Postdoc Fellowships for non-EU researchers

Final Report

Name	Linjun Wang
Selection	
Host institution	University of Mons
Supervisor	David Beljonne
Period covered by this report	from 2012/1/1 to 2013/6/30
Title	Exciton Transport and Dissociation at Organic Interfaces: A Microscopic Picture

1. Objectives of the Fellowship

The title of this BELSPO postdoc fellowship is exciton transport and dissociation at organic interfaces. In detail, the main goal of the research project is two-fold: (1) to reveal the mechanism of exciton diffusion in organic solids and films, and (2) to obtain a microscopic description of exciton dissociation into free electrons and holes at organic interfaces.

For the exciton diffusion part, due to the fact that charge transport is generally similar to exciton diffusion and that molecular crystals are more well-defined than complex organic films, we try to reveal the charge transport mechanism in organic crystals as a starting point. In this field, there already exists a lot of theories, each one of which has advantages and limitations of their own. Among them, the two most widely used approaches are the hopping model and the band model. In the former case, charge carriers hop between neighboring molecules with a timescale obtained from the charge transfer rate in molecular dimers. The hopping model works for systems with weak intermolecular electronic couplings and large electron-phonon interactions, and generally results in a thermally activated temperature dependent mobility. In the band model, charge carriers diffuse in a wave manner, and the scattering by phonons is treated as a perturbation. It is valid for systems with large intermolecular couplings compared to the electron-phonon interaction strength. The resulting temperature dependence of mobility is normally a power law function. For real materials, the charge transport picture should be in between the two limiting models, and thus a more general theoretical description of charge transport is strongly needed. In principle, this can be done within the framework of mixed quantum-classical dynamics. There are two major choices: one is the mean field method and the other one is surface hopping. Within this project, we firstly make assessments of the mean field theory and find that it is not possible to describe properly the hopping picture. For the surface hopping option, so far there is little investigation in literature to apply it for large molecular systems. The major difficulty is the so-called trivial crossing problem due to the existence of high density of electronic states. Within this project, we have proposed a novel flexible surface hopping technique to solve this issue, and produced the crossover from hopping to band transport when tuning the intermolecular couplings. Current flexible surface hopping calculations are limited to model Hamiltonians, so we still use existed methods to describe real systems according to their characteristics. The deformation potential theory, which belongs to the class of band models, has been explored and applied to study charge transport in noncovalently functionalized graphene and graphene nanoribbons. We also move to exciton diffusion in anthracene crystals and P3HT films, where the hopping model has been used.

Exciton dissociation at organic interfaces is a more complex dynamical process started with light absorption. The absorption spectra of molecular aggregates is what we need to resolve in the first place. To this end, we need to evaluate the exciton couplings between neighboring molecules to determine whether the system is a *H* or a *J* aggregate. The Davydov splitting between *H* and *J* bands is also of great interest. The coupling between electron excitation and high frequency vibrational modes induces vibronic features into the optical spectra. The relative intensity of the corresponding peaks is largely determined by the exciton-phonon coupling strength. We apply these techniques to a series of diketopyrrolopyrrole derivatives and polymorphs. The efficiency of exciton dissociation strongly relies on the energy landscape of the electron-hole pair. When the energetics is known, one can perform Monte Carlo simulations to obtain the output and timescale for exciton dissociation. A hot P3HT/PCBM interface is chosen for detailed investigation.

2. Methodology in a nutshell

(1) Quantum chemical theories

In quantum chemistry, there are various different levels of theories. The most commonly used ones are Hartree-Fock (HF), which is a mean field model that includes the Pauli exclusion principle, and density function theory (DFT). which takes a significant further step to incorporate electron correlations arising from both the Pauli principle and Coulomb interactions. Starting from HF, one can neglect three- and four-center two-electron integrals as realized in the so-called neglect-of-differential overlap type semiempirical methods. The accuracy of DFT relies on the choice on exchange-correlation functionals.

(2) Molecular dynamics

Molecular dynamics is a classical method that do not treat electrons explicitly. The trajectories of atoms and molecules are determined by numerically solving the Newton's equations of motion for a system of interacting particles, where forces between the particles and potential energy are defined by force fields with empirical parameters.

(3) Mean field theory

The nuclear dynamics at the mean field level is governed by the gradient of the energy expectation value from the time-dependent electron wave function, namely, a single potential energy surface. This mean field approximation, which is also widely called Ehrenfest method, is mostly appropriate when electron dynamics is fast or the forces from all adiabatic potential energy surfaces are of similar magnitude.

(4) Surface hopping method

Surface hopping approach can incorporate nonadiabatic transitions between different adiabatic potential energy surfaces, and thus is superior to mean field when nuclear motion on different adiabatic surfaces may lead to divergent trajectories. Despite of the great advantages of surface hopping, there have been no extensive studies so far aiming at implementing standard surface hopping formalisms for charge transport in large supramolecular systems due to the difficulty in dealing with the high density of adiabatic potential energy surfaces. Within this BELSPO project, we have propose a flexible surface hopping technique, which treats only a small part of the system in a surface hopping manner and does it in a flexible way in time. In our approach, the problematic crossing problem is avoided because all adiabatic states are spatially close and the computational cost is largely reduced because we only diagonalize a very small Hamiltonian matrix to get all important potential energy surfaces.

(5) Deformation potential theory

Deformation potential theory was proposed to deal with a special situation of electron-phonon scattering. It is assumed that the local deformations induced by the acoustic phonons are similar to the homogeneously deformed crystal. Normally, the effective mass approximation or the Boltzmann transport equation is used. It has proven to be a powerful tool to study the intrinsic carrier mobility of carbon allotrope materials, such as carbon nanotubes, graphene nanoribbons, graphdiyne, and molecular crystals, where electron-phonon scattering arises primarily from the acoustic phonons at low electric fields.

3. Results

(1) Modeling the crossover from hopping to band-like transport in organic crystals

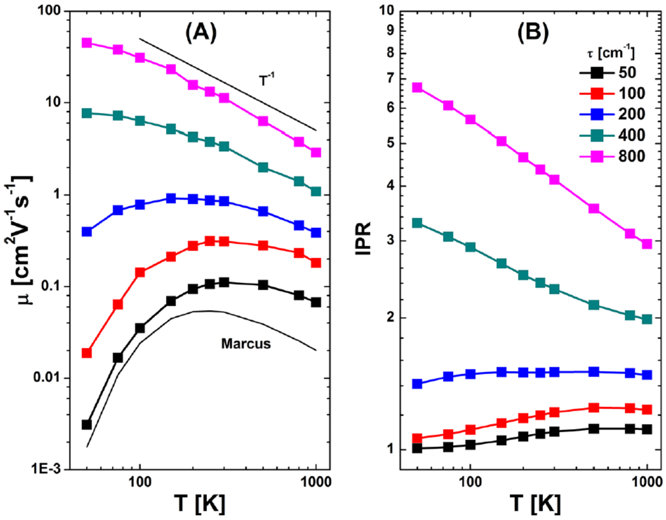

Figure 1. Temperature dependence of the (A) charge carrier mobility and (B) inverse participation ratio (IPR) for model stacks characterized with local electron-phonon couplings. The electronic coupling between the nearest neighboring molecules (τ) varies as indicated, while all other parameters are fixed. The Marcus result and a power law T^{-1} dependence are shown as guides to the eyes.

Two distinct pictures are usually evoked when modeling charge transport in organic crystals, that is, band and hopping models, the signature of which is conveyed by a characteristic temperature dependence of mobility. Applying our recently developed flexible surface hopping (FSH) method to one-dimensional mixed quantum-classical Hamiltonians considering both local and nonlocal electron-phonon couplings, we are able to grasp the crossover from a thermally activated hopping at low electronic coupling to a power law band-like temperature dependence at high couplings (see **Figure 1**). Our work published in J. Phys. Chem. Lett. 4, 1888 (2013) provides a clear rationale of the relationship between the temperature dependence of charge mobility and the corresponding spatial localization strength of charge carriers. In particular, we show that the hopping-to-band crossover already occurs for charge carriers that spread over a few molecular sites. We also reveal how thermal dynamic disorder can either decrease or enhance charge transport depending on the intrinsic charge carrier size. The picture obtained from FSH dynamics is qualitatively similar to that of the polaron model, which has been widely used to study charge transport in molecular crystals, and furthermore it shades deeper insights into the mechanism of charge transport with a much broader parameter range.

(2) Assessment of the mean field theory in the hopping regime of charge transport

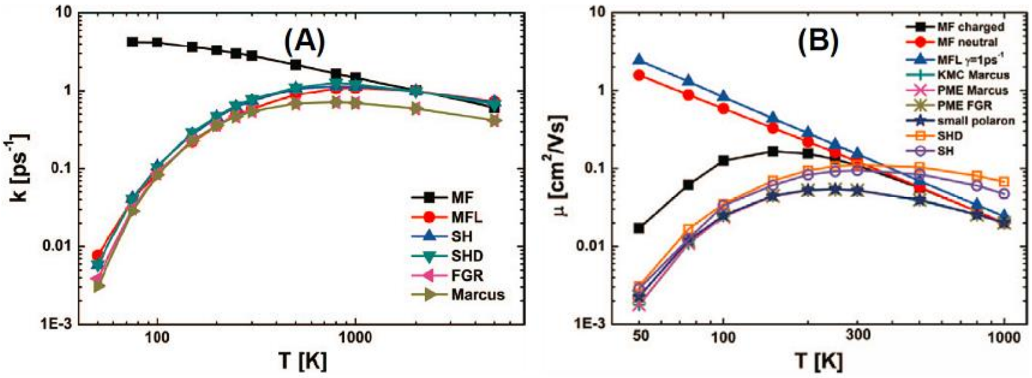

Figure 2. (A) Temperature dependence of the charge transfer rate by the mean field (MF) approach with and without system-bath interaction, the surface hopping (SH) approach with and without decoherence, together with the results from Fermi's golden rule (FGR) and Marcus formula. (B) Temperature dependence of charge transport mobility calculated with the MF theory starting from charged and neutral geometries without system-bath interaction, MF theory with system-bath interaction, the kinetic Monte Carlo (KMC) and Pauli master equation (PME) approaches based on Marcus charge transfer rate, the PME approach based on FGR, the small polaron model, and FSH calculations with and without decoherence.

The performance of the mean field theory to account for charge transfer rate in molecular dimers and charge transport mobility in molecular stacks with small intermolecular electronic coupling and large local electron-phonon coupling (i.e., in the hopping regime) has been carefully investigated against various other approaches in our study published in J. Chem. Phys. 139, 064316 (2013). Using Marcus formula as a reference, it is found that mean field theory with system-bath interaction and surface hopping approaches yield fully consistent charge transfer rates in dimers (see **Figure 2A**). However, in contrast to the dimer case, incorporating system-bath interaction in the mean field approach results in a completely wrong temperature dependence of charge carrier mobility in larger aggregates (see **Figure 2B**). Although the mean field simulation starting from the relaxed geometry of a charged molecule and neglecting system-bath interaction can reproduce thermally activated transport, it is not able to characterize properly the role of additional nonlocal electron-phonon couplings. Our study reveals that the mean field theory must be used with caution when studying charge transport in the hopping regime of organic semiconductors, where the surface hopping approach is generally superior.

(3) Energy level alignment and charge mobility in noncovalently functionalized graphene

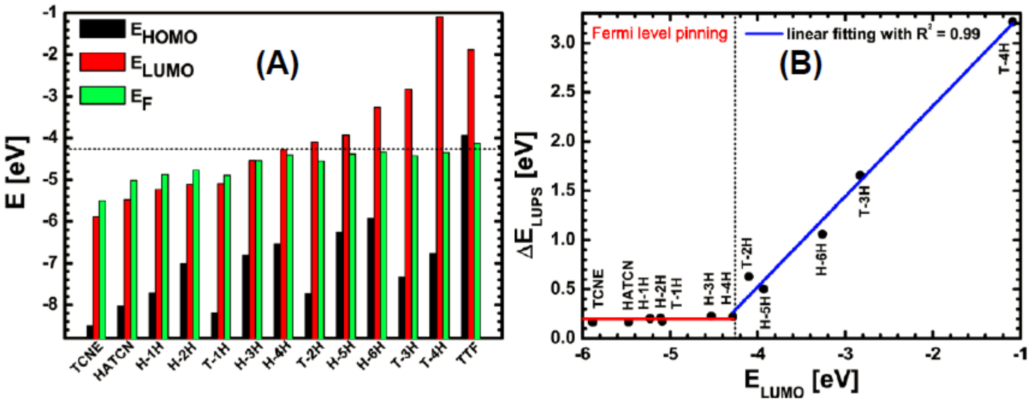

Figure 3. (A) The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) levels and Fermi level of various systems with different molecules physisorbed on graphene, and (B) relationship between ΔE_{LUPS} (i.e., energy difference between the lowest unoccupied π state in the absorbed system and the Fermi level) and the molecular LUMOs. While the red line shows the Fermi level pinning with $\Delta E_{LUPS} = 0.2$ eV, the blue line shows the linear relationship between ΔE_{LUPS} and E_{LUMO}. Dotted lines indicate the graphene Fermi level with the vacuum level shifted to zero.

In our publication J. Phys. Chem. Lett. 4, 2158 (2013), density functional theory calculations have been performed to assess the electronic structure of graphene overlaid with a monolayer of electro-active conjugated molecules, being either electron donors or electron acceptors including TCNE, HATCN, TTF, and HATCN derivatives. Such a noncovalent functionalization results in a work function modification that scales with the amount of electron transfer from or to graphene, in line with the formation of an interfacial dipole. The charge transfer is accompanied by a pinning of the donor HOMO/acceptor LUMO around the Fermi level and a shift in the vacuum level (see **Figure 3**). The use of the Boltzmann transport equation combined with the deformation potential theory shows that large charge carrier mobilities are maintained upon noncovalent functionalization of graphene, thereby suggesting that molecular doping is an attractive approach to design conductive graphene electrodes with tailored work function.

(4) Design coved graphene nanoribbons with charge mobility approaching that of graphene

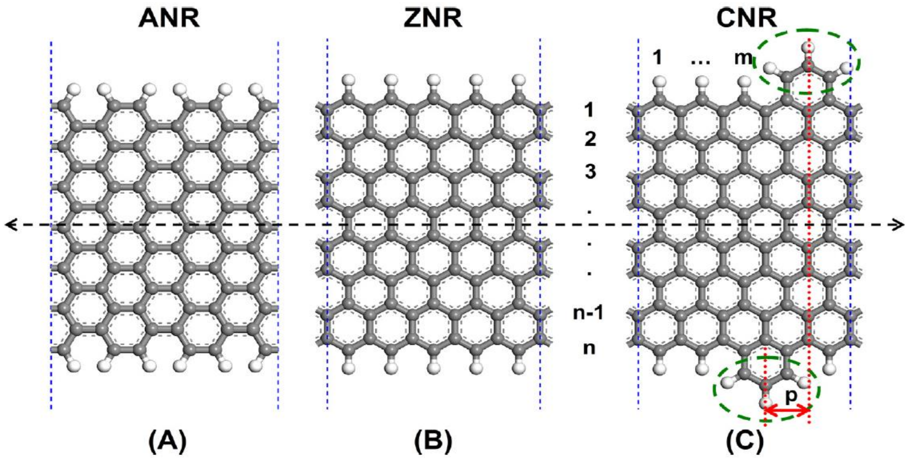

Figure 4. Schematic presentation of (A) armchair nanoribbons (ANRs), (B) zigzag nanoribbons (ZNRs), and (C) coved-shaped nanoribbons based on ZNRs (CNRs). The blue dashed lines represent the periodicity of the ribbons. The black dashed line with arrows shows the stretching direction of the ribbons. *n* specifies the width of the ribbon. *m* is the number of hydrogens along the edge, excluding those hydrogen atoms in the additional phenyl rings on two sides of the ribbon which are indicated by green dashed circles. *p* indicates the relative position of the two additional phenyl rings.

Graphene nanoribbons (GNRs) are fundamental building blocks for carbon-based nanoelectronic devices. In the study published in Carbon 77, 868 (2014), we focus on coved-shape GNRs that contain protruding phenyl rings along both edges (see **Figure 4**). Based on density functional theory calculations coupled to deformation potential theory, we show that these additional phenyl rings profoundly impact the nature of the electronic states near the Fermi surface and modulate the resulting charge transport characteristics of the ribbons. Exploiting Clar's theory, we design unit cells where the number and position of the edge phenyl groups are adjusted to tune the relative magnitude of hole and electron mobilities. Most interestingly, we report on a novel CNRs (named as 4CNR-2-2 with $n = 4$, $m = 2$, and $p = 2$) that posses simultaneously high hole and electron mobility values ($\mu_h = 4.05\times10^5$ cm^2/Vs and $\mu_e = 4.21\times10^5$ cm^2/Vs), approaching those of graphene (about 2×10^6 cm^2/Vs). This phenomena has never been observed before for narrow GNRs, and is quite promising for the future design of carbon-based wires for nanoelectronic devices.

(5) Relation between morphology and charge mobility of poly(3-alkylthiophene)s

A	α_0 [°]$^{a)}$	α [°]	$a/5$ [Å]	b [Å]	$c/5$ [Å]	S-C-C-S dihedral angle [°]	C=C–C–C dihedral angle [°]	$d_{\pi-\pi}$ [Å]	ρ [g cm^{-3}]	ΔE [kcal mol^{-1}]	Exp. α [°]	Calc. α [°]	t_{HOMO} [eV] INDO	t_{LUMO} [eV] INDO	t_{HOMO} [eV] DFT	t_{LUMO} [eV] DFT
4	60–80; 110–120	67 (67)	12.73	7.60	7.85	1.1	86.1	3.50	1.21	0	84°$^{b)}$		0.172	0.027	0.154	0.050
	85–105	93 (87)	14.20	7.34	7.85	6.1	103.0	3.66	1.12	20.5			0.112	0.129	0.103	0.216
6	60–65	67 (67)	16.82	7.53	7.85	0.7	85.0	3.46	1.11	2.2	60°–62°,[51] 64[52]	83[56]	0.184	0.029	0.162	0.052
	70–115	89 (89)	17.20	7.16	7.84	5.6	102.8	3.58	1.14	0	85°[50]		0.135	0.163	0.119	0.252
8	60–65	68 (68)	19.37	7.36	7.83	0.5	84.3	3.41	1.16	5.4			0.194	0.015	0.170	0.072
	70–85	81 (81)	20.86	7.15	7.85	4.3	96.7	3.53	1.10	0	84°[50]		0.156	0.130	0.136	0.219
	95–105	95 (85)	20.01	7.18	7.85	3.7	112.5	3.58	1.14	5.4			0.120	0.145	0.106	0.236

Table 1. The tilt angle for all the thiophene rings in the initial poly(3-alkylthiophene) P3AT geometries (α_0), and in the optimized geometries (α), the lattice constants, the dihedral angles of S–C–C–S and C=C–C–C, the $\pi-\pi$ stacking distance ($d_{\pi-\pi}$), the density (ρ), the potential energy of the optimized geometry with respect to the lowest optimized potential energy starting from different α_0, the α values obtained from experimental X-ray diffraction studies and other calculations, HOMO (LUMO) intermolecular transfer integrals t_{HOMO} (t_{LUMO}) calculated at both INDO and DFT levels. Different α_0 may go to the same α after geometry

optimization, thus all α_0 values are provided. The values between parentheses denote absolute tilt angles between the thiophene rings and the substrate.

Our publication in Adv. Func. Mater. 24, 1994 (2014) highlights the potential of the polymer/air interface in achieving excellent "out-of-plane" orientation and high charge carrier mobilities for field-effect transistor applications. In **Table 1**, we show the optimized thiophene tilt angles and their relative potential energies for all stable structures of poly(3-alkylthiopenes) (P3AT), that is, those that are obtained as output from the calculations when using different initial conditions. Previous X-ray and electron diffraction studies on bulk samples observed two different α_{cryst} values for P36T, namely 60°–62° or 64° and 85°. Here, we also find two structures with close energies yet different α , 67° and 89°. Especially, for the geometry with α = 67°, the interlamella spacing, the intra-lamella chain-to-chain stacking distance, and the intra-chain repeated distance are calculated to be 16.8 Å, 3.8 Å, and 8.1 Å, respectively, agreeing very well with the experimental values of 16.8 Å, 3.8 Å, and 7.9 Å. For the P38T case, our data (α = 81° and 85°) also compare quite well with the experimental value, α = 84°. This holds true as well for P34T, where the calculated value of 87° is close to the value of 84° determined for form I' of P34T. Importantly, for all polymers investigated, we find stable structures with tilt angles around 67–68° and in the range 81–89°, which could yield different domains that coexist in real samples. The calculated relative energies indicate that α should increase from P34T to P36T, suggesting that the experimentally observed variation in $<\alpha>$ at the polymer/air interface could be due to the presence of different polymorphs with different α_{cryst}. Both INDO and DFT results show that the transfer integrals vary significantly with the crystal structure and (therefore) alkyl chain length (see **Table 1**). While all P3ATs exhibit a much larger HOMO than LUMO intermolecular transfer integral for the small tilt angle structure, the opposite situation holds true at larger tilt angles. In a hopping regime, the mobility should scale with the squared transfer integral for disorder-free and defect-free systems. The fact that the mobilities measured at the polymer/air interface do not change significantly with alkyl chain length hints to more or less identical α_{cryst} values for different polymers, although care must be taken here, given the fact that the variation of t^2_{HOMO} with α_{cryst} is only a factor of 2 and the fact that the mobility values that we measure are limited by extrinsic factors such as grain boundaries or structural disorder in general, and can thus differ significantly from the theoretical values calculated for ideal systems.

(6) Triplet exciton diffusion in the anthracene crystal

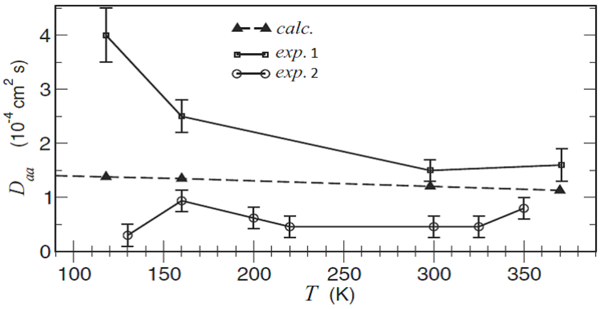

Figure 5. Calculated evolution of the diffusion coefficient with temperature in the anthracene single crystal (dashed line, filled symbols), together with experimental data (empty symbols, full line).

In Phys. Rev. B 88, 035450 (2013), triplet exciton migration in the anthracene single crystal is modeled using a KMC scheme based on fully atomistic hopping rates. These account for the coupling of the triplet excitations to both intramolecular vibrations and lattice phonons from first principles. Thermal fluctuations in site energies and excitonic couplings obtained within the fragmented excitation difference approach yield triplet exciton diffusion constants in quantitative agreement with experiment. As shown in **Figure 5**, the available experimental data bracket the predicted values and point to a very modest decrease in the diffusion coefficient along a direction (D_{aa}) with increasing temperature in the investigated temperature range (from 100 to 400 K).

(7) Molecular weight dependence of exciton diffusion in P3HT

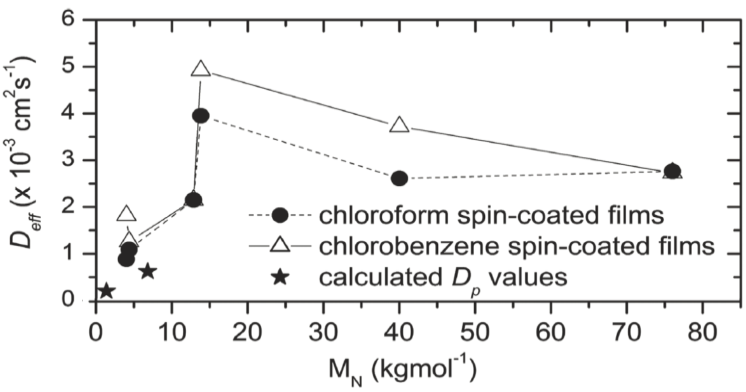

Figure 6. Variation of diffusion coefficient as a function of M_N. The two calculation points are based on a stack size of 101 molecules for two different molecular weights.

In Adv. Energy Mater. 3, 1445 (2013), a joint experimental and theoretical study of singlet exciton diffusion in spin-coated poly(3-hexylthiophene) (P3HT) films and its dependence on molecular weight is presented. The results show that exciton diffusion is fast along the co-facial π–π aggregates of polymer chromophores and about 100 times slower in the lateral direction between aggregates. Exciton hopping between aggregates is found to show a subtle dependence on interchain coupling, aggregate size, and Boltzmann statistics. To explain the experimentally measured effect of molecular weight on exciton diffusion, we have developed a theoretical model for exciton diffusion in P3HT lamellae. The relatively large electronic couplings between the conjugated polymer chains within the stacks yield 2D excitons delocalized over multiple polymer chains. These 2D excitons can then jump from stack to stack according to a Förster-like hopping mechanism. In our model, we first build the exciton Hamiltonian and obtain the intrastack exciton states by diagonalizing the Hamiltonian within each stack. Then we calculate the stack-to-stack hopping rates between the resulting 2D excitons and provide a qualitative analysis of the associated diffusivity using a simple variable range hopping approximation. The model was applied for two different lamella structures built from ideal stacks of P3HT molecules containing 8 and 40 repeated monomers (1360 and 6800 g/mol, respectively). A good agreement with experiment has been observed (see **Figure 6**).

(8) Optical properties of oligothiophene substituted diketopyrrolopyrrole derivatives in the solid phase

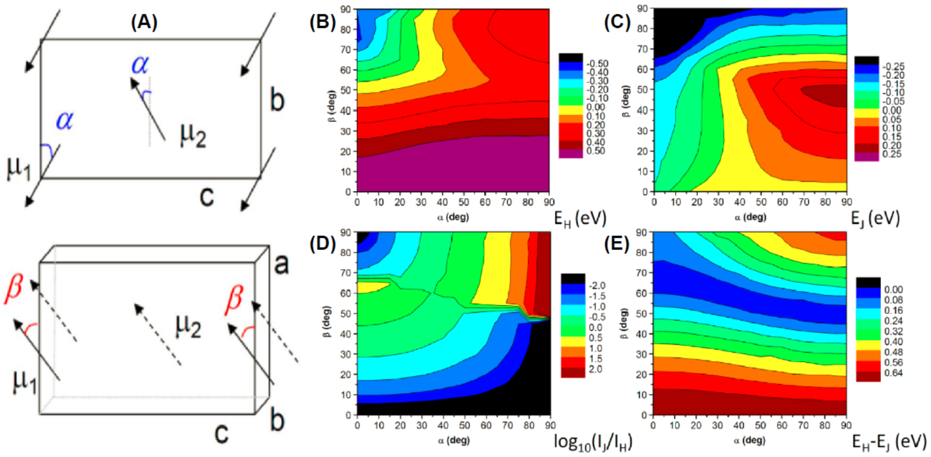

Figure 7. (A) Orientation of the transition dipole moments of the 1,4-Diketo-3,6-diarylpyrrolo[3,4-c]pyrroles (DPP) molecules in the solid phase used in the calculation of the intralayer excited state dipolar couplings relative to the lattice vectors of the triclinic unit cell. Calculations of (B) energy of the higher (*H*-type) energy level, (C) energy of the lower *J*-type level, and (D) $^{10}\log(I_J/I_H)$ with I_J and I_H the calculated intensities for the *J*- and *H*-states, respectively. (E) Calculated Davydov splitting.

In our theoretical work in collaboration with experimentalists, J. Phys. Chem. A 116, 7927 (2012), the photophysical properties of diketopyrrolopyrrole derivatives substituted with oligothiophenes are investigated. We take the lattice parameters from a close structural analog and place the dipole oscillators on the lattice points (see **Figure 7A**). The transition dipoles for the first and second molecule in the unit cell are labeled μ_1 and μ_2. To describe the orientation of the transition dipole moment relative to the lattice vectors a, b, and c, we introduce the angles α and β. We approximate the excited-state intermolecular interaction by the interaction between the transition densities within the same *bc* molecular plane, neglecting the interlayer interaction. We further truncate the intralayer interaction to include only 15×15 unit cells, which yields close to fully converged exciton bandwidths. Quantum-chemical calculations, including exciton-phonon coupling to account for deviations from the Born-Oppenheimer approximation, are performed to simulate the band shape of the lowest absorption band in the molecular solid. The joint presence of *J*- and *H*-bands is explained by the presence of two molecules in the unit cell. The energy of the *H* and *J* bands, and their relative magnitude as a function of the angles α and β (see **Figure 7B−D**). We find that by allowing for relatively small variations in the orientation angles α and β in the molecular arrangement, one can account for the variation in spectroscopic characteristics of the thiophene DPP compounds with different *N*-alkyl side chains. Especially, we find that the Davydov splitting is substantial for molecules with linear alkyl substituents on the nitrogen atom (on the order of 0.2 eV) but can be reduced to almost zero by introducing branching at the β-carbon of the alkyl side chain (see **Figure 7E**).

(9) Optical spectra of dithiophene-DPP(Boc)-dithiophene polymorphs

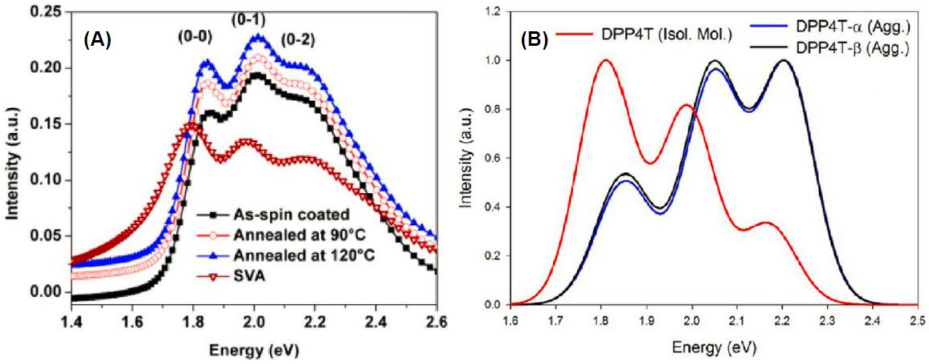

Figure 8. (A) Experimental and (B) theoretical absorption spectra of DPP4T. The films prepared in experiment are spin coated using solvent $CHCl_3$. Calculated spectra for aggregates of DPP4T-α and DPP4T-β polymorphs (blue and black curves) as well as a single DPP4T molecule (red curve) obtained for a gas-to-crystal shift equal to 1.81 eV.

Polymorphism is an interesting phenomenon critical to our understanding of structure-property relationships in solid-state functional materials. In J. Phys. Chem. C 118, 657 (2014), we investigate the spectral features of two polymorphic forms of a DPP-Boc derivative, DPP4T-α and DPP4T-β. 2D aggregates made of 100 molecules in the densest crystalline planes (namely clusters of 10×10 molecules in the *ab* and *bc* planes for DPP4T-α and DPP4T-β, respectively) have been built (test calculations on larger clusters do not show significant differences in the electronic exciton bandwidths). As a consequence of their similar organization in these crystalline planes, the largest excitonic couplings in the two aggregates investigated have relatively similar magnitudes and signs. Most of these couplings are positive, showing characteristics of *H*-like aggregates. As a result, both the α and β phase clusters show a reduced ‘0−0’ intensity associated with dynamic symmetry breaking entailed by coupling to the molecular vibrations (the pure electronic transition to the bottom exciton state is symmetry-forbidden in *H* aggregates). The spectra predicted for the two polymorphs are essentially superimposable with no apparent spectral shift and in reasonable agreement with the experimental data obtained for the films casted from chloroform (see **Figure 8**). The predicted 0−0 intensity is underestimated, which likely arises from static disorder effects not accounted for. As expected for *H*-aggregates, turning off all intermolecular excitonic couplings (i.e., simulating single molecules) yields an increased 0−0 intensity and a red shift of the optical absorption spectrum. Interestingly, the resulting spectrum now appears to be in closer correspondence with that measured for films exposed to solvent annealing. We thus speculate that the SVA films are β-phase crystals that are either highly disordered or, more likely, include a large fraction of noninteracting molecules (possibly in stronger interaction with the substrate compared with the *α* polymorph). In favor of the latter hypothesis, we note that while the single molecule spectrum nicely reproduces the low-energy part of the solvent vapor annealing (SVA) optical spectral (0−0 and 0−1 transitions up to 2.1 eV), it predicts a too-low intensity at higher energy (0−2 at about 2.2 eV), where the crystals (being either *α* or *β*) strongly absorb. Thus a superimposition of the single molecule and crystalline domains would fit the experimental data across the whole spectral range.

(10) Energetics of electron-hole separation at P3HT/PCBM heterojunctions

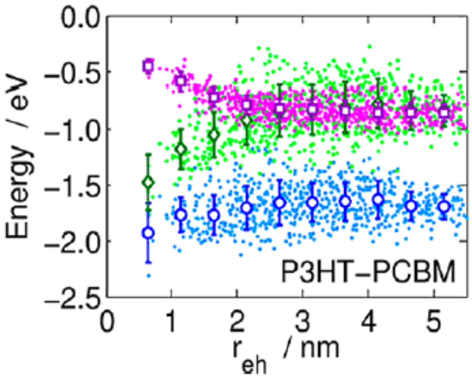

Figure 9. Microelectrostatic polarization energy of electron-hole pairs in P3HT/PCBM as a function of the distance between electron and hole center of charge: total (blue dots), static (green dots), and dynamic (magenta dots) electron-hole polarization energy. Circles, diamonds, and squares show mean values and standard deviations (error bars), respectively, calculated over intervals of 0.5 nm.

In J. Phys. Chem. C 117, 12981 (2013), the energetics of electron-hole separation at the prototypical donor-acceptor interface P3HT/PCBM is investigated by means of a combination of molecular dynamics simulations, quantum-chemical methods, and classical microelectrostatic (ME) calculations. After validation against semiempirical results at the Valence Bond/Hartree-Fock level, ME calculations on a large number of electron-hole (e-h) pairs allowed a statistical study of charge separation energetics in realistic morphologies. Results show that charge separation is an energetically favorable process for about 50% of interfacial e-h pairs, which provides a rationale for the high internal quantum efficiencies reported for P3HT/PCBM heterojunctions. Three effects contribute to overcome the Coulomb attraction between electron and hole: (i) favorable electrostatic landscape across the interface, (ii) electronic polarization (see **Figure 9**), and (iii) interface-induced torsional disorder in P3HT chains. Moreover, the energetic disorder due to the PCBM polar group is shown to play a key role in increasing the dissociation probability.

4. Perspectives for future collaboration between units

Optoelectronics is a very active research field, gathering a huge number of researcher all over the world from both experimental and theoretical sides. A lot of current theoretical studies can be extensively collaborated with experimental groups. For example, band-to-hopping crossover is a famous phenomenon which has been observed clearly only in naphthalene crystals so far. Applying our flexible surface hopping method and ab initio calculations to real molecular crystals can give guidelines of the potential candidates to possess this novel feature. Besides, the methods can be also used to predict intrinsic charge carrier mobilities, and help to achieve maximized transport efficiency in functional devices. Another example is the simulation of optical properties. We have described above some cases with collaboration between theoretical and experimental groups. The electronic structure and optical spectra obtained from theories can reveal the origin for each electron excitation and identify the molecular structure and intermolecular packing that are responsible for the spectroscopic observations. There are also a lot of chances to have collaborations between theoretical groups. We have obtained significant progress in developing surface hopping techniques for supramolecular systems. When we apply these theories to real materials, we need to obtain a accurate description of adiabatic potential energy surfaces and the corresponding wavefunctions, which are quite time consuming. This is not an easy task and requires extensive experience on electronic structure methods, including the modifications and simplifications based on Hartree-Fock and density functional theories. The group where I got the Fellowship has rich experiences in electronic structure calculations, especially semiempirical molecular orbitals methods. Combining these methods and surface hopping simulations allow us to dig deeper our understandings of charge/exciton transport and exciton dissociation at organic interfaces in the near future.

5. Valorisation/Diffusion

(1) Publications

a. M. Kirkus, L. J. Wang, S. Mothy, D. Beljonne, J. Cornil, R. A. J. Janssen, and S. C. J. Meskers, Optical Properties of Oligothiophene Substituted Diketopyrrolopyrrole Derivatives in Solid Phase: Joint J and H-Type Aggregation, **J. Phys. Chem. A**, 116, 7927-7936 (**2012**).

b. L. J. Wang and D. Beljonne, Flexible Surface Hopping Approach to Model the Crossover from Hopping to Band-like Transport in Organic Crystals, **J. Phys. Chem. Lett.**, 4, 1888-1894 (**2013**).

c. L. P. Chen, L. J. Wang, Z. Shuai, and D. Beljonne, Energy Level Alignment and Charge Carrier Mobility in Noncovalently Functionalized Graphene, **J. Phys. Chem. Lett.**, 4, 2158-2165 (**2013**).

d. G. D'Avino, S. Mothy, L. Muccioli, C. Zannoni, L. J. Wang, J. Cornil, D. Beljonne, and F. Castet, Energetics of Electron-Hole Separation at P3HT/PCBM Heterojunctions, **J. Phys. Chem. C**, 117, 12981-12990(**2013**).

e. L. Grisanti, Y. Olivier, L. J. Wang, S. Athanasopoulos, J. Cornil, and D. Beljonne, Role of Local and Nonlocal Electron-Phonon Couplings in Triplet Exciton Diffusion in the Anthracene Crystal, **Phys. Rev. B**, 88, 035450 (**2013**).

f. L. J. Wang and D. Beljonne, Charge Transport in Organic Semiconductors: Assessment of the Mean Field Theory in the Hopping Regime, **J. Chem. Phys.** 139, 064316 (**2013**).

g. Z. Masri, A. Ruseckas, E. V. Emelianova, L. J. Wang, A. K. Bansal, A. Matheson, H. T. Lemke, M. M. Nielsen, H. Nguyen, O. Coulembier, P. Dubois, D. Beljonne, and I. D.W. Samuel, Molecular weight dependence of exciton diffusion in poly(3-hexylthiophene), **Adv. Energy. Mater.**, 3, 1445-1453 (**2013**).

h. S. T. Salammal, J.-Y. Balandier, J.-B. Arlin, Y. Olivier, V. Lemaur, L. J. Wang, D. Beljonne, J. Cornil, A. R. Kennedy, Y. H. Geerts, and B. Chattopadhyay, Polymorphism in Bulk and Thin Films: The Curious Case of Dithiophene-DPP(Boc)-Dithiophene, **J. Phys. Chem. C.**, 118, 657-669 (**2014**).

i. W. D. Oosterbaan, J.-C. Bolsée, L. J. Wang, V. Vrindts, L. J. Lutsen, V. Lemaur, D. Beljonne, C. R. McNeill, L. Thomsen, J. V. Manca, and D. J. M. Vanderzande, On the Relation between Morphology and FET Mobility of Poly(3-alkylthiophene)s at the Polymer/SiO_2 and Polymer/Air Interface, **Adv. Func. Mater.** 24, 1994-2004 (**2014**).

j. L. P. Chen, L. J. Wang (co-first author), and D. Beljonne, Designing Coved Graphene Nanoribbons with Charge Carrier Mobility Approaching That of Graphene, **Carbon** 77, 868-879 (**2014).**

(2) Conferences

a. The 3rd European Symposium on Computing π-Conjugated Compounds (CPIC3), February 02 - 04, 2012, Mons, Belgium (Poster)

b. The MINOTOR workshop “Electronic Processes at Interfaces to Organic Semiconductors: From Modelling to Devices”, May 29 - 31, 2012, Mons, Belgium (Poster)

c. CHINAMUR “The IVth Symposium on Chemistry, Material Science, and Related Fields”, October 21, 2012, Namur, Belgium (Oral Presentation)

d. The CMCS workshop “Computational Methods for Complex System”, December 09 - 12, 2012, Hong Kong, China (Poster)

e. The 4th European Symposium on Computing π-Conjugated Compounds (CPIC4), January 31 - February 02, 2013, Marseille, France (Oral Presentation)

(3) Seminars

a. Charge Transport in Organic Crystals: A Story about Electron-Nuclei Interaction, December 15, 2012, Hong Kong, China

6. Skills/Added value transferred to home institution abroad

The most important skill that I have obtained from this BELSPO projection is the mixed quantum-classical dynamics, especially the surface hopping approach. Most of my scientific carrier has been devoted to charge transport, where I have explored various distinct methods. These methods are generally based on perturbation theories, and thus only work in specific systems The surface hopping method deals with all relevant quantities on equal footing, providing a general strategy suitable to investigate all kinds of materials. Tully's fewest switches surface hopping (FSSH; see J. Chem. Phys. 93, 1061 published in 1990) is the most widely used strategy because of its appealing simplicity, ease of implementation, and computational efficiency. Despite of its popularity and success, FSSH suffers from several shortcomings. One of them is the so-called trivial, or unavoided, crossing problem, which becomes increasingly critical in complex molecular systems. As shown in this project, a lot of interesting dynamical processes are involved with a large aggregate or even bulk, thus it is really urgent to find accurate and efficient solutions to this problem. Starting with the flexible surface hopping method proposed during the BELSPO project, I further work this issue and proposed the self-consistent fewest switches surface hopping (SC-FSSH; see J. Phys. Chem. Lett. 5, 713 published in 2014) and the global flux surface hopping (GFSH; see J. Chem. Theo. Comput. 10, 3598 published in 2014) methods after finishing the project. The experience obtained during the BELSPO Postdoc Fellowship is very helpful for these follow-up studies. Other skills obtained within the project include the computation of absorption and emission spectra with vibronic couplings, manual construction of force fields with corrected torsional potential energy surfaces, fitting the band structure of carbon-based materials with tight-binding Hamiltonian, and so on. They are all beneficial for my further studies in the field of optoelectronics.