Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thin Solid Films 437 (2003) 150–154

www.elsevier.com/locate/tsf

Influence of surface hydrophobicity of substrates on the self-organization of chiral molecule

Yanjie Zhang[a,1], Ran Lu[b], Qingsheng Liu[b], Yanlin Song[c], Lei Jiang[c], Yichun Liu[a,*], Yingying Zhao[b], Tie Jin Li[b]

[a] *Key Laboratory of Excited State Process, Chinese Academy of Sciences, Changchun Institute of Optics, Fine Mechanics and Physics, CAS, Changchun 130021, PR China*
[b] *Department of Chemistry, Jilin University, Changchun 130023, PR China*
[c] *Research Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China*

Received 29 March 2003; received in revised form 29 March 2003; accepted 12 April 2003

Abstract

The interfacial-dependent self-organization of a chiral amino acid amphiphile was observed on various substrates with different surface hydrophobicity. Three kinds of organizations are induced at different substrates, which appear as helical aggregates on hydrophobic surface (e.g. highly oriented pyrolytic graphite), molecular flat layer on hydrophilic surface, (e.g. mica) and a transition state between them on silicon wafer. The strength of the interactions between the helical aggregates formed in solution and the substrate is the key factor to the self-organization of the chiral molecule. The results reported here provide insight into how the surface hydrophobicity of substrates affects the self-organization of chiral molecules.

Keywords: Adsorption; Atomic force microscopy (AFM); Nanostructures; Surface morphology

1. Introduction

Controlling over the structure of the molecular self-assembly and self-organization at interfaces is an interesting field that aroused considerable attention [1–10]. It is increasingly significant for elucidation of life processes and the generation of new supramolecular structures or ensembles and molecular materials, opening the way for new applications [11]. Chirality is a very important phenomenon in nature. Crucial organic molecules associated with life (for example, amino acids, nucleic acids and sugars) are chiral and usually occur in nature in only one of the two enantiomeric forms [12]. It is generally agreed that assembly of chiral molecules is determined by the competition between two factors: the presence of chiral centers often induces helicity; while directional attractive interactions such as hydrogen bonding or face-to-face $\pi-\pi$ aromatic stacking help generate linear arrays of molecules [13,14]. However, the properties of the substrates surfaces also play an important role in the process of the self-organization of molecules [15–18].

In this letter, we focus our interest on the interfacial-dependent self-organization of a chiral amino acid amphiphile (*N*-stearyl-L-glutamic acid, C_{18}-Glu) on three different substrates and attempt to reveal the relationship between the self-organization of chiral molecule and the surface hydrophobicity of the substrates. Three kinds of organizations are observed by atomic force microscopy (AFM), which appear as helical aggregates on hydrophobic highly oriented pyrolytic graphite (HOPG) surface, molecular flat layer on hydrophilic mica surface and a transition state on silicon wafer surface. The self-organization of chiral molecules is manipulated at different interfaces.

2. Experimental

The synthesis of *N*-stearyl-L-glutamic acid (C_{18}-Glu) was previously described in detail [19]. C_{18}-Glu was dissolved in ethanol to form a solution with the concen-

---

*Corresponding author.
E-mail address: ycliu@nenu.edu.cn (Y. Liu).

[1] Current address. Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA.

0040-6090/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
PII: S0040-6090(03)00615-1

tration of 1×10^{-2} M. HOPG and mica plates (10×10 mm) were freshly cleaved just prior to use. Silicon wafers were cut into the dimension 10×10 mm and extensively cleaned. The silicon wafers were ultrasonicated in acetone, ethanol and double-distilled water (Mili-Q System) for 15 min, respectively, and rinsed in a large amount of double-distilled water. The cleaned silicon wafers were dried in vacuum prior to use. The contact angles of water were measured with Contact Angle System OCA (Germany, Dataphysics Inc.) at room temperature. The contact angles were recorded immediately after dispensing 4 μl droplets with a pipet onto the surface. The reported values were the average of five different measurements taken on five individual substrates. The AFM investigations were conducted using a commercial system (Seiko Instruments Inc., SPA300HV, Japan) with a 20 μm scanner. A triangular-shaped Si_3N_4 cantilever with spring constant of 0.02 Nm^{-1} was used to acquire images in contact mode. A drop of C_{18}-Glu solution was applied to the substrates and studied by AFM after solvent had evaporated slowly. All images were recorded under ambient conditions at 22 °C. The scan directions in all images maintained uniform. Each of the images present here was the representation of several images taken at different times to ensure reproducibility.

3. Results and discussion

Adsorbed supramolecular structures remain stable on surfaces if the intermolecular forces are stronger than the forces between the molecules and the surface [17,18]. The surface property of substrates is significant to the self-organization morphologies of chiral molecules. To determine the surface free energies of the different substrates, the contact angles of water are measured at room temperature [20]. Fig. 1 shows the contact angles of water on the bare substrates. The contact angles measurements highlight the large difference in hydrophobicity between HOPG ($83.0\pm1°$, 86° in Ref. [21]), mica ($8.0\pm1°$) and silicon wafer ($56.3\pm1°$). Using contact angles, the difference in interfacial free energies between the surface/air interface and the surface/water interface can be determined from Young's equation [22]:

$$\gamma_{LV}\cos\Theta=\gamma_{SV}-\gamma_{SL} \quad (1)$$

where γ_{LV}, γ_{SV} and γ_{SL} are the specific interfacial free energies for the water (solution)/air, surface/air and surface/water interfaces at 25 °C, respectively. The value for γ_{LV} is 71.97 dyn/cm [23]. Using the measured contact angles, the difference of $(\gamma_{SV}-\gamma_{SL})$ is 8.65 dyn/cm for HOPG, 72.27 dyn/cm for mica and 39.93 dyn/cm for silicon wafer, respectively. As already shown, a drop of water on HOPG has a tendency to bead up while on mica surface wet. It can be deduced that the larger $(\gamma_{SV}-\gamma_{SL})$ is the stronger the interaction between hydrophilic groups in chiral molecules and substrates surface.

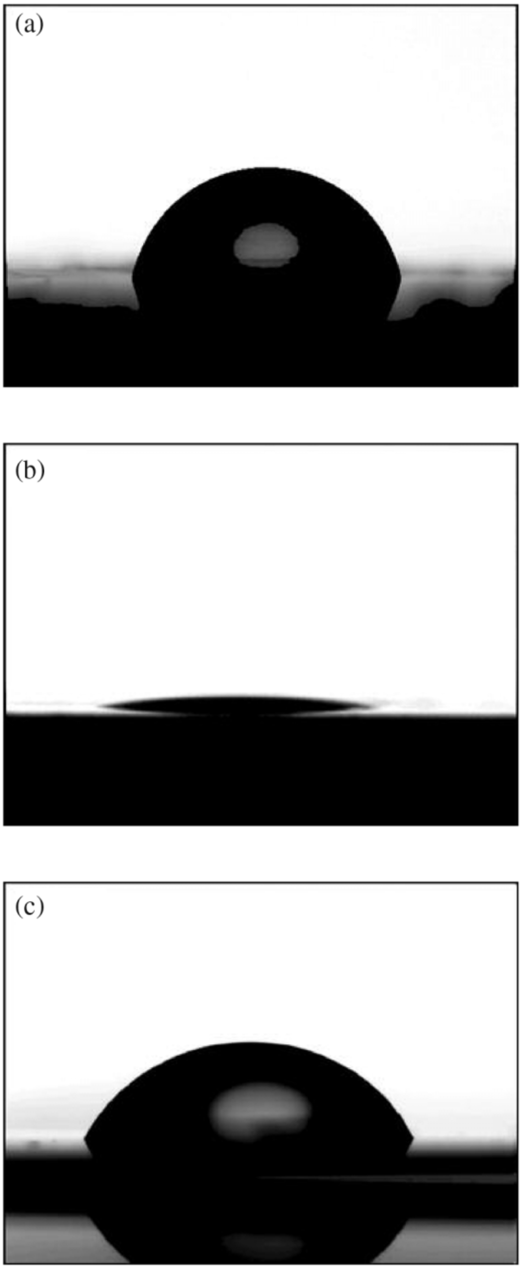

Fig. 1. Contact angles of water on bare substrates: (a) HOPG (b) mica and (c) silicon wafer.

Large-scale AFM image (20×20 μm) obtained on dried C_{18}-Glu adsorbate on HOPG is shown in Fig. 2a, where many left-handed helical aggregates in mesoscale were observed. The packing density is approximately 4.5×10^4 aggregates/mm^2. The helical aggregates can be observed more clearly in the zoomed-in image (Fig. 2b, 6 $\times$6 μm). Each end of the aggregates is in featherlike shape that it covers the surface to the maximum extent. Similar helically twisted fibers from

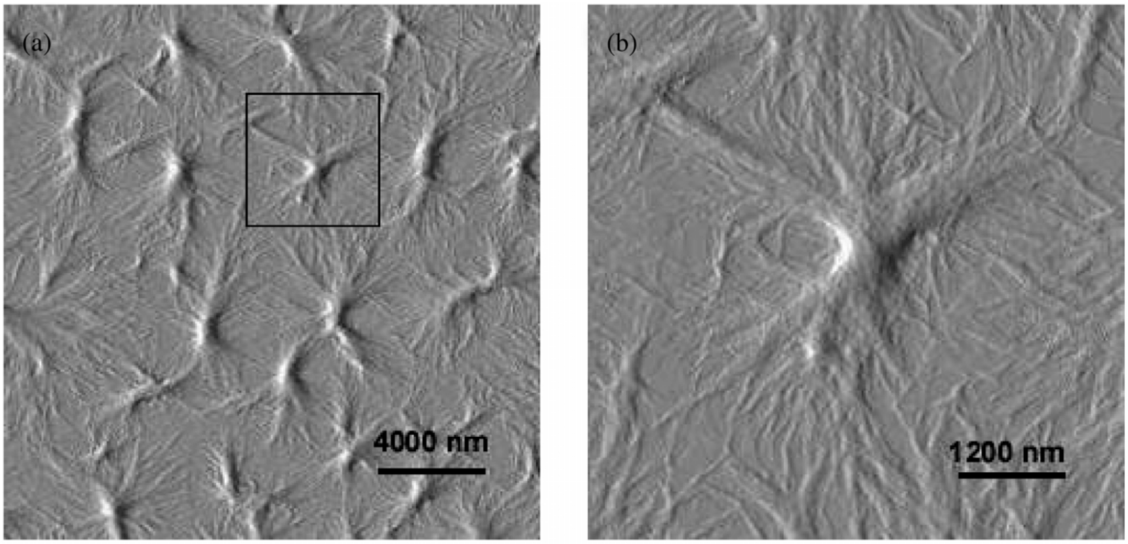

Fig. 2. (a) A large scale AFM image (20×20 μm) of the helical aggregates of C_{18}-Glu adsorbate on HOPG; and (b) Zoomed-in image obtained from the area indicated in (a).

glucosamide bolaamphiphiles have been observed by TEM [24–26]. While on mica surface, the chiral molecules assembled to molecular flat-layered structure in a very long-range order (Fig. 3a). Terraced layers with irregular boundary can be observed clearly. The molecular resolution image obtained from the surface is shown in Fig. 3b. The molecules closely packed linearly and the lines are parallel to each other. It also shows some preferential orientation over the surface. It is surprising that the chiral molecules self-organize into such highly ordered structure without any aids of devices, such as Langmuir–Blodgett trough [27].

Then we turn to the self-organization of C_{18}-Glu on silicon wafer. Left-handed helical aggregates are presented on the surface of silicon wafer (Fig. 4). But this kind of aggregate is different from that formed on HOPG surface. There is no feather-like structure at the end of aggregates and some layered structure can be observed in some areas. This kind of structure can be considered as a transition state of the morphologies on HOPG and mica surface. It preserves the helical character like that on HOPG surface, but has a tendency to form flat-layered structure like that on mica surface.

The different morphologies on HOPG, mica and silicon wafer may come from the different molecular orientations of this chiral amphiphile. Based on Nandi's effective pair potential (EPP) approach [28,29], the EPP for chiral molecules depends on the size of the groups attached to the chiral center, their separation distance, and their relative orientation. The minimal energy conformation of a D-D or L-L pair shows double energy-minimum states, with one minimum at a twist angle between adjacent two molecules and at a short distance (Twist State), while the second, at nearly zero degree, but at large separation (Linear State). For present molecule, –NH– can be involved in two kinds of stable intermolecular hydrogen bonding. The first one is between –NH– and –CO– in carboxyl group attached to the chiral center of the molecule that results in Twist State. The second one is between –NH– and –CO– in amide group that induces a stable Linear State. The changes in hydrogen bonding forms at different interfaces will induce various morphologies.

In the alcoholic solution, Twist State is effective forming helical aggregates and there are free carboxyl groups in the aggregates [30]. Many single helical fibers tangle up together to form the helical aggregates in ethanol solution. When a drop of solution was applied to the hydrophobic surface of HOPG, the exposed hydrophobic hydrocarbon chains of the helical aggregates in ethanol solution will attach to the surface. The two ends of each bundle of the helical aggregates will cover the HOPG surface to the maximum extent and the featherlike structure at each end is formed. As HOPG is a typical hydrophobic substrate, the free carboxyl group of C_{18}-Glu in the helical aggregates almost has no interaction with HOPG surface. The helical aggregates formed in ethanol solution are stable on HOPG and there is no rearrangement taken place.

Mica is a typical hydrophilic substrate with regular crystal lattice on the atomically flat plane. When a drop of C_{18}-Glu ethanol solution is applied to the mica surface, the free carboxyl group of C_{18}-Glu in the helical aggregates sticks to the surface via hydrogen bonding and the hydrophobic hydrocarbon chains extend upwards. Two carboxyl groups in the molecule C_{18}-Glu are at different steric positions. The carboxyl attached to $–CH_2–$ group can move more freely than the other

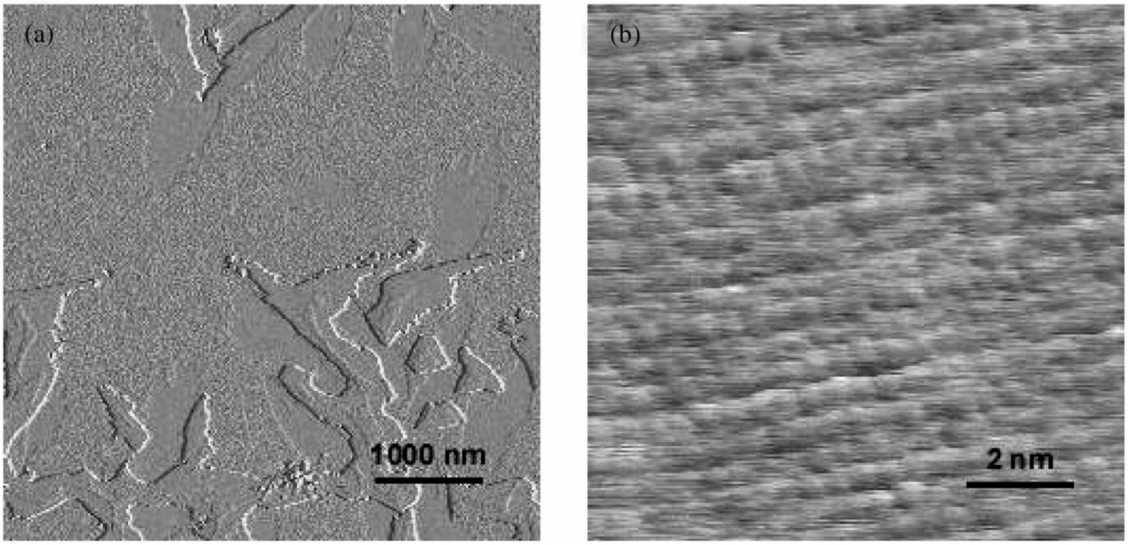

Fig. 3. (a) A large-scale AFM image (5×5 μm) of flat-layered structure formed by C_{18}-Glu adsorbate on mica. (b) A molecular resolution AFM image of layered structure formed by C_{18}-Glu on mica (10×10 nm).

carboxyl and can adjust the location of molecule to match the crystal lattice of mica well. Since amide functional groups possess the Z configuration structure for long-chain molecule [31], chiral molecules assemble regularly and match with each other. These results were suggested by the fact that the racemic derivatives could not form very ordered structure on the substrates. The hydrogen bonding in the helical aggregates is broken completely and lateral hydrogen-bonding network between adjacent amide groups appears. The helical aggregates assemble to a flat-layered structure showing Linear State. Two main factors contribute to the formation of the molecular flat-layered structure. One is the strong interaction between the carboxyl group and the surface of mica and the other is the lateral hydrogen-bonding network between adjacent amide groups. Moreover, the regular crystal lattice on the mica surface helps to the formation of the highly ordered structure.

The hydrophobicity of silicon wafer is between HOPG and mica. There is a thin layer of natural silica on the surface of silicon wafer cleaned as mentioned in experimental section. The interaction between the free carboxyl group in the helical aggregates and the silicon wafer is relatively weak compared to that on mica

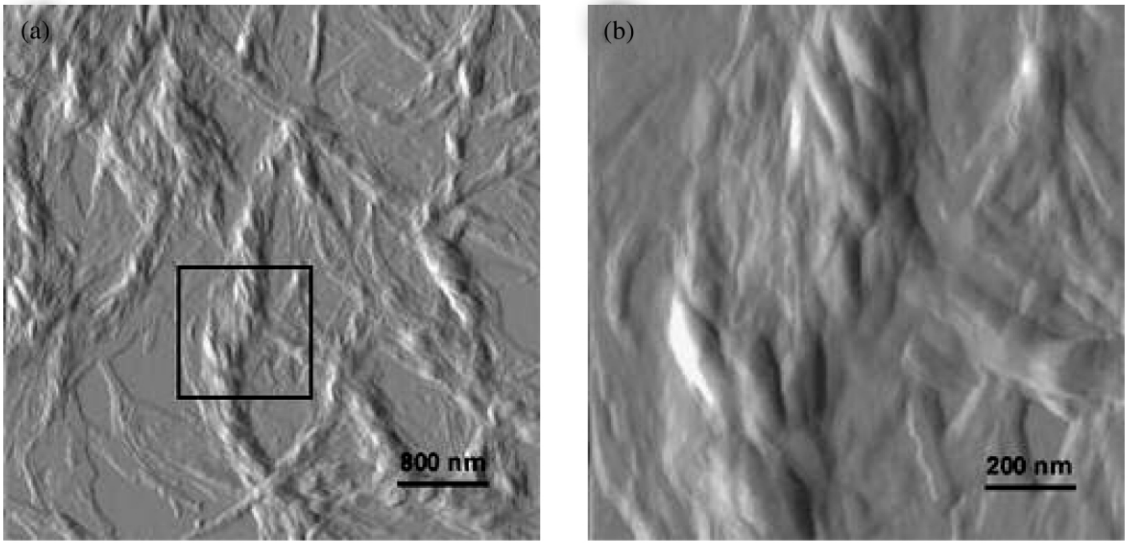

Fig. 4. (a) A large scale AFM image (4×4 μm) of the fibrous assembly of C_{18}-Glu adsorbate on silicon wafer. (b) Zoomed-in image obtained from the area indicated in (a).

surface. The helical aggregates in the solution are broken partially, but they have a tendency to form flat-layered structure. On silicon wafer, the two kinds of intermolecular hydrogen bonding coexist in the system to induce the morphology shown in Fig. 4.

The results reported here provide insight into how the surface hydrophobicity of substrates affects the self-organization of chiral molecules. The strength of the interactions between the helical aggregates formed in solution and the substrates is the key factor to the self-organization of the chiral molecule. The interface can manipulate the bonding behavior in a multi-hydrogen bonding system and the self-organization of chiral molecules can be controlled consequently. Various aggregates of C_{18}-Glu are presented on different substrates. C_{18}-Glu is somewhat similar to protein, having an acyl group neighboring an asymmetric carbon of amino acid and being sufficiently amphiphilic to interact with both hydrophobic and hydrophilic surroundings. Thus, an investigation of the chiral aggregates of C_{18}-Glu would be of interest as regards the structure and function of proteins. The controlling over the self-organization of C_{18}-Glu may be provided as useful method to change the structure of proteins.

Acknowledgments

The authors acknowledge the National Natural Science Foundation of China (NNSFC), State Key Project Fundamental Research and Chinese Academy of Sciences for financial supports.

References

[1] A. Ulman, An Introduction to Ultrathin Organic Films: from Langmuir–Blodgett to Self-Assembly, Academic Press, San Diego, CA, 1991.
[2] A. Kumar, G.M. Whitesides, Science 263 (1994) 60.
[3] D. Qin, Y. Xia, B. Xu, H. Yang, C. Zhu, G.M. Whitesides, Adv. Mater. 11 (1999) 1433.
[4] J.-F. Liu, W.A. Ducker, J. Phys. Chem. B 103 (1999) 8558.
[5] A.M. Rouhi, C and EN 18 (January 1999) 51.
[6] E. Sparr, L. Eriksson, J.A. Bouwstra, K. Ekelund, Langmuir 17 (2001) 164.
[7] G. Luo, T. Liu, L. Ying, X.S. Zhao, Langmuir 16 (2000) 3651.
[8] C.M. Yam, A.K. Kakkar, Langmuir 15 (1999) 3807.
[9] J.L. Wolgemuth, R.K. Workman, S. Manne, Langmuir 16 (2000) 3077.
[10] C. Messerschmidt, S. Svenson, W. Stocker, J.-H. Fuhrhop, Langmuir 16 (2000) 7445.
[11] K.A. Jolliffe, P. Timmerman, D.N. Reinhoudt, Angew. Chem. Int. Ed. 38 (1999) 933.
[12] F. Auer, D.W. Schubert, M. Stamm, T. Arnebrant, A. Swietlow, M. Zizlsperger, B. Sellergren, Chem. Eur. J. 5 (1999) 1150.
[13] R. Oda, I. Huc, S.J. Candau, Angew. Chem. Int. Ed. 37 (1998) 2689.
[14] R. Oda, I. Huc, M. Schmutz, S.J. Candau, F.C. Mackintosh, Nature 399 (1999) 566.
[15] L.M. Grant, F. Tiberg, W.A. Ducker, J. Phys. Chem. B 102 (1998) 4288.
[16] L.M. Grant, T. Ederth, F. Tiberg, Langmuir 16 (2000) 2285.
[17] C. Messerschmidt, C. Draeger, A. Schulz, J.P. Rabe, J.-H. Fuhrhop, Langmuir 17 (2001) 3526.
[18] J. Nissen, S. Gritsch, G. Wiegand, J.O. Rädler, Eur. Phys. J. B 10 (1999) 335.
[19] Y.J. Zhang, Y. Song, Y. Zhao, T.J. Li, L. Jiang, D. Zhu, Langmuir 17 (2001) 1317.
[20] S.D. Gilmor, A.J. Thiel, T.C. Strother, L.M. Smith, M.G. Lagally, Langmuir 16 (2000) 7223.
[21] A.W. Adamson, A.P. Gast, Physical Chemistry of Surfaces, 6th, Wiley, New York, 1997, p. 365.
[22] J.H. Brody, R.M. Rose, J. Wulff, The Structure and properties of Materials: Thermodynamics of Structure, John Wiley and Sons, New York, 1964, p. 55.
[23] D. Lide, The CRC Handbook of Chemistry and Physics, 74th, CRC Press, Ann Arbor, MI, 1993, pp. 6–144.
[24] I. Nakazawa, M. Masuda, Y. Okada, T. Hanada, K. Yase, M. Asai, T. Shimizu, Langmuir 15 (1999) 4757.
[25] M. Masuda, T. Hanada, K. Yase, T. Shimizu, Macromolecules 31 (1998) 9403.
[26] T. Shimizu, M. Masuda, J. Am. Chem. Soc. 119 (1997) 2812.
[27] X. Du, Y. Liang, Chem. Phys. Lett. 313 (1999) 565.
[28] N. Nandi, B. Bagchi, J. Am. Chem. Soc. 118 (1996) 11 208.
[29] N. Nandi, B. Bagchi, J. Phys. Chem. A 101 (1997) 1343.
[30] K. Sakamoto, M. Hatano, Bull. Chem. Soc. Jpn. 53 (1980) 339.
[31] X. Du, B. Shi, Y. Liang, Langmuir 14 (1998) 3631.