as elevated pairs of

parallel stripes. In this regard, two molecules of 12T are thought to adsorb laterally as if each molecule is sitting on top of the Au(111) atoms occupying half or ~ 3.15 nm of the unit cell as viewed from the z axis in Figure 9a. The 12T admolecules with a folded conformation most likely arrange themselves close-packed on Au(111) as viewed from the x and y axes in Figure 9b. This type of intermolecular arrangement is not always the case because there are some domains that would have a different packing arrangement but are still close-packed on the surface. Most probably, the folded conformation is favorable on the reconstructed Au(111) because its dimensions fit onto the reconstruction row, characterized by a slight lateral compression of the surface atoms in one of the three $\langle 110 \rangle$ directions. This means that two folded structures of 12T molecules are dimensionally more favored to occupy and laterally adsorb on the Au(111) surface along the $\langle 110 \rangle$ direction.

Increasing to a more positive potential (but less positive of the potential of zero charge (PZC) of Au(111)- $(\sqrt{3} \times 22)$) would favor oblique or angular conformations (Figure 4). Some structures of folded conformation are still evident, but they tend to unfold to more relaxed angular and extended conformations as revealed by time-dependent STM (Figure 5a–d). The conformational change from folded to angular to an extended conformation is energetically more favorable because this would minimize the steric hindrance between the alkyl chains and torsion in the oligothiophene backbone.

Concomitant with the lifting of the reconstruction, the conformation of 12T changes from folded to oblique and then to extended structures. It appears that at a potential sufficiently negative of the PZC of Au(111)- $(\sqrt{3} \times 22)$, a more compact folded conformation predominates. Because of the higher packing density of a reconstructed surface, 12T admolecules tend to pack closely to each other and fold back completely at a 180° angle on the Au substrate surface. Conversely, at a potential positive of the PZC of Au(111)- $(\sqrt{3} \times 22)$, unfolding of the folded conformation to extended conformations could take place because of the more open structure of the Au(111)- (1×1) surface.

It was observed via small-angle neutron scattering that upon oxidation single poly(3-alkylthiophene) chains undergo large conformational changes from coils to rods.²³ Meanwhile, a recent study on quantum chemical calculations has shown that a neutral polypyrrole chain in the ground state assumes a helical shape resulting from a novel bending mechanism, whereas upon oxidation the chain becomes planar within the polarons, an effect due to enhanced inter-ring π bonding.²⁴ However, as shown by cyclic voltammetry (Figure 2), oxidation of the oligomer commenced at 0.60 V with the main oxidation peak emerging at around 0.90 V (vs RHE). The main anodic peak is attributable to the full electrochemical doping of the neutral oligomer to the trication through polaron formation, as shown and proposed in this study. Thus, it is less likely that the conformational change from the folded to extended structure is due to polarons because stable adlayer structures of 12T are imaged at a double layer potential that is less positive than 0.60 V and far away to 0.90 V where complete electrochemical doping could take place. Apparently, at 0.60 V, two things could possibly happen simultaneously: the first is the lifting of reconstruction, and the second is the unfolding of the folded conformation to extended structures. However, careful potential control is required to

(23) Aime, J. P.; Bargain, F.; Schott, M.; Eckhardt, H.; Miller, G. G.; Elsebaumer, R. L. *Phys. Rev. Lett.* **1988**, 62, 55.

(24) Lin, X.; Li, J.; Smela, E.; Yip, S. *Int. J. Quantum Chem.* **2005**, 102, 980.

prevent degradative oxidation and possible desorption of 12T molecules at the electrode surface in the aqueous electrolyte medium.

Conclusions

The 12T-modified Au(111) electrode was characterized by cyclic voltammetry (CV) and *in situ* electrochemical scanning tunneling microscopy (EC-STM). CV measurements have shown the redox behavior and stability of the 12T-modified Au(111) surface in 0.10 M HClO₄. Submolecular STM studies revealed adlayer structures and the packing arrangement of 12T on a reconstructed Au(111)-(√3 × 22) surface. Likewise, conformational changes in 12T are directly observed by STM under potential control. Molecular mechanics calculations of the isolated 12T molecule provide a theoretical basis for the observed conformational changes. The adsorption of 12T molecules on Au(111) is insightful not only from the standpoint of the interfacial electrochemistry of π-conjugated polymers but

also from the perspective of organic thin film electronics and sensor device applications.

Acknowledgment. This work was supported in part by Core Research for Evolutional Science and Technology (CREST) organized by the Japan Science and Technology Agency (JST) during the period of 2002–2008 and in part by the New Energy and Industrial Technology Development Organization (NEDO). The Ministry of Education, Culture, Sports, Science, and Technology, Japan and the Center of Excellence (COE) Project on Giant Molecules and Complex Systems are also gratefully acknowledged.

Supporting Information Available: CV of a series of short oligothiophenes: 4T, 8T, and 12T on Au(111) in 0.10 M HClO₄. This material is available free of charge via the Internet at <http://pubs.acs.org>.