

Theoretical Studies on Molecular Aggregates

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Keywords Exciton, Energy and Charge Transfer, Organic Semiconductors

Organic molecules can assemble into an ordered structure by non-covalent interactions, forming various types of aggregates. Molecular aggregates exhibit characteristic optical and electronic properties that are not observed in isolated molecules. For example, their photophysical processes include electronic energy transfer and charge separations, which are desirable for low-cost electronic devices.

We study optoelectronic properties and quantum dynamics of molecular aggregates. More specifically, we focus on energy and charge transfer dynamics, energy conversions, and structure-property relationship.

It is still challenging to simulate quantum dynamics in condensed systems. An exciton or electron wave function can be delocalized by electronic couplings due to molecular interactions; it is modulated by molecular vibrations. It is thus essential to consider electronic couplings and electron-phonon couplings on the same footing. We develop a method to simulate quantum dynamics in condensed phase by combining molecular dynamics simulations, electronic structure theories, and quantum dynamics methods, as shown in Figure 1. An electronic structure of an aggregate is described as tight-binding Hamiltonian with electronic couplings obtained from the fragment molecular orbital method. The energy or charge dynamics is described by quantum dynamics methods with

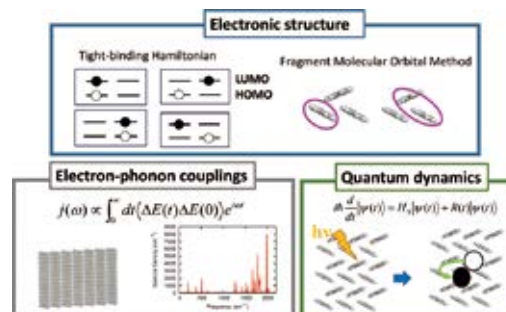


Figure 1. A combine approach to quantum dynamics in molecular aggregates.

incorporating finite-temperature effects and electron-phonon couplings. The combine computational approach allows for bottom-up descriptions of energy or charge transfer dynamics in molecular aggregates.

We currently investigate exciton dynamics in organic semiconductors, and structure-property relationships in ion-based π -conjugated molecular systems. We also study statistical-mechanics theories for predicting supramolecular structures in solution, and a many-body approach for excited-state calculations.

Selected Publications

- T. Fujita, J. C. Brookes, S. K. Saikin and A. Aspuru-Guzik, "Memory-Assisted Exciton Diffusion in the Chlorosome Light-Harvesting Antenna of Green Sulfur Bacteria," *J. Phys. Chem. Lett.* **3**, 2357–2361 (2012).
- T. Fujita, J. Huh, S. K. Saikin, J. C. Brookes and A. Aspuru-Guzik, "Theoretical Characterization of Excitation Energy Transfer in Chlorosome Light-Harvesting Antennae from Green Sulfur Bacteria," *Photosynth. Res.* **120**, 273–289 (2014).

1. Coherent Dynamics of Mixed Frenkel and Charge-Transfer Excitons¹⁾

There has been a growing interest in electronic properties in organic semiconductors due to their broad applications for electronic devices. Optical properties of organic molecular aggregates have been traditionally explained in terms of Frenkel exciton model, which describes an electronic excited state as a bound electron–hole pair. In recent years, great attention has been focused on charge-transfer excitons—a state where electron and hole can be located in separate regions. The CT excitons play essential roles in singlet fission and charge separations at donor/acceptor interfaces.

In this study, we focus on a p-type organic semiconductor, dinaphtho[2,3-b:2'3'-f]thieno[3,2-b]-thiophene (DNNT). A time-resolved spectroscopy study suggests that mixed Frenkel and CT excitons are formed in DNNT thin films after the optical excitation. Although the degree of CT characters in excited states has been discussed, its role in excitation dynamics has remained unclear. We investigate optical properties and exciton dynamics in the DNNT. The excited states of DNNT aggregates are described by tight-binding Hamiltonian combined with electronic couplings. Exciton dynamics coupled to molecular vibrations is modeled by a stochastic Schrödinger equation with spectral densities derived from molecular dynamics simulations and excited-state calculations.

The calculated absorption spectrum is in qualitative agreement with the experimental one. Our theory predicts that the low-energy Frenkel exciton band consists of 8 to 47% of CT character. The obtained excitonic Hamiltonian was used to simulate real-time quantum dynamics with incorporating exciton–phonon interactions in atomistic details. We observe the mixing of CT excitons with Frenkel state in 50 fs after the excitation. Accordingly, an electron–hole separation increases and shows an oscillation pattern as a result of delocalization of electron and hole and electron–hole Coulomb interactions.

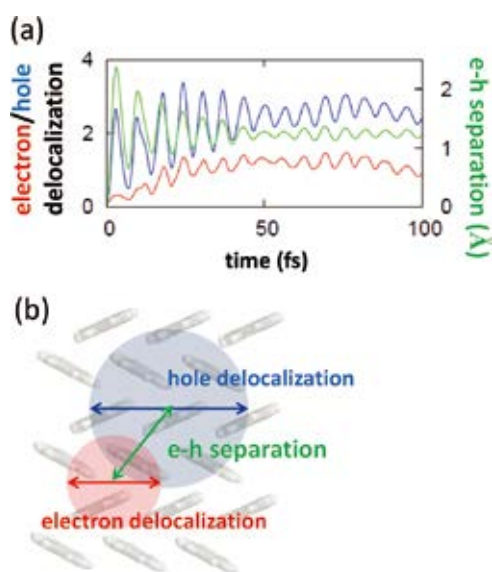


Figure 2. Ultrafast dynamics of mixed Frenkel-CT excitons in DNNT. (a) Electron and hole delocalization lengths, and electron–hole separations. (b) A schematic picture.

2. Polymorphism and Optoelectronic Properties of Anion-Responsible Molecules

π -conjugated molecules, especially aromatic hydrocarbons, show characteristic electronic and optical properties. The planar geometries are useful for constructions of stacking assemblies. Maeda and co-workers have proposed ion-based π -conjugated systems based on dipyrrolyldiketone difluoroboron (BF_2) complexes. Mixed with anion and cationic π -conjugated molecules, they form ion-based molecular assemblies.

Here, we consider the dipyrrolyldiketone BF_2 . This molecule shows the polymorphism of solid-state assemblies with different stacking modes. They have distinct optical and charge transport properties, which depend on their molecular stacking and interactions. In this study, we calculate charge mobility based on fragment molecular orbital calculations for transfer integrals and Marcus theory for charge transfer. Charge mobility is obtained from diffusion constants by Master equation with the hopping rates. Calculated hole mobility correlates well with time-resolved microwave conductivity measurements, suggesting that hole transport is responsible for the photoconductivity.

3. Solution Theories for Nano-Sized Hydrophobic Molecules

Solvation free energy (SFE) is most important thermodynamics quantities in solution chemistry. Molecular dynamics simulations combined with thermodynamic integration or free energy perturbation can offer exact computations of SFEs within statistical error and force fields employed. However, it requires large computational time especially for nano-sized molecular systems. Accurate and efficient estimations of SFEs is still challenging.

Here, we investigate the accuracy of approximate solution theories for calculating hydration free energies (HFEs) of nano-sized hydrophobic molecules. Energy representation and three-dimensional reference interaction site model (3D-RISM) with different closures were compared with molecular dynamics simulations with the Bennett acceptance ratio. The HFEs from approximate theories are in reasonable agreement for relatively small hydrophobic solutes. However, they show considerable errors in HFEs of large hydrophobic solutes and predict artificial solute-size dependence of the HFEs. A recently-proposed empirical correction based on a partial molar volume (PMV) of a solute significantly improves the 3D-RISM results in such a way that they become qualitatively agreement with the BAR. The success of the PMV correction is discussed in terms of asymptotic behaviors of HFEs in a limit of large solute size.

Reference

- 1) T. Fujita, S. Atahan-Evrenk, N. P. D. Sawaya and A. Aspuru-Guzik, *J. Phys. Chem. Lett.* **7**, 1374–1380 (2016).