ChemComm

Accepted Manuscript

ARTICLE TYPE

Porous molecular networks formed by self-assembly of positively-charged trigonal building blocks at the liquid/solid interfaces

Kazukuni Tahara,[a] **Maria L. Abraham,**[b] **Kosuke Igawa,**[c] **Keisuke Katayama,**[a] **Iris M. Oppel*,**[b] **and Yoshito Tobe*,**[a]

Tris-(2-hydroxybenzylidene)triaminoguanidinium salts having six alkyl chains with proper spacing served as new molecular building blocks for the formation of porous
10 honeycomb networks by van der Waals interaction between interdigitated alkyl chains at the liquid/graphite interfaces.

Two-dimensional (2D) molecular networks formed by the self-assembly of organic molecules on solid surfaces have attracted increasing attention in connection with their promising uses in
15 nanoscale patterning, nanoreactor, molecular electronics and 2D polymer synthesis.[1] Among various 2D molecular networks, porous networks have become a subject of intense interest because surface-confined pores in the network can accommodate guest molecules to form multi-component 2D structures, which
20 are important for construction of complex patterns.[2] Scanning tunneling microscopy (STM) is a powerful tool to investigate these networks at sub-molecular level resolution under ultrahigh vacuum (UHV) conditions[1a] or at a liquid/solid interface.[3]

Among the porous patterns hexagonal honeycomb type
25 molecular networks are most common, because epitaxial effects of the hexagonally symmetric surfaces can be utilized to control the network patterns. In general, for the construction of honeycomb type porous molecular networks, C_3 symmetric molecular building blocks are used and they are connected by
30 directional intermolecular interactions to leave open space between them. Though there are many examples for such networks formed by hydrogen bonding[4] or coordination bonding,[5] only a few molecules are known that form honeycomb type networks via van der Waals interactions.[6,7] The major advantage
35 to utilize the latter interaction is its superior versatility in terms of modification of the pore size and functionality for chirality control and selective binding of guest molecules. We reported that triangle-shaped phenyleneetynylene macrocycles, dehydrobenzo[12]annulenes, substituted with six alkyl or alkoxy
40 groups formed honeycomb networks at the liquid/solid interfaces.[6] The group of Attias and Charra reported the formation of porous honeycomb networks by hexaalkoxy-substituted 1,3,5-tristyrylbenzene derivatives.[7a,b] The key structural feature common in these building blocks is a trigonal-
45 shaped core and three pairs of alkyl chains attached to it, wherein each pair is located at an optimal chain-chain spacing (ca. 1 nm) for van der Waals interaction with a pair of alkyl chains of an adjacent molecule, forming a noncovalent linkage by the

interdigitated alkyl chains.[6–8] Another example reported
50 thereafter also meets the above structural criteria of the building block for honeycomb network formation.[9] However, in the previous examples, the trigonal cores of the building blocks consist of nonpolar hydrocarbons.[6] To endow additional functions to porous molecular networks of this type, the exploration of new
55 molecular building blocks is strongly desired. In this respect, porous molecular networks containing polar or charged trigonal cores are intriguing targets, because such networks would possess binding sites that may serve to host ions or molecules[10] and platform freestanding functional groups on surfaces[11] in addition
60 to pores with guest entrapping ability.[2,6,7]

In this context, we herein delineate the construction of the honeycomb type porous molecular network formed from building blocks consisting of a positively charged trigonal core and six alkyl chains attached with proper spacing. For this purpose, we
65 synthesised C_3 symmetric *tris*-(3,5-didecyl-2-hydroxy-benzylidene)triaminoguanidinium salts as molecular building blocks (Fig. 1a) and investigated their self-assembling behaviours at the liquid/graphite interfaces by means of STM. These salts were chosen as their central core unit consist not only a C_3
70 symmetric shape (**H₆L**) but also potential coordination pockets, which are accessible after deprotonation. The construction of a variety of coordination compounds due to a synthetic versatility in functionalization at the peripheral aryl group is a major feature of this compounds.[12] These molecules formed porous honeycomb
75 structures stabilized by van der Waals interactions between interdigitated alkyl chains with adjacent molecules. Moreover, versatility in selection of a counter anion was established by the formation of the identical networks irrespective of the counter anions employed.
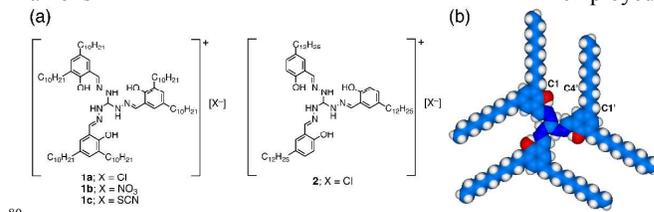

Fig. 1. (a) Chemical structures of *tris*-(3,5-didecyl-2-hydroxybenzylidene)triaminoguanidinium salts, **1a** (X = Cl), **1b** (X = NO₃), and **1c** (X = SCN) and *tris*-(5-dodecyl-2-hydroxy-benzylidene)triaminoguanidinium chloride **2**. (b) Optimised geometry of
85 cation **1⁺** at the B3LYP/6-31g(d) level of theory under vacuum.

The central core of H_6L can adopt four isomeric forms (denoted as *sss*-, *ssa*-, *saa*-, and *aaa*-isomers) in consequence of *syn*- or *anti*- conformation of the three phenyl groups with respect to the C=N-imine units. Intramolecular hydrogen bonding between the imine and hydroxy group stabilizes *syn*-conformation, while intermolecular hydrogen bonds are formed to adjacent electronegative atoms retaining *anti*-conformation. Therefore, H_6L cation is expected to adopt the *sss*-conformation in a non-polar environment.[13] To locate three pairs of alkyl chains at optimal positions for intermolecular van der Waals interaction, we designed *tris*-(3,5-didecyl-2-hydroxybenzylidene)triamino-guanidinium salts **1a–c** in which two decyl chains are attached to each aryl group at 3- and 5-positions (Fig. 1a). To confirm if **1a–c** meet the structural criterion (i.e. ca. 1 nm-spacing), the geometry optimisation of cation **1⁺** was performed with C_{3h} symmetric constraint using the B3LYP/6-31g(d) level of theory (Fig. 1b). As a result, C1-C4' interatomic distance was estimated to be 0.87 nm, in accordance with the optimal chain distances. On the basis of this consideration, cation **1⁺** is expected to form a porous honeycomb type molecular network. To compare the network forming properties, *tris*-(5-dodecyl-2-hydroxybenzylidene)-triamino-guanidinium chloride **2** having only one long alkyl chain at each aryl group was also examined.

The condensation reaction of readily prepared 3,5-didecyl-2-hydroxy-benzaldehyde and triaminoguanidinium salts afforded **1a–c** in 41–50% yields (see ESI, Scheme S1). The reference compound **2** was synthesised in 50% yield. The ^1H NMR spectra in non-polar solvents ($CDCl_3$ or 1,1,2,2-tetrachloroethane-d_2) indicate that all compounds adopt C_3 symmetric geometries (see ESI, Figs. S12-14). On the other hand, in THF-d_8 compounds **1** adopt C_1 symmetric geometries with *saa*-conformation at the C=N-imine units (see ESI, Figs. S15-18). This observation supports that the C_3 symmetric geometry is stabilised by intramolecular hydrogen bonds.

Next, STM observations of monolayers formed by self-assembly of **1** or **2** were performed at the liquid/solid interfaces at room temperature. By dropping a 1-phenyloctane (PO) solution of **1a** at concentration of 1.2×10^{-5} M onto a graphite surface, the formation of two different networks, a porous honeycomb and non-porous linear networks, were observed (see ESI, Fig. S1). Fig. 2a displays an STM image of the monolayer formed by **1a**, where the bright trefoil features correspond to the central π-core and the darker parts are composed out of four interdigitated alkyl chains,[14,15] revealing the formation of a honeycomb structure. The orientations of the four interdigitated alkyl chains are parallel to the main symmetry axes of the underlying graphite surface. Unit cell parameters are a = b = 4.1 ± 0.1 nm, γ = 60 ± 2°. From these parameters and the appearance in the image, a tentative network model was constructed as shown in Fig. 2b. The molecular core adopts the *sss*-conformation. Note that there is small open space between the point end of alkyl chains and the central core (yellow circle in Fig. 2b) probably due to steric repulsion between the methyl group and the hydroxy oxygen atom.

A high resolution image of the linear structure is shown in Fig. 2c. In the image, the bright bow-tie features correspond to two adjacent molecular cores of **1a** and the darker parts are composed of at least four interdigitated alkyl chains. Unit cell parameters are a = 2.5 ± 0.1 nm, b = 3.9 ± 0.1 nm, γ = 84 ± 1°. A tentative

network model is shown in Fig. 2d. The molecular core adopts the *sss*-conformation. Though five alkyl chains including the fifth one adopting an "L" shape are shown in Fig. 2d to fill the open space between **1a**, it is not certain how many of them are indeed adsorbed on the surface, because they are not visualised. If only four alkyl chains are adsorbed on the surface, with the remaining two exposed in solution, the open space must be filled with solvent molecules.
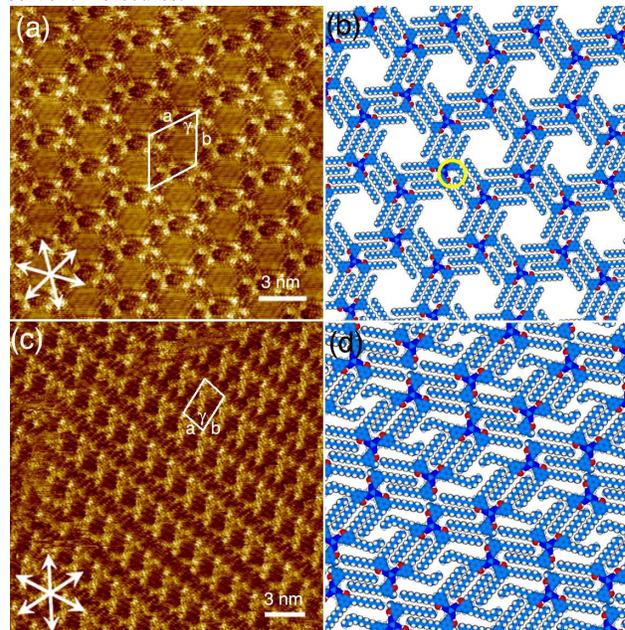

Fig. 2. (a, b) An STM image and a network model of the porous structure of **1a** formed at the PO/graphite interface (concentration; 3.0×10^{-6} M, tunneling parameters; I_{set} = 0.20 nA and V_{set} = –0.39 V). The yellow circle highlight the space between the point end of the alkyl chain and the π-core. (c, d) An STM image and a network model of the non-porous structure of **1a** formed at the PO/graphite interface (1.0×10^{-4} M, I_{set} = 0.20 nA and V_{set} = –0.39 V). In model (d), one alkyl chains per molecule is omitted for clarity. White arrows in (a) and (c) indicate the directions of main symmetry axes of underlying graphite.

It is well known that solvent[16] and solute concentration[17] play significant roles in network patterns. Indeed, the molecular network of **1a** showed a distinct concentration dependency (see ESI, Fig. S1). At the concentration of 3.0×10^{-6} M exclusive formation of the porous pattern was observed, whereas at 1.0×10^{-4} M the surface was covered only with the non-porous pattern. This phase behaviour is consistent with that of the networks formed by alkoxy-substituted triangle π-conjugated molecules.[17c,d] On the other hand, only the porous pattern was observed over a wide concentration range at the 1,2,4-trichlorobenzene (TCB)/graphite interface (see ESI, Fig. S2) presumably due to the stabilizing effect for porous patterns by solvent co-adsorption.[6a,18]

In contrast to **1a**, compound **2** formed only a non-porous pattern even at the lowest concentration (1.8×10^{-6} M) in PO (Fig. 3a and S3). In this case, all three alkyl chains per molecule are adsorbed on the surface. Unit cell parameters are a = 2.8 ± 0.1 nm, b = 3.1 ± 0.2 nm, γ = 60 ± 4°. A tentative network model is shown in Fig. 3b. Note that the molecular core adopts the *ssa*-conformation. To build a close-packed molecular network, the intermolecular van der Waals interactions must have prevailed

over the intramolecular hydrogen bonding interactions. The formation of the non-porous network pattern from **2** supports the criterion of our molecular design.
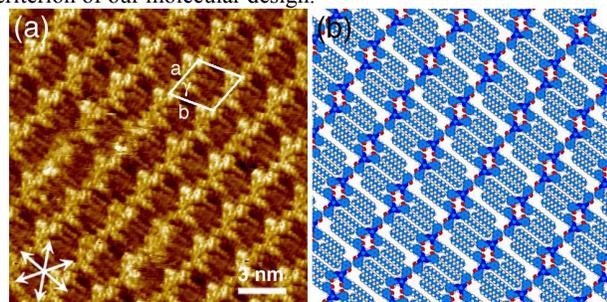

Fig. 3. (a, b) An STM image and a network model of the non-porous structure of **2** at the PO/graphite interface (1.8×10^{-5} M, I_{set} = 0.21 nA and V_{set} = −0.31 V). White arrows in (a) indicate the directions of main symmetry axes of underlying graphite.

Similar to **1a**, compounds **1b** and **1c** formed the porous patterns at the PO/graphite interface (3.0×10^{-6} M, Figs. S4, and S5), revealing that the counter anion does not influence the self-assembling behaviour of these molecules. In all cases, however, the counter anions were not visualised in the image, presumably because of their dynamic behaviour in the liquid phase or low tunneling efficiency of them.[19]

In summary, we have shown that *tris*-(2-hydroxy-benzylidene)triaminoguanidinium salts having six alkyl chains with proper spacing served as new molecular building blocks for the formation of porous networks by van der Waals interactions at the liquid/graphite interfaces. The counter anions did not influence the self-assembling behaviour, forming the identical honeycomb networks. Given the co-adsorption capability for nonpolar guest molecules at the pores of the honeycomb networks,[2,6,7] the present molecular networks would serve as templates for complex 2D patterns formed by multiple interactions. Additionally, since **H₆L** salts are known to form transition metal complexes,[12b,20] construction of 2D metal arrays which may serve as tailor made catalysts would become possible.

Notes and references

a Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan. Tel: +81-(0)6-6850-6225; E-mail: tobe@chem.es.osaka-u.ac.jp
b Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany. Tel: +49-(0)241 8094649; E-mail: iris.oppel@ac.rwth-aachen.de
c Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan.

† Electronic Supplementary Information (ESI) available: [Experimental details, STM images, detail of theoretical simulations, synthesis]. See DOI: 10.1039/b000000x/

1 (*a*) J. V. Barth, *Annu. Rev. Phys. Chem.*, **2007**, *58*, 375–407; (*b*) J. A. A. W. Elemans, L. Shengbin and S. De Feyter, *Angew. Chem. Int. Ed.*, **2009**, *48,* 7298–7332.

2 D. Bonifazi, S. Mohnani and A. Llanes-Pallas, *Chem. Eur. J.,* **2009**, *15*, 7004–7025.

3 J. P. Rabe and S. Buchholz, *Science*, **1991**, *253*, 424–427.

4 (*a*) J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness and P. H. Beton, *Nature*, **2003**, *424*, 1029–1031; (*b*) M. Lackinger and W. M. Heckl, *Langmuir*, **2009**, *25*, 11307–11321; (*c*) Y.-T. Shen, M. Li, Y.-Y. Guo, K. Deng, Q.-D. Zeng and C. Wang, *Chem. Asian. J.*, **2010**, *5*, 787–790.

5 (*a*) S. Stepanow, M. Lingenfelder, A. Dmitreiev, H. Spillmann, E. Delvigne, N. Lin, X. Deng, C. Cai, J. V. Barth and K. Kern, *Nat. Mater.*, **2004**, *3*, 229–233; (*b*) D. Kühne, F. Klappenberger, R. Decker, U. Schlickum, H. Brune, S. Klyatskaya, M. Ruben and J. V. Barth, *J. Am. Chem. Soc.*, **2009**, *131*, 3881–3883.

6 (*a*) K. Tahara, S. Furukawa, H. Uji-i, T. Uchino, T. Ichikawa, J. Zhang, W. Mamdouh, M. Sonoda, F. C. De Schryver, S. De Feyter and Y. Tobe, *J. Am. Chem. Soc.*, **2006**, *128*, 16613–16625; (*b*) K. Tahara, S. Lei, J. Adisoejoso, S. De Feyter and Y. Tobe, *Chem. Commun.*, **2010**, *46*, 8507–8525.

7 (*a*) G. Schull, L. Douillard, C. Fiorini-Debuisschert, F. Charra, F. Mathevet, D. Kreher and A.-J. Attias, *Nano Lett.*, **2006**, *6*, 1360–1363; (*b*) C. Arrigoni, G. Schull, D. Bléger, L. Douillard, C. Fiorini-Debuisschert, F. Mathevet, D. Kreher, A.-J. Attias and F. Charra, *J. Phys. Chem. Lett.*, **2010**, *1*, 190–194; (*c*) S. Xu, Q. Zeng, J. Lu, C. Wang, L. Wan and C.-L. Bai, *Surf. Sci.*, **2003**, *538*, L451–L459.

8 K. Tahara, C. A. Johnson II, T. Fujita, M. Sonoda, F. C. De Schryver, S. De Feyter, M. M. Haley and Y. Tobe, *Langmuir*, **2007**, *23*, 10190–10197.

9 S.-S. Jester, E. Sigmund and S. Höger, *J. Am .Chem. Soc.,* **2011**, *133*, 11062–11065.

10 T. Chen, G.-B. Pan, H. Wettach, M. Fritzsche, S. Höger, L.-J. Wan, H.-B. Yang, B. H. Northrop and P. J. Stang, *J. Am. Chem. Soc.*, **2010**, *132*, 1328–1333.

11 (*a*) B. Baisch, D. Raffa, U. Jung, O. M. Magnussen, C. Nicolas, J. Lacour, J. Kubitschke and R. Herges, *J. Am. Chem. Soc.*, **2009**, *131*, 442–443; (*b*) Jung, U.; Schütt, C.; Filinova, O.; Kubitschke, J.; Herges, R. and Magnussen, O. *J. Phys. Chem. C*, **2012**, *116*, 25943–25948.

12 (*a*) F. L. Scott, M. Cashman and J. Reilly, *J. Am. Chem. Soc.*, **1952**, *74*, 5802–5802; (*b*) I. M. Müller and R. Robson, *Angew. Chem. Int. Ed.*, **2000**, *39*, 4357–4359; (*c*) I. M. Müller and D. Möller, *Eur. J. Inorg. Chem.*, **2005**, 257–263.

13 In crystaline state, **H₆L** chloride and *tris*(5-bromo-2-hydroxybenzylidene)triaminoguanidinium chloride adopted *saa*- and *aaa*-conformation, respectively, because of interactions between the chloride anion and hydroxy groups. See refs. 12b and c.

14 R. Lazzaroni, A. Calderone, G. Lambin, J. P. Rabe and J. L. Brédas, *Synth. Met.*, **1991**, *41*, 525–528.

15 Orbital distributions of HOMO and HOMO–1 of **1⁺** are located at the peripheral three aryl units (see ESI, Fig. S6).

16 Y. Yang and C. Wang, *Curr. Opin. Colloid & Interface Sci.,* **2009**, *14*, 135–147.

17 (*a*) L. Kampschulte, T. L. Werblowsky, R. S. K. Kishore, M. Schmittel, W. M. Heckl and M. Lackinger, *J. Am. Chem. Soc.*, **2008**, *130*, 8502–8507; (*b*) C.-A. Palma, J. Bjork, M. Bonini, M. S. Dyer, A. Llanes-Pallas, D. Bonifazi, M. Persson and P. Samorì, *J. Am. Chem. Soc.*, **2009**, *131*, 13062–13071; (*c*) S. Lei, K. Tahara, F. C. De Schryver, M. Van der Auweraer, Y. Tobe and S. De Feyter, *Angew. Chem. Int. Ed.*, **2008**, *47*, 2964–2968; (*d*) A. Bellec, C. Arrigoni, G. Schull, L. Douillard and C. Fiorini-Debuisschert, *J. Chem. Phys.,* **2011**, *134*, 124702.

18 M. O. Blunt, J. Adisoejoso, K. Tahara, K. Katayama, M. Van der Auweraer, Y. Tobe and S. De Feyter, *J. Am. Chem. Soc.*, **2013**, *135*, 12068–12075.

19 (*a*) S. Takahashi, A. Aramata, M. Nakamura, K. Hasebe, M. Taniguchi, S. Taguchi and A. Yamagishi, *Surf. Sci.,* **2002**, *512*, 37–47; (*b*) Y. Xiao, G.-B. Pan and W. Freyland, *Chem. Phys. Lett.,* **2009**, *481*, 91–93.

20 I. M. Oppel (née Müller) and K. Föcker, *Angew. Chem. Int. Ed.*, **2008**, *47*, 402–405.