J|A|C|S
COMMUNICATIONS

Molecular Geometry Directed Kagomé and Honeycomb Networks: Toward Two-Dimensional Crystal Engineering

Shuhei Furukawa,[†] Hiroshi Uji-i,*,[†] Kazukuni Tahara,[‡] Tomoyuki Ichikawa,[‡] Motohiro Sonoda,[‡]
Frans C. De Schryver,[†] Yoshito Tobe,*,[‡] and Steven De Feyter*,[†]

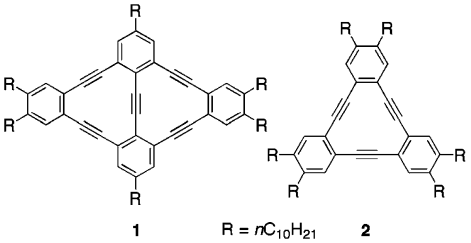
Department of Chemistry, Katholieke Universiteit Leuven (K.U.Leuven), Celestijnenlaan 200-F,
B-3001 Leuven, Belgium, Division of Frontier Materials Science, Graduate School of Engineering Science,
Osaka University, and CREST, Japan Science and Technology Agency (JST), Toyonaka, Osaka 560-8531, Japan

Received December 8, 2005; E-mail: hiroshi.ujii@chem.kuleuven.be; tobe@chem.es.osaka-u.ac.jp; steven.defeyter@chem.kuleuven.be

Recent progress in three-dimensional (3D) solid-state crystal engineering has led to numerous examples of infinite molecular networks with specific topologies by controlling the spatial arrangement of molecules.[1] The dimensionality of the molecular network depends on the number of noncovalent intermolecular interactions and the geometry of each building block.[2] Two-dimensional (2D) periodic monolayers, known as 2D crystals, formed by physisorption on an atomically flat conductive surface, can be investigated with the aid of scanning tunneling microscopy (STM).[3] Reducing the dimensionality (from 3D to 2D) simplifies the design of molecular networks on surfaces if the noncovalent intermolecular interactions and molecule−substrate interaction are understood and controlled.[4] Though 2D molecular networks containing voids provide interesting host−guest chemistry opportunities,[5] only a few examples of such networks have been reported, for instance those based on trimesic acid[6] and triphenylene[7] scaffolds.

Among a variety of 2D networks, a Kagomé lattice is the most intriguing one because of its relevance in the field of spin-frustrated magnetic materials.[8] However, molecular Kagomé lattices are very rare. In the 3D crystals, there are only a few examples.[9] "Engineering" concepts for their formation are lacking thus far, and therefore, it is essential to correlate molecular geometry and network symmetry. Here, we report on the 2D crystal structure of two dehydrobenzo[12]annulene (DBA) derivatives[10] (Chart 1) which form specific topologies at the liquid (1,2,4-trichlorobenzene (TCB))/solid (highly oriented pyrolytic graphite (HOPG)) interface: a Kagomé lattice for **1** and a honeycomb structure for **2**. This is the first example, to our knowledge, of the formation of a Kagomé network in a 2D crystal.

Chart 1. Molecular Structures of **1** and **2**



In general, essential elements that control the topology of a 2D network are the molecular shape and functionalization, with respect not only to the intermolecular interactions but also to the molecule−substrate interactions. The DBA derivatives contain π-conjugated cores, one of which is rhombic for **1** and the other of which is triangular for **2**, substituted with alkyl chains. Actually, the rhombic shape of **1** can be considered as being composed of two regular triangles of **2** fused on one side. The alkyl chains on the rim of the DBA cores spread out radially; they play a significant role in the physisorption as well as in the topological control of the network by chain−chain interdigitation and directional correlation with the symmetry axes of HOPG. In contrast to previous reports on network formation, these molecules do not contain functional groups known to lead to noncovalent directional interactions such as hydrogen-bonding.

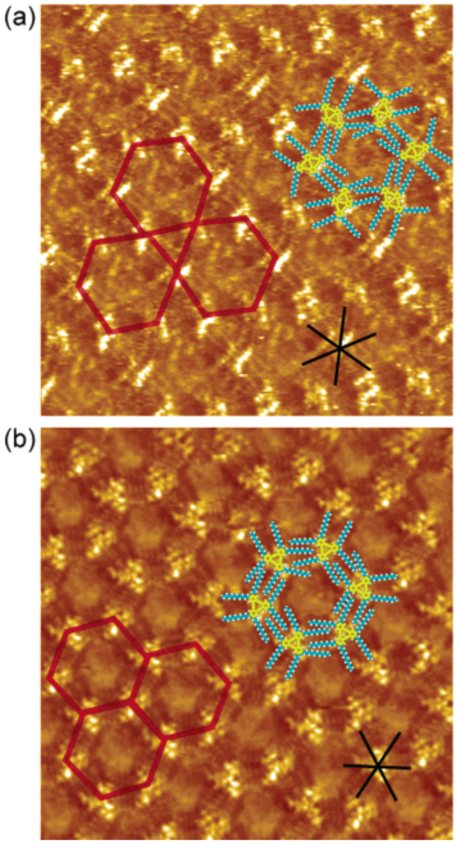


Figure 1. (a) STM image of monolayer of **1**. $I_{set} = 0.5$ nA. $V_{bias} = -1.04$ V. Scan area is 20.0×20.0 nm^2. (b) STM image of a monolayer of **2**. $I_{set} = 0.5$ nA. $V_{bias} = -0.99$ V. Scan area is 18.7×18.7 nm^2. Tentative packing models of **1** and **2** are superimposed in (a) and (b), respectively. The red lines highlight the network symmetry, which is Kagomé type for **1** and honeycomb type for **2**. The black axes indicate the main symmetric axes of HOPG underneath the molecular monolayers.

A typical STM image of a monolayer of **1** physisorbed on HOPG from TCB (Figure 1a) shows a Kagomé lattice pattern in which the bright feature located on each lattice point can be recognized

---

[†] K.U.Leuven.
[‡] Osaka University.

10.1021/ja0583362 CCC: $33.50 © 2006 American Chemical Society

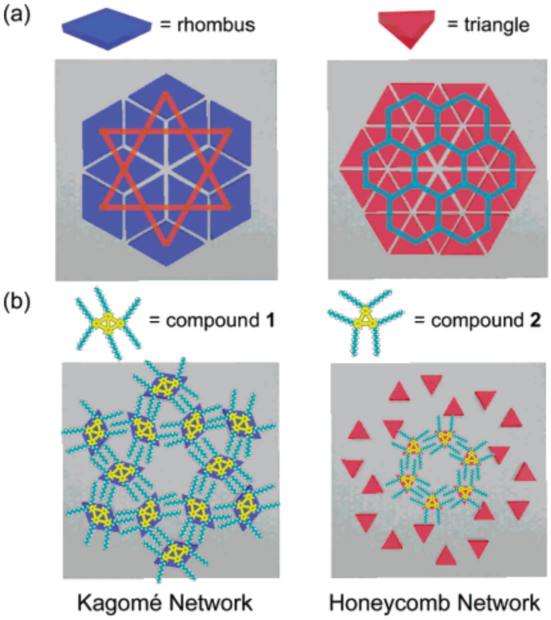


Figure 2. (a) Schematic representation of the dense packing of *ideal* rhombic plates (left) and triangular plates (right) on a surface. Connecting the gravity centers of adjacent plate (shown as lines) gives rise to the formation of the Kagomé network in case of rhombi and the honeycomb network in case of triangles. (b) Schematic representation of networks of **1** (left) and **2** (right).

as a DBA core. Even its rhombic shape is clearly observed. This network is interpreted as a hexagonal packing pattern with corner-sharing as indicated with red lines in Figure 1a. Sets of three bright lines between the DBA cores along the sides of the Kagomé structure correspond to interdigitated alkyl chains. A tentative packing model based upon the orientation of the rhombic DBA cores is superimposed in Figure 1a. In the hexagonal cavities, spots were observed, which might suggest the coadsorption of TCB[11] or **1** (see Supporting Information).

On the other hand, compound **2** forms a honeycomb network as shown in Figure 1b. This network can be considered as a side-sharing hexagonal packing. In this image the triangular shape of the DBA core can clearly be recognized. A tentative packing model is superimposed in Figure 1b. The DBA cores are linked by interdigitating alkyl chains.

A Kagomé network and a honeycomb network consist of four-connected nodes and three-connected nodes at specific angles, respectively. Figure 2a shows the dense packing patterns of *ideal* rhombic and triangular models. Interestingly, linking the gravity center of adjacent rhombi results in the formation of the Kagomé pattern, whereas in case of triangles this gives rise to a honeycomb pattern.[12] Note that the orientation of these *ideal* models corresponds very well to the orientation of the DBA cores of **1** and **2** in the STM images and models shown in Figures 1 and 2b, even though the surface area occupied by each molecule containing six alkyl chains has not such an intrinsic rhombic and triangular shape.

Ideal rhombi and triangles share all sides with their neighbors. We also observed this for the networks formed by alkylated molecules in this report. It should be stressed that, for alkylated systems with a rhombic or triangular core, the core shape itself is not the only responsible element in defining the formation of respectively a Kagomé or honeycomb type network, as suggested by the symmetry arguments of the models in Figure 2a. Thanks to the fact that the alkyl chains run nearly perpendicular to the sides of the core, in combination with their interdigitation, each core is translated, obeying the symmetry aspects of the respective networks. The direction of the alkyl chains is determined by two factors: the position of alkylation, and their preferential orientation along the three C_3 axes of HOPG. Indeed, the graphite symmetry perfectly matches the symmetry elements of the respective networks; the C_3 symmetry points are located on the center of the triangle lattice in the Kagomé network and on the lattice point in the honeycomb network.

In conclusion, we present here the first example of a molecular Kagomé network within a 2D crystal on a surface. Key elements to control molecular network formation are core symmetry, location and orientation of interacting and connecting substituents, and symmetry matching between the networks and the surface. This knowledge opens up the way to accurately control molecular networks regarded as “2D crystal engineering”.

Acknowledgment. We thank the Federal Science policy through IUAP-V-03, the Institute for the promotion of innovation by Science and Technology in Flanders (IWT), and the Fund for Scientific Research-Flanders (FWO). S.F. and K.T. are grateful for a JSPS Research Fellowship for Young Scientists. S.F. also expresses his gratitude to Prof. S. Kitagawa for his continual scientific support.

Supporting Information Available: Experimental details, an STM image and a tentative model of TCB molecules inside the cavities of **1**, and schematic representation of packing patterns of an *ideal* rhombus. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (b) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.
(2) Hosseini, M. W. *CrystEngComm* **2004**, *6*, 318.
(3) (a) Rabe, J.; Buchholz, S. *Science* **1991**, *253*, 424. (b) Cyr, D. M.; Venkataraman, B.; Flynn, G. W. *Chem. Mater.* **1996**, *8*, 1600. (c) Samori, P. *J. Mater. Chem.* **2004**, *14*, 1353.
(4) (a) De Feyter, S.; De Schryver, F. C. *Chem. Soc. Rev.* **2003**, *32*, 139. (b) Otero, R.; Schock, M.; Molina, L. M.; Laegsgaard, E.; Stensgaard, I.; Hammer, B.; Besenbacher, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 2270. (c) Tao, F.; Bernasek, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 12750. (d) Saettel, N.; Katsonis, N.; Marchenko, A.; Teulade-Fichou, M.-P.; Fichou, D. *J. Mater. Chem.* **2005**, *15*, 3175. (e) Gyarfas, B. J.; Wiggins, B.; Zosel, M.; Hipps, K. W. *Langmuir* **2005**, *21*, 919. (f) Uji-i, H.; Yoshidome, M.; Hobley, J.; Hatanaka, K.; Fukumura, H. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4231. (g) Mena-Osteritz, E.; Bäuerle, P. *Adv. Mater.* **2001**, *13*, 243.
(5) (a) Theobald, J. A.; Oxtoby, N. S.; Phillips, M. A.; Champness, N. R.; Beton, P. H. *Nature* **2003**, *424*, 1029. (b) Stepanow, S.; Lingenfelder, M.; Dmitriev, A.; Spillmann, H.; Delvigne, E.; Lin, N.; Deng, X.; Cai, C.; Barth, J. V.; Kern, K. *Nat. Mater.* **2004**, *3*, 229. (c) Bonifazi, D.; Spillmann, H.; Kiebele, A.; de Wild, M.; Seiler, P.; Cheng, F.; Guntherodt, H.-J.; Jung, T.; Diederich, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 4759.
(6) (a) Ishikawa, Y.; Ohira, A.; Sakata, M.; Hirayama, C.; Kunitake, M. *Chem. Commun.* **2002**, 2652. (b) Su, G. J.; Zhang, H. M.; Wan. L. J.; Bai, C.-L.; Wandlowski, T. *J. Phys. Chem. B* **2004**, *108*, 1931. (c) Lackinger, M.; Griessl, S.; Heckel, W. M.; Hietschold, M.; Flynn, G. W. *Langmuir* **2005**, *21*, 4984.
(7) (a) Charra, F.; Cousty, J. *Phys. Rev. Lett.* **1998**, *80*, 1682. (b) Wu, P.; Zeng, Q.; Xu, S.; Wang, C.; Yin, S.; Bai, C.-L. *ChemPhysChem* **2001**, *12*, 750.
(8) (a) Monauskis, E. *Rev. Mod. Phys.* **1991**, *63*, 1. (b) Nocera, D. G.; Bartlett, B. M.; Grohol, D.; Papoutsakis, D.; Shores, M. P. *Chem.-Eur. J.* **2004**, *10*, 3850. (c) Rao, C. N. R.; Sampathkumaran, E. V.; Nagarajan, R.; Paul, G.; Behera, J. N.; Choudhury, A. *Chem. Mater.* **2004**, *16*, 1441.
(9) (a) Moulton, B.; Lu, J.; Hajndl, R.; Hariharan, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2821. (b) Manson, J. L.; Ressouche, E.; Miller, J. S. *Inorg. Chem.* **2000**, *39*, 1135. (c) Awaga, K.; Okuno, T.; Yamaguchi, A.; Hasegawa, M.; Inabe, T.; Maruyama, Y.; Wada, N. *Phys. Rev. B* **1994**, *49*, 3975. (d) Liu, B.; Li, Y.-Z.; Zheng, L.-M. *Inorg. Chem.* **2005**, *44*, 6921.
(10) Sonoda, M.; Sakai, Y.; Yoshimura, T.; Tobe, Y.; Kamada, K. *Chem. Lett.* **2004**, 972.
(11) Jackel, F.; Ai, M.; Wu, J. S.; Müllen, K.; Rabe, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 14580.
(12) Hauck, J.; Mika, K. *Surf. Rev. Lett.* **2000**, *7*, 37.

JA0583362