Intermolecular interaction modulation on pentacene clusters by introduction of a neighboring charged pentacene

Shigekazu Ohmori [a],[*], Ken Tokunaga [b], Hiroshi Kawabata [c]

[a] *Venture Business Laboratory, Kyoto University, Yoshida honmachi, Sakyo-ku, Kyoto, Kyoto 615-8510, Japan*
[b] *Division of Liberal Arts, Kogakuin University, Nakano machi 2665-1, Hachioji, Tokyo 192-0015, Japan*
[c] *Young Researchers Education Center, Hiroshima University, Kagamiyama 1-1-1, Higashihiroshima, Hiroshima 739-8524, Japan*

ARTICLE INFO

ABSTRACT

Energy gap, Mulliken population, and bond-overlap population analyses were carried out to investigate the intermolecular interaction modulation in pentacene clusters by neighboring artificially charged pentacene molecules, which model a charge-carrier injection into a crystal. Two common pentacene clusters, type-1 and type-2, obtained from the crystal structure of pentacene, were examined. A larger decrease in the band gap was observed for the type-2 orientation, whereas a positive intermolecular interaction was observed for the type-1 cluster. Both closing of the energy gap and the positive intermolecular interaction (bonding nature) were found only in the extreme n-type state.

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1. Introduction

Pentacene is one of the most common materials used for manufacturing organic semiconductor devices because of its potential for high charge mobility (>1 cm^2 V^{-1} s^{-1}) [1]. The carrier-transport mechanism in crystalline pentacene has been investigated from a number of perspectives, including band theory [2], hopping of carrier charges [3], and Marcus theory [4]. The band dispersion of crystalline pentacene was reported to be approximately 0.2–0.7 eV by photoelectron [5] and ultraviolet absorption [6] spectroscopies, a large value relative to other organic materials because of its strong intermolecular interaction. This large band dispersion has been identified as the driver for the observed band-transport behavior [7,8].

On the other hand, the device performance of a fabricated transistor [9] suggests that the hopping-based carrier-transport model applies. In this model it can be considered that the carrier is not delocalized among the lattice as in inorganic crystals, but is a charged state of a molecule. Thus, according to the model, the carrier mobility can be calculated based on the hopping probability of one charged state to another using Marcus theory, as a function of reorganization energy and the electronic coupling constant [10]. This theory does not take into consideration the electric field induced by the charged molecules themselves. Although the effect of the electric field should be small relative to the parameters described above, it may still be important in understanding the transport behavior for two reasons. First, the change in the intermolecular interaction as a result of the electric field would become

important because of this interaction has a small magnitude in the molecular crystal. Second, the electric field can extend over longer distances than the other forces. For these reasons, we have investigated the influence of the electronic structure modulation in an external electric field that was induced by the charged carrier.

2. Calculation

In this work, we investigated the intermolecular interaction between two pentacenes in a cluster under an electric field induced by a neighboring charged pentacene molecule. The original model of pentacene clusters, which contains two to four molecules in series, was obtained from X-ray diffraction data of a pentacene thin film [11], as shown in Fig. 1. Two types of pentacene clusters, one shown in Fig. 1a (type-1) for the first-nearest direction in the crystal, and the other, which forms a π-stacking configuration along the second-nearest direction, in Fig. 1b (type-2), were examined to investigate the anisotropy of charge transport. A pentacene located at one side in the original model was replaced by a set of point charges, which was simulated by the Mulliken charges of a separately calculated pentacene molecule in the ionic and/or neutral states, for constructing the electric field of charged pentacene [12]. Each pentacene is labeled as Pen(n) with a variable n, numbering from the pentacene nearest to the artificially charged pentacene. The electronic structures of these systems were then calculated using coulomb-attenuated [13] density-functional theory without geometrical optimization. The intermolecular interaction between the pentacenes was investigated by analyzing the bond-overlap population (BOP) coefficient [14–16] of the nearest-neighbor carbon atoms between molecules, specified by the dashed lines in Fig. 1. All of the calculations were carried out using the CAM-B3LYP/6-311++G(d,p) framework in Gaussian 09

* Corresponding author at: Technology Research Association for Single Wall Carbon Nanotubes, Tsukuba, Ibaraki 305-8562, Japan. Tel.: +81 29 861 4034.
E-mail address: ohmori-sh@aist.go.jp (S. Ohmori).
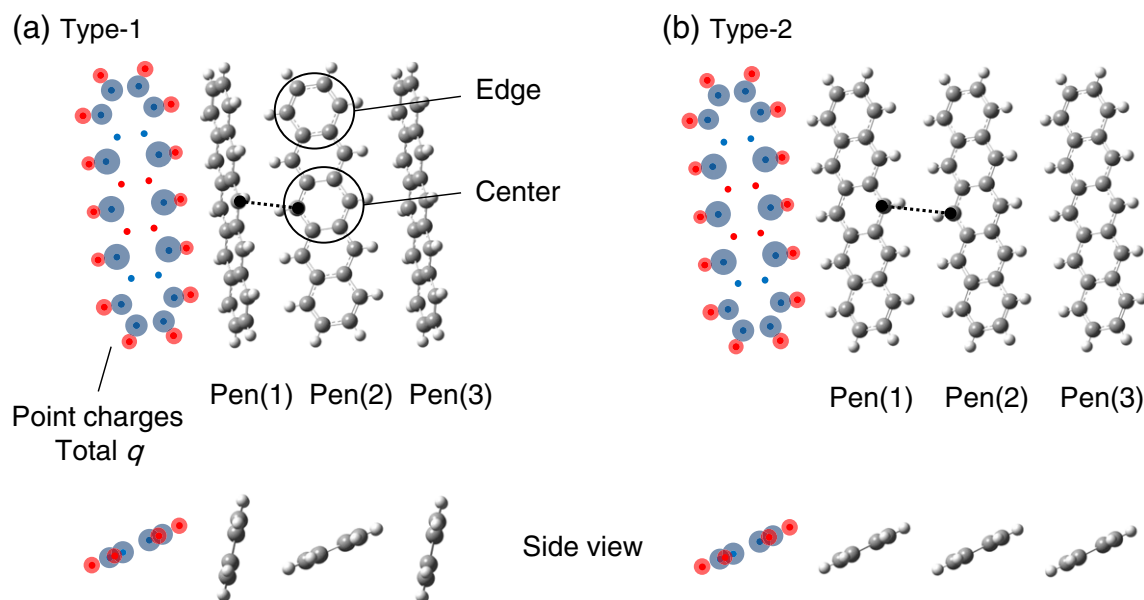
Fig. 1. Pentacene trimer models with an artificially charged pentacene: (a) type-1 and (b) type-2. The artificially charged pentacene (left side) was constructed from point charges placed at individual atom positions that have the same magnitude of Mulliken charges as the q-charged or neutral pentacene. Pentacenes are numbered as Pen(1), Pen(2), and Pen(3), respectively. A dashed line indicates the nearest-neighbor carbon atoms at the center of two adjacent pentacenes.

[17]. Basis-set superposition errors of the neutral models are estimated to be less than 4 kcal mol^{-1}, with the counterpoise correction used.

3. Results

Fig. 2a shows changes to the energy gaps between the lowest unoccupied (LU) and the highest occupied (HO) molecular orbitals (MOs) of type-1 clusters as a function of changing the magnitude of the total of the point charges from $q = -2$ to $+2$. It should be noted that $q = 0$ does not mean without charge, but with the point charges placed as Mulliken charges of neutral pentacene. The energy gap of the monomer, containing one neutral pentacene and one artificial pentacene constructed of point charges, did not change significantly (less than 0.2 eV change) as a function of applied charge, q. This result suggests that the electronic structure of the neutral pentacene is not affected by the neighboring charged pentacene. Upon increasing the cluster size from monomer to trimer with $q = 0$, the energy gap only changed by 0.5 eV. As the magnitude of q was increased, the energy gap for the dimer and trimer decreased, indicating that the intermolecular interaction is affected by the induced charge. The higher decrease in the energy gap observed in the trimer than that in the dimer suggests that the electric field extends for a distance of more than 1 nm. In addition, it was found that the positive charge had a greater influence on the energy gaps than did the negative charge.

In contrast, symmetrical energy gap modulation by the induced charge was observed for the type-2 clusters. Interestingly, the energy gap of the trimer decreased to around 2 eV at high induced charge, which was much greater than the modulation observed for the type-1 clusters. This result suggests that the electric field induced by the carrier affects the energy gap lowering, especially in the type-2 direction.

Mulliken population analysis can be estimated for both intra- and intermolecular charge rearrangements. In the neutral trimer, it is observed that $+0.843$ and -0.100 charges are transferred from the center to the sides of the pentacenes in type-1 and type-2 clusters, respectively. By introducing an artificial pentacene molecule in the neutral state ($q = 0$), the transferred Mulliken charges slightly decreased to $+0.764$ and -0.081, respectively. This intermolecular charge transfer varied less than 0.11 as a function of q, whereas an intramolecular charge rearrangement in the individual pentacenes was observed. In the type-1 trimer cluster, more than one electron was transferred at

the center C$_6$ ring of Pen(2) by changing the applied charge q from $+2$ to -2, suggesting that this location is important in charge transport (Table 1).
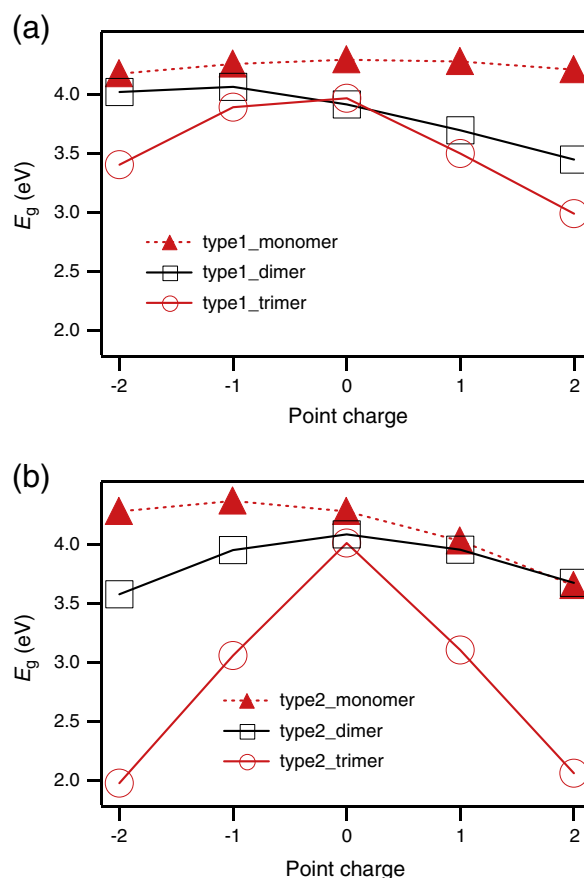
Fig. 2. Changes in the energy gaps of monomeric, dimeric, and trimeric (a) type-1 and (b) type-2 clusters as a function of applied charge, q, from -2 to $+2$.