Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Substituent Effect on Epitaxy of Mono-Molecular Layer on HOPG

Eiichi Fujiwara [a c], Seiji Isoda [a c], Akitaka Hoshino [b c], Takashi Kobayashi [a c] & Yoshiro Yamashita [b c]

[a] Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611-0011, Japan

[b] Department of Physics, Faculty of Science, Kyoto University, Sakyo, Kyoto, 606-8224, Japan

[c] Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan

Version of record first published: 24 Sep 2006

To cite this article: Eiichi Fujiwara, Seiji Isoda, Akitaka Hoshino, Takashi Kobayashi & Yoshiro Yamashita (2000): Substituent Effect on Epitaxy of Mono-Molecular Layer on HOPG, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 349:1, 215-218

To link to this article: http://dx.doi.org/10.1080/10587250008024903

Mol. Cryst. Liq. Cryst., 2000, Vol. 349, pp. 215-218
Reprints available directly from the publisher
Photocopying permitted by license only

Substituent Effect on Epitaxy of Mono-Molecular Layer on HOPG

EIICHI FUJIWARA[a], SEIJI ISODA[a], AKITAKA HOSHINO[b], TAKASHI KOBAYASHI[a] and YOSHIRO YAMASHITA[b]

[a]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611–0011, Japan,* [b]*Department of Physics, Faculty of Science, Kyoto University, Sakyo, Kyoto 606–8224, Japan and* [c]*Institute for Molecular Science, Myodaiji, Okazaki 444–8585, Japan*

The monolayer of tetramethyl-bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole) (TMBTQBT) on graphite was examined by scanning tunneling microscopy. The monolayer crystal lattice of TMBTQBT was found to exhibit point-on-line coincidence epitaxy with respect to the (0001) graphite, and expands a little compared with the corresponding layer in the bulk crystal. This result indicates that the S•••S intermolecular interaction or bond in the TMBTQBT monolayer is not strong or doesn't exist in contrast to the case of pristine BTQBT. The high contrast positions in the STM image were found to correspond to the sulfur atoms of the TMBTQBT molecule.

Keywords: Bis[1; 2; 5]thiadiazolo-*p*-quinobis(1; 3-dithiole) (BTQBT); tetramethyl-BTQBT (TMBTQBT); STM; epitaxy

INTRODUCTION

Yamashita *et al.* have reported that Bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole) (BTQBT) (FIGURE 1) exhibits high conductivity as a single component organic material. This is partially due to the strong interaction between the sulfur atoms in the neighboring molecules forming a molecular sheet [1].

Hoshino *et al.* have reported that the crystal lattices of organic monolayers on graphite exhibit "point-on-line coincidence" with respect to the (0001) graphite. The point-on-line coincidence is one of the geometrical matching between the crystal lattices of the organic monolayer and the substrate [2]. The two-dimensional lattice of BTQBT on graphite shrinks slightly compared with the corresponding layer structure in the bulk crystal enabling the point-on-line coincidence to be realized [3]. This shrinkage is probably due to the strong S···S intermolecular interaction in the monolayer. In this study, the monolayer structure of tetramethyl-BTQBT (TMBTQBT) on graphite was investigated, where the specific S···S intermolecular interaction was expected to be weaker.

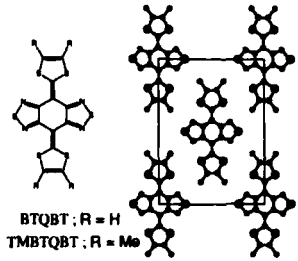

FIGURE 1 Molecular structure of BTQBT and TMBTQBT and layer structure of TMBTQBT in the bulk crystal [1].

EXPERIMENTAL

The monolayer of TMBTQBT was formed on freshly cleaved (0001) plane of HOPG under 3×10^{-7} Torr by using the vacuum-deposition method. The STM observations were carried out using the constant current mode in air with a scanning tunneling microscope (Nanoscope IIIa). A sharp Pt/Ir (80/20) tip mechanically cut with a wire cutter was used for the STM measurements. The tunneling current used was between 5-10pA and the bias voltage was between ±200-600 mV. After the molecular images were observed, the HOPG surface beneath the monolayer was also observed at the same place by decreasing the bias voltage and increasing the tunneling current. This result was used to determine experimentally the orientation relations between the two-dimensional crystalline monolayer and the graphite substrate.

RESULTS AND DISCUSSION

FIGURE 2 shows an STM image of the TMBTQBT monolayer. Besides individual molecular contrast, one-dimensional long-range contrast modulation (moiré like contrast) can also be seen as indicated with white arrows in the image. This type of contrast modulation is caused by certain epitaxy with respect to the substrate, which is called the point-on-line coincidence.

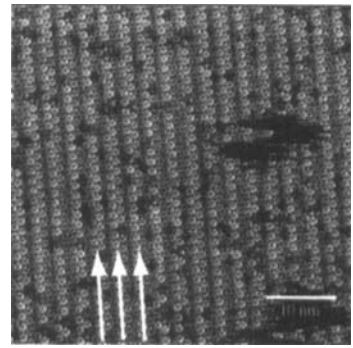

FIGURE 2 An STM image of the TMBTQBT monolayer.

Similarly, the BTQBT monolayer on graphite has this type of epitaxy [3]. The orientation relationship between the lattices of the TMBTQBT monolayer and the graphite was correctly determined by the method described in Ref. [2]. However, many dark contrasts are observed in molecular size of TMBTQBT and they are presumably scratched holes in the monolayer. Such holes in film were not observed in the BTQBT monolayer, which indicates the weaker intermolecular interaction of TMBTQBT than those of BTQBT. FIGURE 3 represents the orientation relationship of the TMBTQBT monolayer with respect to the (0001) graphite. In this figure, all lattice points of this monolayer locate on the a_g line. In this case, the lattice of the monolayer on graphite expands slightly compared with the corresponding lattice in the bulk crystal. This result was opposite to that of BTQBT. TABLE 1 shows the two-dimensional lattice constants of BTQBT and TMBTQBT. The reason for differences in lattice dimensions, expansion or shrinkage, are considered to come from the differences in the strength of the S···S intermolecular interaction between neighboring molecules in the monolayer. In the case of the TMBTQBT monolayer,

$$a = 5.02a_g - 1b_g$$
$$b = 5.74a_g + 9b_g$$

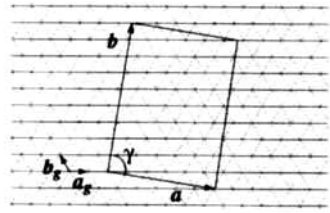

FIGURE 3 The orientation relationship of the TMBTQBT monolayer with respect to the (0001) graphite.

strong S ··· S intermolecular interaction or bond formation between the neighboring molecules is not possible due to the existence of CH_3 groups between two S atoms. That is, the monolayer of TMBTQBT is formed only by van der Waals interaction. Therefore, the two-dimensional lattice is expected to be able to be expanded compared with that of a layer in the bulk crystal. In contrast to this, the BTQBT molecules tend to come closer together so as to form a stronger S···S interaction in the monolayer. The energetically favorable two-dimensional structure of these molecules will be described elsewhere based on computer simulation in a future publication.

TABLE 1 Two-dimensional lattice constants of the monolayer.

	BTQBT		TMBTQBT	
	bulk	observed	bulk	observed
a(nm)	1.1191	1.137	1.392	1.372
b(nm)	1.8757	1.824	1.897	1.938
γ(°)	90.0	88.9	90.0	89.9
$ab\sin\gamma$	2.099	2.074	2.641	2.659

FIGURE 4 shows a high-resolution STM image of the TMBTQBT monolayer on graphite. In the image, the positions of bright contrast are found to fit with the positions of the sulfur atoms in the molecule.

The TMBTQBT monolayer on the (0001) graphite is concluded to show point-on-line coincidence like BTQBT, but not to have a strong S ···S interaction or bond between neighboring molecules like BTQBT.

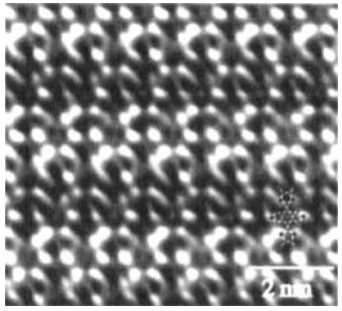

FIGURE 4 High-resolution STM image of the TMBTQBT monolayer.

References

[1] Y. Yamashita, S. Tanaka, K. Imaeda, H. Inokuchi, and M. Sano, *J. Org.Chem.*, **57,** 5517 (1992).

[2] A. Hoshino, S. Isoda, H. Kurata and T. Kobayashi, *J. Appl. Phys.*, **76,** 4113 (1994); *J. Cryst. Growth,* **146,** 636 (1995); *Jpn. J. Appl. Phys.*, **34,** 3858 (1995); S. Irie, A. Hoshino, K. Kuwamoto, S. Isoda, M. J. Miles and T. Kobayashi, *Appl. Surf. Sci.*, **133/114,** 310 (1997).

[3] A. Hoshino, Doctor Thesis, Kyoto Univ., (1997).