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Computational Analysis of Thermal Energetic Disorder in a Pentacene Crystal:  
Temperature Dependence of Trap Levels and Possible Novel Thermoelectric  
Contribution

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In organic semiconductors, the sudden appearance of deep traps (30 - 100 meV) below  
100 - 200 K is frequently observed experimentally even in highly crystalline films and  
single crystals. We analyzed this phenomenon by molecular dynamics combined with  
semi-empirical quantum chemical calculation, and found that defect levels are  
concealed by thermal disorder at high temperatures but appear as hole traps at low  
temperatures. We propose that the thermal energetic disorder may lead to a  
considerably large thermoelectric effect in organic semiconductors.

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It is often observed that the conductivity and mobility of organic semiconductors drastically decrease at temperatures lower than 100 - 200 K. This rather sudden “insulator transition” is characterized by the appearance of deep trap levels with tens of meV activation energies<sup>1</sup>. Simply considering the Boltzmann statistics, the characteristic temperature  $T_o$  of the trap occupation should correspond to the trap energy  $E_T$  via  $T_o \sim E_T / k_B$ , where  $k_B$  is the Boltzmann constant. The observed “transition” temperature (100 - 200 K) and  $T_o$  (several hundreds to thousand kelvins) are very different. Explanations assuming abundant shallow traps work in some materials, but the nature of the shallow traps has not been clarified<sup>2</sup>.

In this study, we will try to qualitatively account for this sudden appearance of deep traps by computational analysis using the combination of molecular dynamics and semi-empirical quantum chemical calculation. Strong carrier scattering by thermally induced lattice disorder is characteristic to organic semiconductors in which molecules are loosely bound together with weak van der Waals forces. This scheme has been successfully applied to the estimation of the temperature dependence of carrier mobility<sup>3</sup>, but the defect levels and thermoelectric effects have not been studied. We here focus on the energy fluctuation which might dominate the behavior of traps and thermoelectric characteristics in organic semiconductors. The material treated here is a thin-film-phase pentacene, which is one of the best studied organic semiconductors. After describing the computational details, we discuss the trap levels and then the thermoelectric effects.

We investigated a perfect crystal and a crystal with a point defect (a vacancy or a missing molecule), as shown in Figs. 1(a) and 1(b), respectively. We used easily

accessible program packages for the classical molecular dynamics (TINKER<sup>4</sup>) and for semi-empirical quantum chemistry (AM1<sup>5</sup> in MOPAC 6<sup>6</sup>) and followed the scheme developed by Troisi et al. to combine them<sup>3</sup>. We chose AM1 because the intermolecular interaction is adequately included in the parameters. The lattice constant and initial structure were taken from the literature<sup>7</sup>. We performed a simulated annealing at 450 K and decreased the temperature to the desired value. We first recorded snapshots of atomic positions in a periodic crystal consisting of 3 x 3 x 2 unit cells in the thermal equilibrium using molecular dynamics. A Berendsen thermostat was used with a 2 fs interval and the molecular positions were recorded every 100 fs. Then, those atomic positions were used for the semi-empirical calculation of the energy states of a five-molecule cluster. The five-molecule cluster consists of a center molecule and in-plane nearest-neighbors. The semi-empirical quantum chemical calculation (AM1) of 5 molecules yields 5 orbitals derived from 5 interacting highest occupied molecular orbital (HOMO) levels, and their energy levels were recorded to make histograms, which produce density of states (DOS) distribution. When the five molecular cluster includes the point defect (vacancy), the electronic states were calculated for four molecules. These treatments are intended to approximate the hole transport in the intermediate of the band scheme and the hopping scheme. We

consider that the energy scale of the thermal disorder can be estimated by this procedure, without going into detail of the transport mechanism.

The nearest-neighbor limitation is justified because the transfer integrals beyond the nearest neighbors are small as estimated from low temperature angle-resolved ultraviolet photoelectron spectroscopy<sup>8</sup>. Although it is desirable to include the contribution beyond nearest neighbors considering band structure calculation<sup>9</sup>, it was omitted here to obtain the qualitative results with small scale computation.

The point defect (Fig.1(b)) was stable with the periodic boundary condition of 3 x 3 x 2 even after simulated annealing at 450 K for 1 ns. We therefore analyzed electronic structures around the defect in comparison with the crystal without the defect. Figure 2(a) shows the DOS of the crystal without the defect of the HOMO. The bottom axis of the all results in the following was shifted by -7.3 eV from the calculated value for clarity. It is easily observed that the DOS distribution is broadened when the temperature is increased. The FWHM of the distribution at each temperature is plotted in Fig. 2(b), in which the narrowing of the distribution becomes significant below 100 K. The broadening has the same orders of magnitude as the reported thermal disorder of transfer integrals<sup>11</sup>.

Figure 3 shows the results of similar calculation on pentacene crystal containing a point defect. It is observed that the DOS is similarly broadened at high temperature ( $\geq 100$  K), but a small peak at the energy higher than the main peak appears at 50 and 10 K. It was found that this peak is localized around the point defect. It is due to the less stabilized HOMO levels with a missing neighboring molecule. This additional DOS peak at higher energy will act as a hole trap. The energy separation between the main peak and the trap level is 50 meV, which is similar to the reported value of the trap depth. These results strongly suggest the following. (1) Trap levels are concealed by the strong thermal disorder of the electronic states at high temperature but appear at low temperature (50 K in the present simulation). (2) Trap states for holes with tens of meV depth can be created by a point defect. These results can qualitatively explain the sudden appearance of trap levels in highly purified single crystals. We do not know the reason for the difference between the present simulation and the reported experiments about the temperature at which the trap level appears, but it is speculated that the classical molecular dynamics simulation might not be accurate enough at low temperatures. Effects of the conduction mechanism such as percolation and band transport might also be responsible for the discrepancy. The broadened HOMO level distribution at high temperature will not be distinguishable from abundant shallow traps

within the experimental accuracy in a narrow temperature range around room temperature.

Next, we will discuss the thermoelectric aspect of the results. We can easily observe that the DOS of perfect crystal (Fig. 2(a)) shows the shift of the distribution to a higher energy, especially considering the high-energy-side tailing. If the organic semiconductor is heavily doped, the Fermi level position measured from the vacuum level is significantly affected by this shift and tailing. This effect certainly contributes to the thermoelectric effect of the material and is worth further examination in detail. Figure 4(a) shows the relative Fermi energy position of a perfect crystal calculated in Fig. 2 as a function of temperature with various degrees of doping. The Fermi energies ( $E_F$ ) were determined numerically from the DOS of HOMO levels in the following equation:

$$p \int_{-\infty}^{\infty} D(E) dE = \int_{E_F}^{\infty} D(E) dE ,$$

where  $p$  is the doping concentration. From Fig. 4 (a), it is obvious that the shift of the Fermi energy is dependent on the doping level and temperature. Figure 4(b) shows the thermoelectric effect in the same unit as Seebeck coefficients derived from Fig. 4(a) as the difference in Fermi energy divided by the temperature difference of the adjacent calculated temperatures (10 ~ 25K). This thermoelectric effect is unique to organic semiconductors. It comes from the strong thermal disorder of the electronic structure, which causes the transition from band transport to hopping transport. The obtained

values of 100 - 1000  $\mu\text{eV/K}$  are comparable to the values expected from the band structures of organic semiconductors<sup>11,12</sup> and may act as an additional source of thermoelectricity. The thermal disorder effect will be enhanced when the band dispersion is flat, because the narrow DOS at low temperature will become broadened at higher temperature due to the thermal disorder effect. It is also suggested that the low-mobility semiconductors with the carrier mobility suppressed by the thermal disorder effect might show large thermoelectric effects. The reported experimental and theoretical values of the Seebeck coefficients of organic semiconductors<sup>11-14</sup>, charge transfer salts<sup>15-19</sup>, and polymers<sup>20-22</sup>, some of which are considerably large and promising in future applications, should be reexamined from this viewpoint.

In summary, we analyzed the electronic structure around a point defect of organic semiconductor pentacene with a combination of molecular dynamics and semi-empirical quantum chemistry. We found that the defect levels make traps for holes, but the binding energy is smaller than the energy deviation caused by thermal disorder at room temperature. The defect levels appear as traps when the temperature is several tens of Kelvin. This result is consistent with the common experimental observations. Thermoelectric effects due to the thermal disorder of electronic structures were examined and it was found that the contribution to the Seebeck coefficient can be comparable to the ordinary mechanism from the band structure.

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## Figure Captions

Fig. 1. Structure of thin film phase pentacene used in the calculation. Views from c-axis of (a) perfect crystal and (b) crystal with a point defect (vacancy) indicated by a white circle.

Fig. 2. (a) DOS histogram of interacting HOMO states at each temperature. (b) FWHM of DOS peaks plotted as a function of temperature.

Fig. 3. DOS histogram of HOMO states with a point defect (vacancy). The states indicated by arrows are localized to the molecules adjacent to the defect.

Fig. 4. Fermi energy (a) and thermoelectric effect (b) plotted as a function of temperature with various dopant concentrations.

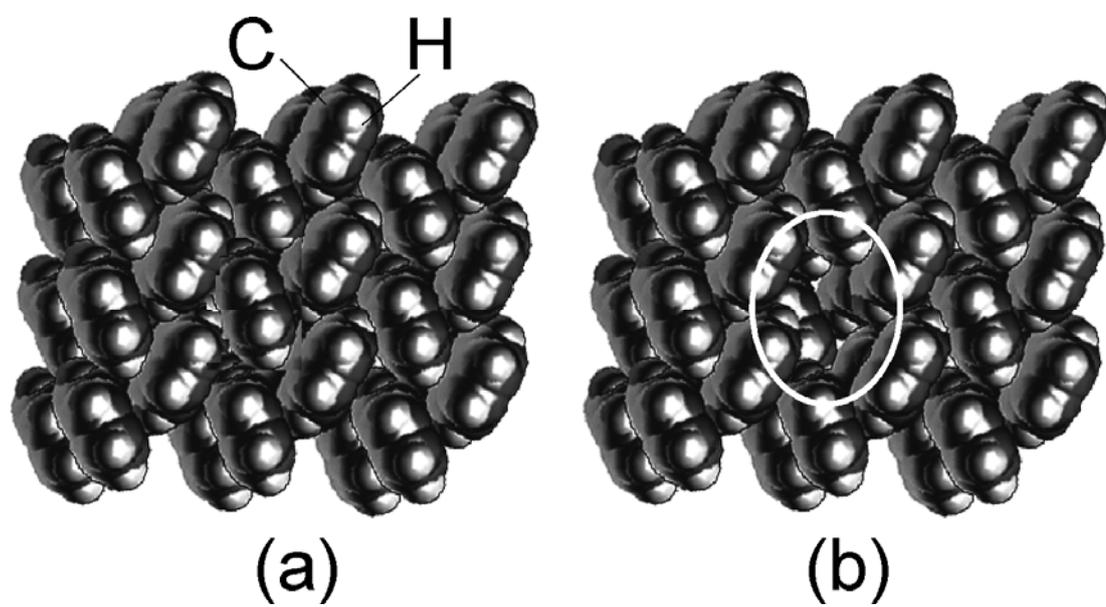


Fig. 1

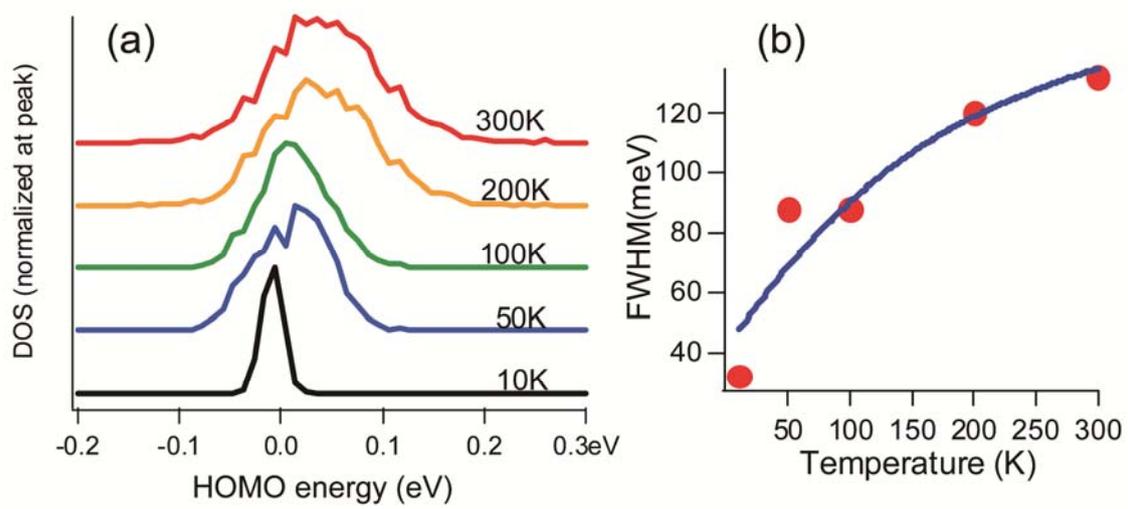


Fig.2

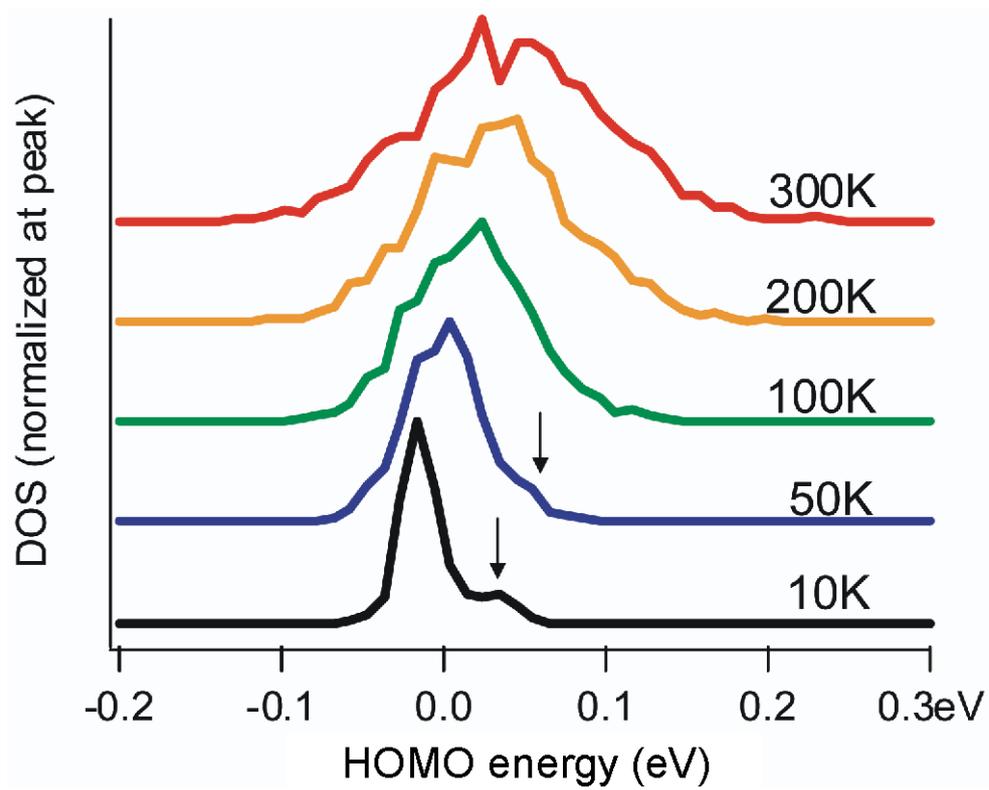


Fig.3

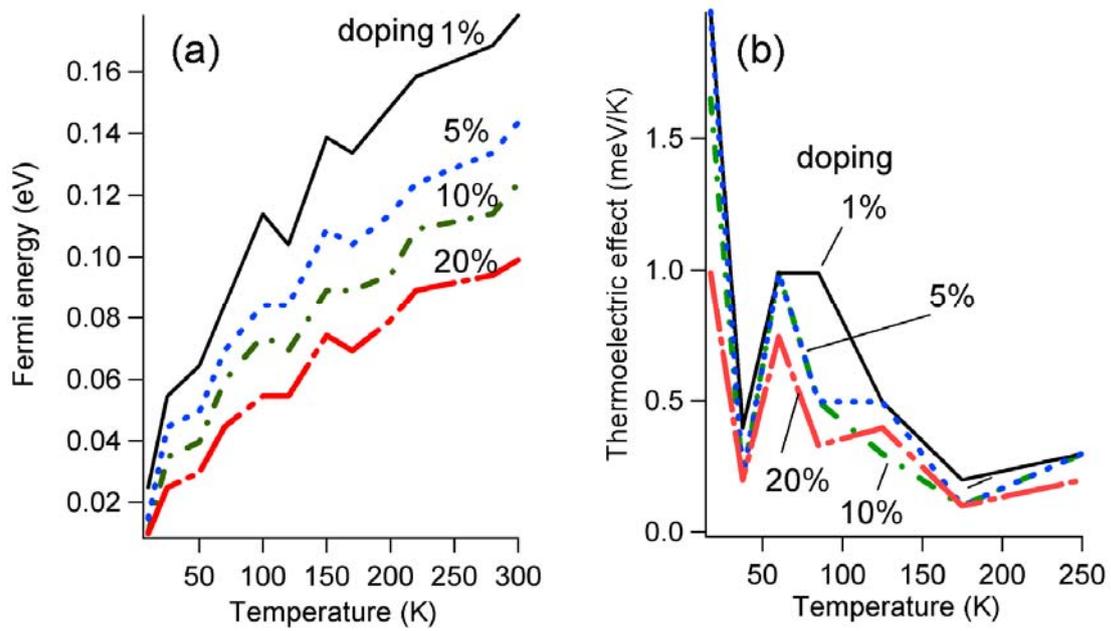


Fig.4