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Multiscale simulation of charge transport in a host material, \(N,N'\)-dicarbazole-3,5-benzene (mCP), for organic light-emitting diodes

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We have performed multiscale charge transport simulations in organic amorphous thin films by explicitly considering organic molecules. The simulations were based on quantum chemical and Monte Carlo calculations. The amorphous layer was composed of \(N,N'\)-dicarbazole-3,5-benzene, which is a widely used host material in the emissive layer of blue-emitting organic light-emitting diodes. The hole mobility was calculated to be three to four times larger than the electron mobility. This trend was consistent with the experimentally obtained mobility ratio. It was also found that the charges are transported dominantly by diffusion-type character at low applied electric fields and the contribution of drift-type character increased as the applied electric field increased. The difference between the number of hops in the forward and the backward directions contributes to the actual charge transport. From the detailed molecular level analysis, it was turned out that the molecular pairs with a large electronic coupling do not necessarily have large contributions to the charge transport; rather can temporarily trap charges. We found important molecular pairs, which form effective charge-transfer paths, although the electronic coupling was not substantially large.

Introduction

Organic light-emitting diodes (OLEDs) are one of the most attractive and promising devices for application to flat/flexible ultra-thin displays and solid-state lighting sources. In 1953, the first electroluminescence (EL) from organic compounds was observed by Bernanose et al. 1 Thereafter, Helfrich et al. observed EL resulting from the recombination of holes and electrons in anthracene single crystal under an applied electric field. 2 The first multi-layered OLEDs were reported in the pioneering work of Tang and VanSlyke in 1987. 3 They have greatly improved the EL efficiency of OLEDs by the insertion of a hole transport layer between electrode and emissive/electron transport layer. Adachi et al. have further improved the EL efficiency using the multi-layered structures. 4 These early studies have emerged significant interest in OLEDs and have formed the basis of device structures of today’s OLEDs.

At present, considerable efforts have been devoted to improve the luminescence efficiency. 5–10 The optimization of the charge injection and charge blocking at each interface, and charge transport in each layer is one of the crucial issues to decrease the energy loss. Among these factors, the injection and the blocking of charges have often been discussed in terms of energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of organic molecules. The HOMO and the LUMO can be well estimated using quantum chemical calculations for isolated molecules. However, the charge transport in organic aggregate systems is considered to greatly depend not only on the structure of the molecule in an isolated state but also in an intermolecular aggregated state. Recently, some research groups 11–14 including our own 15, 16 have evaluated charge transport properties by quantum chemical calculations of the rate constant for charge hopping between two molecules, \(k_{\text{CT}}\). This approach will provide some hints for the material design. However, calculated \(k_{\text{CT}}\) instead of the calculated mobility was compared against the experimental mobility in these studies. Moreover, crystal structures are used for the calculation of \(k_{\text{CT}}\) in most cases. Approaches not for crystal systems but for amorphous systems are necessary for a full understanding of OLEDs, because actual OLEDs are composed of amorphous thin layers.

We can find an approach for the understanding of charge transport properties of amorphous systems; Bässler et al. 17–19 evaluated the charge transport properties between the electrodes using Monte Carlo simulation. This is one of the most successful studies for charge transports. However, because this approach, including related studies, 20–30 does not consider the organic molecule explicitly, it is somewhat difficult to link the macroscopic charge transfer and the microscopic molecular structure directly.
We can assume that a detailed study of the charge transfer processes between electrodes is possible by the combination of these two approaches and such attempts have been made in recent years.\textsuperscript{31,37} For example, Kwiatkowski et al. performed simulations of the charge mobility for an amorphous tris(8-hydroxyquinoline) aluminum (III) (Alq\textsubscript{3}) system by approximating the Alq\textsubscript{3} molecule as a rigid body.\textsuperscript{32} This is the first attempt for the charge transfer simulation considering organic molecules explicitly, as far as we know. Although the absolute value of the experimental charge mobility of Alq\textsubscript{3} could not be reproduced, they succeeded in explaining the difference between hole and electron mobility. They considered that this difference originated from the delocalization of the HOMO and the LUMO on the Alq\textsubscript{3} molecule. Lukyanov et al. constructed an Alq\textsubscript{3} aggregated structure using molecular dynamics (MD) simulations without applying the rigid body approximation and investigated the influence of the force fields on the charge mobility in detail.\textsuperscript{32} However, theoretical treatment of amorphous systems is not yet well established. One of the reasons is that large-scale, high computational cost MD simulations are required to reproduce actual amorphous systems. Also, the method has been applied to Alq\textsubscript{3},\textsuperscript{31,36} and 2,8-bis(triphenylsilyl)-dibenzofuran (BTDF),\textsuperscript{37} 9,10-di-(2′-naphthyl)anthracene (ADN),\textsuperscript{38} 5,5′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPD)\textsuperscript{38} so far. The theory should be applied to other important molecular systems for the understanding of charge transfer phenomena in organic amorphous systems and for the development of excellent charge transfer materials.

In this study, we have performed multiscale charge transport simulations for the amorphous structure of N,N′-dicarbazole-3,5-benzene (mCP; shown in Fig. 1a), which has been used as a bipolar host material for the emissive layer in blue-emitting OLEDs. We also investigated the contribution of respective molecular pairs to the charge transport in amorphous thin films. We show that molecular pairs with large electronic couplings are not most important in charge transport processes. We will show some molecular pairs effectively transport charges in the forward direction, although they do not have substantially large electronic couplings. Charge transport in single crystal systems is mainly determined by electronic coupling. However, that is not necessarily true of amorphous systems. Actual OLEDs are composed not of crystalline but of amorphous thin layers. Since the crucial factor is different in amorphous and crystal systems, the approach for amorphous systems in this study is significant for the understanding of charge transports in actual OLEDs.

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Results and discussion

The entire computational flow is shown in Fig. 2. The geometry optimization of the mCP in its neutral, cationic, and anionic states were performed using density functional theory (DFT) implemented in the Gaussian 09 program package using the B3LYP/6-31G(d) level of theory.\textsuperscript{40} The reorganization energy for hole transport (\(\lambda^+\)) was obtained from the energies of the optimized structures of the neutral and cationic states. The reorganization energy for electron transport (\(\lambda^-\)) was calculated in a similar way. The details are provided elsewhere.\textsuperscript{15,16} The construction of the amorphous structure was carried out by MD simulation for 100 molecules of mCP in a cubic cell (denoted as “mCP-100”). To mimic the deposition process, the initial construction of the structure was performed at a density of 0.1 g cm\textsuperscript{-3} and at a temperature of 598 K. Pre-optimization was then conducted. The MD simulation was performed until the density of the system becomes constant, which was over 300 ps with the constant-pressure, constant-temperature (NPT) ensembles at 298 K. A system consists of ten molecules of mCP (denoted as “mCP-10”) was also constructed in the same way. The final density of the structure was 1.0 g cm\textsuperscript{-3} for both the mCP-100 structure and the mCP-10 structure. The amorphous structures thus obtained are shown in Fig. S1 in ESI. The calculation of the electronic coupling for hole and electron transfer (\(H_{AB}^+\) and \(H_{AB}^-\), respectively) was performed for the molecular pairs that have a center-to-center distance within 20 Å in the amorphous structure. Using the values of \(H_{AB}^+\) and \(\lambda^+\) or \(H_{AB}^-\) and \(\lambda^-\) obtained above, the rate constants for hole and electron transfer (\(k_{CT}^+\) and \(k_{CT}^-\), respectively) under the applied external electric field was calculated according Eq. 1,\textsuperscript{17,41}

\[
k^{+/−}_{CT} = \frac{4\pi^2}{h} H_{AB}^{+/−} \frac{1}{\sqrt{4\pi k_B T k_B^+}} \exp\left(-\frac{(\lambda^{+/−} + \Delta G)^2}{4\Delta x^2/k_B T}\right),
\]

(1)

where \(\Delta G\) is the free energy difference between the initial and final states, \(T\) is the temperature, \(h\) is Plank’s constant and \(k_B\) is Boltzmann’s constant. At present, Marcus theory is widely used and no crucial problems are found for treating the charge transport of organic molecules.\textsuperscript{42-44} Under the applied external electric field, the free energy change, \(\Delta G\), is given by Eq. 2,

\[
\Delta G = qF\Delta x,
\]

(2)

where \(q\) is the elementary charge (unit charge), \(F\) is the applied external electric field strength, and \(\Delta x\) is the distance between the neighboring relevant molecules along the electric field.
This is a continuation of the text from the previous page. It seems there might be a typographical error, as the words “Journal Name” and “ARTICLE” are repeated multiple times, which is unusual for a scientific document. Assuming the “Page 3 of 8” is indeed part of the document, the proceeding text might be part of a discussion or results section, possibly related to molecular dynamics or materials science, given the context of the calculations and simulations mentioned. The text references charge hopping calculations, electronic coupling, and reorganization energies, indicating a detailed exploration of molecular transport properties.

For a more accurate representation, the full text and diagrams should be examined. If there are specific points of interest or questions about the content, please let me know, and I can provide a more detailed analysis or clarification.
structure. At 300 V/cm, the hole (Fig. 5a) reached the counter electrode by using complicated routes, going back and forth, indicating a strong diffusive behavior. At 1,000 V/cm, the hopping of the hole in the direction of the applied field was more efficient (Fig. 5b). The trajectories for electron transport had a similar trend depending on the applied electric field (Fig. 5c and d). These results clearly indicate that there is increased contribution of the drift transport as the applied electric field strength was increased.

As shown in Fig. 3, \( H_{AB}^{\max} \) is greater than \( H_{AB}^{+} \). For the two molecular pairs which have \( H_{AB}^{\max} \), the value of \( H_{AB}^{+} \) was calculated according to Eqs. 1 and 2. They are denoted as \( k_{CT}^{+} \) and \( k_{CT}^{-} \), respectively. For 300–1,000 V/cm, the hopping of the hole in the direction of the applied field was more efficient (Fig. 5b). The trajectories for electron transport had a similar trend depending on the applied electric field (Fig. 5c and d). These results clearly indicate that there is increased contribution of the drift transport as the applied electric field strength was increased.

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The large difference between the initial and final states, \( \Delta \), is mainly efficient. Charge hopping for molecular pairs with large \( \Delta \) was mainly diffusive and back and forth between the two molecules, especially at low electric fields. For molecular pairs with \( \Delta \) max the contribution of the drift transport increased. For the pairs with large \( \Delta \), the free energy difference between the initial and final states, \( \Delta G \), is large as found from Eqs. 2 and 3. The large \( \Delta G \) is the origin of the effective forward hopping.

Table 1 Number of hops in the forward direction \( (N^+) \), backward direction \( (N^-) \), the sum \( (N_{\text{diff}}) \), and the difference \( (N_{\text{diff}}) \) for the respective molecular pairs shown in Fig. 8. The ratio of \( N_{\text{diff}} / N_{\text{diff}} \) and the average migrated distance \( (\Delta X) \) are also shown.

<table>
<thead>
<tr>
<th>Molecule Pairs</th>
<th>( H_{\text{AB}} ) ( \Delta X ) (meV)</th>
<th>( F^{1/2} ) (V(1/2 ) cm(^{-1/2} ))</th>
<th>Number of hops</th>
<th>( N^+ )</th>
<th>( N^- )</th>
<th>( N_{\text{diff}} )</th>
<th>( N_{\text{diff}} )</th>
<th>( \Delta X ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_{\text{AB}} \max )</td>
<td>29</td>
<td>300</td>
<td>584.7</td>
<td>582.4</td>
<td>1167.1</td>
<td>2.3</td>
<td>515</td>
<td>1.4</td>
</tr>
<tr>
<td>( \Delta X_{\max} \max )</td>
<td>2.9</td>
<td>300</td>
<td>8.0</td>
<td>3.6</td>
<td>11.6</td>
<td>4.4</td>
<td>3</td>
<td>4.2</td>
</tr>
<tr>
<td>( H_{\text{AB}} \max )</td>
<td>89</td>
<td>300</td>
<td>3595.3</td>
<td>3594.5</td>
<td>7189.8</td>
<td>0.8</td>
<td>9289</td>
<td>0.16</td>
</tr>
<tr>
<td>( \Delta X_{\max} \max )</td>
<td>5.7</td>
<td>300</td>
<td>27.2</td>
<td>22.1</td>
<td>49.3</td>
<td>5.1</td>
<td>10</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Conclusions

In this study, we performed the charge transport simulations in an amorphous mCP thin layer. Organic molecules were explicitly considered to link the macroscopic charge transfer and the microscopic molecular structure directly. The hole mobility of mCP was calculated to be three to four times larger than the electron mobility. This result was in good agreement with the experimentally determined ratio of the charge mobility for hole and electron transfer. It was clearly shown that while the diffusion transport is dominant at low applied electric fields, the contribution of the drift transport increased as the applied electric field increased. At a low electric field strength, both holes and electrons reached the counter electrode not through simple routes directly toward the direction of the applied electric field but through complicated routes, including the direction opposite to and perpendicular to the electric field. At a high electric field strength, charge hopping in the direction of the applied electric field can be advantageous and becomes significantly efficient. Charge hopping for molecular pairs with large \( H_{\text{AB}} \) was mainly diffusive and back and forth between the two molecules tended to occur more frequently. Therefore, these molecular pairs are not crucial for charge transports. In contrast, the contribution of the drift transport was dominant for molecular pairs with large \( \Delta X \). The molecular pair substantially improve charge mobilities by forming effective charge transfer paths.

We revealed that one of the important factor of charge transport in amorphous systems is relative configuration of the molecules rather than \( H_{\text{AB}} \). This is different from the charge transport in crystal systems. Our findings are important not only...
for fundamental science but also for the design of charge-transporting materials by controlling electronic states and intermolecular orientation. Further development of this approach is in progress for multi-layered amorphous systems composed of hole transport, emission, and electron transport layers, and for more complex systems, including charge blocking layers, etc.

Computational methods

The Dreiding force field was used for the MD simulation. The MD simulations were carried out under periodic boundary conditions. The parameters for the Dreiding force field such that the MD simulation reproduced the molecular structure of mCP optimized with DFT method (for more details, see Fig. S7 in ESI and Tables S1, S2). The total number of pairs, approximately 270,000, was reduced to about 5,000 pairs at the 20 Å cut-off for the calculation of $H_{AB}$ and $H_{AB}^{-}$. As shown in Fig. S8 in ESI, the values of $H_{AB}$ of the molecular pairs, whose adjacent center-to-center distance is more than 20 Å, is negligibly small, less than $1 \times 10^{-10}$ meV. We verified that these molecular pairs with small $H_{AB}$ do not take part in the charge transport. For Monte Carlo simulations, periodic boundary conditions were set in all directions. The thickness of the film was 100 nm and the electric field was applied in this direction for the charge transport simulation. The square root of the external electric field was $300\text{--}1000$ V cm$^{-1/2}$, which corresponded to a voltage of 0.9–10 V. The temperature was set to 298 K. Amorphous cell and Forcite programs (Accelrys Inc., San Diego, CA, USA) were used for the construction of the amorphous structure. Calculations of $H_{AB}$ was performed by the Gaussian 09 program package using the extended Hückel approach is in progress for multi-layered amorphous systems composed of hole transport, emission, and electron transport layers, and for more complex systems, including charge blocking layers, etc.

Acknowledgements

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Notes and references


By considering organic molecules explicitly, we could successfully link the macroscopic charge transfer and the microscopic molecular structure directly.