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From electronic excited state theory to the property predictions of organic optoelectronic materials

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We introduce here a work package for a National Natural Science Foundation of China Major Project. We propose to develop computational methodology starting from the theory of electronic excitation processes to predicting the opto-electronic property for organic materials, in close collaborations with experiments. Through developing methods for the electron dynamics, considering superexchange electronic couplings, spin-orbit coupling elements between excited states, electron-phonon relaxation, intermolecular Coulomb and exchange terms we combine the statistical physics approaches including dynamic Monte Carlo, Boltzmann transport equation and Boltzmann statistics to predict the macroscopic properties of opto-electronic materials such as light-emitting efficiency, charge mobility, and exciton diffusion length. Experimental synthesis and characterization of D-A type ambipolar transport material as well as novel carbon based material will provide a test ground for the verification of theory.

electron dynamics methods, statistical physics approaches, light-emitting efficiency, charge mobility, exciton diffusion

1 Introduction

Applying large scale computation, starting from molecular structure and their stacking modes to predict the properties, is an urgent and press challenge. It is the foundation of molecular design for advanced materials. In 2011, President of the United States Mr. Obama announced the “Material Genome Initiative (MGI) for global competitiveness”. This new focused initiative will strengthen the computational capabilities, data storage and management, and an integrated approach to materials science and engineering, which is expected to accelerate the development of advanced materials through advancing computational methodologies and techniques, more effective use of standards, and enhanced data management [1].

The performances of organic optoelectronic materials as one important kind of advanced materials, have been improved rapidly recently, especially for those related to the electronic excited states. For example, the charge mobility for molecular films has reached 30 $cm^2/(V\ s)$ [2], and for conjugated polymers, the mobility is increased from 10^{-1} to the order of 10 [3]; the power conversion efficiency for polymer solar cells attains more than 10% [4]; and the white organic light-emitting-diodes lumen efficiency goes over 100 lm/W [5]. Organic light-emitting is resulted from competition of several elementary excited state decay processes. The charge transport is dictated by the linear response of the charged state driven by external electric field. In organic photovoltaic cells, the fundamental photoexcitation is exciton, instead of free carriers in conventional inorganic semiconductors. The former is termed as “excitonic cells” in comparison with the “electronic cells” for the latter. In “excitonic cells”, the photo-excited exciton migrates to the do-

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nor-acceptor interface to generate free carriers. It consists of both excited state transfer and charge transfer processes. Understanding the electronic processes in organic solids is at the central issue for predicting the opto-electronic function or property of materials. Based on that, one may devise computational methods for material design.

The most distinguishing feature for organic solids from traditional covalently bonded inorganic solids is the charge localization effects, namely, the delocalized band structure description is no more complete. In 1959, Holstein proposed the theory of polaron in molecular solids. The basic concept is that the charge or exciton is strongly coupled with intramolecular vibration, which induced localization [6]. Namely, the HOMO or LUMO level (for charge transport) or molecular excitation energy is coupled with molecular vibration, sensitive to vibration quanta or temperature. In the extremely strong coupling case, localization occurs within one single molecule and the charge transport can be regarded as charge or energy transfer followed by diffusion process [7]. Silbey and Munn [8] have first proposed the non-local coupling effect in addition to the Holstein's local model, where the electron-phonon coupling not only comes to the on-site term, but also to the inter-site hopping integral. Along the non-local line, the most prominent model was proposed in 1979 by Su-Schrieffer-Heeger [9] to modeling the soliton excitation in conducting polymer. And then, Brazovskii and Kirova [10] established the polaron model in polymers. The premise is that the bond-stretching mode is coupled to the resonance integral term, but not to the site energy term. All these models led to localization effect and can describe the electronic processes in organic solids. Full parallel to these advances is the phenomenological charge transport model in disordered systems. The most successful model was developed by Bässler, within which, the charge or exciton level is assumed to be disordered following Gaussian distribution. Such model has been very successful in reproducing the electric conduction as functions of temperature, electric field strength, carrier concentration *etc* [11]. Unfortunately, this phenomenological model is not directly related to molecular or polymeric structures, and does not help molecular design.

Recent years, great progresses have been made in computational electronic structure and computer technology, which render quantitative prediction of property as well as structure. Regardless of charge transport mechanism, Bredas *et al.* [12] and Ratner *et al.* [13] suggested quantum chemistry evaluations of the core molecular parameters governing charge transports including intermolecular electronic coupling and charge reorganization energy. Molecular design strategies have been proposed based on extensive quantum chemistry calculations regarding molecular packing and molecular architecture [14]. Starting from the hopping model coupled with Marcus semiclassical charge transfer theory, Song *et al.* [15] obtained the mobility values for triphenylamines dimers, concluding that the macrocycle dimer structure possesses hole mobility about one order of magnitude higher than the linear chain dimer, quite counter-intuitive but can be fully rationalized through charge reorganization energy analysis. This result has inspired computational chemists to devise molecular design strategies [16–21] for a variety of organic materials. By and large, the computational results are in good agreement with experiments [22]. Further developments include random walk simulation [23], quantum nuclear tunneling effect [24] and inclusion of dynamic disorder [25–27]. Regardless of the success of hopping model, there have been long time debates over the transport mechanism, namely, several experiments on organic single crystals indicated that the transport is governed by bandlike model, instead of hopping model with localized charge [25–27]. In fact, both Holstein and SSH models can give polaron picture. However, if combined with first-principles calculations, the resulting charge mobility is about two orders of magnitude higher than the experiments [28]. It is still a challenging issue to describe the charge transport both qualitatively and quantitatively. The complexity stems from the extent of charge localization.

Organic light-emitting diodes have great potential in industrial application for display and lighting technology. There have been great progresses in white-light emitting recently. For example, through ITO surface modification to improve the hole injection coupled with optical outcoupling, the luminescence efficiency reached 230 lm/W [29], in comparison with 0.8 lm/W when Kido *et al.* [30] first proposed the concept of WOLEDs in 1994. The internal quantum efficiency of electroluminescence for organometallic molecules can reach 100% since in principle, both the electro-excited singlet and triplet states can decay radiatively to give rise fluorescence and phosphorescence. So far, the highly efficient molecules are still limited to Iridium compounds as originally proposed by Forrest and Thompson *et al.* [31, 32] It is a challenging issue as how to explore novel metallic organic molecules with both high efficiency and stability. From the perspective of molecular design, enhancing radiative decay and reducing non-radiative decay at molecular level are the core issues. From computational chemistry, the electronic excited states, both structure and dynamics are at the center of light-emitting. Earlier time, people employed semiempirical model such as ZINDO to describe the excited state. For hydrocarbon molecules, the parametrization often gave satisfactory results. However, only first-principles calculation can be of predictive power. So far, the excited state theory based on first-principles calculation is under the stage of fast development, as proposed in this Major Research Project. We know that for small molecules, methods based on multireference configuration interaction such CASPT2, or MRCI can indeed give reliable descriptions for the potential energy surface at the excited states. Nevertheless, for relatively large system, time-dependent density functional theory (TDDFT) is the most widely employed approach in literature, which is under fast development for the improvement of both computational efficiency and accuracy.

Based on the displaced and distorted harmonic oscillator model coupled with TDDFT provided electronic structures, we have worked out a formalism to calculate the excited state decay rates both for radiative and non-radiative processes, considering both the mode-mixing Duschinsky rotation effect and the coordinate-dependent transition dipole (Herzberg-Teller effect). The calculated radiative decay rate and the absorption/emission spectra are in nice agreement with the experiments [33]. The calculated non-radiative decay rates partly agree with experiments but sometimes disagree. The discrepancy might be due to the deviation from the harmonic oscillator model. In fact, for large molecules, there are usually many vibrational modes involved in relaxation process to dissipate the electronic excited state energy, most of which involve small number of vibrational quanta, some of which could involve relatively large number of vibrational quanta, deviating appreciably the harmonic behavior [34]. Incorporation of spin-orbit coupling to break spin symmetry is essential for understanding the phosphorescence phenomena for WOLEDs [35].

In brief, based on developing TDDFT excited state theory as applied to organic functional materials, both the carrier transport and the light-emitting phenomena can be investigated which allow quantitative prediction of optoelectronic properties.

2 Objectives and tasks

The major objective of this work Unit of the Project is to integrate the developments from other three Units, namely, the linear scaling methodology for excited state in molecules and aggregates and spin-orbit coupling from Unit 1 as applied to the evaluation of forces from Unit 2 and the excited state dynamics developed in Unit 3, all of which can be applied to more or less extent to assess the charge mobility and light-emitting efficiency. Quantitative prediction of the optoelectronic property is a formidable objective for theoretical chemistry. Accordingly, we propose the following research tasks in order to fulfill the goal:

2.1 Computational methodology development and application for designing novel organic semiconductors

Charge transport is at the center of organic electronics. The charge mobility is increased steadily through synthesizing molecules with novel architectures. However, our understanding of the charge transport mechanism in organic semiconductors is still very limited. We recently proposed "tunneling enabled hopping" model for localized charge which not only presented reasonable explanation for the "paradoxical" experimental finding of "bandlike" in electrical measurement but "local" in optical measurement, but also give quantitative prediction for mobility values [36]. Neverthless, as we stressed before that the application scope for such model is for the molecular parameter in the range of $\lambda >> V$, where λ is molecular charge reorganization energy and V is the intermolecular electronic coupling. On another hand, once the charge localization condition is not satisfied, the charge transport can be described by band theory coupled with Boltzmann equation under the constant relaxation time approximation [37]. Under such circumstance, computational evaluations of the various scattering processes pose great challenges for computational chemistry at the first-principles level. Electron-phonon scattering dominates the intrinsic transport. The phonon dispersion effect is far from clear. Thus, we propose to investigate charge transport mechanism in a larger scope, namely going beyond the local approximation for more general molecular parameters, covering both band and local ranges. We also propose to develop efficient methods to calculate the electron-phonon relaxation time with phonon dispersion contribution. And finally, we propose to investigate the charge transport in donor-acceptor co-crystals for understanding the ambipolar transports under the superexchange mechanism.

2.2 Excited state non-adiabatic dynamics and non-radiative decay in OLEDs

OLEDs left over series problem for theoretical chemistry, namely, the excited state structure and dynamics for large molecules. In OLEDs, the electronic processes involve charge injection and transport, charge recombination and formation of molecular excited state, and the excited state decays. The injected charges forming electron-hole pairs with either spin 1 (triplet) or spin 0 (singlet). In organic materials the exchange energy is usually large ca. 0.7 eV [38], which prohibit any direct inter-conversion between spin manifolds. According to spin statistics, the singlet formation is limited to 25%, which was believed to be the maximum internal quantum efficiency for organic electro-fluorescence in light-emitting diodes. This limit has been removed for polymeric materials since the singlet exciton formation rate can large exceed that of triplet [39]. Another possibility was to introduce heavy elements to enhance the spin-orbit coupling which breaks the spin conservation. Right after the exciton formation, the competition between radiative and non-radiative decays comes to the central stage, namely, conversion of electronic energy to light or heat. In fact the light emission theory has been well established after Einstein spontaneous emission model coupled with quantization of electromagnetic field. However, the non-adiabatic coupling of electron with nuclear motion has been a long-standing problem. We propose to investigate both the singlet and triplet excited state decays through the non-radiative channels. We are going to combine our multimode mixing correlation function formalism with spin-orbit coupling quantum chemistry calculation methods developed by Unit 1 as well as the excited state dynamics developed by Unit 3 to develop a working computational scheme for predicting the light-emitting quantum efficiency. The solid state effect will be incorporated through combined quantum mechanics and classical mechanics (QM/MM) [40].

2.3 Computational simulation of exciton diffusion and photovoltaic conversion

Based on what we have worked out for charge transport and excited state dynamics, we would then tackle the complicated electronic process in photovoltaic conversion for organic and polymeric materials. Under the illumination, excitons are generated first as a bound state of electron and hole. This is a collective excitation. Namely, when one molecule or chromophore is excited, the excitation energy can propagate to the neighboring molecules. The eigen state of the aggregate is described by a linear combination of these excitations. The propagation of exciton could be quantum coherently or incoherently (Foerster process). In general, in polymers, there present sizable static disorders which localize exciton, making the Foerster process dominant. Since the life time for exciton is short (~ ns), the diffusion length is usually also short, such as a few to a few tens nm [41]. The exciton diffusion length is of critical importance: if it is too short, the exciton will decay before it reaches the interface for free charge generation. Thus, the exciton diffusion length is of both fundamental and practical interests. We propose to develop computational scheme to estimate the exciton diffusion length starting from the excited state lifetime and the exciton mobility assuming Foerster transfer process. Thus, except the charge collection at the electrodes, the electronic processes occurred in organic solar cells are all taken into consideration in this project.

2.4 Experiment part

We have so far discussed the charge transport, excited state decay, and exciton diffusion from theoretical perspectives. Some of the computational results can be verified by experiments. Thus, in this Unit, we plan to carry out materials preparation and device characterization. Two types of materials system will be considered here, the donor-acceptor cocrystal and ambipolar field-effect transistors [42] and novel carbon materials with triple bonds. In donor-acceptor cocrystal, donor moiety is responsible for hole transport and the acceptor for electron. We are going to look at how the dimensionality of D/A molecules, packing modes, and the D/A strengths influence the charge transport properties. Device characterization will be done with FET structure. Novel carbon materials such as graphdiyne or graphyne have attracted great attentions due to the application potential in next generation electronics. Most importantly, the charge mobility in carbon materials is expected to be two orders of magnitude higher than the traditional silicon wafer. Bandlike transport is anticipated in carbon materials and the intriguing issue is the dispersion effect of phonon in the electron-phonon interaction. Fabrication techniques of novel ultrathin carbon film with large area and high quality are essential to realize FET device. The novel physical and chemical properties for graphdiyne will be revealed through combined experimental and theoretical/computational studies.

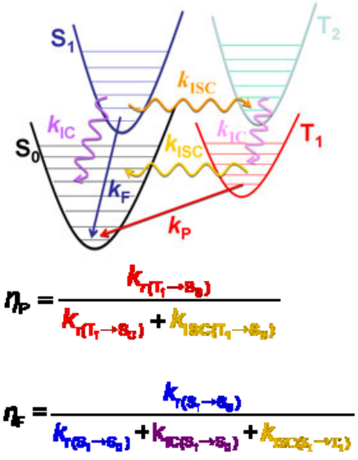
3 Scientific issues and the proposed methodologies applicable

From the above introduction of the project, we identify the following scientific issues: (i) electron-nuclear coupled non-adiabatic dynamics for polymers and molecular aggregates to understand the charge mobility with variable localization; (ii) excited state dynamics for singlet and triplet decay to dictate the luminescence quantum efficiency, shown in Figure 1; (iii) exciton dynamics and transport to understand the mechanism of exciton diffusion.

We proposed the following methodologies to solve the key scientific issues:

(i) Developing charge transport modeling tools from localized to delocalized pictures (Figure 2): In fact, localized model has been well developed. The state-of-the-art approach is to combine quantum tunneling charge transfer model with dynamic Monte Carlo simulation as well as first-principles calculations. To go beyond the local picture, we need to look at the diffusion process of wave packet evolution, which not only can describe the extent of charge localization, but also the diffusion constant and charge mobility;

(ii) Ambipolar transport and superexchange effects: Under the current transport model based on localized charge,



$$\eta_P = \frac{k_{r(T_1\rightarrow S_0)}}{k_{r(T_1\rightarrow S_0)} + k_{ISC(T_1\rightarrow S_0)}}$$

$$\eta_F = \frac{k_{r(S_1\rightarrow S_0)}}{k_{r(S_1\rightarrow S_0)} + k_{IC(S_1\rightarrow S_0)} + k_{ISC(S_1\rightarrow T_1)}}$$

Figure 1 The excited state dynamics for singlet and triplet decay processes.

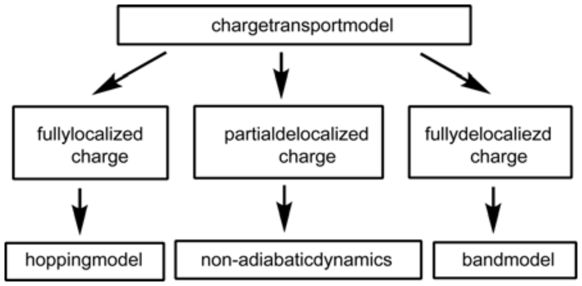


Figure 2 Charge transport model from localized to delocalized pictures.

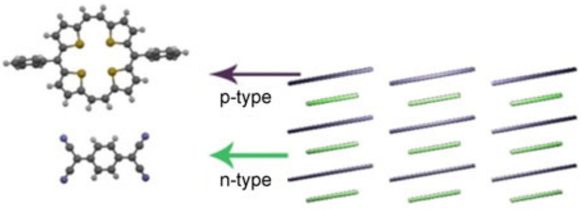


Figure 3 Alternate stacking donor-acceptor cocrystal. Reprinted with permission from Ref. [43]. Copyright © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

the long range coupling effect cannot be considered. For example, in a donor-acceptor cocrystal, the donor-donor moieties are separated by acceptor (Figure 3). The direct coupling between two donors is zero. However, the coupling could be realized by indirect through bridge, namely, the superexchange effect. Starting from dimer model, we apply the Lowdin transformation to orthogonalize the diabatic orbital and superexchange is obtained through elimination of the acceptor coordinate in the D-A-D coupled Hamiltonian;

(iii) Electron-phonon scatterings and relaxation: For the novel carbon materials (graphene, nanotube, graphyne/graphdiyne), the charge is well delocalized and band like transport is the most appropriate. The scattering/relaxation time dictates the charge transport according to Boltzmann's equation. It is a formidable challenge to go beyond the Gamma-point approximation to calculate the electron-phonon scattering matrix with full consideration of phonon dispersion at the first-principles level. The transformation from Bloch to Wannier representations will allow efficient cut-off in real space to carry out and when back-transformed to Bloch space, much fewer computational grid-points are needed. This is to be tested and is expected to be a low-scaling approach;

(iv) Excited state non-adiabatic dynamics for non-radiative decay rate: there have been tremendous progresses in understanding the ultrafast non-adiabatic dynamics for conical intersection, which are still limited for small molecules and to picoseconds. For organic light-emitting molecules or polymers, the radiative decay time is usually at nanosecond scale and in general conical intersection occurs at sub-picosecond, irrelevant to light-emitting. Nanosecond dynamics requires very efficient electronic structure calculations. We propose to start with tight-binding DFT and QM/MM approach and later, we sort to apply the linear scaling TDDFT method;

(v) Spin-orbit coupling and phosphorescence. The non-radiative coupling Hamiltonian consisting of both Born-Oppenheimer coupling and spin-orbit coupling can be expresses as:

$$\hat{H}'\Psi_{\mathrm{i}\nu} = \hat{H}'_{\mathrm{BO}}\Phi_{\mathrm{i}}(\mathbf{r};\mathbf{Q})\Theta_{\mathrm{i}\nu}(\mathbf{Q}) + \hat{H}'_{\mathrm{SO}}\Phi_{\mathrm{i}}(\mathbf{r};\mathbf{Q})\Theta_{\mathrm{i}\nu}(\mathbf{Q}), \quad (1)$$

where Φ and Θ are wavefunctions for electron and nuclear, respectively. From Fermi Golden Rule, the transition rate between initial and final states is:

$$k_{\mathrm{f}\leftarrow\mathrm{i}} = \frac{2\pi}{\hbar}\sum_{v,u} P_{\mathrm{i}v}\left| H'_{\mathrm{f}u,\mathrm{i}v} + \sum_{n,\mu}\frac{H'_{\mathrm{f}u,n\mu}H'_{n\mu,\mathrm{i}v}}{E_{\mathrm{i}v} - E_{n\mu}}\right|^2 \delta\left(E_{\mathrm{f}u} - E_{\mathrm{i}v}\right) \quad (2)$$

Vibration correlation function approach can make the above expression as a compact time integration formalism, ready for quantum chemistry. The spin-orbit coupling operator is the Brei-Pauli term:

$$\hat{H}_{\mathrm{SO}} = \frac{e^2}{2m_e^2c^2}\sum_{i=1}^{N_{el}}\sum_{\alpha}^{N_{\mathrm{A}}} Z_\alpha \left(\frac{\boldsymbol{r}_{i\alpha}}{r_{i\alpha}^3}\times\boldsymbol{p}_i\right)\cdot$$

$$s_i - \frac{e^2}{2m_e^2c^2}\sum_{i=1}^{N_{el}}\sum_{j\neq i}^{N_{el}}\left(\frac{\boldsymbol{r}_{ij}}{r_{ij}^3}\times\boldsymbol{p}_i\right)\cdot(s_i + 2s_j) \quad (3)$$

In the framework of TDDFT, both the H'_{BO} and H'_{SO} can be evaluated for ground state to excited state transition. The work from Unit 1 on relativistic DFT and from Unit 2 on analytical second derivative will be directly employed in this part for efficiently evaluating spin-orbit coupling and the excited state normal modes. The whole solving process is shown in Figure 4.

(vi) Aggregation effects on light-emitting: Intermolecular interaction is generally weak for organic aggregate. The excited state is dominated by excitation on a single molecule. Intermolecular Coulombic interaction results in energy transfer, while intermolecular wavefunction overlap causes electron transfer. Both effects could reduce charge recombination chances and decrease light-emitting quantum efficiency. Coherent intermolecular stacking also causes Davydov splitting, often making the lowest-lying energy level with canceling transition dipole moment. As a matter of fact, the light-emission in films is very often much weak than in solution, or aggregation-caused emission quenching. This is detrimental to display or lighting application, since the device is working in solid state. Recent discovery of aggregation induced emission (AIE) by Tang et al. and the computational study by Shuai et al. indicated the possibility that the aggregation could block the non-radiative decay channels, thus the quantum efficiency is enhanced by intermolecular interaction. We propose to treat one single molecule

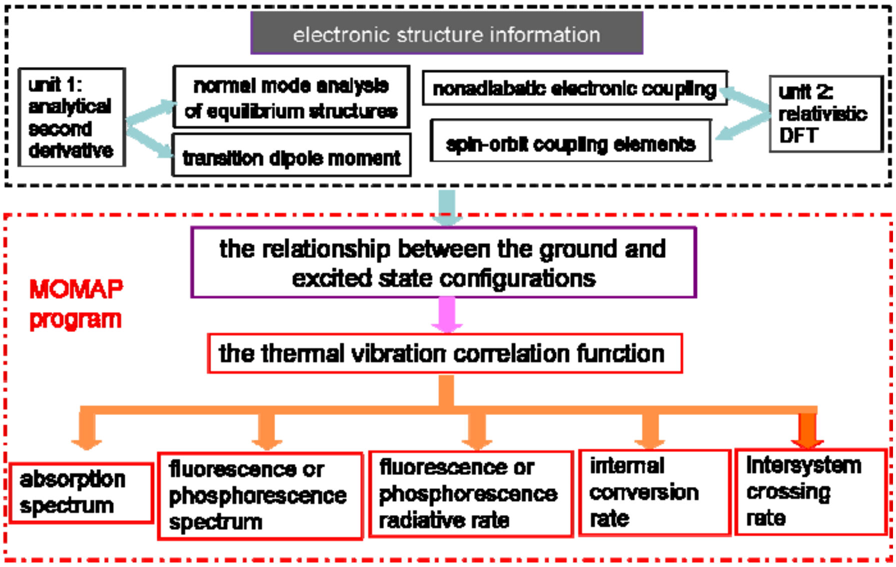


Figure 4 The whole scheme to calculate the luminescence quantum efficiency.

as light-emitting center by quantum mechanics while the surroundings by molecular mechanics (QM/MM) with full consideration of intermolecular electro-static interaction. The intermolecular excitonic effect is neglected in such an approach, which is justified by the fact that the emission spectrum in film is close to that in solution at room temperature.

(vii) Evaluating the exciton diffusion length can be started also with the Fermi Golden Rule for localized exciton, where the excitation energy transfer rate is expressed as:

$$k_{\mathrm{DA}} = \frac{2\pi}{\hbar}\sum_{v_{\mathrm{D}},v_{\mathrm{D}^*}}\sum_{v_{\mathrm{A}},v_{\mathrm{A}^*}} P_{\mathrm{D}^*}P_{\mathrm{A}}\left|\left\langle \Psi_{\mathrm{D}^*v_{\mathrm{D}^*}}\Psi_{\mathrm{A}v_{\mathrm{A}}}\right|H_{\mathrm{DA}}\left|\Psi_{\mathrm{A}^*v_{\mathrm{A}^*}}\Psi_{\mathrm{D}v_{\mathrm{D}}}\right\rangle\right|^2$$

$$\cdot\delta(E_{D^*v_{D^*}}+E_{Av_A}-E_{A^*v_{A^*}}-E_{Dv_D}) \qquad (4)$$

where the donor-acceptor coupling terms both for singlet and triplet can be evaluated at TDDFT level. The spectrum overlap, namely, the emission of donor with absorption of acceptor, can be calculated through the correlation function formalism we developed earlier. Combining excitation energy transfer rate, excited state decay (both radiative and non-radiative) rates, the intrinsic exciton diffusion length can be roughly estimated assuming diffusion process. We also propose to go beyond the local exciton assumption by carrying out exciton dynamics in aggregates.

(viii) Synthesis and charge transport measurements for donor-acceptor cocrystal as ambipolar materials and novel carbon materials. This work unit is not only to integrate the theoretical developments from other three units, but also to apply the integrated theoretical methodology to the recent development in experiments, namely, D-A cocrystal and graphdiyne materials. In the past decade, vast amounts of organic molecules have been designed for organic field-effect transistor. These are either hole or electron transport materials, with very few ambipolar transport materials. Employing the existing molecules to form D-A co-crystal is an efficient way to fabricate novel transport materials with ambipolar properties, without resorting complicated molecular design with novel architectures. Our strategy is to select two types of molecules with matching frontier molecular levels first, and then to synthesize the cocrystals. Transport property is measured by FET device. For the novel carbon materials, we will continue the efforts for controllable fabrication of ultrathin film of graphdiyne as well as its molecular fragments.

4 Summary

To summarize, we present here an introduction to a proposed research work on “Theoretical predictions for the optoelectronic properties of materials from the electronic excited states” as an integrated work unit in a Major Research Project “Theoretical study of the low-lying electronic excited states for molecular aggregates” from the National Natural Science Foundation of China. This work unit of the Project intends to integrate the methodologies developed in other three Units to study the electronic processes in organic and carbon materials. We propose here to develop computational methodology for the carrier transport covering both localized charge to delocalized band model and the low-scaling method for electron-phonon interaction with dispersion effects for evaluating the relaxation time. For ambipolar transport, we propose the superexchange mechanism for D-A cocrystal and the corresponding method development for computation. We propose to study the excited state radiative and non-radiative decays including both spin-orbit coupling and non-adiabatic coupling. We intend to evaluate the exciton diffusion length starting from the energy transfer rate, excited state lifetime, and a random walk simulation. We also propose to carry out materials synthesis and device fabrication for experimental verification of the theoretical results, especially for the D-A co-crystal ambipolar transport and the novel carbon materials.

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