

Hybridization of HOMO and Next HOMO in Organic Semiconductor Crystals Revealed by Band Calculations

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Abstract

Band calculations based on density functional theory (DFT) for high-mobility organic semiconductor molecules with V-, W- and N-shape motifs are presented. The comparison between the band calculation of solid crystals and the calculation for a monomer molecule reveals that the highest occupied band state in a periodic crystal can significantly deviate from the highest occupied molecular orbital (HOMO) at each monomer unit. This deviation is due to the non-zero coupling between the HOMO at one molecule and next HOMO (NHOMO) at adjacent molecules and/or the coupling between HOMO and NHOMO at the same molecule via the crystal field. The results point out the limitation of the quantum chemistry calculations based on monomer and dimer molecules and that a full band calculation is necessary for understanding the electronic states in organic semiconductor crystals correctly.

1. Introduction

High-mobility organic semiconductors have attracted much attention in recent years because of the low-temperature and solution processability on plastic substrates, which enables low-cost, light-weight and flexible electronics. In order to maximize the advantage of the wide variety of molecules, the understanding of the structure-property relationships is required. Here we show the band calculations for several new organic semiconductor materials with V-, W- and N-shape motifs and discuss the difference from the monomer- and dimer-based quantum chemistry calculations. The results point out that the highest occupied band states can deviate significantly from the single-molecular orbitals and that the common method for calculating transfer integrals can be misleading in some cases.

2. Calculation Methods

We employed the new high-mobility organic semiconductor materials which have the motifs of V-, W- and N-shapes [1-4]. The materials exhibit high mobility up to 15 cm²/Vs and high thermal-stability in air. The crystal structures were obtained by single-crystal X-ray diffraction analysis. The band calculations were performed on a

supercomputer, SR16000, HITACHI, using a software, Gaussian 09. The PW91 exchange and correlation functionals and 6-31G(d) basis set were employed. Transfer integrals t were also calculated for the dimer molecules taken from the crystal structures by the direct method according to the literature [5]:

$$t = \frac{F_{12} - \frac{1}{2}(F_{11} + F_{22})S_{12}}{1 - S_{12}^2},$$

where F and S are the Fock and overlap matrices, and the suffixes 1 and 2 denote the first and second molecules in dimer.

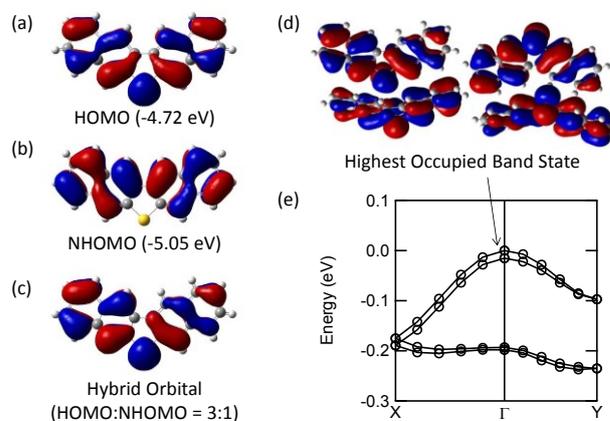


Fig. 1 (a) HOMO, (b) next HOMO and (c) hybrid orbitals of a DNT-V monomer. (d) Highest occupied band state and (e) energy dispersion in a DNT-V crystal.

3. Results and Discussion

Figures 1(a) and (b) show the highest and the next highest molecular orbitals (HOMO and NHOMO) calculated for a monomer molecule of dinaphtho[2,3-*b*:2'3'-*d*]-thiophene (DNT-V). The HOMO is symmetric in the direction of the long molecular axis and has a large component at the sulfur site whereas the NHOMO is anti-symmetric and has no component at the sulfur site. By contrast, Fig. 1(d) shows the highest occupied band state calculated in the DNT-V crystal with a periodic boundary condition. We found that the band state does not match

neither the HOMO or NHOMO. Actually the orbital shape of the band state can be reproduced by a linear combination of HOMO and NHOMO in the monomer unit with an appropriate ratio. The best ratio was about HOMO:NHOMO = 1:3 in the case of DNT-V (Fig. 1(c)), indicating a large degree of hybridization of the two orbitals inside crystals. Similar hybridizations were observed also in other V-shaped molecules, while no large hybridization was observed in W-shaped molecules. The reason is that the crystal structure of W-shaped molecules have a mirror symmetry plane at the center of the two-dimensional molecular sheet, which imposes a symmetric orbital shape inside the crystals.

Such a significant reconstitution of the molecular orbitals inside crystals indicate relatively-large interactions between the adjacent molecules in high-mobility organic semiconductors. The impact of the hybridization of molecular orbitals on the transport properties was investigated in terms of transfer integrals. Figure 2 shows the transfer integrals calculated for (a) HOMO and (b) the hybrid orbital constituted by HOMO:NHOMO = 3:1. We found that all the transfer integrals were increased significantly by 10-70 % as a result of the hybridization. Figure 2(c) also shows that the hybridization ratio of 3:1 is very close to the maximum point of the all transfer integrals. Another V-shaped molecule, DAT-V, also exhibit 10-210 % increase of the transfer integrals. We expect that the positive effect of the hybridization on the transport properties should be general rather than accidental because the reconstitution of the electronic states usually create new levels outside of the existing energy levels and hence should increase the band width.

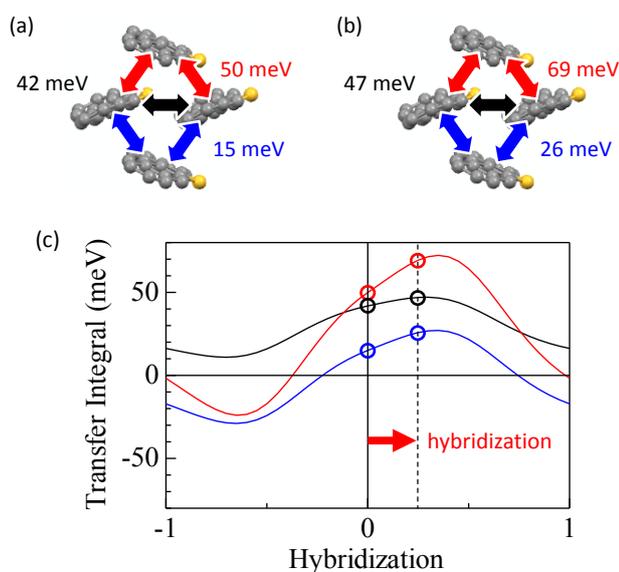


Fig. 2 Effective transfer integrals calculated for (a) HOMO and (b) hybrid orbital composed of HOMO:NHOMO = 3:1. (c) The variation in transfer integrals along the gradual change of the orbital from HOMO to NHOMO. Hybridization factor a is defined as HOMO:NHOMO = $(1-a) : a$.

Finally, we discuss the band structure and effective mass calculated with the crystal structures including periodic boundary condition. The effective mass tensor was calculated by fitting the energy dispersion at the top of the valence band with a quadratic function (Fig. 1(e)). Effective mass is a more important parameter than transfer integrals in that (1) it counts the effects of all the transfer integrals at once, including their interference, (2) it includes the effect of the hybridization, and (3) mobility is expected inversely proportional to the effective mass according to the band theory: $\mu = e\tau/m^*$. The effective mass of holes in DNT-V crystal was found $2.8m_0$ along a axis and $3.2m_0$ along b axis, where m_0 is the mass of free electrons. These values are comparable to those of other high-mobility materials such as pentacene and DNTT. The small anisotropy of the effective mass in DNT-V is desirable to reduce the device-to-device variation in case the crystals were oriented at random. Further improvement of effective mass was realized by substituting side alkyl chains to the DNT-V molecules, which introduce a high solubility at the same time. The effective mass of hexyl- and octyl-substituted DNT-V was found $1.6m_0$ and $1.5 m_0$, which explain one of the reasons for a large improvement of mobility from $1.5 \text{ cm}^2/\text{Vs}$ for DNT-V to 9.5 and $6.5 \text{ cm}^2/\text{Vs}$ for hexyl- and octyl-substituted DNT-V.

4. Conclusions

The hybridization of HOMO and NHOMO in organic semiconductor crystals were revealed by the full band calculations for V-, W- and N-shaped molecules. As a result of the hybridization, effective transfer integrals were found to increase significantly by 10-210 %. Band calculation also enables the evaluation of effective mass, which should be a more important parameter than transfer integrals. The small effective mass for DNT-V and alkyl-substituted DNT-V would explain one reason for the high mobility of these materials.

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