Prediction of Electronic Properties in Amorphous Organic Semiconductors

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ABSTRACT

Amorphous structures of hole-transporting materials were generated via molecular dynamics simulations, and their site-specific orbital energies were computed using quantum chemical calculations that explicitly account for intermolecular interactions. Based on the resulting electronic structure, key electronic transport properties were quantitatively evaluated, including hole mobility, the density of states of the valence band, the distribution of localized states near the valence band edge, and the effective density of states of the valence band. The calculated values show good agreement with experimental results, demonstrating that this integrated computational approach enables predictive evaluation of the electronic properties of amorphous organic semiconductors.

1 Introduction

Organic light-emitting diodes (OLEDs) have become increasingly prevalent in applications ranging from automotive displays to consumer electronics due to their superior contrast, design flexibility, and potential for transparent and flexible implementations. These devices typically consist of multilayered organic materials, each engineered to optimize charge injection, transport, and recombination within the emissive layer, where photon emission occurs. The tunability of organic semiconductors allows precise control over properties such as emission color and charge mobility through molecular design. However, identifying optimal materials remains a challenge, as trial-and-error approaches based on chemical intuition are inefficient given the vast design space.

To address this, integrated computational-experimental workflows have emerged as a promising strategy. Multiscale simulations—spanning quantum chemical calculations, molecular dynamics (MD), and kinetic Monte Carlo (KMC) techniques—enable the connection of molecular structure to macroscopic properties such as ionization energy, morphology, and charge mobility [1, 2]. The reliability of this multiscale simulation framework is validated through comparison between the computed physical properties of representative molecules and experimental benchmarks, providing a solid foundation for predictive modeling in OLED material discovery. However, KMC simulations are time-consuming and therefore not suitable for predicting the electronic properties of a large number of molecules.

In this presentation, electronic properties of five representative hole transporting materials (their chemical structures are shown in Fig. 1) for OLEDs in the amorphous aggregates were predicted using the novel successive conduction (SC) model [3]. The SC model can give the key electronic transport properties in a reasonable computational time. We will demonstrate the feasibility of predicting the electronic properties of amorphous aggregates of the representative hole transporting molecules.

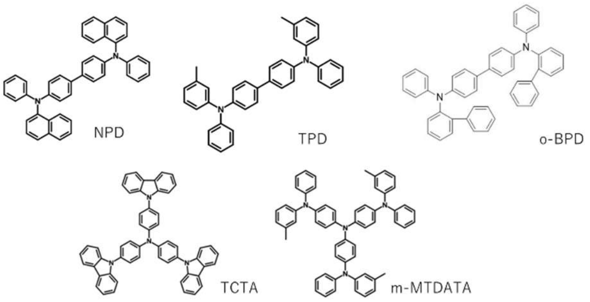

Fig. 1 Chemical structures of representative hole transporting materials. N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPD), N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD), N,N'-di(biphenyl-2-yl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine (o-BPD), 4,4',4"-Tris(carbazol-9-yl)triphenylamine (TCTA), and 4,4',4"-Tris(N-3-methylphenyl-N-phenylamino) triphenylamine (m-MTDATA).

2 Methods of calculation

2.1 Preparation of the model amorphous phase structure

The computational protocol for generating amorphous phase structures was provided in our earlier publication [4, 5]. Initial molecular assemblies were constructed using the Amber9 package with generalized AMBER force fields, applying periodic boundary conditions. The systems were first equilibrated at 1000 K and 1 atm to promote random molecular arrangement, followed by gradual cooling to 300 K over 4 ns. The resulting structures were adopted as amorphous models for the calculations of the key electronic transport properties of five representative hole transporting materials in Fig. 1.

2.2 Transfer rate constants

Charge transfer rate constants between molecular pairs (molecule *i* and *j*) in amorphous aggregates were calculated using Marcus theory

$$\boldsymbol{k_{ij} = \frac{4\pi^2}{h}\frac{t_{ij}^2}{\sqrt{4\pi\lambda kT}}\exp\left(-\frac{\left(\Delta G^0+\lambda\right)^2}{4\lambda kT}\right)}$$

where t_{ij} is the transfer integral between molecule *i* and *j*, λ is the reorganization energy, ΔG^0 is the Gibbs free energy change associated with the charge transfer, kT is the thermal energy, with the transfer integrals computed via density functional theory (DFT) at the cam-B3LYP/6-31+G(d) level. This functional was chosen for its ability to correct long-range charge transfer deficiencies inherent in standard B3LYP. Spin contamination and self-consistent field (SCF) convergence issues, particularly in radical species, were effectively mitigated using cam-B3LYP, yielding stable $\langle S^2 \rangle$ values around 0.75. All calculations were performed with Gaussian09. Transfer integrals were obtained using symmetrically orthogonalized monomer orbitals [6].

3 Results and discussion

3.1 Mobility

Based on the three-dimensional random walk theory [7], the diffusion constant of molecule *i* was calculated using the charge transfer rate constant k_{ij} obtained from Marcus theory under zero electric field conditions, along with the intermolecular distance r_{ij}. The corresponding hole mobility was then derived from the Stokes–Einstein relation. Mobilities for individual molecules were determined, and the average mobility was evaluated as the geometric mean of the individual values [3]:

$$\boldsymbol{\bar{\mu} = \left(\prod_{i=1}^{k}\mu_i\right)^{1/k}}$$

Figure 2 shows the average mobilities of representative hole-transporting materials calculated using the SC model. A reasonably good correlation with experimental data was observed, yielding a correlation coefficient of 0.88.

3.2 Density-of-states of valence band

The orbital energies of individual molecules in the amorphous aggregates were calculated while accounting for intermolecular interactions. The density of states was then obtained by counting the number of orbital energies within specified energy intervals. Figure 3 presents the calculated valence-band density of states along with the ultraviolet photoelectron spectroscopy (UPS) spectrum of TCTA [8] (although Figure 3 presents the results for TCTA, similar agreement between the calculated and experimental valence-band density of states has also been obtained for other representative hole-transporting molecules.).

A good agreement is observed between the calculated and experimental valence-band density of states, particularly in the reproduction of the major spectral features seen in the UPS data. This consistency validates the accuracy of both the modeled disordered molecular packing and the electronic structure calculations.

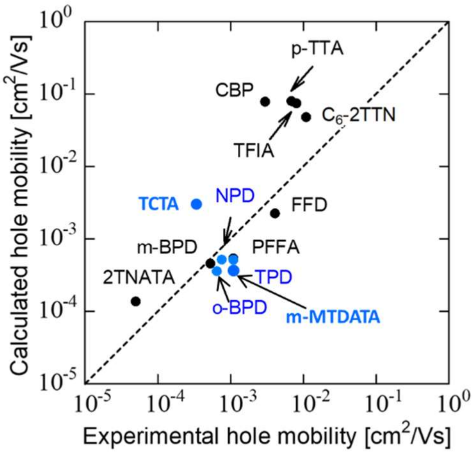

Fig. 2 Correlation between theoretically calculated and experimentally measured hole mobilities for the representative hole-transporting materials, including additional data from the literature [3]. The results demonstrate good agreement (the correlation coefficient is 0.88), indicating the validity of the SC method.

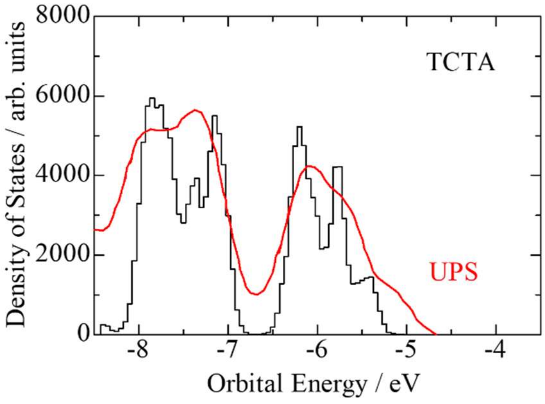

Fig. 3 Theoretically calculated valence-band density of states along with the UPS spectrum of TCTA.

3.3 Valence-band tail states

The absence of long-range order in amorphous semiconductors gives rise to band tail states, which play a critical role in determining their electronic transport properties. These tail states can be probed using transient or modulated spectroscopic techniques, such as time-of-flight (TOF) transient photocurrent and impedance spectroscopies [9]. In general, the energy distribution of band tail states can be approximated by a Gaussian function:

$$g(E) = \frac{N_0}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(E-E_v)^2}{2\sigma^2}\right]$$

where N_0 is the total density of localized tail states, E_v is the valence band mobility edge, and σ represents the energetic width of the distribution. Minimizing σ is essential for the molecular design of high-mobility hole-transporting materials. Among various techniques, TOF measurements are particularly effective for determining σ, as the energetic disorder can be extracted from the temperature dependence of the drift mobility [10], rather than relying on spectroscopic methods. Within the framework of the Gaussian Disorder Model (GDM) [11], the relationship between mobility and energetic disorder is given by:

$$\mu \propto \exp\left[-\left(\frac{2\sigma}{3k_BT}\right)^2\right]$$

Figure 4 summarizes the values of σ estimated from the theoretically calculated tail-state distributions, as shown in Fig. 3, along with experimental values reported in the literature [12–16]. The results indicate that the energetic disorder values derived from quantum chemical calculations are in good agreement with the experimental values.

3.4 Effective valence band density-of-states

The effective density of states, N_v, in the valence band was calculated from the following expressions [17]

$$N_v \exp\left(-\frac{E_f - E_v}{kT}\right) = \int_{-\infty}^{E_v} g(E) f(E, E_f) dE$$

using valence band density-of-states distribution, as shown in Fig. 3, where $f(E, E_f)$ is the Fermi-Dirac distribution function. In amorphous semiconductors, the effective density-of-states is a material parameter that cannot be determined by simple theoretical models as in crystalline semiconductors. Assuming that the Fermi level, E_f, is located near the center of the energy gap, the following values were obtained: 1.9 × 10^{18} cm^{-3} for TPD, 2.9 × 10^{18} cm^{-3} for NPD, 7.4 × 10^{17} cm^{-3} for o-BPD, 5.6 × 10^{17} cm^{-3} for TCTA, and 2.6 × 10^{18} cm^{-3} for m-MTDATA. These results indicate that the effective density-of-states in the valence band is on the order of 10^{18} cm^{-3}. There have been very few reports on the effective density-of-states of amorphous organic semiconductors, and the present findings are expected to provide useful insights for device simulations and related studies.

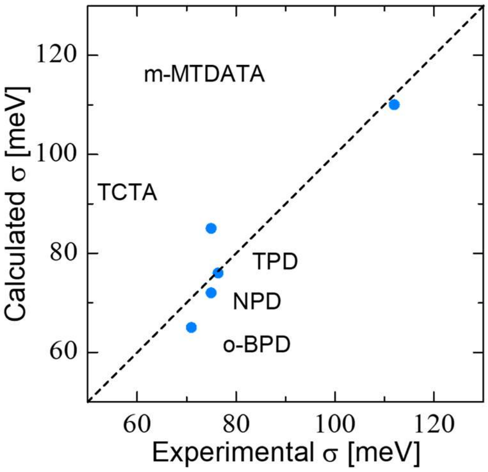

Fig. 4 Values of σ estimated from the theoretically calculated tail-state distributions as shown in Fig. 3, along with experimental values reported in literature.

3.5 Conclusions

Amorphous structures of representative hole-transporting materials were constructed using MD simulations, and molecular orbital energies were obtained through quantum chemical calculations. The hole mobility, the density of states in the valence band, and the distribution of localized states (tail states) near the valence band edge were evaluated within a relatively short time, making it suitable for high-throughput screening, and found to be in good agreement with experimental data. These findings confirm that the electronic properties of amorphous organic semiconductors can be effectively predicted.

Furthermore, the effective density of states in the valence band, estimated from the calculated density-of-states distributions, was found to be on the order of 10^{18} cm^{-3}.

Acknowledgments

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