

# Temperature Dependence Simulation of Carrier Mobility for Ambipolar Hexyl-substituted Phthalocyanine

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## Abstract

The carrier mobility for an ambipolar organic semiconductor, non-peripherally hexyl-substituted phthalocyanine (C6PcH<sub>2</sub>), was discussed by performing charge transport simulation based on Marcus theory and density functional theory. In order to understand the unique negative temperature dependence of hole and electron mobilities, the theoretical calculation was carried out taking the inter-molecular distance extended by thermal expansion into consideration. For the electron mobility, the degeneracy effect of LUMOs, which is an important factor to determine electron mobility, was also studied.

## 1. Introduction

Organic semiconductors have been attracting much attention for their device application, such as organic solar cells and organic field-effect transistors, because of the lightweight, flexibility, and low-cost production, and so on. The charge transport behavior in the thin film devices must be an important factor for the device performance. The overlap of  $\pi$  electron orbitals with adjacent molecules, which is determined by the molecular packing structure, tends to be strongly related to the actual carrier mobility of organic semiconductors [1].

1,4,8,11,15,18,22,25-octahexylphthalocyanine (C6PcH<sub>2</sub>), the molecular structure of which is shown in Fig. 1, is a promising organic semiconductor material, because C6PcH<sub>2</sub> exhibited ambipolar characteristics with high hole and electron mobilities of 1.4 and 0.6 cm<sup>2</sup>/Vs, respectively [2]. Both of hole and electron mobilities of C6PcH<sub>2</sub> demonstrated a negative temperature dependence, but the origin was still not clarified.

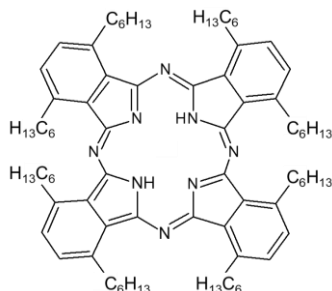


Fig. 1 Molecular structures of C6PcH<sub>2</sub>.

In this study, the carrier mobility calculation with Marcus

theory and density functional theory (DFT) was carried out taking the thermal expansion of the molecular packing structure of C6PcH<sub>2</sub> into account for discussing the temperature dependence of carrier mobilities. For the electron mobility calculation, the contribution of the degeneracy of LUMO and LUMO+1 were also discussed.

## 2. Methods

In organic semiconductor materials, the inter-molecular charge transfer in the dimer can be usually interpreted by hopping model. The carrier hopping rate  $k_{ij}$  from a molecule  $i$  and to its adjacent molecule  $j$  can be estimated by the Marcus theory [1], [3]-[5].

$$k_{ij} = \frac{|V_{ij}|^2}{\hbar} \left( \frac{\pi}{\lambda k_B T} \right)^{1/2} \exp \left( -\frac{\lambda}{4 k_B T} \right) \quad (1)$$

where  $k_B$  is Boltzmann's constant,  $\hbar$  is Planck's constant,  $T$  is the temperature,  $\lambda$  is the reorganization energy, and  $V_{ij}$  is the electronic coupling.  $V_{ij}$  is the magnitude of the electronic interaction and defined as [6]

$$V_{ij} = \frac{J_{ij} - S_{ij}(\epsilon_i + \epsilon_j)/2}{1 - S_{ij}^2} \quad (2)$$

where  $J_{ij}$ ,  $S_{ij}$ ,  $\epsilon_i$ ,  $\epsilon_j$  are the transfer integral, the spatial overlap integral, and the site energies, respectively.  $J_{ij}$ ,  $S_{ij}$ ,  $\epsilon_i$ ,  $\epsilon_j$  and  $\lambda$  values are obtained by applying the "fragment approach" to the dimer in the Amsterdam density functional (ADF) package. The calculation was performed using the generalized gradient approximation (GGA) and the Perdew and Wang 91 (PW91) exchange-correlation (XC) functional with a polarized triple- $\zeta$  Slater-type orbital (STO) basis set (TZP) [3].

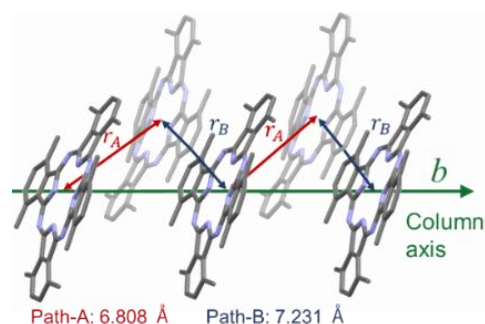


Fig.2 Molecular packing structure along  $b$ -axis [7].

To calculate carrier mobility of C6PcH<sub>2</sub>, the molecular packing structure and the temperature dependence of lattice constant, which were determined by single-crystal X-ray analysis, were used. The inter-molecular distance of dimer was determined based on the experimental data of thermal expansion [7]. The molecular packing structure along *b*-axis of  $\beta$ -type C6PcH<sub>2</sub> crystal [7], which contributes to the high mobility, is shown in Fig. 2. Since the alternating molecular alignment must become the zigzag route for carriers, the different distances of  $r_A$  and  $r_B$  shown in Fig. 2 were distinguished as path-A and path-B. The mobility for each path was calculated as  $\mu_A$  and  $\mu_B$ , then the effective mobility  $\mu_{\text{eff}}$  was defined as  $1/\mu_{\text{eff}} = \{ (1/\mu_A) + (1/\mu_B) \} / 2$  [3], [8].

For the electron mobility, the additional calculation including the degeneracy at LUMO, that is, LUMO-LUMO+1 electron coupling, was also carried out. Namely,  $J_{ij}$  and  $S_{ij}$  were recalculated with one molecular orbital as LUMO+1 ( $\psi_{\text{LUMO}+1}$ ) and the other as LUMO ( $\psi_{\text{LUMO}}$ ).

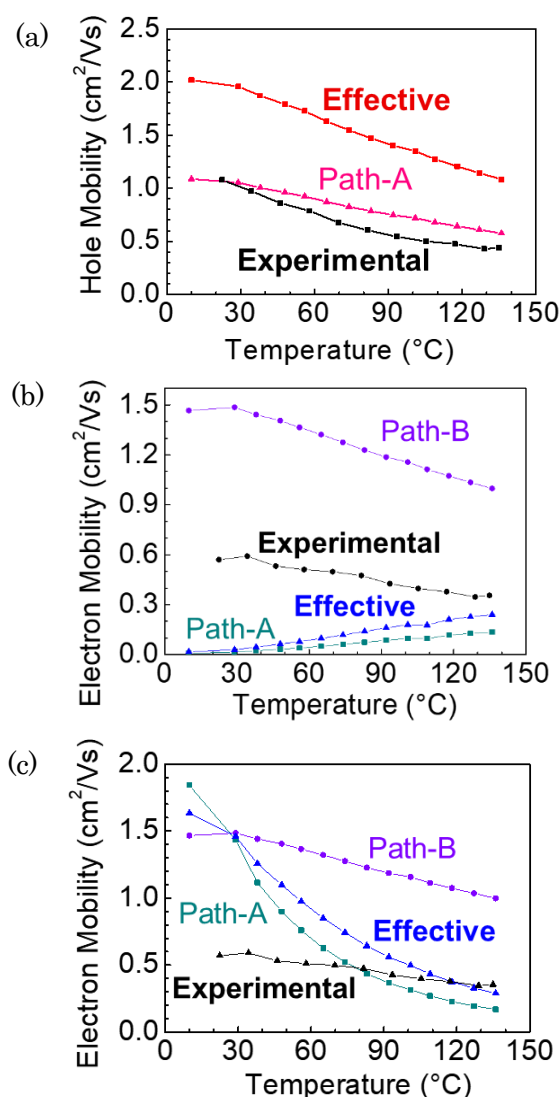


Fig. 3 Temperature dependence of (a) hole and (b) electron mobility. (c) shows the electron mobility by the modified calculation in consideration of the degeneracy at LUMO.

### 3. Results and discussion

Figure 3 shows the temperature dependence of the calculated hole mobility in path-A and effective hole mobility. The calculated hole mobility demonstrated the negative temperature dependence, which exhibited the similar slope and value with the experimental one. The decrease of mobility with increasing temperature can be explained by the reduced overlapping of  $\pi$  electron orbitals, which is due to the extended inter-molecular distance owing to the thermal expansion.

On the other hands, the calculated effective electron mobility was gradually enhanced with increasing temperature, namely, positive temperature dependence, which is not corresponding to the experimental result. Although the electron mobility of path-B shows the similar negative temperature dependence with experimental one, that of path-A is predominant for the effective mobility. The electron mobility of path-A was estimated to be low due to the rate-limiting by the electron mobility of path-A.

Focused on the LUMO of C6PcH<sub>2</sub>, which must be an important factor to determine electron mobility, it was noticed that LUMO+1 was located near LUMO in the DFT calculation. Therefore, the degeneracy of these orbitals should be considered for the electron mobility estimation. Recalculated electron mobility of path-A by taking the degeneracy of LUMO and LUMO+1 into account, the modified results was obtained as shown in Fig. 3 (c). The electron mobility of path-A also shows the negative temperature dependence. The slope was not completely consistent with the experimental results, however, it is suggested that LUMOs degeneracy effect must be significant for discussing the carrier transport of C6PcH<sub>2</sub>.

### 4. Conclusions

The carrier mobilities of C6PcH<sub>2</sub> was calculated by using Marcus theory and DFT to discuss the negative temperature dependence of carrier mobilities. By taking the thermal expansion of the molecular packing structure into account, the simulated hole mobility exhibited the similar temperature dependence as the experimental results. For understanding the temperature dependence of the electron mobility, the contribution of the degeneracy of LUMO and LUMO+1 must be necessary to introduce, and the modified calculation actually demonstrated the negative temperature dependence.

### Acknowledgements

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