SURFACE COORDINATION SPACE ORGANIZED AT THE MOLECULAR LEVEL
分子レベルで構造が規定された表面配位空間の構築

Joe Otsuki
College of Science and Technology, Nihon University, 1-8-14 Kanda Surugadai, Chiyoda-ku, Tokyo, Japan
E-mail: otsuki@chem.cst.nihon-u.ac.jp

ABSTRACT

Learning how molecules assemble themselves into higher order architecture is important because the knowledge may be utilized in bottom-up construction of molecule-based nanomaterials. Highly oriented pyrolytic graphite (HOPG) offers us a unique opportunity to observe individual molecules self-assembled on the surface by means of scanning tunneling microscopy under ambient conditions.[1] We have investigated a variety of surface patterns formed from metal complexes including porphyrins and octahedral organometallics.

The assembly of porphyrin derivatives is particularly interesting owing to potential roles of porphyrin-based nanoarchitecture in applications of photonic/electronic materials and devices. *meso*-Tetraphenylporphyrins substituted with four alkyl chains via ether linkages adsorb on the surface of HOPG with alkyl chains being interdigitated forming lamella patterns. We found that replacing one or two alkoxy chains by hydrogen bonding sites (i.e., carboxyl groups) results in the formation of new surface patterns owing to hydrogen bonding interactions among surface adsorbed species.[2] We also found that *meso*-tetraphenylporphyrins substituted with alkyl chains each containing a diacetylene unit via an ester linkage exhibited remarkably diverse assembly structures, ranging from usual alkyl-mediated face-on packing to face-to-face stacking of porphyrin macrocycles to a dense packing of porphyrin macrocycle apparently without adsorption of alkyl chains, depending on the length of the alkyl chains and the state of metalation. Kinetically inert coordination to rhodium porphyrins as well as kinetically labile coordination to zinc porphyrins may be utilized to organize the ligand moieties according to the underlying surface pattern of the metal porphyrin complexes (Fig.).[3] Another subclass of the porphyrin family we have investigated is double-decker porphyrin/phthalocyanins. Introducing long alkyl chains into one of the macrocycles results in the formation of ordered array of double decker complexes, which is of interest in terms of molecular scale rotor as a component in molecular machines.[4]

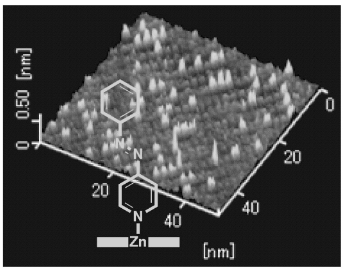

Fig. Surface assembly of an axially coordinated zinc porphyrin derivative.

Another class of typical photo- and electro-active compounds is octahedral d^6-metal complexes. Due to stereochemical complexity, it is usually difficult to prepare ordered arrays of this class of metal complexes on the surface of HOPG. Organometallic iridium phenylpyridine complexes are unique among them in that the facial isomer can be prepared selectively that allow us to introduce alkyl chains in selective positions. We have obtained ordered surface arrays of alkyl-substituted iridium phenylpyridine complexes, which may extend over a few micrometers with a high ordering at the molecular level.[5]

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