Surface Electron Density Analysis of Organic Semiconductors

Surface relaxation in organic semiconductors should affect the performance of organic devices, but there have been few experimental studies. In order to clarify the general tendency of surface relaxation in organic semiconductors, we performed a systematic investigation of the electron density distribution as a function of depth on a series of organic semiconductor [*n*]phenacenes by using surface X-ray scattering measurements combined with holographic analysis and a first principles calculation. We demonstrated that, unlike the case of tetracene that shows a large relaxation, all the [*n*]phenacenes measured have little surface relaxation.

There has been remarkable recent progress in the development of organic device techniques. Organic electroluminescence displays are widely used for cell phones, and laser devices are also being studied. The application of organic semiconductors to various electronic devices requires higher carrier mobility, environmental stability, and smaller contact resistance. All of them are related to the energy level of molecular orbitals, and the mobility depends on the transfer integrals. Since the transfer integrals in molecular crystals depend on intermolecular distance as well as the relative angle of neighboring molecules, a knowledge of the molecular arrangement is desired to design better organic semiconductors. In many organic devices, the place where the carriers move is the surface or interface, and there-

fore the surface/interface structure is of importance. Structural modulation induced by the surface is known as surface relaxation or surface reconstruction, and is one of the central issues of surface science. Surface relaxation may be regarded as a surface induced polymorphism.

To date, the surface structure relaxation of organic semiconductors has been examined for rubrene and tetracene by using the surface X-ray scattering technique [1, 2]. Rubrene has no surface relaxation, while tetracene has significant relaxation. It is unclear whether organic semiconductors often have a relaxed surface. Therefore, we have examined the surface relaxation of organic semiconductors.



Figure 1: Depth profile of the electron densities for (a) rubrene, (b) tetracene [2], and (c)-(e) [n]phenacenes [3]. (a')-(e') show the molecular packing in the bulk unit cell.



Figure 2: CTR scattering profiles of rubrene, tetracene, and [*n*]phenacenes (*n* = 5, 7 and 9) single crystals. The unit for the horizontal axis is the length of 2 *c** for rubrene, and *c** for others [2, 3].

There are several similarities and differences between rubrene and tetracene. Their highest occupied molecular orbitals and lowest unoccupied molecular orbitals are very similar. The main difference between them is the molecular packing as presented in **Fig. 1**. In order to study the effect of the molecular packing as well as the molecular size, we selected [*n*]phenacenes as our samples [3].

Single-crystal samples of [*n*]phenacenes were grown by the physical vapor transport method. The crystals were placed on Si(001) substrate. Surface X-ray scattering experiments along the c^* axis were performed at room temperature in air with the four-circle diffractometer installed at BL-3A. The two-dimensional pixel array detector allows us to measure the intensity profiles in a short time, typically one hour for measurements up to the 2θ angle close to the 004 Bragg reflection of Si substrate. Measured intensity profiles are shown in Fig. 2.

In order to perform phase retrieval analysis, the bulk crystal structure is required. Previous phase retrieval analyses for organic semiconductor surfaces [1, 2] were made with coherent Bragg rod analysis (COBRA) [4] based on the reported results of single-crystal structure analysis. Unfortunately, there is no report on the singlecrystal structure analysis of [*n*]phenacenes ($n \ge 6$) because of the difficulty of growing solid thick crystals; all the crystals were grown in a film shape, which prevents single-crystal structure analysis. To obtain the bulk crystal structure, we performed first principles calculations. Using the theoretically derived bulk structure, we performed COBRA on surface scattering intensity profiles.

The resulting electron density profiles of the [*n*]phenacenes together with that of tetracene are shown

in **Fig. 1**. As can be seen, there is little relaxation in [*n*]phenacenes, which have similar herringbone molecular packing with tetracene. The result shows that the herringbone packing is not the origin of the relaxation.

What makes the surface relaxed? Tetracene has a very similar structure to pentacene, which is known to have various polymorph structures. On the other hand, [*n*]phenacenes have very stable structures, and no other polymorph structure has been reported. Although the number of examples that show a large surface relaxation is too small to make any decisive conclusion, we propose that the number of possible polymorph structures for the bulk crystal structure reflects the possible degree of surface relaxation.

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