Abstract

The development in nanostructural materials has been continuously pursued due to the higher efficiency than that of conventional materials. In recent, the engineering of nanomaterials onto the surface for device applications has been progressively promoted through the concept of coordination chemistry and surface science. In aspect of material performance, not only the molecular components but also molecular ordering and alignment direction play significant impact on it. The strategy to control the architectures is extremely important to achieve the desired properties. Surface-Induced Assembly (SIA) is considered for this achievement. The sequential immobilization between metal ions and organic building units on the surface can promote huge variety of coordination structures with controllable manner. The stepwise growth phenomena using SIA approach differs from the bulk system. The novel structures on surface can be possibly discovered by this method.

In this research, the oriented porphyrin-based multilayer thin films on amine-terminated surface substrates were synthesized using cobalt(II) ions and porphyrin building blocks via SIA approach at room temperature. The multilayer thin films exhibited the stepwise growth with compact packing and homogeneous surface morphology which were characterized by UV-Vis, AFM, IR, and XPS studies. The studies on XRR and GI-SAXS revealed that the mass density of film was almost constant throughout the multilayer formation along with the existence of periodic structure in in-plane (IP) direction. These results indicated a well-organized structure of film growth. The alignment of the porphyrin macrocycle plane in the framework has been proposed as a hexagonal packed model using single-anchor binding with tilting of approximately $60°$ relative to the surface substrate. This result suggested that structural arrangement on the surface can be efficiently controlled by SIA technique. The structure of the synthesized thin film was distinct from the bulk synthesis, which suggests a significant role of the surface and SIA approach for the coordination network formation.

This report of our research provides insight into the ordered porphyrin-based metal-organic coordination network thin films. The design of metal-organic coordination network thin film with controllable growth behavior represents as an important challenge that must be addressed to promote these solid state phenomena for nanoscale device. The interior perspective for the molecular growth behavior is highly necessary to elucidate the growth mechanisms along with the development of material properties for specific applications.