Formation of a Non-Crystalline Bimolecular Porous Network at a Liquid/Solid Interface

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1. Details of STM Investigations

All STM investigations except for temperature control experiment were performed at 22–26 °C using a Nanoscope IIIa (Digital Instruments Inc.) with an external pulse/function generator (model Agilent 33220A) and PicoSTM (Agilent) with negative sample bias. All STM images were acquired in the constant current mode. Tips were mechanically cut from Pt/Ir wire (80%/20%, diameter 0.20 or 0.25 mm).

Prior to imaging, a compound under investigation was dissolved in commercially available 1,2,4-trichlorobenzene (Aldrich) or 1-phenyloctane (TCI) at ca. 5 × 10⁻⁶ M, the solutions of DBA and bisDBA were mixed 1 to 1 volumetric ratio, and a drop of this solution was applied on a freshly cleaved surface of HOPG (grade ZYB, Momentive Performance Material Quartz Inc., Strongsville, OH or Advanced Ceramics Inc., Cleveland, USA). The STM investigations were then performed at the liquid/solid interface. By changing the tunneling parameters during the STM imaging, namely, the voltage applied to the substrate and the average tunneling current, it was possible to switch from the visualization of the adsorbate layer to that of the underlying HOPG substrate. This enabled us to correct for drift effects by the use of SPIP software (Image Metrology A/S).
2. A Large Area STM Image of Monolayer Formed from a Mixture of DBA 1 and BisDBA 2 at the TCB/Graphite Interface

**Fig. S1** An STM image (a) and a model (b) of a self-assembled monolayer formed by DBA 1 and bisDBA 2 at the TCB/graphite interface (concentrations: $2.5 \times 10^{-6}$ M for 1 and $2.3 \times 10^{-6}$ M for 2 and tunneling parameters: $I_{set} = 0.05$ nA; $V_{set} = -0.26$ V).

**Fig. S2** (a) An STM image of a self-assembled monolayer formed by 1 and 2 at the TCB/graphite interface (conditions: same as Fig. S1). White line corresponds a domain boundary. (b) Model of the monolayer of the top right side of the STM image.
3. Self-Assembled Monolayers of DBA 1 and BisDBA 2 at the 1-Phenyloctane/Graphite Interface.

Figs. S3 and S4 summarize the observed structures and their tentative molecular models formed from each molecular component. As reported previously,\textsuperscript{1} DBA 1 forms both the porous honeycomb and a non-porous linear A structures at higher concentration (ca. $10^{-4}$ M). We proved here that even at much lower concentrations ($3.0 \times 10^{-6}$ M), both structures (52 ± 10% and 48 ± 10% for the honeycomb and the linear A structures) were observed too (Fig. S3). In the case of bisDBA 2, three structures, the porous Kagomé and linear B structures, and non-porous linear structure (linear C structure), were observed at the 1-phenyloctane/graphite interface ($3.0 \times 10^{-6}$ M, Fig. S4). The coverage of the Kagomé, linear B, and linear C structures is 76 ± 14%, 18 ± 8%, and 6 ± 8%, respectively.

![Fig. S3](image)

**Fig. S3** (a, b) An STM image and the tentative network model of the honeycomb structure of DBA 1 ($I_{set} = 0.26$ nA; $V_{set} = -0.16$ V). (c, d) An STM image and the tentative network model of the linear A structure of DBA 1 ($I_{set} = 0.23$ nA; $V_{set} = -0.18$ V). The solvent molecules (1-phenyloctane) are colored in purple.
Fig. S4  (a, b) An STM image ($I_{set} = 0.25$ nA; $V_{set} = -0.17$ V) and the tentative network model of the Kagomé structure of bisDBA 2. (c, d) An STM image ($I_{set} = 0.25$ nA; $V_{set} = -0.15$ V) and the tentative network model of the rhombic B structure of bisDBA 2. (e, f) An STM image ($I_{set} = 0.28$ nA; $V_{set} = -0.16$ V) and the tentative network model of the linear C structure of bisDBA 2. In the image, the rhombic B domains are co-existed. Two alkyl chains of 2 orientating to the solution phase are omitted for clarity.
4. Monolayer Formed from a Mixture of DBA 1 and BisDBA 2 at the 1-Phenyloctane/Graphite Interface

In our experimental conditions, a stable imaging of molecular networks of a mixture of 1 and 2 typically started after 2 h from dropping the 1-phenyloctane solution (1 to 1 molar ratio, total concentration; $5.0 \times 10^{-6}$ M), exhibiting a 2D random pattern accompanying small domains of the pure components. Fig. S5a displays a typical STM image of the self-assembled monolayer formed from a mixture of 1 and 2 at the 1-phenyloctane/graphite interface. A tentative network model based on the image is shown in Fig. S5b. The hexagonal structure of 1, the trimer and hexamer of 2, the hexagonal structures formed by 1 and 2, and the rhombic structure with alternatingly aligned 1 and 2 were observed (Fig. S6). The structural differences between the monolayers formed in TCB and 1-phenyloctane are the formation of small domains of the rhombic B structure of 2 due to the inherent tendency of formation of this structure of pure 2 in 1-phenyloctane and less abundance of the large pores. In addition, there are fuzzy or ill ordered areas in the image (ca. 10%). The ratio of the number of adsorbed molecules of 1 and 2 is close to 1 to 1 (48 ± 4% and 52 ± 4%, respectively). The probability of homo-molecular (1-1 and 2-2) pairs and hetero-molecular (1-2) pairs in ca. 1500 intermolecular connections are 17 ± 5% for the 1-1 pair, 38 ± 7% for the 2-2 pair, and 45 ± 3% for the 1-2 pair, respectively. These values qualitatively match those from MC simulations.
Fig. 5 (a) An STM image of a self-assembled monolayer formed by a mixture of DBA 1 and bisDBA 2 (molar ratio; 1 to 1 and total concentration; $5.8 \times 10^{-6}$ M and tunneling parameters: $I_{set} = 0.25$ nA; $V_{set} = -0.10$ V). (b) A tentative molecular model corresponding to image (a).

Fig. S6 An large area STM image of a self-assembled monolayer formed by a mixture of DBA 1 and bisDBA 2 at the 1-phenyloctane/graphite interface (molar ratio; 1 to 1, total concentration; $5.8 \times 10^{-6}$ M, and tunneling parameters: $I_{set} = 0.05$ nA; $V_{set} = -0.26$ V). The white box indicates the Kagomé pattern of 2.
5. Estimation of Molecule-Substrate and Intermolecular Interactions.

The molecule-substrate and intermolecular interactions of 1 and 2 were estimated by using the parameters reported previously (Table S1). The carbon atoms of the triple bonds of the DBA core are approximated as sp² carbon atoms, and the methyl groups are treated as methylene units, respectively. Following values are employed for the estimations of molecule-substrate as well as intermolecular interactions.

**Molecule-graphite interactions.**

Aromatic parts: \(-61 \pm 5\) meV/(sp² carbon)

Alkyl chains: \(-64.2\) meV/CH₂

**Intermolecular interactions.**

\(-49.2\) meV/CH₂ if flanked at both sides by the alkyl chains

\(-22\) meV/CH₂ if only flanked by another alkyl chain at one side.

**Table S1.** Estimated molecule-substrate and intermolecular interactions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Networks</th>
<th>Molecule-substrate interaction (eV)</th>
<th>Intermolecular interaction (eV)</th>
<th>Sum of molecule-substrate and intermolecular interactions (eV)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>Honeycomb</td>
<td>(-5.316)</td>
<td>(-2.136)</td>
<td>(-7.452)</td>
</tr>
<tr>
<td>2</td>
<td>Kagomé</td>
<td>(-5.926)</td>
<td>(-1.864)</td>
<td>(-7.790)</td>
</tr>
</tbody>
</table>
6. Details of the MC Simulations

In order to simulate the self-assembly of DBA and bisDBA on graphite, we employed their simplified structural models. To that purpose, a molecule of DBA was modeled as a rigid planar tripod consisting of a central segment (core) and three arms with two segments. Similarly, a molecule of bisDBA was represented by a tetrapod consisting of a central two segment (core) and four arms with two segments (Fig. S7). In the simulations, we assumed that both molecules are built of identical segments, so that the segment-segment interaction energy was characterized by one parameter $\varepsilon$, common for each type of interaction (1-1, 2-2 and 1-2). The segment-segment interaction energy in our model was expressed in $kT$ units. According to the convention adopted here positive values of $\varepsilon$ correspond to the intermolecular attraction.

Fig. S7  Schematic representation of the models of DBA and bisDBA used in the MC simulations. DBA 1 is represented by the tripod structure consisting of 7 identical segments shown in left. The right shows the tetrapod structure corresponding the model of a molecule of bisDBA 2 with 10 identical segments.

To study the pattern formation in both one- and two-component systems, we employed the conventional Canonical Ensemble Monte Carlo method with Metropolis sampling. The simulations were performed on a triangular $L\times L$ lattice of equivalent adsorption sites using periodic boundary conditions in both directions. It was assumed that molecules of DBA and bisDBA adsorb parallel to the
surface, so that a single segment occupies one vertex of the lattice (adsorption site). The energy of interaction between a molecular segment and the surface was assumed to be equal to zero. The adsorbed molecules were allowed to interact via a short ranged segment-segment interaction potential limited to nearest-neighbors on a triangular lattice. All of the simulations described in this work, including those for one- and two-component systems were performed for $\varepsilon = 1$.

### 6–1. Adlayer of Tetrapod Model

Results of the MC simulations for the tripod molecules were reported in our previous work. The simulations of both pure adlayers comprising molecules of bisDBA and bicomponent adlayers of the DBA and bisDBA (mixing ratio is 1 to 1) were performed using 2000 molecules. In the case of one-component system, the simulations were carried out on a lattice with $L = 200$. To keep constant segment density in one- and two-component systems, a smaller lattice with $L = 184$ was employed for the latter case. The resulting segment density, which is defined as a fraction of occupied lattice sites, was equal to 0.35 for both systems. To equilibrate the systems, we run $10^9$ MC steps where one MC step is defined as a single attempt to rotate and move each adsorbed molecule to a next position.

First, the possible 2D patterns formed by the model molecules of bisDBA (tetrapod) on a triangular grid was performed. To avoid trapping of the system in metastable states, the annealing method in which the adlayer was initially equilibrated at $T = 6.0$ and next slowly cooled down to $T = 1.0$ was employed. The annealing run consisted of initial $10^8$ MC steps at $T = 6.0$ followed by the cooling procedure in which we used $8 \times 10^8$ MC steps assuming linear temperature gradient ($1.25 \times 10^{-5}$ per one MC step). The final $10^8$ MC steps aimed at equilibration of the adlayer at the target temperature $T = 1.0$. During the simulation the average acceptance ratio of movements was not exceeding 6% and the acceptance of insertion (movements not rejected due to steric overlap) was up to 40%. Fig. S8 displays two snapshots of the ordered superstructures obtained from the simulations. The tetrapod model spontaneously self-organizes into the porous Kagomé structure (Fig. S8, left) as well as into the linear type packing (Fig. S8, right) both observed experimentally. Note that the difference in the conditions for the formation of these superstructures is the initial (random) configuration of the adsorbed molecules. In the linear type
packing, there are two structures. For better understanding, the snapshot with the coexistence of these patterns is shown in the right part of Fig. S8. The difference between these structures is the number of contacts between the core of tetrapod model and neighboring arm segments (two vs. four). We call the pattern with four core-arm interactions linear and the other linear U (two core-arm interactions), respectively. Note that the possible 2D molecular structures obtained in the simulations agree with the STM observations. Moreover, these results are obtained by MC annealing, and therefore both these structures are not kinetically trapped.

**Fig. S8**  Snapshots of the ordered patterns formed by 2000 tetrapod molecules adsorbed on a 200 × 200 triangular lattice, $\varepsilon = 1.0$. The results shown in the left part correspond to the target temperature of the MC annealing, $T = 1.0$. The structure presented in the right part was obtained at a somewhat higher temperature $T' = 1.5$. At this temperature, both linear and linear U domains can be clearly distinguished.
Fig. S9  Changes in the potential energy of the adsorbed phase which comprises the equimolar mixture of each 1000 molecules of DBA and bisDBA on a 184 by 184 lattice by annealing. The solid lines (black, blue and red) correspond to three independent Monte Carlo runs. The green dashed line shows the temperature program used in the annealing.

6–2. Adlayer of a Mixture of Tetrapod and Trigonal Models

To simulate the co-assembly of DBA and bisDBA we assumed that molecules of both species consist of identical segments, for which the interaction parameter $\varepsilon$ is equal to 1.0. To equilibrate the adlayer comprising molecules of DBA and bisDBA, we used the same annealing procedure as for the one component system. The results are shown in Fig. 4 in the main text. Cooling of the bicomponent adlayer to the target temperature $T = 1.0$ results in the formation of a mixed assembly. In all attempts, the development of any ordered structure in the course of the cooling run was not observed.

The number of segment-segment interactions of a given type (tripod-tripod (blue), tetrapod-tetrapod (red), and tripod-tetrapod (black) interactions) divided by the total number of segment-segment interactions is summarized in Fig. S10.
Fig. S10  Changes in the segment-segment interaction (tripod-tripod interaction for blue, tetrapod-tetrapod interaction for red, and tripod-tetrapod interaction for black) fractions during three independent MC simulation runs.

6–3. Fraction Dependent Change of Adlayer of a Mixture of Tetrapod and Trigonal Models

In order to estimate the effect of relative coverage of the tetrapod and trigonal models on the formation of mixed phase, simulations at different mixing ratios were performed. At higher tetrapod model ratio (9:1 and 7:3 in the tetrapod model to tripod model ratios), the formation of small domains of the linear structures of tetrapod models was observed and the trigonal models are located at the domain boundaries (Figs. S11a and b). On the other hand, at higher trigonal model ratio (3:7 and 1:9 ratios), the formation of the honeycomb structure of trigonal models becomes favorable (Figs. S11c and d). The tetrapod models formed small linear domains between the honeycomb domains of the trigonal models.
Fig. S11  Snapshots of the mixed overlayer consisting of the tripod (blue) and tetrapod (gray) molecules obtained in the MC simulations at different mixing ratio, 9:1 in the tetrapod model to trigonal model ratio for (a), 7:3 ratio for (b), 3:7 ratio for (c), and 1:9 ratio for (d).

7. Temperature Control Experiments at the TCB/Graphite Interface.

Temperature control experiments were performed by using a liquid cell equipped with Cu internal heater. Initially observation started at room temperature in TCB, and the formation of randomly mixed phase was observed (Fig. S12a). Upon heating to 70 °C at rate of 10 °C/min, the exclusive formation of the Kagomé structure of 2 was observed (Fig. S12b). The domain size becomes very large. Upon slow cooling at a rate of 0.5 °C/min to room temperature, whole surface was covered with only the Kagomé structure of 2 (Fig. S12c), indicating that kinetic factors influence the formation of the randomly mixed phase.
**Fig. S12** STM images of a monolayer formed by a mixture of triangular DBA and rhombic bisDBA at the TCB/graphite interface at different temperatures (25 °C for (a), 70 °C for (b), 40 °C for (c), and 25 °C for (d)). Tunneling parameters are $I_{\text{set}} = 0.15$ nA; $V_{\text{set}} = -0.17$ V for (a), $I_{\text{set}} = 0.16$ nA; $V_{\text{set}} = -0.18$ V for (b), $I_{\text{set}} = 0.15$ nA; $V_{\text{set}} = -0.18$ V for (c), and $I_{\text{set}} = 0.15$ nA; $V_{\text{set}} = -0.18$ V for (d).
8. References


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