

# STM Observation of Cooperative Process of 2-D Self-Assembly: Influence of Multidirectional Interactions on Domain Size and Shape

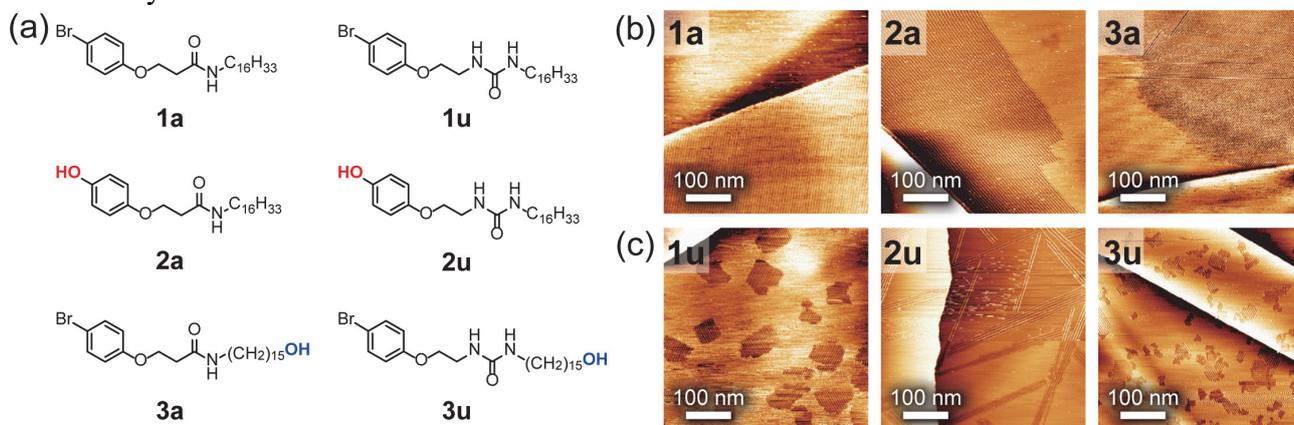
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Self-assembly on two-dimensional (2-D) surface is a powerful approach to construct functionalized surfaces. Intermolecular interactions are key factors to determine the stabilization energy during cooperative self-assembly processes at the liquid/solid interface.<sup>1</sup> We envision that the design of intermolecular interactions will be a rational strategy to fabricate sophisticated 2-D self-assemblies having specific size and shape.

In this work, we investigated the effect of multidirectional interactions on the domain size and shape of 2-D orderings using rod-coil-type compounds **1a–3a** bearing amide group and **1u–3u** bearing urea group (Figure 1a). Hydroxy group was introduced as an additional intermolecular interaction; **2a** and **2u** have hydroxy group at the 4-position of phenyl group, while **3a** and **3u** at the edge of alkyl side chain.

Molecular orderings of **1a–3a** and **1u–3u** were observed by STM at the octanoic acid/graphite interface. We found that amide derivatives tend to form large domains of 2-D orderings, whereas the domain size of corresponding urea derivatives was significantly small in the same condition (Figure 1b and 1c). The quantitative analysis of the concentration dependence of surface coverage using a nucleation–elongation model suggested that the replacement of amide by urea group increased the equilibrium constant of the nucleation process of 2-D self-assembly. The large equilibrium constant for nucleation is likely responsible for the generation of a number of nuclei at the initial steps in the 2-D self-assembly, resulting in the small domain size at the liquid/solid interface. Furthermore, needle-shaped domains were uniquely observed for **2u**, which have a large aspect ratio around 10 (Figure 1c, middle). The anisotropic domain growth was likely attributed to the formation of multidirectional hydrogen bonds via urea groups and hydroxyl groups introduced into the aromatic core moiety.<sup>2</sup>



**Figure 1.** (a) Chemical structures of compounds **1–3**. (b) STM images of the 2-D ordering of amide derivatives (**1a**, left; **2a**, middle; **3a**, right) and (c) those of urea derivatives (**1u**, left; **2u**, middle; **3u**, right) at the octanoic acid/HOPG interface.

[1] N. Nishitani, T. Hirose, K. Matsuda, *Chem. Asian J.* **2015**, *10*, 1926–1931.

[2] N. Nishitani, T. Hirose, K. Matsuda, *Langmuir* **2017**, *33*, 9151–9159.