Effect of the Bridge Alkylene Chain on Adlayer Structure and Property of Functional Oligothiophenes Studied with Scanning Tunneling Microscopy and Spectroscopy

Zhi-Yong Yang, Hui-Min Zhang,[†] Ge-Bo Pan, and Li-Jun Wan*

Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing, 100080, China. [†]Current address: School of Science, Beijing Institute of Technology.

ABSTRACT Five dual-quinquethiophene self-assemblies are prepared on a highly oriented pyrolytic graphite (HOPG) surface. The dual-quinquethiophenes are quinquethiophenes (5T)-di to hexamethylene (*n*, 2–6)-quinquethiophenes (5T), abbreviated as 5T-*n*-5T (*n* = 2–6). The effect of the bridge alkylene chains on the structure and property of the five assemblies are investigated by scanning tunneling microscopy (STM). It is found that all 5T-*n*-5T molecules form ordered adlayers on a HOPG surface with stripe feature. The alkylene bridge part in a molecule appears in a dark contrast in an STM image. Intriguingly, the thiophene backbones of individual molecules in the adlayer always keep an angle with the direction of molecular stripes. With alkylene bridge length increasing, different structures are found in 5T-5-5T and 5T-6-5T assemblies. To understand the effect of bridge chains on single molecular property, scanning tunneling spectroscopy is used to probe the electronic property of the different adlayers. The results will be important in surface engineering by self-assembly and molecular device fabrication with oligothiophenes.

KEYWORDS: self-assembly · oligothiophene · STM · STS

The study on single molecule, molecular self-assembly and molecular thin film has become an attractive research field in recent years because of the increasing requirement in improving surface function of materials and performance of organic electronics.[1–5] In particular, self-assembly is an important technique in the so-called "bottom-up" approach to make electronic devices with single molecules and atoms.[6] To prepare a designed self-assembly, molecules with defined chemical structure and special property are essential and will make differences in surface chemistry, material property, and molecular device function.[7–10] As a model molecule,[11,12] thiophene and its derivatives are currently receiving considerable attention because of their improved solubility, well defined chemical structure, and special electronic property.[13–18] For example, molecules with good solubility have advantages in solution-based methods such as spin-coating, stamping, ink-jet printing, and self-assembling.[13,14] Linear π-conjugated alkylated oligothiophenes with defined length and structure are reported to be promising candidates in electronic and optical devices such as Schottky diodes,[19] organic light-emitting diodes (OLEDs),[20,21] field-effect transistors,[22] and organic thin film transistors.[13,23] The former research results demonstrate that the transistors fabricated with thiophene derivatives show high charge-carrier mobility, high on/off modulation ratio, and long life.[22] By modifying molecular structures with functional groups, alkyl chains, and thiophene rings, the emitting color of an OLED can be regulated from blue to red.[24]

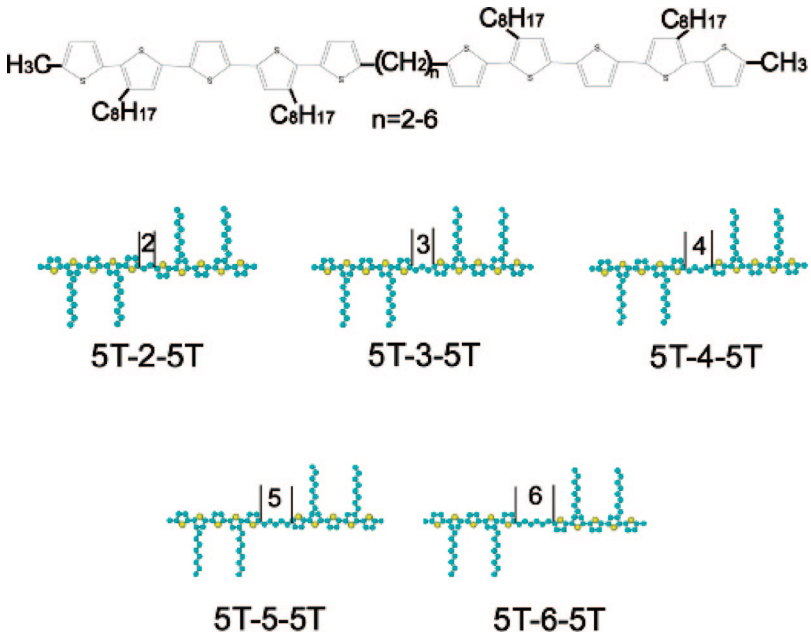
The property of a molecular assembly is affected by not only the property of individual molecules but also the spatial arrangement of the molecules in the assembly.[14,25] Therefore, understanding the molecular arrangement and single molecular property on the substrate surface is an important issue in fabricating molecular devices.[26] With fine balance between intermolecular interactions and molecule/substrate interactions, the molecular structure can be constructed, resulting in desirable function.[3,27–33]

The adlayer structure and property of thiophene derivatives have been investigated with scanning tunneling microscopy (STM) in submolecular resolution, and

*Address correspondence to wanlijun@iccas.ac.cn.

Received for review December 24, 2007 and accepted March 06, 2008.

Published online March 26, 2008.
10.1021/nn7004443 CCC: $40.75



Scheme 1. Molecular structures of 5T-*n*-5T (*n* = 2–6).

single molecular property was also measured.[34–37] For example, STM experimental results indicated that thiophene formed a two-dimensional ordered adlayer on a Au(111) surface through chemisorption while 2,5-dimethylthiophene formed physisorbed multilayers having a liquid-like phase.[38] A series of oligothiophenes with carboxylic groups and different alkyl chains were synthesized.[39] The alkyl chains and carboxylic groups, which were subjected to hydrogen-bond interactions, were designed to different positions of the oligothiophenes. With these molecules, assembling architectures such as dimer, line, square, rectangle, and parallelogram have been fabricated. It was found that the hydrogen bond played an essential role in the formation of the ordered assemblies. In addition, two dual oligothiophene molecules, unsymmetrical quarterthiophene (4T)-trimethylene (tm)-octithiophene (8T) and symmetrical 4T-tm-4T molecules, were used to construct surface nanostructures.[40] STM observation indicated that 4T-tm-8T formed quasi-hexagonal and linear adlayers, while the wavelike adlayer occupied most of the surface for 4T-tm-4T. The results show the effect of molecular structure on the self-assembly structure. To understand the structural transformation and temperature effect on the adlayer structure in terms of device stability and efficiency,[41–43] thermal stability of 4T-tm-8T adlayer was also investigated. After annealing at 100 °C for 30 min, only a linear domain can be observed in the 4T-tm-8T samples, indicating that linear structure of 4T-tm-8T is more stable than quasi-hexagonal structure. The electronic properties of 4T-tm-8T and 4T-tm-4T were investigated with scanning tunneling spectroscopy (STS). Experiments results indicated that both dual oligothiophenes are p-type semiconductors with the experimental energy gap of 4T-tm-8T smaller than that of 4T-tm-4T.[40]

In the present paper, five dual-quinquethiophene self-assemblies are prepared on a highly oriented pyrolytic graphite (HOPG) surface. Graphite surface is a quite inert surface. Most kinds of molecule, also including oligothiophene derivatives, physisorb on a HOPG surface owing to weak molecule−substrate interactions. Also the weak molecule−substrate interactions make graphite a proper kind of substrate for STS measurement by ensuring that the STS results reflect mostly the molecular property itself. In detail, the dual-quinquethiophenes are quinquethiophenes (5T)-di to hexamethylene (*n*, 2–6)-quinquethiophenes (5T), abbreviated as 5T-*n*-5T (*n* = 2–6). The effect of the bridge alkylene chains on the structure and property of the five assemblies are investigated by STM and STS. The chemical structures of the five molecules are shown in Scheme 1. The experimental results on the oligothiophenes will be helpful to explore the role of the bridge alkylene chain in assembling process and surface engineering by self-assembly and molecular device fabrication with oligothiophenes.

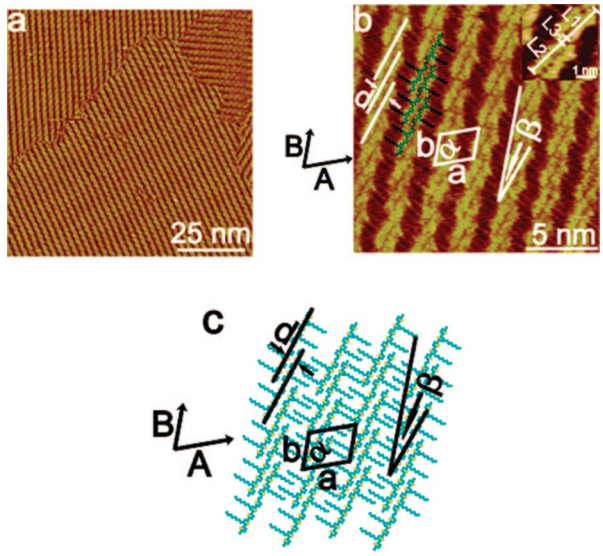


Figure 1. (a) Large-scale and (b) high-resolution STM images of 5T-2-5T adlayer; (c) structural model of 5T-2-5T adlayer. Tunnelling conditions: (a) V_{bias} = 660 mV, I_{tip} = 569 pA; (b) V_{bias} = 817 mV, I_{tip} = 641 pA. The inset is V_{bias} = 750 mV, I_{tip} = 695 pA.

RESULTS AND DISCUSSION

Adlayer Structure of 5T-2-5T. Figure 1a represents a typical large-scale STM image of 5T-2-5T adlayer on HOPG. Several domains consisting of regular molecular rows can be easily discerned within the scan area. The different domains observed in the image are rotated by 120° or 60°, which is related to the graphite substrate due to the molecule−substrate interaction in the self-

assembly.[44] Figure 1b is a higher resolution STM image revealing the structural details of the 5T-2-5T adlayer. The ordered adlayer appears in a stripe feature, forming regular molecular rows. Each bright stripe consists of shot sticks illustratively indicated by white lines in the figure. The distance between the neighboring sticks within one molecular row is $d = 0.7 \pm 0.2$ nm. The sticks stack parallel and orient at an angle of $\beta = 19 \pm 2°$ with the direction of molecular rows. Furthermore, there is a slight displacement between the neighboring sticks along the direction B. The inset is an enlarged STM image of an individual stick. A small black gap (L3) is clearly resolved in the center of a bright shot stick and divides the shot sticks into two parts (L1 and L2). The lengths extracted from STM images are L1 = L2 $= 2.1 \pm 0.2$ nm and L3 $= 0.40 \pm 0.2$ nm. These values match well with the theoretical lengths of each part in the molecule. The whole length of a stick is 4.3 ± 0.2 nm, consistent with the size of a 5T-2-5T molecule. Therefore, each bright shot stick with a central small black gap can be assigned to a 5T-2-5T molecule. The central gap L3 in dark contrast is the bridge alkylene chain due to its low electronic density. For clarity, several 5T-2-5T molecular models are illustrated in Figure 1b.

On the basis of molecular arrangement, a unit cell is deduced and outlined in Figure 1b. The lattice constants are $a = 2.5 \pm 0.2$ nm, $b = 2.2 \pm 0.2$ nm, and $\alpha = 81 \pm 2°$. A structural model is tentatively proposed in Figure 1c, giving a visual representation of the adlayer structure. In the model, the thiophene skeletons of 5T-2-5T stack with an angle of $\beta = 19°$ to the molecular rows and the dimeric quinquethiophenes correspond to the two parts of a shot stick. The distance between the neighboring sticks within one molecular row is $d = 0.7$ nm. The side alkyl chains ($-C_8H_{17}$) are interdigitated with each other between neighboring molecular rows. In this model, the molecular plane of 5T-2-5T backbone is assumed to adsorb parallel to the underlying HOPG surface.

Adlayer of 5T-*n*-5T (*n* = 3–6). Figure 2 panels a–d are the STM images recorded at 5T-3-5T, 5T-4-5T, 5T-5-5T, and 5T-6-5T adlayers on a HOPG surface. In comparison with Figure 1, it can be seen that all these five molecules formed well-ordered adlayers with similar stripe feature. The details of each adlayer can be found in the corresponding higher resolution STM images shown in Figure 2 panels a1, b1, c1, and d1, respectively. Each molecular row consists of bright shot sticks. Each stick is corresponding to a 5T-*n*-5T ($n = 3–6$) molecule, as illustrated by white lines. The molecular model for each adlayer is also superimposed in the high resolution STM images. Each molecule appears in two parts with a dark gap in its STM image, consistent with its characteristics in chemical structure. Owing to the difference in chemical structure, the gap length of alkylene bridge link part increases as *n* increases from a careful observation. Similar to 5T-2-5T adlayer, the 5T-*n*-5T ($n = 3–6$) molecules in the same row stack parallel and orient in an angle with the row direction. In this arrangement, a stable assembly will be organized.

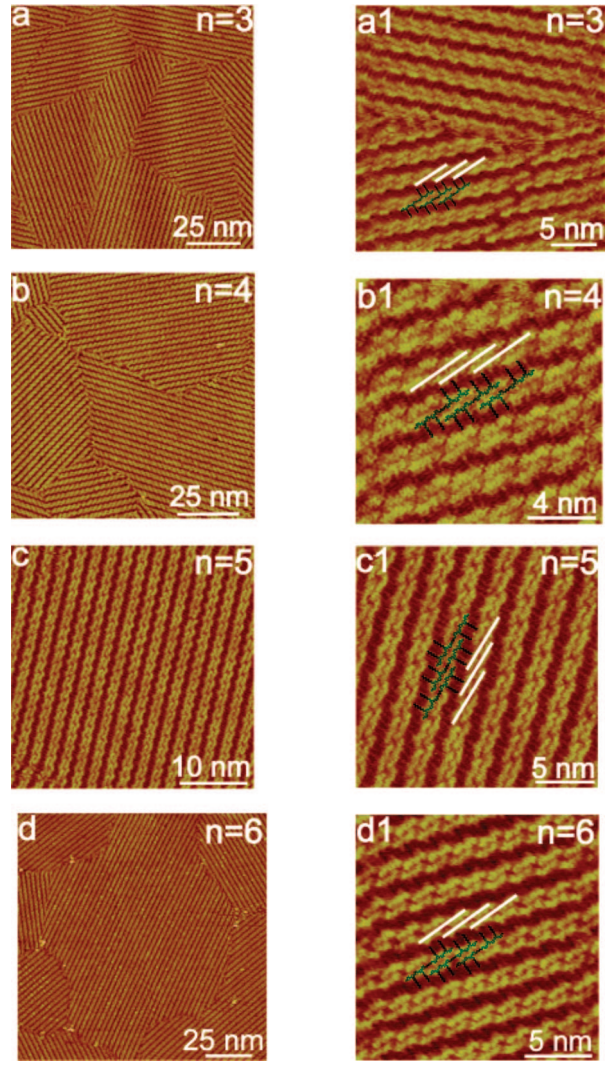


Figure 2. (a) Large-scale and (a1) high-resolution STM images of 5T-3-5T adlayer; (b) large-scale and (b1) high-resolution STM images of 5T-4-5T adlayer; (c) large-scale and (c1) high-resolution STM images of 5T-5-5T adlayer; (d) large-scale and (d1) high-resolution STM images of 5T-6-5T adlayer. Tunnelling conditions: (a) $V_{bias} = 647$ mV, $I_{tip} = 689$ pA; (a1) $V_{bias} = 647$ mV, $I_{tip} = 689$ pA; (b) $V_{bias} = 580$ mV, $I_{tip} = 523$ pA; (b1) $V_{bias} = 605$ mV, $I_{tip} = 578$ pA; (c) $V_{bias} = 594$ mV, $I_{tip} = 580$ pA; (c1) $V_{bias} = 594$ mV, $I_{tip} = 580$ pA; (d) $V_{bias} = 680$ mV, $I_{tip} = 683$ pA; (d1) $V_{bias} = 650$ mV, $I_{tip} = 678$ pA.

In the well-defined adlayers, a unit cell can be determined as that in Figure 1. The corresponding parameters in each unit cell, β, L1, L2, L3, a, b, and α, for 5T-*n*-5T ($n = 2–6$) are summarized in Table 1. From Table 1, it can be seen that the parameters in the five adlayers are almost the same within the experimental errors. L3, the width of central black gaps increases with the increase of carbon number in the bridge alkylene chain.

The adlayer structures of 5T-*n*-5T ($n = 3–6$) in Figure 2 are well reproducible though a different structure is occasionally observed. However, with the in-

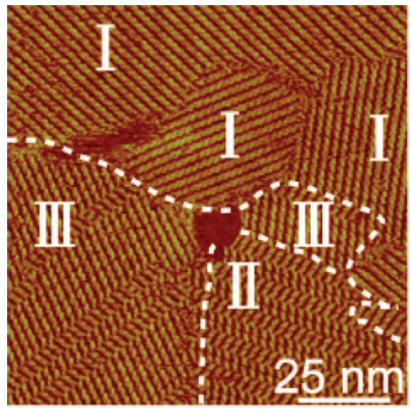


Figure 3. An STM image of 5T-5-5T showing two kinds of adlayers. Tunnelling conditions: V_{bias} = 625 mV, I_{tip} = 658 pA.

creasing of the length of bridge alkylene link, different structures are clearly found in 5T-5-5T and 5T-6-5T adlayers, showing the effect of the molecular chemical structure on their self-assembly. It is clear that with the increasing of length of bridge alkylene chains, the molecules will be more flexible, and the flexibility results in different self-assemblies with different structures. The structural details in the different 5T-5-5T and 5T-6-5T adlayers are revealed by STM and compared with other adlayers.

Zigzag Structure in 5T-5-5T Adlayer. A different structure from that in Figure 2c was found in the adlayer of 5T-5-5T. Figure 3 is a large scale STM image acquired on a 5T-5-5T adlayer. In this image, several molecular domains can be seen. Among theses domains, different molecular arrangements can be found as indicated by I, II, and III. In domain I, linear and stripe feature similar to that in Figures

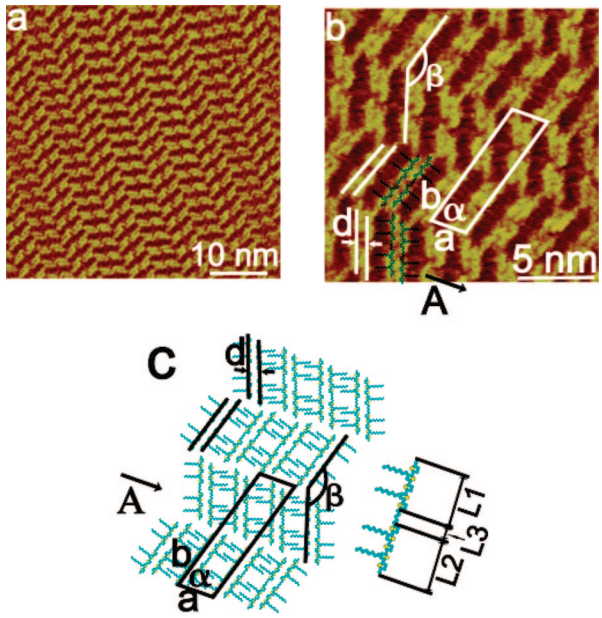


Figure 4. (a) Large-scale and (b) high-resolution STM images of 5T-5-5T zigzag adlayer; (c) structure model of 5T-5-5T zigzag adlayer. Tunnelling conditions: (a) V_{bias} = 600 mV, I_{tip} = 580 pA; (b) V_{bias} = 650 mV, I_{tip} = 601 pA.

TABLE 1. Parameters of Unit Cell in 5T-*n*-5T (*n* = 2–6) Adlayers

	β (±2°)	L1 (±0.2 nm)	L2 (±0.2 nm)	L3 (±0.2 nm)	*a* (±0.2 nm)	*b* (±0.2 nm)	α (±2°)
5T-2-5T	19	2.1	2.1	0.40	2.5	2.2	81
5T-3-5T	19	2.0	2.0	0.49	2.6	2.2	83
5T-4-5T	19	2.1	2.1	0.60	2.6	2.1	80
5T-5-5T	18	2.1	2.1	0.71	2.7	2.2	79
5T-6-5T	19	2.1	2.0	0.84	2.7	2.1	81

1 and 2 can be correlated. Intriguingly, a different zigzag structure can be seen in domains II and III. In particular, domain II consists of only a zigzag structure, while mixed stripe and zigzag structures are in domain III.

Figure 4a is a large scale STM image showing the zigzag structure. The molecular arrangement in this structure is clearly different from that in the stripe structure. The details of the structure are revealed by a higher resolution STM image in Figure 4b. Although the molecules form ordered rows along direction A, an angle is formed between the neighboring molecular rows, which leads to the neighboring molecular row appearing as a "V" configuration and the whole assembly appearing as a wavelike morphology. The molecular rows are composed of bright shot sticks indicated by white lines in the image. The distance between the neighboring "sticks" in the same molecular row is $d = 0.7 \pm 0.2$ nm. The length of a stick is measured to be 4.9 ± 0.2 nm, consistent with the theoretical length of a 5T-5-5T molecule. The molecular characteristics with two quinquethiophene parts and a dark gap are clearly seen in the image. The length of each part is L1 = 2.1 ± 0.2 nm, L2 = 2.1 ± 0.2 nm, and L3 = 0.72 ± 0.2 nm. The angle β between the neighboring molecular rows is measured to be $148 \pm 2°$. From the molecular arrangement, a unit cell can be deduced and outlined in Figure 4b with the parameters of $a = 2.6 \pm 0.2$ nm, $b = 10.2 \pm 0.2$ nm, and $\alpha = 82 \pm 2°$. A structural model for the 5T-5-5T zigzag adlayer is tentatively proposed in Figure 4c. In this model, the side alkyl chains of 5T-5-5T molecules interdigitate with each other. The molecular orientation along its thiophene backbone takes an alternative transformation and results in a wavelike zigzag feature.

Through analysis of the STM image of the 5T-5-5T molecular adlayer, it can be found that the probability of forming a pure stripe structure (domain I) is 60% or so, while that of a pure zigzag structure (domain II) is less than 15%. The probability of formation of domain III is about 25%. Therefore, for 5T-5-5T, the dominative structure is still a stripe structure instead of a zigzag one. However, owing to the length increase in the bridge alkylene chain, the flexibility of the molecules increases, resulting in the zigzag structure.

New Structure in 5T-6-5T Adlayer. Figure 5a is a large scale STM image recorded on 5T-6-5T adlayer. A different domain II can be seen in the image, although do-

main I is almost the same as that in Figure 2d with a stripe structure. Figure 5b is a high resolution STM image showing the difference between domains I and II. The image consists of two types of domains. The molecular rows align along the direction A and B. On basis of the molecular orientation and size, each 5T-6-5T molecule can be recognized as schematically illustrated. The lengths of dual quinquethiophene and bridge alkylene chain are measured to be L1 = L2 = 2.1 ± 0.2 nm, L3 = 0.86 ± 0.2 nm, consistent with the theoretical value of the molecule. In domain II, the angle between the molecular row direction B and thiophene backbone is β = 10 ± 2° smaller than that in domain I. Another difference of domain II and I is the displacement difference between neighboring molecules in the same molecular row. In domain I, one quinquethiophene and bridge alkylene chain of 5T-6-5T is covered by neighbor 5T-6-5T molecules. While in domain II, only one quinquethiophene part is covered by neighbor 5T-6-5T molecules, which means displacement of domain II is less than that of domain I. Simplified molecular models (thick rod, quinquethiophene; thin cord, bridge alkylene chain) were superimposed on Figure 5 panels b and c. With these models, the difference of displacement between these two kinds of domain can be seen more clearly. These differences result in a new adlayer structure. A proposed model is described in Figure 5c. In this model, the molecular rows extend along direction A and B and the side alkyl chains in neighboring rows interdigitate each other. The unit cell for domain II is deduced based on the molecular arrangement and outlined in Figure 5b and c with parameters $a = 2.5 \pm 0.2$ nm, $b = 2.7 \pm 0$, and $\alpha = 88 \pm 2°$.

Dual oligothiophene with a long bridge alkylene chain formed diverse structures. The long bridge alkylene chains make dual oliothiophene more flexible and allow molecules to adsorb on the surface with multiple fashions.

Electronic Property of 5T-*n*-5T. To probe the electronic properties of 5T-*n*-5T molecules on HOPG under ambient conditions, we performed STS measurements on 5T-2-5T, 5T-4-5T, and 5T-6-5T adlayers. For comparison, the d*I*/d*V*−*V* curve on bare graphite was also measured. As shown in Figure 6a, the curve has a characteristic parabola shape, and no apparent energy gap is found due to the high conductivity of graphite.

Figure 6b is typical d*I*/d*V*−*V* curves from the adlayers of 5T-2-5T, 5T-4-5T, and 5T-6-5T. The d*I*/d*V*−*V* curve reflects the density states of adsorbates. When applying an appropriate bias on the substrate, the Fermi energy of the substrate will resonate with certain orbitals of adsorbing molecules, either highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO), and induce sharp change in the d*I*/d*V*−*V* curve. The edge defined by the cross-point of the tangents of the platform and uplift part of the curve is related to the energy states of HOMO and LUMO of the

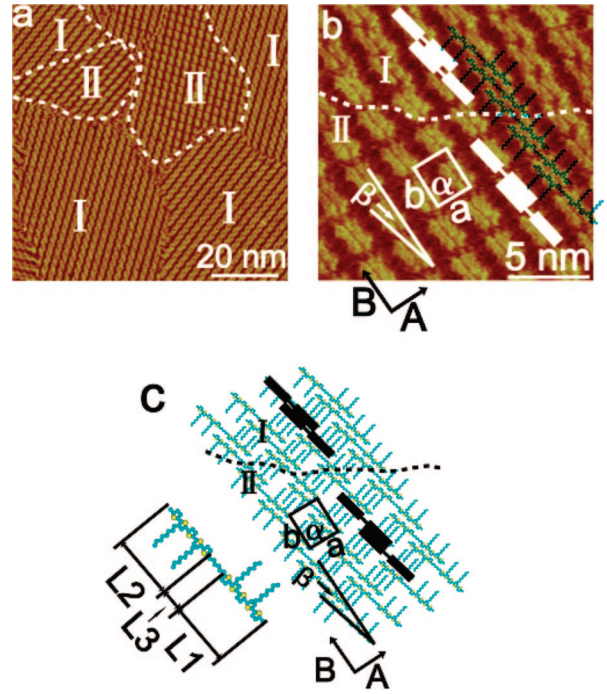


Figure 5. (a) Large-scale STM image of two kinds of 5T-6-5T adlayer; (b) high-resolution STM image of two kinds of 5T-6-5T adlayers; (c) structure model of two kinds of 5T-6-5T adlayers. Tunnelling conditions: (a) V_{bias} = 650 mV, I_{tip} = 678 pA; (b) V_{bias} = 741 mV, I_{tip} = 715 pA.

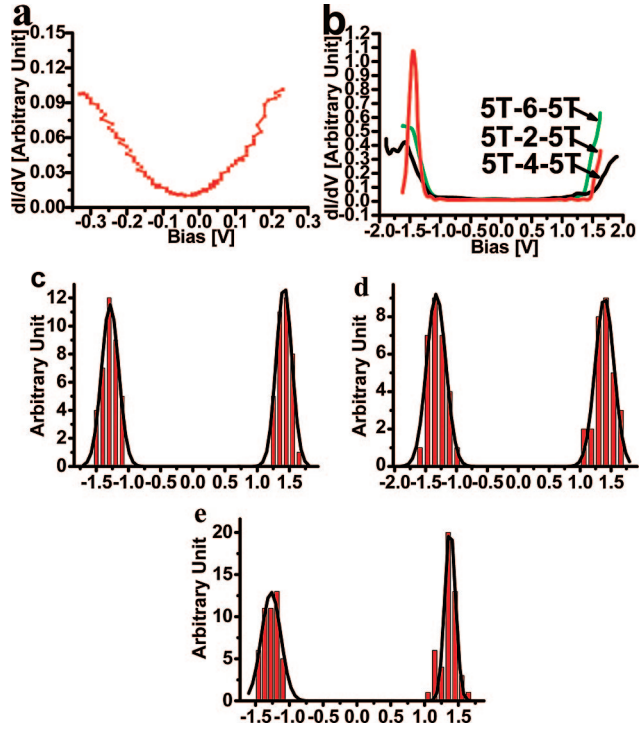


Figure 6. (a) Typical d*I*/d*V*−*V* curve obtained on bare HOPG; (b) typical d*I*/d*V*−*V* curve obtained on 5T-2-5T, 5T-4-5T, and 5T-6-5T adlayers on HOPG; (c) The histogram of experimental gap edges of 5T-2-5T molecules. The black solid lines show a Gauss fit of the columns. (d) The histogram of experimental gap edges of 5T-4-5T molecules. The black solid lines show a Gauss fit of the columns. (e) The histogram of experimental gap edges of 5T-6-5T molecules. The black solid lines show a Gauss fit of the columns.

TABLE 2. Summary of STS Results of 5T-2-5T, 5T-4-5T, and 5T-6-5T molecules

	left edge (±0.2 eV)	right edge (±0.2 eV)	experimental gap (±0.4 eV)
5T-2-5T	−1.29	1.42	2.71
5T-4-5T	−1.32	1.39	2.71
5T-6-5T	−1.27	1.38	2.65

adsorbing molecules.[41] Thus the experimental energy gap is measured as the separation between these two edges.

The histograms in Figure 6c,d,e show the statistic distributions of the edges of HOMO and LUMO measured from a large number of spectra obtained on 5T-2-5T, 5T-4-5T, and 5T-6-5T adlayers. The experimental energy gap is given by Gaussian simulation. The statistic results of the left and right edge for each kind of molecule are summarized in Table 2. On the basis of this table, it can be seen that the experimental energy gap centers of all three kinds of molecules are slightly shifted to positive regions; consistent with the previous report that oligothiophene is a p-type material in air.[18] For 5T-2-5T, 5T-4-5T, and 5T-6-5T, their experimental energy gap is all around 2.7 eV which is close to the energy gap for quinquethiophene, 2.78 eV, given by theoretical results.[45] STS results in the present study indicate that dual-quinquethiophenes with different bridge alkylene chains show similar electronic properties, which means that a bridge alkylene chain has little effect on the electronic properties of 5T-*n*-5T (n = 2–6).

CONCLUSIONS

The effect of bridge alkylene chain on the assembling behaviors and electronic properties of dual-quinquethiophenes were investigated systematically using STM and STS. 5T-*n*-5T (n = 2–6) can form similar adlayers although they have different bridge alkylene chains. For the molecules with a long length of bridge alkylene chain, 5T-5-5T and 5T-6-5T, they can form their special adlayers, which indicate that molecules with long bridge chain are more flexible. So they may have more arrangement forms on a HOPG surface. In addition, STS results showed that the electronic property of dual-quinquethiophenes is very close to that of quinquethiophenes and the difference of the bridge alkylene chain does not lead to much difference in electronic properties. The results will be useful in surface engineering by self-assembly and device fabrication with oligothiophenes.

EXPERIMENTAL SECION

5T-*n*-5T (n = 2–6) were synthesized according to the procedure reported in the literature.[12,46] Phenyloctane was from Aldrich and used as solvent without further purification. The self-assemblies of the five molecules were prepared by depositing a drop of solution containing the assigned molecules in a concentration less than 10^{-4} M on a freshly cleaved HOPG surface.

All STM experiments were performed in phenyloctane on a Nanoscope IIIa scanning tunneling microscope (Digital Instruments Co. CA) with mechanically cut Pt/Ir (90/10%) tips. All the STM images given in this paper were collected with the constant current mode and used with only flatten processing. The tunneling conditions for each STM image are given in the corresponding figure caption.

Scanning tunneling spectroscopic experiments were performed by applying a modulation (peak-to-peak 0.02−0.03 V) to the bias voltage. A lock-in amplifier was used to collect the dI/dV−V signals. The feedback of the STM control was shut down during STS measurements.

Acknowledgment. The financial support from National Natural Science Foundation of China (grants 20575070, 20673121, 20473103 and 20121301), National Key Project on Basic Research (grants 2006CB806100 and 2006CB932100), and the Chinese Academy of Sciences are gratefully acknowledged.

REFERENCES AND NOTES

1. Uosaki, K.; Yamada, R. Formation of Two-Dimensional Crystals of Alkanes on the Au(111) Surface in Neat Liquid. *J. Am. Chem. Soc.* **1999**, *121*, 4090–4091.
2. Yoshimoto, S.; Higa, N.; Itaya, K. Two-Dimensional Supramolecular Organization of Copper Octaethylporphyrin and Cobalt Phthalocyanine on Au(111): Molecular Assembly Control at an Electrochemical Interface. *J. Am. Chem. Soc.* **2004**, *126*, 8540–8545.
3. Baker, R. T.; Mougous, J. D.; Brackley, A.; Patrick, D. L. Competitive Adsorption, Phase Segregation, and Molecular Motion at a Solid-Liquid Interface Studied by Scanning Tunneling Microscopy. *Langmuir* **1999**, *15*, 4884–4891.
4. Mu, Z. C.; Yang, X. Y.; Wang, Z. Q.; Zhang, X.; Zhao, J. L.; Bo, Z. S. Influence of Substituents on Two-Dimensional Ordering of Oligo(phenylene-ethynylene)s−A Scanning Tunneling Microscopy Study. *Langmuir* **2004**, *20*, 8892–8896.
5. Yang, X. Y.; Wang, J.; Zhang, X.; Wang, Z. Q.; Wang, Y. STM Study on 2D Molecular Assemblies of Luminescent Quinacridone Derivatives: Structure Fine-Tuned by Introducing Bulky Substitutes and Co-Adsorption with Monofunctional/Bifunctional Acid. *Langmuir* **2007**, *23*, 1287–1291.
6. Hamers, R. J. Scanned Probe Microscopies in Chemistry. *J. Phys. Chem.* **1996**, *100*, 13103–13120.
7. Rosei, F.; Schunack, M.; Naitoh, Y.; Jiang, P.; Gourdon, A.; Laegsgaard, E.; Stensgaard, I.; Joachim, C.; Besenbacher, F. Properties of Large Organic Molecules on Metal Surfaces. *Prog. Surf. Sci.* **2003**, *71*, 95–146.
8. Hickman, S.; Hamilton, A.; Patrick, D. L. Controlling Molecular Alignment in an Organic Monolayer with a Sacrificial Liquid Crystal Template. *Surf. Sci.* **2003**, *537*, 113–122.
9. Fujii, S.; Akiba, U.; Fujihira, M. Geometry for Self-Assembling of Spherical Hydrocarbon Cages with Methane Thiolates on Au(111). *J. Am. Chem. Soc.* **2002**, *124*, 13629–13635.
10. Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chem. Rev.* **2005**, *105*, 1103–1169.
11. Kaikawa, T.; Takimiya, K.; Aso, Y.; Otsubo, T. Synthesis and Spectroscopic Properties of [2.2]Quinquethiophenophane as an Ideal π-Dimer Model. *Org. Lett.* **2000**, *2*, 4197–4199.
12. Sakai, T.; Satou, T.; Kaikawa, T.; Takimiya, K.; Otsubo, T.;

Aso, Y. Syntheses, Structures, Spectroscopic Properties, and π-Dimeric Interactions of [*n.n*]Quinquethiophenophanes. *J. Am. Chem. Soc.* **2005**, *127*, 8082–8089.
13. Murphy, A. R.; Fréchet, J. M. J.; Chang, P.; Lee, J.; Subramanian, V. Organic Thin Film Transistors from a Soluble Oligothiophene Derivative Containing Thermally Removable Solubilizing Groups. *J. Am. Chem. Soc.* **2004**, *126*, 1596–1597.
14. Stabel, A.; Rabe, J. P. Scanning Tunneling Microscopy of Alkylated Oligothiophenes at Interfaces with Graphite. *Synth. Met.* **1994**, *67*, 47–53.
15. Azumi, R.; Götz, G.; Debaerdemaeker, T.; Bäuerle, P. Coincidence of the Molecular Organization of β-Substituted Oligothiophenes in Two-Dimensional Layers and Three-Dimensional Crystals. *Chem. Eur. J.* **2000**, *6*, 735–744.
16. Bäuerle, P.; Fischer, T.; Bidlingmeier, B.; Stabel, A.; Rabe, J. P. Oligothiophenes—Yet Longer? Synthesis, Characterization, and Scanning Tunneling Microscopy Images of Homologous, Isomerically Pure Oligo(alkylthiophene)s. *Angew. Chem., Int. Ed.* **1995**, *34*, 303–307.
17. Leclère, P.; Surin, M.; Viville, P.; Lazzaroni, R.; Kilbinger, A. F. M.; Henze, O.; Feast, W. J.; Cavallini, M.; Biscarini, F.; Schenning, A. P. H. J.;. *et al.* About Oligothiophene Self-Assembly: From Aggregation in Solution to Solid-State Nanostructures. *Chem. Mater.* **2004**, *16*, 4452–4466.
18. Mena-Osteritz, E.; Bäuerle, P. Complexation of C_{60} on a Cyclothiophene Monolayer Template. *Adv. Mater.* **2006**, *18*, 447–451.
19. Yassar, A.; Demanze, F.; Fichou, D. Synthesis and Electrical Properties of Cyano-Substituted Oligothiophenes Towards *n*-Type Organic Semiconductors. *Opt. Mater.* **1999**, *12*, 379–382.
20. Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M. Electroluminescence in Conjugated Polymers. *Nature* **1999**, *397*, 121–128.
21. Mazzeo, M.; Pisignano, D.; Favaretto, L.; Barbarella, G.; Cingolani, R.; Gigli, G. Bright Oligothiophene-Based Light Emitting Diodes. *Synth. Met.* **2003**, *139*, 671–673.
22. Huisman, B.-H.; Valeton, J. J. P.; Nijssen, W.; Lub, J.; ten Hoeve, W. Oligothiophene-Based Networks Applied for Field-Effect Transistors. *Adv. Mater.* **2002**, *15*, 2002–2005.
23. Videlot-Ackermann, C.; Ackermann, J.; Brisset, H.; Kawamura, K; Yoshimoto, N.; Raynal, P.; El Kassmi, A.; Fages, F. α,ω-Distyryl Oligothiophenes: High Mobility Semiconductors for Environmentally Stable Organic Thin Film Transistors. *J. Am. Chem. Soc.* **2005**, *127*, 16346–16347.
24. Li, Z. H.; Wong, M. S.; Fukutani, H.; Tao, Y. Full Emission Color Tuning in Bis-Dipolar Diphenylamino-Endcapped Oligoarylfluorenes. *Chem. Mater.* **2005**, *17*, 5032–5040.
25. Ishida, T.; Mizutani, W.; Choi, N.; Akiba, U.; Fujihira, M.; Tokumoto, H. Structural Effects on Electrical Conduction of Conjugated Molecules Studied by Scanning Tunneling Microscopy. *J. Phys. Chem. B* **2000**, *104*, 11680–11688.
26. Tang, J. X.; Lau, K. M.; Lee, C. S.; Lee, S. T. Substrate Effects on the Electronic Properties of an Organic/Organic Heterojunction. *Appl. Phys. Lett.* **2006**, *88*, 232103.
27. Berg, A. M.; Patrick, D. L. Preparation of Chiral Surfaces from Achiral Molecules by Controlled Symmetry Breaking. *Angew. Chem., Int. Ed.* **2005**, *44*, 1821–1823.
28. Ishida, T.; Mizutani, W.; Azehara, H.; Sato, F.; Choi, N.; Akiba, U.; Fujihira, M.; Tokumoto, H. Adsorption Processes of Self-Assembled Monolayers Made from Terphenyl Thiols. *Langmuir* **2001**, *17*, 7459–7463.
29. Wano, H.; Uosaki, K. In Situ, Real-Time Monitoring of the Reductive Desorption Process of Self-Assembled Monolayers of Hexanethiol on Au(111) Surfaces in Acidic and Alkaline Aqueous Solutions by Scanning Tunneling Microscopy. *Langmuir* **2001**, *17*, 8224–8228.
30. Yamada, R.; Uosaki, K. Two-Dimensional Crystals of Alkanes Formed on Au(111) Surface in Neat Liquid: Structural Investigation by Scanning Tunneling Microscopy. *J. Phys. Chem. B* **2000**, *104*, 6021–6027.
31. Yoshimoto, S.; Tsutsumi, E.; Narita, R.; Murata, Y.; Murata, M.; Fujiwara, K.; Komatsu, K.; Ito, O.; Itaya, K. Epitaxial Supramolecular Assembly of Fullerenes Formed by Using a Coronene Template on a Au(111) Surface in Solution. *J. Am. Chem. Soc.* **2007**, *129*, 4366–4376.
32. Yoshimoto, S.; Sato, K.; Sugawara, S.; Chen, Y.; Ito, O.; Sawaguchi, T.; Niwa, O.; Itaya, K. Formation of Supramolecular Nanobelt Arrays Consisting of Cobalt(II) "Picket-Fence" Porphyrin on Au Surfaces. *Langmuir* **2007**, *23*, 809–816.
33. Hermann, B. A.; Scherer, L. J.; Housecroft, C. E.; Constable, E. C. Self-Organized Monolayers: A Route to Conformational Switching and Read-Out of Functional Supramolecular Assemblies by Scanning Probe Methods. *Adv. Funct. Mater.* **2006**, *16*, 221–235.
34. Wan, L. J. Fabricating and Controlling Molecular Self-Organization at Solid Surfaces: Studies by Scanning Tunneling Microscopy. *Acc. Chem. Res.* **2006**, *39*, 334–342.
35. Gesquière, A.; De Feyter, S.; De Schryver, F. C.; Schoonbeek, F.; van Esch, J.; Kellogg, R. M.; Feringa, B. L. Supramolecular π-Stacked Assemblies of Bis(urea)-Substituted Thiophene Derivatives and Their Electronic Properties Probed with Scanning Tunneling Microscopy and Scanning Tunneling Spectroscopy. *Nano Lett.* **2001**, *1*, 201–206.
36. Mena-Osteritz, E. Superstructures of Self-Organizing Thiophenes. *Adv. Mater.* **2002**, *14*, 609–616.
37. Mena-Osteritz, E.; Meyer, A.; Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Meijer, E. W.; Bäuerle, P. Two-Dimensional Crystals of Poly(3-Alkylthiophene)s: Direct Visualization of Polymer Folds in Submolecular Resolution. *Angew. Chem., Int. Ed.* **2000**, *39*, 2680–2684.
38. Noh, J.; Ito, E.; Araki, T.; Hara, M. Adsorption of Thiophene and 2,5-Dimethylthiophene on Au(111) from Ethanol Solutions. *Surf. Sci.* **2003**, *532–535*, 1116–1120.
39. Xu, L. P.; Gong, J. R.; Wan, L. J.; Jiu, T. G.; Li, Y. L.; Zhu, D. B.; Deng, K. Molecular Architecture of Oligothiophene on a Highly Oriented Pyrolytic Graphite Surface by Employing Hydrogen Bondings. *J. Phys. Chem. B* **2006**, *110*, 17043–17049.
40. Yang, Z.-Y.; Zhang, H.-M.; Yan, C.-J.; Li, S.-S.; Yan, H.-J.; Song, W.-G.; Wan, L.-J. Scanning Tunneling Microscopy of the Formation, Transformation, and Property of Oligothiophene Self-Organizations on Graphite and Gold Surfaces. *Proc. Natl. Acad. Sci., U.S.A.* **2007**, *104*, 3707–3712.
41. Gong, J. R.; Wan, L. J.; Lei, S. B.; Bai, C. L.; Zhang, X. H.; Lee, S.-T. Direct Evidence of Molecular Aggregation and Degradation Mechanism of Organic Light-Emitting Diodes under Joule Heating: An STM and Photoluminescence Study. *J. Phys. Chem. B* **2005**, *109*, 1675–1682.
42. Rohde, D.; Yan, C. J.; Yan, H. J.; Wan, L. J. From a Lamellar to Hexagonal Self-Assembly of Bis(4,4′-(*m*,*m*′-di(dodecyloxy)phenyl)-2,2′-difluoro-1,3,2- dioxaborin) Molecules: A trans-to-cis-Isomerization-Induced Structural Transition Studied with STM. *Angew. Chem., Int. Ed.* **2006**, *45*, 3996–4000.
43. Mi, B.-X.; Wang, P.-F.; Liu, M.-W.; Hoi-Lun, Kwong; Wong, N.-B.; Lee, C.-S.; Lee, S.-T. Thermally Stable Hole-Transporting Material for Organic Light-Emitting Diode: An Isoindole Derivative. *Chem. Mater.* **2003**, *15*, 3148–3151.
44. Abdel-Mottaleb, M. M. S.; Götz, G.; Kilickiran, P.; Bäuerle, P.; Mena-Osteritz, E. Influence of Halogen Substituents on the Self-Assembly of Oligothiophenes—A Combined STM and Theoretical Approach. *Langmuir* **2006**, *22*, 1443–1448.
45. Bouzzine, S. M.; Bouzakraoui, S.; Bouachrine, M.; Hamidi, M. Density Functional Theory (B3LYP/6-31G*) Study of Oligothiophenes in Their Aromatic and Polaronic States. *J. Mol. Struct. (Theochem)* **2005**, *726*, 271–276.
46. Satou, T.; Sakai, T.; Kaikawa, T.; Takimiya, K.; Otsubo, T.; Aso, Y. α,ω-Bis(quinquethienyl)alkanes as a π-Dimer Model of Polythiophene. *Org. Lett.* **2004**, *6*, 997–1000.