

Molecular dynamics and electronic structure studies of organic semiconductors under mechanical stress

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Abstract

Properties of organic semiconductors under mechanical stress are important to develop flexible electronic circuits. We studied deformation of organic semiconductor under mechanical stress and its influence to the electronic structures. Small molecules such as pentacene flexibly compressed but cannot be expanded with crystal coherence. On the other hand, molecules with alkyl chains such as C8-BTBT can be compressed or expanded with keeping substantial band dispersion.

1. Introduction

In order to develop flexible electronic circuits, semiconductors which can be deformed is important. Although various organic semiconductors have been synthesized, deformation of the molecular arrangements and change in the electronic structures under mechanical stress has not been studied in detail. Since crystalline organic semiconductors show superior performance over polymer semiconductors, we focus on the crystalline organic semiconductors. Change in the crystal lattice is crucially important for their electronic structures. In this paper, we report molecular dynamics and electronic structure studies of several organic semiconductors. Main focus is on the difference between pentacene and C8-BTBT[1].

2. Computational details

We used Gromacs 5.0 [2] for the calculation of the deformation under mechanical stress. Force field for the molecular dynamics was OPLS[3] and the thermostat was Berendsen type. Pressure of the system was not controlled. First, molecular lattice was created according to single crystal data to fill a 10 nm x 10 nm x 5 nm box. After waiting for thermal equilibrium at 300 K with the initial periodic boundary condition (PBC) of 10 nm x 10 nm x 5 nm, the PBC box was compressed or expanded step by step as a function of time. The speed was 0.05nm / 20 ps. After changing the PBC box size, molecular dynamics at 300K was run. The energy and the structure parameters were extracted from the trajectory by Gromacs subprograms. The electronic structure of the deformed lattice was calculated by taking average of lattice constant of a single unit cell and running structure optimization in the unit cell. The electronic structure was calculated by Quantum Espresso 5.1 [4] with PBE functional with GGA ap-

proximation, 65 Ry cut off and 8 x 8 x 4 unit cell sampling.

3. Results and Discussions

Figure 1 shows the process of compressing pentacene. The initial structure was taken from bulk phase pentacene lattice[5]. When the PBC box was shrunk step by step at the rate of 0.05 nm / 20 ps. The pentacene molecules climbed up to make thicker layers and the crystal structure is maintained. This result suggests that the pentacene is robust to the compression.

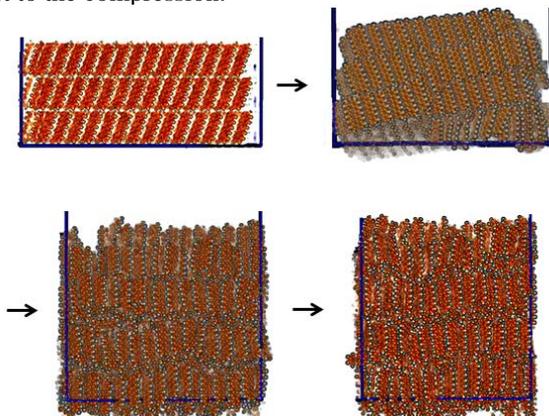


Fig. 1 Molecular dynamics simulation of compression of pentacene at 300K. The initial box size of 10 nm x 10 nm was compressed to 7 nm x 7 nm. The lines indicate the periodic boundary condition (PBC) used in the calculation.

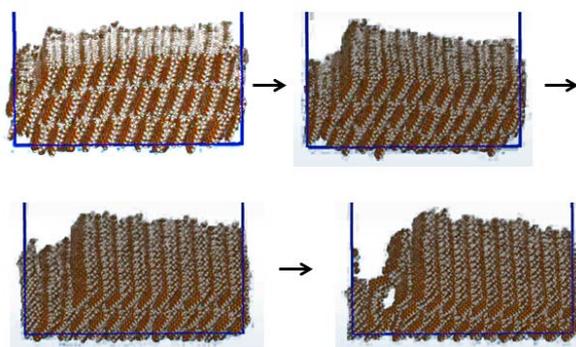


Fig. 2 Molecular dynamics simulation of stretching of pentacene at 300K. The initial box size of 10 nm x 10 nm was expanded to 13 nm x 13 nm.

On the other hand, when the PBC of pentacene was enlarged from 10 nm x 10 nm to 13 nm x 13nm, the vacuum entered between the periodic boundary condition in one

direction, or, in other words, the crystal was broken in this direction. The pentacene solid was continuous in the other direction until the PBC was expanded to slightly below 13nm, but it was finally broken also in this direction as shown in Fig. 2.

Striking difference was observed in the case of C8-BTBT. When compressed, the lattice of C8-BTBT seems to change, but the molecules do not clime to each other to make multilayers. Instead, the whole monolayer was disassembled when the lattice was compressed by 22% (Fig. 3). Figure 4 shows the total energy as a function of the PBC size. It shows a minimum at ~ 10% compression, which corresponds to a possible polytype crystal of this material.

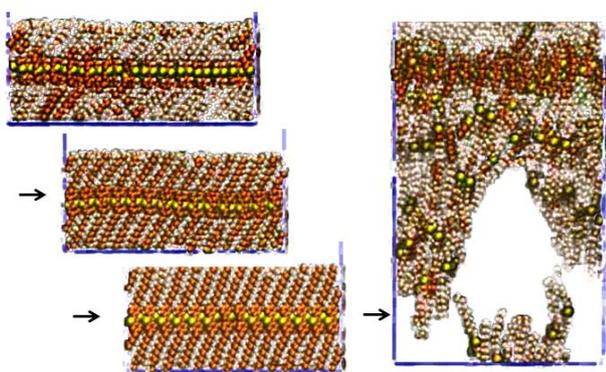


Fig. 3 Molecular dynamics simulation of compression of C8-BTBT at 300K. The initial box size of 10 nm x 10 nm was compressed to 7 nm x 7 nm.

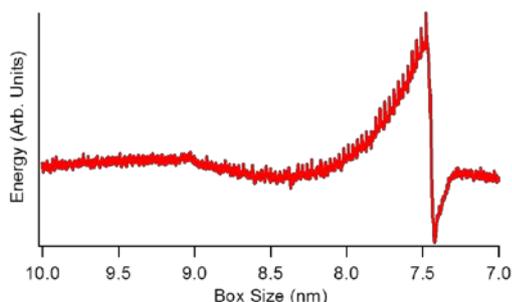


Fig. 4 Total energy plotted versus PBC box size during the compression of C8-BTBT. The cusp at 7.5nm is the “explosion” of the compressed layer to the vertical direction. From the slope, the pressure at the point is estimated as 3 GPa. Note that shallow minimum exists at PBC box size of 8.5nm.

When C8-BTBT was expanded, the vacuum entered in one dimension as in the case of pentacene, but the solid did not break in other dimension at least when the expansion or the stretch was 50% (10nm to 15nm) as shown in Fig. 5.

The band structure of the energy optimized structure with the average unit cell size at 50% stretching was calculated as shown in Fig. 6. It is impressive that the band dispersion is observed. Although the effective mass calculated from the band curvature at the valence top is larger than that of bulk C8-BTBT by the factor of 5~10, it still works as semiconductor. The robustness to the expansion

is due to the van der Waals attraction between alkyl chains of C8-BTBT, or “molecular fastener” effects.

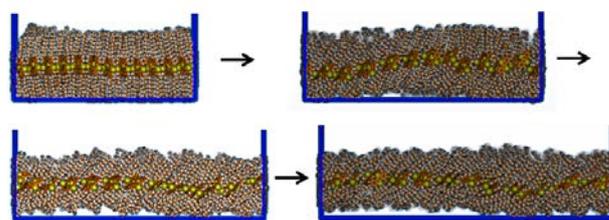


Fig. 5 Molecular dynamics simulation of expansion of C8-BTBT at 300K. The initial box size of 10 nm x 10 nm was compressed to 15 nm x 15 nm.

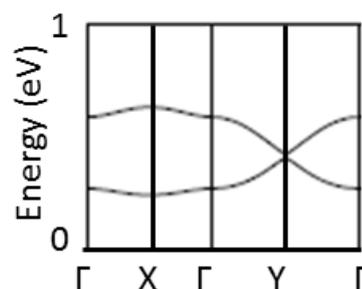


Fig. 6 HOMO band dispersion of 50% expanded C8-BTBT. The energy origin was taken arbitrarily to show only the scale.

4. Conclusion

In the present work, the effects of mechanical stress to organic semiconductor was studied by molecular dynamics simulations and DFT band calculation. It was revealed that the response to the compression and stretching is much different by molecules. C8-BTBT was found to be robust to the stretching, probably due to the “molecular fastener effect”.

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