有機ラジカル結晶における電荷キャリア移動度に関する理論的研究

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Theoretical study on Charge Carrier Mobility in Organic Radical Crystals

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[Introduction]

Organic radicals have attracted intensively attentions from both theoretical and experimental studies in recent years. Due to the existence of unpaired electrons in open-shell molecules, strong interactions between radicals play an important role in the promising optical, electrical, and magnetic properties.[1-5] The packing of organic crystals could be tuned by chemical modification through different substituents. To bring insights for material design of radical crystals, the charge carrier mobility in organic radical crystals was discussed by a multi-scaled model with respect to molecular packing in the one-dimensional π-stacking crystal model. The hopping model for the charge transfer was applied in the study. First, the charge transfer rate was obtained based on DFT calculations. Next, the Monte-Carlo method was used to investigate the charge carrier mobility in a one-dimensional crystal model. The results show that the charge carrier mobility in the uniform packing structures is larger than the one in the dimerized packing structures. On the other hand, the non-local electron-phonon coupling effect was taken into account by introducing the fluctuation of inter-molecular distances.

[Theory]

A multi-scale method is proposed to estimate the charge carrier mobility in a one-dimensional organic crystal. The hopping model was used to obtain the charge transfer rate k based on the Marcus theory. [6]

$$k = \frac{|J|^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{\lambda}{4 k_B T}\right) \tag{1}$$

Here, DFT calculations were used to calculate the electronic coupling J and reorientation energy λ. To facilitate the simulation on the diffusive motion of charge carrier, which was time-demanding for DFT calculation, an empirical exponential equation was applied to model the electronic coupling J and the inter-molecular distance d.

$$|J(d)| = A \exp(-\beta d) \tag{2}$$

Next, the Monte-Carlo simulation was used to calculate the diffusion constant D based on the charge transfer rates, which is strongly dependent on inter-molecular distance d.

$$D = \frac{1}{2n} \lim_{t \to \infty} \frac{d\langle \Delta x(t)^2 \rangle}{dt} \tag{3}$$

Where $\langle \Delta x(t) \rangle^2$ is the mean squared displacement of the charge carrier at time t, and $n = 1$ for the one-dimensional organic crystal system. The diffusion constant D was obtained from a linear fit of $\langle \Delta x(t) \rangle^2$ with simulation time (Fig. 1).

Finally, the charge carrier mobility μ was derived from the diffusive motion of the charge carrier according to the Einstein-Smoluchowski equation

$$\mu = \frac{eD}{k_B T} \tag{4}$$

To further consider the effects of nonlocal electron-phonon couplings, which play important roles on charge transfer by influencing the electron coupling between molecules, a weighting function $P(d)$ was introduced to include the geometrical fluctuations of inter-molecule distances d.

$$\mu' = \frac{\sum P(d)\mu(d)}{\sum P(d)} \tag{5}$$

The weight function $P(d)$ was estimated based on the MD simulations.

[Results and Discussion]

The charge transfer process was studied using a one-dimensional organic crystal model. The charge carrier mobility was investigated with respect to the molecular packing. Δd is defined as the difference between the upper and lower inter-molecular distances in the crystal. A larger Δd corresponds to the crystal packing with stronger dimerization.

Fig. 1 shows typical time evolution of square displacement of individual charge carriers by Monte-Carlo simulation. The diffusion constant D of charge carriers is obtained by the slope of mean square displacement over 5000 individual trajectories.

Fig. 2 shows the charge carrier mobility with respect to molecular packing. The uniform packing ($\Delta d = 0$ Å) shows the largest charge carrier mobility. The mobility decreases while Δd increases. The comparison of unweighted and weighted charge carrier mobility is shown in Table 1. The results will bring insights to the material design for high charge carrier mobility. The calculations will be shown in detail in the poster.
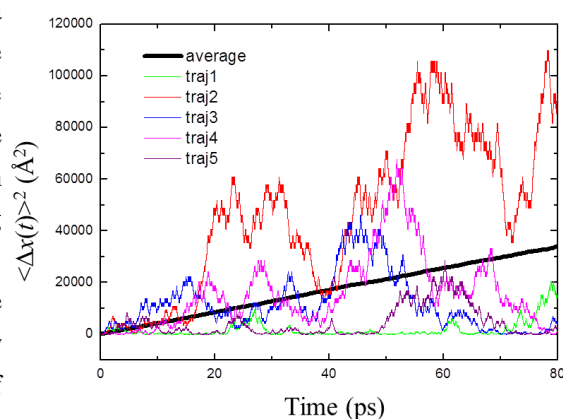

Fig.1. Monte-Carlo simulations for the square displacement of charge carriers.

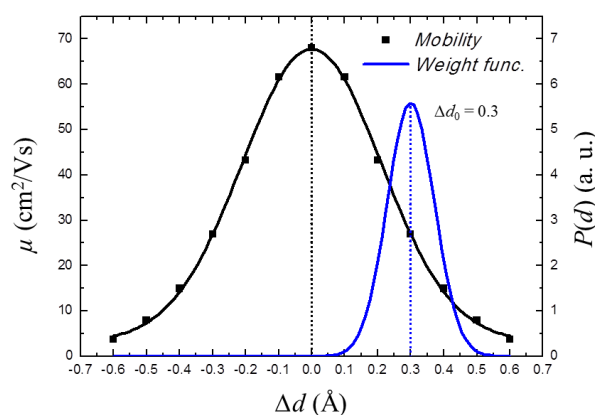

Fig. 2. The charge carrier mobility and molecular packing. The weight function is illustrated for $\Delta d_0 = 0.3$ Å.

Table 1. Comparison of unweighted and weighted charge carrier mobility (in cm^2/Vs) with respect to Δd (in Å).

Δd	μ (Unweighted)	μ' (Weighted)	$\Delta\mu=\mu'-\mu$
0.0	68.0	64.4	-3.6
0.1	61.6	58.6	-3.0
0.2	43.3	44.2	0.9
0.3	27.0	28.1	1.1

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