Porous Self-Assembled Monolayers as Templates for Chiral Chemical Functionalization of Graphite Surface

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Development of a nanopatterned surface functionalization method in molecular level precision is highly desirable in various fields. In this context, we reverntly reported that template-guided one-dimensional (1D) covalent functionalization with only few nanometer wide rows of grafted molecule by stimulating fluctuation of each alkane molecule in a lamella type monolayer.[1] To further control covalent grafting with a variety of pattern symmetries as well as chirality, we present herein that covalently functionalize graphite surfaces with a hexagonal symmetry of grafted molecules in different periodicities using self-assembled porous networks as the templating masks. We chose porous molecular networks formed by **DBAOCn** (Figure 1a) because the hexagonal pore sizes can be tuned simply by varying alkyl chain length and conditions for porous structure formation on graphite are well established.[2] As an aryl radical source, 3,4,5-trimethoxybenzenediazaonium chloride was chosen because the corresponding aryl radical exhibits a very high grafting density to graphite.[3] During electrochemical treatment, a phase separated solution double layer is employed to ensure stable formation of the DBA networks. For example, when the porous strucutre of **DBAOC8** is used as the template, a hexagonal periodicity of the covalently bound molecular units are seen in STM image and its FFT image (Figure 1b). Patterning periodicities of the covalently bound molecular units can be controlled in 2.3, 2.7, and 3.0 nm using the molecular networks with the different pore sizes formed by **DBAOC4**, **DBAOC6**, and **DBAOC8**. Moreover, it should be noted that the chirality of the template DBA networks is successfully transferred to the alignment of covalently attached molecules.

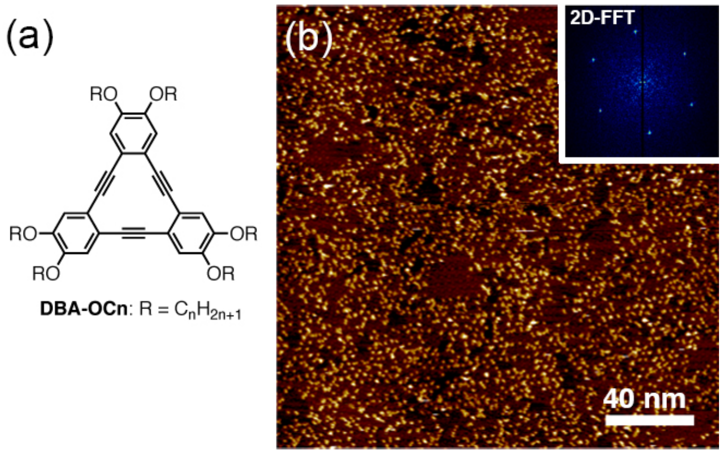

Figure 1: (a) Chemical structures of **DBA-OCn**s. (b) STM image of a functionalized graphite using a **DBA-OC8** honeycomb network as the template. Inset: 2D fast Fourier Transform image with 3.0 nm 2D (hexagonal) periodicity.

References

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