Single-Crystal Structure and Transport Analyses of Rubrene under High Pressure

Junto Tsurumi¹, Ken-ichi Sakai^{1, 2}, Hiroyuki Matsui¹, Yugo Okada¹, Toshihiro Okamoto^{1,3}, Hiroyasu Sato⁴, Akihito Yamano⁴, Kunihisa Sugimoto⁵, Akihiko Fujiwara⁵ and Jun Takeya¹

 ¹ Department of Advanced Materials Science, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan
 ² Institute for Solid State Physics, The University of Tokyo,

5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan ³ PRESTO, JST,
4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan ⁴ Rigaku Corporation,
3-9-12 Matsubara, Akishima, Tokyo 196-8666, Japan ⁵ JASRI, SPring-8,

1-1-1 Kohto, Sayo, Sayo, Hyogo 679-5198, Japan

Abstract

Structure and transport properties of rubrene single crystals under high pressure were investigated by single-crystal X-ray diffraction (SC-XRD) analysis followed by the density functional theory (DFT) calculation of transfer integrals. The analyses revealed a significant intramolecular deformation of rubrene under high pressure, which leads to the non-monotonic dependence of mobility on the applied pressure. The results demonstrate the softness of the van der Waals crystals as well as organic molecules themselves.

1. Introduction

The charge transport in organic conductors and semiconductors originates from the weak intermolecular interactions in van der Waals crystals. Owing to the softness of the crystals, their properties can be modulated significantly by the application of external pressure. Using this unique feature of organic materials, several reports have demonstrated the pressure effects on the transport properties such as superconductive transition [1] and the improvement of mobility [2]. So far, we have studied the crystal structures of rubrene and dinaphtho[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophene (DNTT) under high pressure by powder X-ray diffraction (XRD) analysis, and discussed the variation in transport properties on the basis of the rigid molecule model [2,3]. However, the non-monotonic dependence of mobility on the applied pressure was not fully understood yet, which implies the limitation of the rigid molecule model in organic semiconductor materials.

Here we show the single-crystal XRD analysis of rubrene under high pressure followed by the density functional theory (DFT) calculations based on the structures. The analyses revealed that the application of pressure up to 0.6 GPa increases mobility because of the approach of neighbor molecules whereas the pressure above 0.6 GPa decreases mobility because of the deformation of each molecule. This is the first report, to our knowledge, which demonstrates the softness of organic semiconductor molecules themselves.

2. Experimental

We employed rubrene as an organic semiconductor material because it exhibits the highest field-effect mobility of $\mu = 40 \text{ cm}^2/\text{Vs}$ so far [4–6]. The rubrene single crystals were grown by physical vapor transport (PVT) method according to the previous report [3]. For the SC-XRD analysis under high pressure, the crystals were encapsulated in diamond anvil cell (DAC) with Fluorinert as pressure medium in order to apply hydrostatic pressure. The base of the diamond was designed to be larger than conventional ones, which enabled us to adjust the pressure finely below 2.0 GPa. Powder of NaCl was used as the reference for the calibration of pressure. Since the intensity of diffracted light from the thin crystal of rubrene was very low, SC-XRD measurement was done in a synchrotron radiation facility, SPring-8.



Fig. 1 Crystal structures of rubrene under ambient pressure (pale outline) and 2.0 GPa (dark solid).

3. Results & Discussion

Figure 1 shows the comparison of the crystal structures of rubrene under ambient pressure and 2.0 GPa. The anisotropic decrease of lattice constants were ~3 % along *a* and *b* axes and ~6 % along *c* axis at 2.0 GPa, which makes adjacent molecules closer to each other and consequently should increase the transfer integrals. The SC-XRD analysis also enables us to observe the deformation and rotation of each molecule: (1) The tetracene backbones in the rubrene molecules clearly bent at 2.0 GPa although they were flat at ambient pressure. (2) The angle of phenyl groups was also changed by the application of pressure. (3) Each molecule rotated along *a* axis under high pressures, which explains the larger decrease of the lattice constant along *c* axis.

Transfer integrals were calculated from these crystal structures at respective pressures and compared with the field-effect mobility of single-crystal transistors. Here we focus on the transfer integrals and mobility along b axis because the mobility in this direction is about three times higher than that along c axis [7]. The transfer integral tbetween neighboring rubrene molecules along b axis was calculated by Gaussian 09 based on the density functional theory (DFT) using the PBE exchange and correlation functionals and the 6-31G(d) basis set. Figure 2 shows the pressure dependence of the calculated transfer integrals t as well as the field-effect mobility in single-crystal transistors which has been reported in ref. [3]. It is roughly consistent that both transfer integral and mobility increase below ~0.6 GPa and decrease above ~0.6 GPa. Comparing the crystal structures, we found that the increase in mobility mainly originates from the approach of neighbor molecules while the decrease of the mobility mainly from the deformation of individual molecules. It should be noted that the linewidth of the XRD peaks was increased monotonically as the pressure increases, which suggests some disorder was also induced by the application of high pressure. We think that this is the reason why the increase in mobility is three times smaller than that of transfer integral in Fig. 2.

4. Conclusions

We discussed the non-monotonic effects of pressure on the transport properties of rubrene single crystals by the fine analyses of crystal structures and transfer integrals. Interestingly, the external pressure up to 2.0 GPa changed not only the intermolecular distance which is governed by the weak van der Waals interactions but also the intramolecular geometry which is formed by hard covalent bonds. We believe that the results give us a new insight into the softness of organic conductors and semiconductors which are the most useful class of materials for flexible electronics.



Fig. 2 Normalized transfer integral $\Delta t/t_0$ (circle) and mobility $\Delta \mu/\mu_0$ (square) plotted against pressure, where $t_0 = 82.7$ meV and $\mu_0 = 18.3$ cm²/Vs.

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