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Charge transport properties and band-dispersion modulation induced by low-frequency intramolecular vibration modes of organic semiconductors

A New Step Toward Improving Performance of n-Type Organic Semiconductors Development of molecules that suppress low-frequency intramolecular vibration modes is the key

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Summary

- **The mechanism by which n-type organic semiconductors have extremely low electron mobility compared to that of p-type organic semiconductors is revealed.**
- **Low-frequency intramolecular vibration modes could be ignored when calculating hole mobility but are an important factor in determining the magnitude of electron mobility.**
- **This research may accelerate the performance improvement of n-type organic semiconductors.**

A research group led by Hiroyuki Ishii and Nobuhiko Kobayashi of the University of Tsukuba and Hiroyuki Yoshida of the Chiba University, has elucidated the mechanism by which n-type organic semiconductors have extremely low electron mobility compared to that of p-type organic semiconductors, which has long been unexplained. Employing the time-dependent wave packet diffusion method, they increased the precision of calculations for electron mobility by including low-frequency intramolecular vibration effects that are neglected in calculations for hole mobility. This research will greatly improve the accuracy of simulations for the molecular design of n-type organic semiconductors and contribute to the improvement of their performance in the future.

Detail

Elucidating the Mechanism Behind the Low Electron Mobility of n-Type Organic Semiconductors, a Longstanding Mystery

Organic semiconductors, a type of plastic, are expected to find use in a wide variety of flexible devices owing to their low thickness and weight. Currently, they are being used in flat panel displays for TVs and smartphones, and applications in solar cells and various sensors are being explored. In addition, organic semiconductors are expected to find a wide range of social applications because they are inexpensive, printable materials with low environmental impact.

Organic semiconductors are either hole-transporting (p-type) or electron-transporting (n-type). In organic semiconductor devices, semiconductors with different transport properties are joined. However, n-type organic semiconductors have extremely low electron mobility (*1) compared to those of p-type organic semiconductors. This is one of the factors that has reduced the overall performance of organic semiconductor devices.

A research group led by Hiroyuki Ishii of the University of Tsukuba's Faculty of Pure and Applied Sciences succeeded for the first time in observing the energy band structure (*2/Fig. 1) of the conduction band (*3) of pentacene, a typical organic semiconductor, by using angle-resolved low-energy inverse photoelectron spectroscopy (*4). The obtained results helped clarify the mechanism by which n-type organic semiconductors have extremely low electron mobility compared to those of p-type organic semiconductors. By using the time-dependent wave packet diffusion method (*5), the low-frequency intramolecular vibrational mode, which could be ignored in the calculation of hole mobility, was shown to be a factor that significantly reduces electron mobility. This research will greatly improve the accuracy of simulations of the molecular design of n-type organic semiconductors and will contribute to the improvement of their performance.

Ishii and his research team were the first to observe that electrons flowing in pentacene, an organic semiconductor, deform the molecule and generate quasiparticles called polarons. They found that the existence of polarons is closely related to the mystery of why the mobility of electrons is only one-tenth that of holes. Electrons induce intramolecular vibrations with a low frequency of 254 cm^{-1} , thereby deforming molecules and reducing their mobility. By applying this mechanism to the time-dependent wave packet diffusion method, they were able to accurately calculate the electron mobility in other n-type organic semiconductors.

Ishii said that "Until now, calculations of electron mobility in n-type organic semiconductors have been based on the assumption that high-frequency intramolecular vibrational modes generate the polaron, as is the case with holes. This caused an overestimation of the magnitude of the mobility. When we recalculated the mobility considering low-frequency intramolecular vibrational modes, we found that there was a large difference in the mobility of electrons and holes. The low-frequency intramolecular vibrational modes were inhibiting the movement of electrons in n-type organic semiconductors."

Ishii further said that "By simulating electrical conduction, taking into account the low-frequency intramolecular vibrational modes, we were able to calculate the difference in mobility between n-type and p-type organic semiconductors without any discrepancies. This has also allowed us to look at ways to improve n-type organic semiconductors. If we can develop molecules that can suppress low-frequency intramolecular vibrational modes, we will be able to increase the mobility

of electrons in n-type organic semiconductors. We hope that our findings will be utilized in the field of molecular design in the future.”

Electron mobility is the key to improving the performance of organic semiconductor devices

The higher the electron mobility of organic semiconductors, the wider the range of their applications. For example, e-Paper, which can project a still image, has a mobility of approximately $0.5 \text{ cm}^2/\text{Vs}$; with a mobility above $1 \text{ cm}^2/\text{Vs}$, it can be used to create a display, and with a mobility above $10 \text{ cm}^2/\text{Vs}$, it can be used to create an RF-ID tag that can perform simple calculations. In the future, it is expected to be used in wearable devices for which a mobility of $50 \text{ cm}^2/\text{Vs}$ is required. The key to achieving the same is improving the performance of n-type organic semiconductors.

Ishii said that “Currently, there are several p-type organic semiconductors that exceed $20 \text{ cm}^2/\text{Vs}$. However, the mobility of n-type organic semiconductors is still mostly below $3\text{--}5 \text{ cm}^2/\text{Vs}$. In the future, we will use simulations to gain knowledge on how to design molecules that will enable n-type organic semiconductors to have a mobility of $10 \text{ cm}^2/\text{Vs}$ or higher.”

Unlike inorganic semiconductors, organic semiconductors can be developed at a very low cost. For example, the future Internet of things (IoT) will require a large number of sensors. In this regard, the use of organic semiconductors will afford a great cost advantage. Further, widely applying inexpensive solar cells made from organic semiconductors can reduce environmental impacts. Realizing all of these possibilities requires a better understanding of electron mobility.

Annotations

1 **Electron mobility:** A quantity that indicates the ease of electron transfer in a material.

2 **Energy band structure:** The relationship between the energy and momentum of electrons and holes in a crystal based on the laws of quantum mechanics.

3 **Conduction band:** An empty energy band in charge neutrality state. The conduction band is the path through which injected electrons flow and is the element that determines electron mobility.

4 **Angle-resolved low-energy inverse photoelectron spectroscopy:** An experimental technique developed by Prof. Yoshida that can measure the energy and momentum of electrons flowing in the conduction band.

5 **Time-dependent wave packet diffusion method:** A method developed by Dr. Ishii to accurately calculate the mobility of electrons and holes in organic semiconductors based on quantum theory.

figure

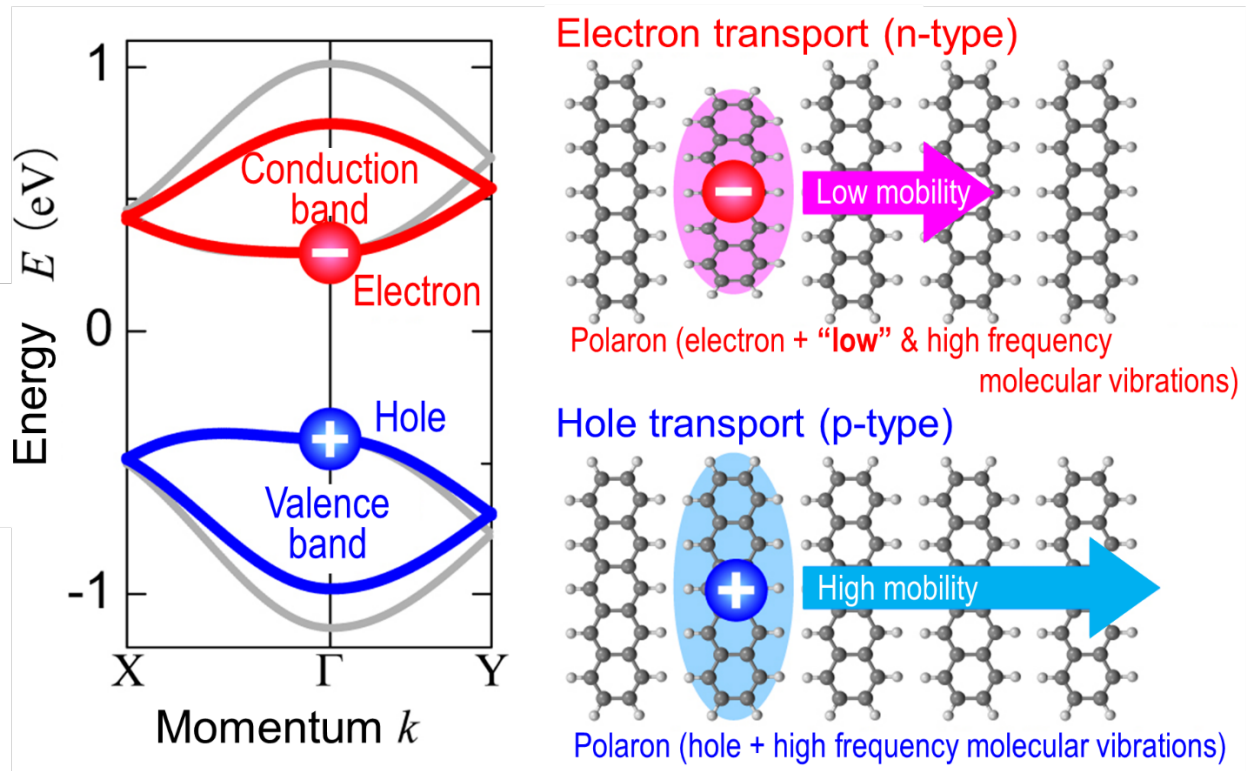


Fig. 1 Energy band structure of valence band and conduction band.

Holes flow in the valence band and electrons flow in the conduction band. Each band structure determines the hole transport property (hole conduction/p-type organic semiconductor) and electron transport property (electron conduction/n-type organic semiconductor) in organic semiconductors.