
Ultrafast Photophysics of Organic Semiconductor Junctions

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Abstract. This contribution gives an overview of our recent studies of the electronic structure and ultrafast photophysics of semiconductor polymer junctions. We focus on the phonon-assisted exciton dissociation at donor-acceptor heterojunctions, using state-of-the-art electronic structure methods in conjunction with vibronic coupling models and multiconfigurational quantum dynamical techniques. The decay of the photogenerated exciton towards an interfacial charge-separated state is an ultrafast (femtosecond to picosecond scale) process which precedes photocurrent generation. We describe this process using a linear vibronic coupling model parametrized for two to three electronic states and 20-30 phonon modes. Several representative interface configurations are considered, which are shown to differ significantly in their cross-chain interactions but exhibit an efficient exciton dissociation in all cases investigated. The exciton decay depends critically on the presence of intermediate states and on the dynamical interplay between high-frequency (C=C stretch) and low-frequency (ring-torsional) modes. The resulting molecular-level picture of exciton dissociation could contribute to the design of efficient polymer junctions.

1 Introduction

The photophysics of semiconducting conjugated polymers is a key ingredient for the understanding and design of optoelectronic devices such as organic light-emitting diodes (OLEDs) and solar cells [1–10]. In view of these materials' composition of molecular building blocks, a natural approach is to

interpret polymer photophysics by analogy with the photophysics and photochemistry of smaller organic species. One would thus typically expect vibrational relaxation and ultrafast internal conversion processes that lead to deexcitation on a femtosecond to picosecond time scale. These efficient deexcitation mechanisms are reflected, e.g., in Kasha's rule [11–13], a key rule of molecular photochemistry which states that fluorescence always occurs from the lowest excited state. (A related formulation known as the Kasha-Vavilov rule [14] states that the fluorescence quantum yield is independent of excitation frequency.) Even though exceptions to these rules occur – due to photophysical pathways that do not lead to the lowest excited state – their remarkable generality has been confirmed for a majority of organic systems. The Kasha-Vavilov rule has indeed been found to also hold for polymers of poly-phenylene-vinylene (PPV) type, according to the observations, e.g., of Ref. [15] which reports on the independence of the observed photoluminescence signal of the excitation wavelength.

However, beyond these similarities with conventional organic photochemistry, a host of new phenomena occur which reflect the extended nature of the conjugated π electronic system. This entails the formation of delocalized exciton states [6], along with excitation energy transfer (exciton migration) and dissociation of excitons to polaron pairs, i.e., formation of charge transfer states which are precursors of photocurrent carrying states. These processes can also be ultrafast and are expected to compete with the internal conversion pathways addressed above. Thus, the dissociation into charge carriers has been found to compete with the decay to the lowest excited state in PPV type systems, leading to a (partial) breakdown of Kasha's rule [16,17]. In all of these processes, both site-site interactions and electron-phonon coupling play a decisive role. Time-resolved experiments have provided evidence for the ultrafast [16, 18, 19] and coherent [20], quantum-mechanical nature of many of the processes involved. Very recent experiments indicate long-lived electronic coherences in the ultrafast exciton migration dynamics along polymer chains even at room temperature [21]. To provide an appropriate theoretical description of these dynamical phenomena, a perspective has to be adopted that interpolates between a molecular-level picture and a description in terms of a disordered, solid-like phase.

In the present contribution, we illustrate a molecular-level approach to the electronic structure and charge transfer dynamics at polymer heterojunctions [22–26], i.e., interfaces between phase-separated semiconducting polymer domains. So-called bulk heterojunctions [26] provide conditions for an extremely efficient charge separation at the interface; the advent of this type of heterojunctions in fact brought significant advances in device efficiency. In photovoltaic diode devices, the primary excitation is a photogenerated exciton stabilized by the electron-hole Coulombic interaction, with a typical binding energy of $\epsilon_B \sim 0.5$ eV [26–29], i.e., considerably larger than in inorganic semiconductors where ϵ_B typically lies in the 50 meV range. Due to the highly folded interfacial area in bulk heterojunction materials, the exciton has

an enhanced probability of reaching the interface within the diffusion length (typically ~ 10 nm [28,30,31]). The exciton decay towards a charge-separated state (“exciplex”) [26, 32, 33, 35–38] is largely determined by molecular-level electronic interactions at the interface. Recent time-resolved photoluminescence studies have shown that the exciton decay falls into a (sub)picosecond regime [32, 34].

In the following, we first give an account of the electronic structure side, summarizing recent time-dependent density functional theory (TD-DFT) calculations for interface fragments with different stacking geometries [41, 43]. We then focus on the crucial role of electron-phonon coupling in mediating the ultrafast decay of the initially generated exciton to an interfacial charge transfer state. The currently accepted picture of the processes at a heterojunction involves the formation of both photoluminescent exciplex states and optically dark charge transfer states [41, 44]. The dynamical treatments which we describe here therefore include both 2-state and 3-state models which attempt to capture the relevant features of the dynamics. In the present analysis, we focus on the earliest events at the interface, which are followed by exciton regeneration and photocurrent generation [32, 34, 39, 40] on longer time scales.

The approach adopted here combines high-level excited-state electronic structure calculations, vibronic coupling models that are adapted to the spatially extended nature of the system, and state-of-the-art techniques for the quantum dynamical description of electron-phonon coupling in high-dimensional systems. Using full quantum-dynamical calculations by the multi-configuration time-dependent Hartree (MCTDH) method [45–49] for 2-3 electronic states and 20-30 explicit phonon modes, a molecular-level picture of the exciton dissociation event is obtained. As detailed in Refs. [50–53], the exciton dissociation involves a coherent nonadiabatic transfer dynamics between the photogenerated exciton state and one or several charge transfer states; this process is found to be ultrafast (~ 100 fs–1 ps). A key factor in the dynamics is the interplay between high-frequency (C=C stretch) and low-frequency (ring-torsional) modes. Importantly, the exciton decay is found to be inefficient in the absence of the low-frequency modes [50, 51]. The dynamical mechanism is interpreted in terms of a hierarchical electron-phonon model which allows one to identify generalized reaction coordinates for the nonadiabatic process. This analysis highlights that the electron-phonon coupling is dominated by high-frequency modes, but the presence of low-frequency modes is crucial in mediating the transition to a charge-separated state. Further, the presence of intermediate states is favorable to the exciton dissociation, and the process is found to remain dynamically robust with respect to variation of the cross-chain interactions [53]. The ultrafast nature of the dynamics is in agreement with time-resolved spectroscopic observations [32].

In the remainder of this chapter, we first give an overview of electronic structure calculations for the donor-acceptor heterojunction systems under consideration (Sec. 2). We then introduce the electron-phonon coupling model adopted to describe the extended polymer system (Sec. 3), followed by an

account of the dynamical analysis based on a linear vibronic coupling Hamiltonian (Sec. 4). We employ, in particular, recently developed techniques by which a relevant set of effective modes is constructed that account for the short-time dynamics in high dimensional systems involving conical intersection topologies [51, 54, 55]. In Sec. 5, these methods are applied to the exciton dissociation at a heterojunction. Given that the systems under study typically involve high- vs. low frequency phonon distributions, we identify certain mechanistic aspects which should carry over to a related class of systems. Finally, Sec. 6 gives an outlook on possible extensions of the present analysis.

2 Overview of interfacial electronic states of polymer heterojunctions

Here, a brief summary is provided of the current understanding of the electronic structure properties of the heterojunction interface. We start with the basic picture of the energetics (Sec. 2.1), based on the offset between the frontier orbitals of the two polymer species; this offset triggers the dissociation of the photogenerated exciton if the exciton binding energy $\epsilon_B \sim 0.5$ eV can be overcome. To refine this picture, explicit electronic structure calculations are necessary, which pose a formidable challenge for the interfacial systems under consideration. Secs. 2.2 and 2.3 summarize recent efforts in this direction [41, 43, 44, 56].

2.1 Energetics of a type-II heterojunction

The basic picture of the heterojunction energetics is formulated in terms of the offset between the frontier orbitals of the two polymer species, i.e., the respective highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs). The heterojunctions we are considering here are “type II” junctions [10, 33], where the respective offsets between the HOMO and LUMO levels have the same sign and are of comparable magnitude, $\Delta E_{\text{HOMO}} \sim \Delta E_{\text{LUMO}} \sim \Delta E$. A schematic illustration is shown in Fig. 1. If the offset ΔE exceeds the exciton binding energy $\epsilon_B \sim 0.5$ eV, the photogenerated exciton (XT) is destabilized and tends to decay to an interfacial charge transfer state (CT) [3, 23, 28]. This is desirable for photovoltaic applications. Conversely, if $\Delta E < \epsilon_B$, the exciton is stable, and this is best suited for OLED applications. However, intermediate cases where $\Delta E \simeq \epsilon_B$ cannot straightforwardly be addressed in these terms. This applies, for example, to the TFB:F8BT junction [26, 32, 33, 57] which we focus on in this chapter. Here, the interface is composed of the poly[9,9-dioctylfluorene-co-bis-N,N-(4-butyl-phenyl)-bis-N,N-phenyl-1,4-phenylenediamine] (TFB) and poly[9,9-dioctylfluorene-co-benzothiadiazole] (F8BT) polymer components, see Fig. 2 where the molecular structure of the junction is illustrated. For this system,

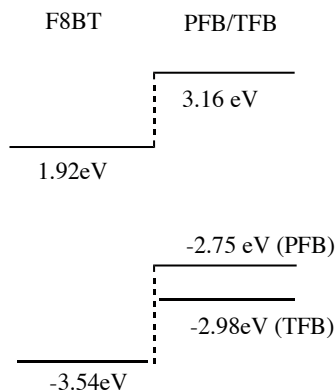


Fig. 1: Band offsets, i.e., relative HOMO/LUMO energies, for two representative type II polymer junctions, i.e., the TFB:F8BT and PFB:F8BT heterojunctions. Both are fluorene-based polymer materials [26,33]. In this chapter, we focus on the TFB:F8BT junction.

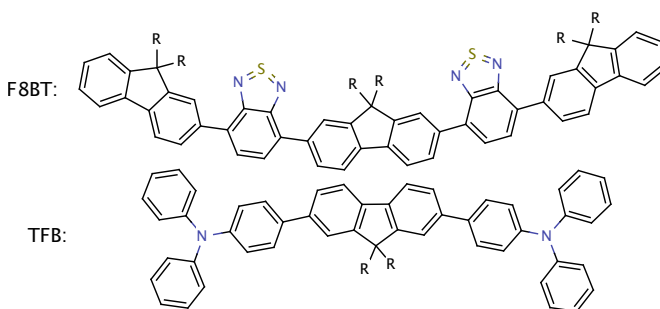


Fig. 2: Molecular structure of a model F8BT(top):TFB(bottom) polymer heterojunction in the “eclipsed” stacking configuration, see also Fig. 3. In the actual polymer, the residues are $R = C_8H_{12}$; in the calculations reported here, $R = H$ was used (Adapted from Ref. [43]).

recent time-resolved photoluminescence studies suggest that both exciton decay and regeneration phenomena are observed [32, 34, 42], with the earliest events falling into the (sub)picosecond regime.

2.2 Electronic structure calculations of interfacial singlet states

Excited-state electronic structure calculations, even for small fragments of the polymer interfaces under consideration, are barely feasible using high-level *ab initio* methodology, and are a formidable task even if performed at a semiempirical level. This is all the more true if such calculations are to be carried out for a range of relevant geometries. Here, we summarize the results of Refs. [41, 43] for selected geometries, using single-excitation configuration interaction (CIS) and time-dependent density functional theory (TD-DFT) methods. The results of these studies are in qualitative agreement with semiempirical calculations [44, 56].

In the calculations reported in Refs. [41, 43], a finite-sized fragment of the interface region is considered, composed of a F8BT moiety consisting of six co-monomer units (i.e., three benzothiadiazole (BT) units alternating with three fluorene (F) units) and a TFB moiety consisting of five co-monomer units (three F units alternating with two triarylamine units). The rationale for considering a finite portion of the interface region is that the delocalization length of the photogenerated exciton generally does not exceed a few monomer units [6, 29, 57, 58]. The CIS and TD-DFT methods were employed to determine the heterojunction excited states at the Franck-Condon geometry, either for the isolated TFB:F8BT or including a solvent modeled by a dielectric continuum [41].

Since intermolecular interactions at the interface play a key role, two representative interface structures were considered, which will be referred to as eclipsed (E) vs. staggered (S), see Fig. 3. These structures correspond to attractive vs. repulsive π -stacked interface configurations, which result from the following stacking patterns in the lowest-lying exciton state:

$$\text{attractive (E configuration): } \begin{bmatrix} (-\mathbf{F8}^{\delta+} - \mathbf{BT}^{\delta-})_n \\ (-\mathbf{F8}^{\delta-} - \mathbf{TB}^{\delta+})_n \end{bmatrix} \quad (1)$$

$$\text{repulsive (S configuration): } \begin{bmatrix} (-\mathbf{F8}^{\delta+} - \mathbf{BT}^{\delta-})_n \\ (-\mathbf{TB}^{\delta+} - \mathbf{F8}^{\delta-})_n \end{bmatrix} \quad (2)$$

As indicated by the partial charges, the F8 sub-unit acquires a net partial positive charge when co-polymerized with BT (in the F8BT moiety), but a net partial negative charge when co-polymerized with TB (in the TFB moiety) [34, 41]. This leads to a strongly attractive electrostatic interaction in the E configuration, but a repulsive interaction in the S configuration. Both structures were optimized in the electronic ground state using molecular mechanics force fields (i.e., the MM3 force field as implemented in TINKER [41]). Subsequently, CIS and TD-DFT calculations were carried out at this geometry. Geometry relaxation in the excited states was not accounted for. Overall, TD-DFT was found to give results that compare well with experimental absorption spectra [41] while CIS tends to significantly overestimate the relevant

excitation energies. However, due to the known deficiencies of TD-DFT in describing long-range charge transfer states, as a consequence of the local nature of the approximate exchange-correlation functionals [59], charge transfer state energies tend to be underestimated by about 0.5 eV [41].

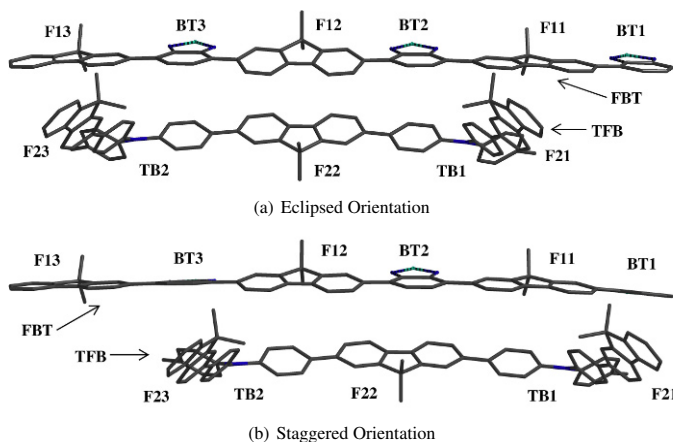


Fig. 3: TFB:F8BT structures (slightly tilted forward) showing two different orientations of the polymer constituents. In each, the FBT (top chain) consists of 3 fluorene (F) units and 3 benzothiadiazole (BT) units while the TFB (bottom chain) consists of 3 F units and 2 triarylamine (TB) units. These co-monomer units are labeled with indices. The eclipsed orientation (panel a) has the middle F units (F12 and F22) of both chains π -stacked while the staggered orientation (panel b) has the middle BT of FBT (BT2) and the middle F of TFB (F22) π -stacked, see Eqs. (1)-(2). Reprinted with permission from Ref. [41]. Copyright 2007, American Institute of Physics.

Fig. 4 illustrates the low-lying singlet states obtained from TD-DFT calculations for the E vs. S structures [41]. The observed states fall into two classes: excitonic states (XT), which feature electron-hole (e - h) configurations on the same polymer chain (FBT* or TFB*) and charge transfer states (CT), which feature e - h configurations on adjacent chains. In particular, the lowest-lying XT state is essentially of FBT* character, while the lowest-lying CT state corresponds to a $\text{TFB}^+\text{-FBT}^-$ inter-chain e - h configuration. In Fig. 4, these lowest-lying XT vs. CT states are highlighted. The XT $\rightarrow$ CT transition thus involves the inter-chain transfer of an electron from a TFB to an FBT unit.

Importantly, the excited electronic states are not of pure XT vs. CT character, and the observed admixtures of electronic state character strongly depend upon the interface geometry. While the XT states exhibit significantly larger oscillator strength and, hence, photoluminescence intensity, some of the nominal CT states can acquire non-negligible photoluminescence by intensity

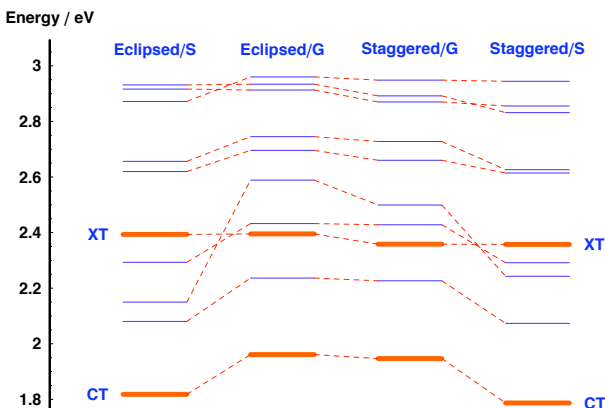


Fig. 4: Energy correlation diagram between the gas phase (/G) and solvated (toluene) (/S) lowest excited states in a TFB:F8BT model system calculated by TD-DFT (B3LYP/6-31G(d)). The eclipsed vs. staggered structures as shown in Fig. 3 are compared. The lowest-lying excitonic (XT) and charge transfer (CT) states are highlighted in red. Solvation effects tend to stabilize the CT state. Reprinted with permission from Ref. [41]. Copyright 2007, American Institute of Physics.

borrowing. For example, for the E configuration, the CT (1.96 eV) state is 92% $\text{TFB}^+\text{-FBT}^-$ and 8% FBT^* in character while the XT (2.40 eV) state is 74% FBT^* and 26% $\text{TFB}^+\text{-FBT}^-$ in character. Conversely, for the S configuration, the CT (1.95 eV) state is purely $\text{TFB}^+\text{-FBT}^-$ while the XT (2.36 eV) state almost has a 1:1 admixture, i.e., 51% $\text{TFB}^+\text{-FBT}^-$ and 49% FBT^* .

Thus a non-negligible FBT^* admixture (as in the E configuration) is thought to account for the luminescence of the lowest-lying CT state [41], which is characterized as a long-lived “exciplex” state that essentially corresponds to an inter-chain e - h pair pinned to the interface [44]. Other charge transfer states are optically dark; these states could be precursors to partially dissociated geminate e - h pairs that eventually contribute to the field-induced photocurrent observed in this system [34]. Indeed, as will be further discussed below, a picture which is solely based on the two dominant XT and CT states is not accurate enough to obtain a detailed understanding of the photophysical processes at the heterojunction.

2.3 Triplet states at the heterojunction

Finally, we briefly comment on the role of triplet states, a detailed characterisation of which has been given in Ref. [43]. Triplet states are generally lower in energy than their singlet counterparts, due to the exchange interaction which can lead to a stabilization of up to 0.5 eV. Since triplet states are optically

dark, they do not play a role in the photoexcitation process and subsequent ultrafast internal conversion events. Even on longer time scales, intersystem crossing (ISC) to form triplets is presumably not important. This is not only due to the fact that ISC is very slow in the absence of heavy atoms (of the order of 5 ns to 1 ms), but more importantly, is a consequence of the fact that the relevant spin-orbit matrix elements between singlet vs. triplet $\pi\pi^*$ states are generally zero [43].

Therefore, the only mechanism by which triplet generation is feasible is by recombination from bi-polaron like, charge separated states. This is comparable to direct electron-hole recombination in organic light-emitting diode (OLED) devices, where triplet formation indeed leads to a significant reduction in the theoretical efficiency of the device [60]. Using the results of TD-DFT calculations as reported above, we conclude that for $\text{TFB}^+\text{-FBT}^-$ type states, the electron can essentially be assumed to be localized on an N 2p or S 3p orbital of the BT sub-unit. A “back of the envelope” estimate based on the spin-orbit coupling of hydrogenic systems then suggests that the time scale for spin flipping is around 700-800 ps. Since the $\text{TFB}^+\text{-FBT}^-$ configuration appears as a significant admixture in the triplet exciton state of the eclipsed stacking (E) configuration, we expect spin interconversion to be more efficient in the E configuration.

It is tempting to speculate on the significance of the triplet states in these heterojunction systems. For OLED applications, triplets are generally undesirable since they are not emissive and hence potentially limit the efficiency of the device. However, for a heterojunction, it is possible that triplets pinned to the interface may undergo conversion to singlets and decay via exciplex or excitonic emission at long times. This would give an enhancement to the time-integrated emission and thereby account in part for the high electroluminescence efficiency reported for this system [26, 33].

3 Electron-phonon Hamiltonian

While the electronic structure calculations addressed in the preceding Section could in principle be used to construct the potential surfaces that are a prerequisite for dynamical calculations, such a procedure is in practice out of reach for large, extended systems like polymer junctions. At most, semiempirical calculations can be carried out as a function of selected relevant coordinates, see, e.g., the recent analysis of Ref. [44]. To proceed, we therefore resort to a different strategy, by constructing a suitably parametrized electron-phonon Hamiltonian model. This electron-phonon Hamiltonian underlies the two- and three-state diabatic models that are employed below (Secs. 4 and 5). The key ingredients are a lattice model formulated in the basis of localized Wannier functions and localized phonon modes (Sec. 3.1) and the construction of an associated diabatic Hamiltonian in a normal-mode representation (Sec. 3.2) [61].

3.1 Two-band configuration interaction lattice model

Following Refs. [61, 62], a two-band (valence and conduction band) configuration interaction model is introduced, using a basis of monoexcited configurations on the polymer chain. These correspond to electron-hole states $|\mathbf{n}\rangle = |n_e \bar{n}'_h\rangle = |n_e\rangle_C \otimes |\bar{n}'_h\rangle_V$ localized at sites n and n' of the chain. Here, $|n_e\rangle_C$ denotes a conduction-band (C) Wannier function (WF) localized at site n and occupied by an electron (e), while $|\bar{n}'_h\rangle_V$ denotes a valence-band (V) WF localized at site n' and occupied by a hole (h). The configurations $|\mathbf{n}\rangle$ thus correspond to neutral ($n_e = n'_h$) or charge transfer ($n_e \neq n'_h$) e - h pairs (excitons).

We now introduce creation and annihilation operators $a_{\mathbf{n}}^\dagger$ and $a_{\mathbf{n}}$ which create/annihilate e - h pairs at a given combination of sites $\mathbf{n} \equiv (n, n')$, i.e., $a_{\mathbf{n}}^\dagger|0\rangle = |\mathbf{n}\rangle = |n_e \bar{n}'_h\rangle$, where $|0\rangle$ is the ground state. Using these operators, a generic monoexcitation configuration interaction Hamiltonian can be formulated as follows in second quantization notation,

$$H_{\text{el}} = \sum_{\mathbf{mn}} \left(F_{\mathbf{mn}} + V_{\mathbf{mn}} \right) a_{\mathbf{m}}^\dagger a_{\mathbf{n}} \quad (3)$$

Here, the $F_{\mathbf{mn}}$'s are one-particle matrix elements which yield the energy levels ($\mathbf{m} = \mathbf{n}$) and transfer integrals ($\mathbf{m} \neq \mathbf{n}$) for the e - h pairs composed of conduction electrons and valence holes,

$$F_{\mathbf{mn}} = \langle m_e | f | n_e \rangle \delta_{m'_h n'_h} - \langle \bar{m}'_h | f | \bar{n}'_h \rangle \delta_{m_e n_e} \quad (4)$$

The $V_{\mathbf{mn}}$'s of Eq. (3) contain two-particle interactions, including Coulomb, exchange, and dipole-dipole contributions, which are parameterized according to semi-empirical functional forms [61]. The parameters are adapted to PPV and are then transposed by scaling to other polymer species.

The electronic Hamiltonian H_{el} is now augmented by the electron-phonon interaction [61],

$$\begin{aligned} H &= H_{\text{el}} + H_{\text{el-ph}} + H_{\text{ph}} \\ &= \sum_{\mathbf{mn}} \left(F_{\mathbf{mn}} + V_{\mathbf{mn}} \right) a_{\mathbf{m}}^\dagger a_{\mathbf{n}} + \sum_{\mathbf{nm}} \sum_{l\alpha} \left(\frac{\partial F_{\mathbf{mn}}}{\partial q_{l\alpha}} \right) a_{\mathbf{m}}^\dagger a_{\mathbf{n}} q_{l\alpha} \\ &\quad + \sum_{ll'} \sum_{\alpha} \frac{1}{2} (\omega_{l\alpha}^2 q_{l\alpha}^2 + p_{l\alpha}^2) + \lambda_l q_{l\alpha} q_{l'\alpha} \delta_{l',l+1} \end{aligned} \quad (5)$$

The electron-phonon coupling term is constructed so as to account for the modulation of the band gap – stemming from the diagonal single-particle matrix elements of Eq. (4) – as a function of the ($l\alpha$) phonon modes belonging to the α th phonon branch and l th site [29],

$$\left(\frac{\partial f_{mn}}{\partial q_{l\alpha}} \right) = \left(\frac{\partial \bar{f}_{mn}}{\partial q_{l\alpha}} \right) = \frac{S}{2} (2\hbar\omega^3)^{1/2} (\delta_{ml} + \delta_{nl}) \quad (6)$$

Here, S is the Huang-Rhys factor [63], which is related to the intensity of the 0- n vibronic transition, $I_{0-n} = e^{-S} S^n / n!$, and reflects the time-dependent Stokes shift associated with a given type of vibrational mode (e.g., $S \sim 0.6$ for the high-frequency C=C stretch modes [61,64,65]). For the class of systems studied here, two types of phonon modes are considered per monomer unit, i.e., high-frequency C=C stretch modes and low-frequency ring-torsional modes.

The parametrization for different polymer species is constructed by reference to the PPV case, by adjusting the relative HOMO and LUMO energies. For copolymer species which are not characterized by uniform sites, the site energies are varied along the chain. For the case of parallel chains, inter-chain single-particle terms are introduced, e.g., if the electrostatic coupling between the chains is strong. With regard to the electron-phonon coupling, it is assumed that no inter-chain phonon coupling terms occur.

3.2 Diabatic representation

Given the lattice Hamiltonian Eq. (5), which casts the interactions in terms of site-specific and site-site interaction terms, a complementary diabatic representation can be constructed which diagonalizes the Hamiltonian excluding the electron-phonon interaction, $H_0 = H_{\text{el}} + H_{\text{ph}}$. This leads to the form

$$H_{\text{dia}} = \sum_a \epsilon_a |a\rangle\langle a| + \sum_{ab} \sum_{\xi} g_{ab\xi} x_{\xi} (|a\rangle\langle b| + |b\rangle\langle a|) + \frac{1}{2} \sum_{\xi} (\omega_{\xi}^2 x_{\xi}^2 + p_{\xi}^2) \quad (7)$$

Here, the x_{ξ} are normal mode coordinates. Note that off-diagonal electron-phonon coupling terms appear both in the representation Eq. (7) and in the excitonic site representation of Eq. (5).

The Hamiltonian Eq. (7) provides the basis for the quantum dynamical treatment to be detailed in the following sections, typically involving a parametrization for 20-30 phonon modes. Eq. (7) is formally equivalent to a class of linear vibronic coupling (LVC) Hamiltonians which have been used for the description of excited-state dynamics in molecular systems [66] as well as the Jahn-Teller effect in solid-state physics. In the following, we will elaborate on the general properties of the Hamiltonian Eq. (7) and on quantum dynamical calculations based on this Hamiltonian.

Regarding the parametrization of the Hamiltonian Eq. (7), the present approach relies on the parameters of the underlying lattice model Eq. (5). However, one could envisage an alternative approach, similar to the one described in Refs. [66–69] for small molecular systems, where a systematic diabaticization is carried out based on supermolecular electronic structure calculations as described in Sec. 2.2.

4 Vibronic coupling in many dimensions: conical intersections and effective modes

The excited-state dynamics of the polymer systems studied here is a paradigm case of vibronic coupling in high-dimensional polyatomic systems. These systems are generally characterized by complex topologies of intersecting surfaces, involving in particular conical intersections (CoIn's) [66–69]. The linear vibronic coupling (LVC) Hamiltonian Eq. (7) is the simplest Hamiltonian which correctly accounts for the excited-state structure and topology. Generalizations of this Hamiltonian involve the inclusion of higher-order terms in a systematic Taylor expansion [66], or the embedding of the locally linearized structure into a correct representation of the overall adiabatic potential surfaces [70,71]. For the purpose of describing the polymer systems under consideration, the LVC model is appropriate since essentially small-amplitude motions are involved.

The LVC model further allows one to introduce coordinate transformations by which a set of relevant effective, or collective modes are extracted that act as generalized reaction coordinates for the dynamics. As shown in Refs. [54, 55, 72], $n_{\text{eff}} = n_{\text{el}}(n_{\text{el}} + 1)/2$ such coordinates can be defined for an electronic n_{el} -state system, in such a way that the short time dynamics is completely described in terms of these effective coordinates. Thus, three effective modes are introduced for an electronic two-level system, six effective modes for a three-level system etc., for an arbitrary number of phonon modes that couple to the electronic subsystem according to the LVC Hamiltonian Eq. (7). In order to capture the dynamics on longer time scales, chains of such effective modes can be introduced [50, 51, 73]. These transformations, which are briefly summarized below, will be shown to yield a unique perspective on the excited-state dynamics of the extended systems under study.

4.1 LVC model and effective modes

We start by re-writing the generic Hamiltonian Eq. (7) for an electronic two-level system coupled to N nuclear modes,

$$\mathbf{H} = \mathbf{V}_{\Delta} + \sum_{i=1}^N \frac{\omega_i}{2} \left(p_i^2 + x_i^2 \right) \mathbf{1} + \sum_{i=1}^N \begin{pmatrix} \kappa_i^{(1)} x_i & \lambda_i x_i \\ \lambda_i x_i & \kappa_i^{(2)} x_i \end{pmatrix} \quad (8)$$

where mass and frequency weighted coordinates were used for convenience. Here, $\mathbf{1}$ and $\mathbf{V}_{\Delta}$ denote the unit matrix and a coordinate-independent matrix of offsets, respectively. The diagonal ($\kappa_i^{(1,2)}$) and off-diagonal (λ_i) potential terms correspond to diabatic tuning and coupling terms [66]. The Hamiltonian Eq. (8) allows for the presence of a conical intersection (CoIn) topology at nuclear configurations where the diabatic couplings vanish and the adiabatic states become degenerate. A CoIn corresponds to an $(N - 2)$ -dimensional

hypersurface of degeneracy points of the adiabatic potential energy surfaces (PES). The degeneracy is lifted by displacements within the two-dimensional branching plane [66–69, 74].

The Hamiltonian Eq. (8) can alternatively be represented in terms of sum and difference parameters $\kappa^{(\pm)} = 1/2(\kappa_i^{(1)} \pm \kappa_i^{(2)})$,

$$\mathbf{H} = \mathbf{V}_\Delta + \sum_{i=1}^N \frac{\omega_i}{2} \left(p_i^2 + x_i^2 \right) \mathbf{1} + \sum_{i=1}^N \kappa^{(+)} x_i + \begin{pmatrix} \kappa_i^{(-)} x_i & \lambda_i x_i \\ \lambda_i x_i & -\kappa_i^{(-)} x_i \end{pmatrix} \quad (9)$$

This illustrates that only the electron-phonon coupling terms associated with the $\kappa_i^{(-)}$ (tuning) and λ_i (coupling) parameters contribute to the lifting of the CoIn degeneracy [55, 74].

Following the analysis of Refs. [54, 55, 72], we now make use of the fact that the nuclear modes of the Hamiltonian Eq. (8) produce cumulative effects by their coupling to the electronic subsystem. From Eq. (9), the electron-phonon interaction can be absorbed into the following collective modes,

$$\begin{aligned} X_+ &= \sum_{i=1}^N \kappa_i^{(+)} x_i \\ X_- &= \sum_{i=1}^N \kappa_i^{(-)} x_i \\ X_A &= \sum_{i=1}^N \lambda_i x_i \end{aligned} \quad (10)$$

which represent collective shift (X_+), tuning (X_-), and coupling (X_A) effects. These modes entirely define the coupling to the electronic subsystem. The modes of Eq. (8) can be orthogonalized [54, 55, 72] so as to yield a set of effective coordinates (X_1, X_2, X_3). By introducing an orthogonal transformation in the full coordinate space, $\mathbf{X} = \mathbf{T}\mathbf{x}$, the remaining coordinates are identified as a complementary set of residual modes ($X_4, \dots, X_N$). These modes do not couple directly to the electronic subsystem but couple bilinearly to the effective modes.

The Hamiltonian in the new coordinates reads

$$\mathbf{H} = \mathbf{H}_{\text{eff}} + \mathbf{H}_{\text{res}} \quad (11)$$

with the 3-mode effective Hamiltonian part

$$\begin{aligned} \mathbf{H}_{\text{eff}} = \mathbf{V}_\Delta + \sum_{i=1}^3 \frac{\Omega_i}{2} (P_i^2 + X_i^2) \mathbf{1} + \sum_{i,j=1, j>i}^3 d_{ij} (P_i P_j + X_i X_j) \mathbf{1} \\ + \sum_{i=1}^3 K_i X_i \mathbf{1} + \begin{pmatrix} D_1 X_1 + D_2 X_2 & \Lambda X_1 \\ \Lambda X_1 & -D_1 X_1 - D_2 X_2 \end{pmatrix} \end{aligned} \quad (12)$$

Here, a topology-adapted representation [55] was chosen, where (X_1, X_2) lift the degeneracy at the intersection and thus span the branching plane [74]. These modes are obtained by orthogonalizing the modes (X_-, X_+) of Eq. (10). The third mode X_3 is in turn orthogonal to (X_1, X_2) and carries information on the intersection space, i.e., the X_+ component of Eqs. (9)–(10). Alternative construction schemes are possible; in particular, the bilinear coupling terms can be eliminated within the three-mode subspace [54, 72].

The residual Hamiltonian $\mathbf{H}_{\text{res}}$ contains the remaining $(N - 3)$ modes, and their bilinear coupling to the effective modes,

$$\mathbf{H}_{\text{res}} = \sum_{i=4}^N \frac{\Omega_i}{2} (P_i^2 + X_i^2) \mathbf{1} + \sum_{i=1}^N \sum_{j=4}^N d_{ij} \left(P_i P_j + X_i X_j \right) \mathbf{1} \quad (13)$$

Using this transformation, it has been shown in Refs. [54, 72] that the effective-mode Hamiltonian $\mathbf{H}_{\text{eff}}$ by itself reproduces the short-time dynamics of the overall system exactly. This is reflected by an expansion of the propagator, for which it can be shown that the first few terms of the expansion – relating to the first three moments of the overall Hamiltonian – are exactly reproduced by the reduced-dimensional Hamiltonian $\mathbf{H}_{\text{eff}}$.

The effective-mode transformation described here is closely related to earlier works which led to the construction of so-called interaction modes [75, 76] or cluster modes [77, 78] in Jahn-Teller systems. The approach of Refs. [54, 55, 72] generalizes these earlier analyses to the generic form – independent of particular symmetries – of the linear vibronic coupling Hamiltonian Eq. (8).

In Refs. [55, 79], the truncation at the level of $\mathbf{H}_{\text{eff}}$ has been tested for several molecular systems exhibiting an ultrafast dynamics at CoIn's, and it was found that this approximation can give remarkably good results in reproducing the short-time dynamics. This is especially the case if a system-bath perspective is appropriate, and the effective-mode transformation is only applied to a set of weakly coupled bath modes [55, 72]. In that case, the system Hamiltonian can take a more complicated form than given by the LVC model.

4.2 Hierarchical electron-phonon (HEP) representation

For the polymer systems studied here, the approximation defined by $\mathbf{H}_{\text{eff}}$ is not necessarily sufficient, as demonstrated below (Sec. 5). We therefore resort to a strategy which generalizes the effective-mode approach in such a way that a chain of effective modes is generated, which successively unravel the dynamics as a function of time.

To this end, an additional orthogonal coordinate transformation is introduced, by which the bilinear couplings occurring in Eq. (13) are transformed to a band-diagonal form that only allows a coupling to the (three) nearest neighbors. By concatenating the effective-mode construction described in the previous section with this additional transformation in the residual-mode subspace,

a series of n th-order approximate Hamiltonians are generated [50, 51, 80],

$$\mathbf{H}^{(n)} = \mathbf{H}_{\text{eff}} + \sum_{l=1}^n \mathbf{H}_{\text{res}}^{(l)} \quad (14)$$

with the l th-order residual Hamiltonian

$$\mathbf{H}_{\text{res}}^{(l)} = \sum_{i=3l+1}^{3l+3} \frac{\Omega_i}{2} (P_i^2 + X_i^2) \mathbf{1} + \sum_{i=3l+1}^{3l+3} \sum_{j=i-3}^{i-1} d_{ij} \left(P_i P_j + X_i X_j \right) \mathbf{1} \quad (15)$$

For $(3 + 3n) = N$, Eqs. (14)-(15) yield an exact, transformed version of the original LVC Hamiltonian Eq. (8), as well as the effective-mode form Eqs. (11)-(13). We refer to this transformed LVC Hamiltonian as a hierarchical electron-phonon (HEP) model [50, 51, 80]. This form of the model is schematically illustrated in Fig. 5.

Successive orders $\mathbf{H}^{(n)}$ can be shown to correspond to successive orders in a moment (or cumulant) expansion of the propagator, which takes one to increasing times. Truncation of the chain at a given order n (i.e., $3 + 3n$ modes) leads to an approximate, lower-dimensional representation of the dynamical process, which reproduces the true dynamics up to a certain time. In Ref. [51], we have demonstrated explicitly that the n th-order ($3n + 3$ mode) truncated HEP Hamiltonian exactly reproduces the first $(2n + 3)$ rd order moments (cumulants) of the total Hamiltonian. A related analysis is given in Ref. [73].

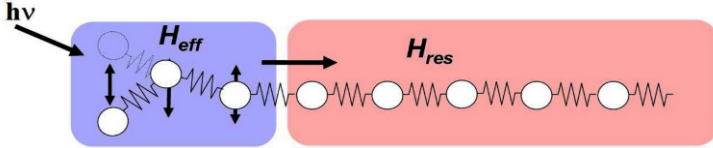


Fig. 5: Schematic illustration of the HEP construction. In addition to the transformation which identifies the three effective modes that couple directly to the electronic subsystem, further transformations are introduced for the residual bath in such a way that the chain-like representation of Eqs. (14)-(15) is obtained.

In the examples addressed below, for a two-band phonon distribution, the HEP scheme will be shown to yield essential insight into the interplay between high-frequency (C=C stretch) and low-frequency (ring-torsional) modes of the polymer heterojunction model of Eq. (7).

4.3 Dissipative closure of the HEP model

If the phonon distribution of the model Eq. (8) spans a dense spectrum – as is generally the case for the extended systems under consideration, which are effectively infinite-dimensional – the dynamics induced by the Hamiltonian will eventually exhibit a dissipative character. However, the effective-mode construction demonstrates that the shortest time scales are fully determined by *few* effective modes, and by the coherent dynamics induced by these modes. The overall picture thus corresponds to a Brownian oscillator type dynamics, and is markedly non-Markovian [81, 82].

If the HEP chain is truncated at a given order, a natural approach to impose an irreversible character on the dynamics is to close the hierarchy by adding a dissipation mechanism, e.g., employing a Markovian master equation or a corresponding collection of explicit bath modes. By this technique, one prevents the occurrence of artificial recurrences that “propagate back” along the chain, and an effectively irreversible dynamics results. This scheme is known from Mori theory [83–86] as well as the Generalized Langevin Equation [82, 87] and translates to the following form of an n th-order system-bath Hamiltonian,

$$\begin{aligned} \mathbf{H}_{\text{diss}}^{(n)} &= \mathbf{H}^{(n)} + \mathbf{H}_{\text{bath}}^{(n)} \\ &= \mathbf{H}_{\text{eff}} + \sum_{l=1}^n \mathbf{H}_{\text{res}}^{(l)} + \mathbf{H}_{\text{bath}}^{(n)} \end{aligned} \quad (16)$$

Here, $\mathbf{H}_{\text{bath}}^{(n)}$ is an external bath Hamiltonian which generates a Markovian (Langevin-type) friction acting at the level of the highest order n of the hierarchy. In Ref. [88], we have constructed a hierarchy of approximate spectral densities representing the combined effect of the residual modes and bath modes; these converge towards the true spectral density as more chain modes are added in the residual space. One should again emphasize that the overall process is strongly non-Markovian [81, 82] even though the “end of the chain” undergoes a simple Markovian damping.

In Refs. [51, 53], we used an explicit representation of the bath in terms of a collection of oscillators which are bilinearly coupled to the last three members of the HEP hierarchy,

$$\mathbf{H}_{\text{bath}}^{(n)} = \sum_{i=1}^{N_B} \frac{\omega_{B,i}}{2} (p_{B,i}^2 + x_{B,i}^2) \mathbf{1} + \sum_{i=n-3}^n \sum_{j=1}^{N_B} d_{ij}^B \left(P_i p_j + X_i x_j \right) \mathbf{1} \quad (17)$$

The coupling parameters d_{ij}^B are sampled according to a specified spectral density, which is here taken to be Ohmic [89–91]. More generally, the external bath itself can be taken to be non-Markovian. An example of this scheme is given in Fig. 8 of Sec. 5.1, for an Ohmic bath at zero temperature, i.e., exhibiting no thermal fluctuations. Here, the damping effect is generated by “quantum fluctuations” at $T = 0$ [90, 91].

More generally, a treatment which allows for the inclusion of temperature leads to a master equation of the form [88]

$$\frac{\partial \rho^{(n)}}{\partial t} = -\frac{i}{\hbar} [\mathbf{H}^{(n)}, \rho^{(n)}] + \mathbf{L}_{\text{diss}} \rho^{(n)} \quad (18)$$

where $\mathbf{L}_{\text{diss}}$ is a dissipative Liouvillian which can be derived from an explicit representation of the bath as given in Eq. (17). The density operator $\rho^{(n)}$ is a reduced density operator comprising all modes of the HEP hierarchy that are accounted for explicitly.

From the viewpoint of system-bath theory, the hierarchical structure of the HEP Hamiltonian thus allows for a flexible partitioning into system and bath subspaces. A chosen subset of effective modes can be absorbed into the system space, while approximations are introduced for the residual space. For a partitioning that identifies the electronic subsystem as the system part, the dynamics is generally non-Markovian and exhibits an inertial, coherent regime on short time scales. This coherent regime is determined by a limited number of effective environmental modes. The irreversible, multi-mode nature of the bath determines the dynamical behavior on intermediate and long time scales. Using cumulant expansion techniques [81], one can introduce a series of finite-dimensional bath propagators corresponding to successive orders of the HEP hierarchy, whose cumulant expansions are identical to the one of the full propagator up to a certain order.

4.4 Generalization to three and more states

A generalization of the effective-mode construction to three or more electronic states is straightforward, using a set of $n_{\text{eff}} = n_{\text{el}}(n_{\text{el}} + 1)/2$ effective modes as mentioned above. In Refs. [52, 53], we have thus employed a three-state representation with six effective modes, based on the following form of the Hamiltonian which generalizes Eq. (14),

$$\begin{aligned} \mathbf{H}^{(n)}(X_1, \dots, X_{6n+6}) &= \mathbf{H}_{\text{eff}}(X_1, \dots, X_6) \\ &+ \sum_{l=1}^n \mathbf{H}_{\text{res}}^{(l)}(X_{6l+1}, \dots, X_{6l+6}) \end{aligned} \quad (19)$$

where the effective Hamiltonian reads as follows,

$$\begin{aligned} \mathbf{H}_{\text{eff}} &= \sum_{i=1}^6 \frac{\Omega_i}{2} (P_i^2 + X_i^2) \mathbf{1} + \sum_{i=1}^6 \begin{pmatrix} (K_i + D_i)X_i & \Lambda_i^{(12)} X_i & \Lambda_i^{(13)} X_i \\ \Lambda_i^{(12)} X_i & (K_i - D_i)X_i & \Lambda_i^{(23)} X_i \\ \Lambda_i^{(13)} X_i & \Lambda_i^{(23)} X_i & K_i^{(3)} X_i \end{pmatrix} \\ &+ \sum_{i=1}^6 \sum_{j=i+1}^6 d_{ij} \left(P_i P_j + X_i X_j \right) \mathbf{1} + \mathbf{C} \end{aligned} \quad (20)$$

The detailed derivation of $\mathbf{H}_{\text{eff}}$ is given in Ref. [53]. Here, two of the six modes (i.e., X_1 and X_2) are chosen as topology-adapted modes that span the branching plane for a chosen pair of electronic states (here, states 1 and 2). Each l th-order residual term now also comprises 6 modes,

$$\mathbf{H}_{\text{res}}^{(l)} = \sum_{i=6l+1}^{6l+6} \frac{\Omega_i}{2} (P_i^2 + X_i^2) \mathbf{1} + \sum_{i=6l+1}^{6l+6} \sum_{j=i-6}^{i-1} d_{ij} \left(P_i P_j + X_i X_j \right) \mathbf{1} \quad (21)$$

The moment conservation rules described above – i.e., conservation of the $(2n+3)$ rd Hamiltonian moments (cumulants) at the n th order of the hierarchy – carry over to an arbitrary number of electronic states [51, 53, 73].

5 Quantum dynamics of exciton dissociation at a polymer heterojunction

The dynamics associated with the Hamiltonian Eq. (8) or its variants Eq. (11) and Eq. (14) can be treated at different levels, ranging from the explicit quantum dynamics to non-Markovian master equations and kinetic equations. In the present context, we will focus on the first aspect – an explicit quantum dynamical treatment – which is especially suited for the earliest, ultrafast events at the polymer heterojunction. Here, the coherent vibronic coupling dynamics dominates over thermally activated events. On longer time scales, the latter aspect becomes important, and kinetic approaches could be more appropriate.

In Refs. [50–53], we have used the MCTDH method [47–49] in order to calculate the femtosecond to picosecond scale evolution of the relevant state populations at the TFB:F8BT heterojunction. MCTDH is numerically exact and currently one of the most efficient methods for time-dependent quantum propagation for systems with many degrees of freedom. In the applications of Refs. [50–53], we have employed the method at a wavefunction level, using pure-state initial conditions and an explicit time propagation for all phonon modes. On longer time scales, the irreversible nature of the dynamics – due to the infinite-dimensional nature of the phonon mode space – can be accounted for by an augmented version of the model including a Markovian closure [51, 53], see Sec. 4.3. A related approach using a non-Markovian master equation formulation has been developed in Ref. [92]; this approach is able to capture both the coherent and dissipative aspects of the dynamics.

In the following, we summarize the pertinent results of our analysis of Refs. [50–53] where we applied the LVC Hamiltonian Eq. (1) in conjunction with a 20-30 mode phonon distribution composed of a high-frequency branch corresponding to C=C stretch modes and a low-frequency branch corresponding to ring-torsional modes. In all cases, the parametrization of the vibronic coupling models is based on the lattice model of Sec. 3.1 and the complementary diabatic representation of Sec. 3.2.

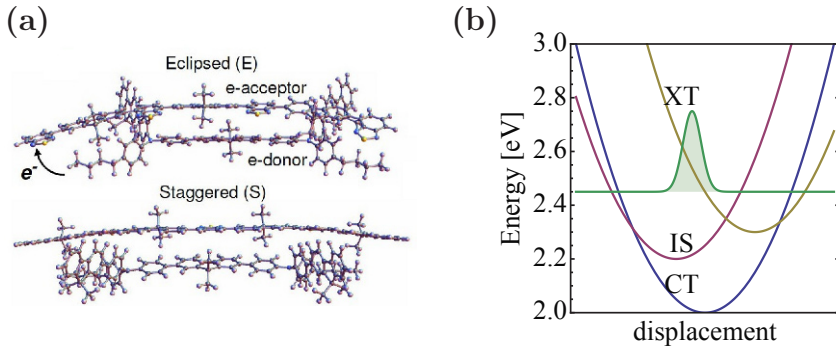


Fig. 6: Schematic illustration of the phonon-assisted exciton dissociation process. Due to the electronic state couplings, the photogenerated exciton (XT) wavepacket undergoes transitions to an interfacial charge transfer (CT) state, along with indirect $XT \rightarrow IS \rightarrow CT$ transitions via an intermediate (IS) state (see panel (b)). In Ref. [52], the diabatic Hamiltonian of Eqs. (19)–(20) was parametrized for two relevant interface configurations (eclipsed (E) vs. staggered (S) as shown in panel (a)) which correspond to the configurations of Fig. 3.

In Refs. [50–53], two levels of analysis were successively addressed: (i) a two-state XT-CT model which is able to capture the basic features of the phonon-mediated exciton dissociation process; (ii) a three-state XT-IS-CT model which also comprises an intermediate state (IS), i.e., an additional charge transfer state whose presence can have a significant influence on the dynamics, see Fig. 6. In the latter case, comparative calculations for several interface configurations were carried out, leading to a realistic, molecular-level picture of the photophysical events at the heterojunction. In the following, we start with a summary of the findings reported in Refs. [50, 51], where the two-state model was explored (Sec. 5.1). Following this, we address in more detail the analysis of Refs. [52, 53] for the three-state model (Sec. 5.2).

5.1 Two-state XT-CT model

We now briefly summarize the key results of the analysis of Refs. [50, 51] for a reduced XT-CT model of the TFB:F8BT heterojunction, using explicit quantum dynamical (MCTDH) calculations for a two-state model parametrized for 20–30 phonon modes. At this level of analysis, an ultrafast (~ 200 fs) XT state decay is predicted, followed by coherent oscillations, see Fig. 8 (trace “exact” in panel (a)). Further analysis in terms of an effective-mode model and the associated HEP decomposition (see Sec. 4.2) highlights several aspects:

- i. The high-frequency vs. low-frequency modes appear in alternation at successive orders of the HEP hierarchy. The lowest order of the hierarchy, i.e., $\mathbf{H}^{(0)} = \mathbf{H}_{\text{eff}}$ comprising modes (X_1, X_2, X_3), is entirely composed of high-frequency modes, reflecting that the high-frequency C=C stretch modes

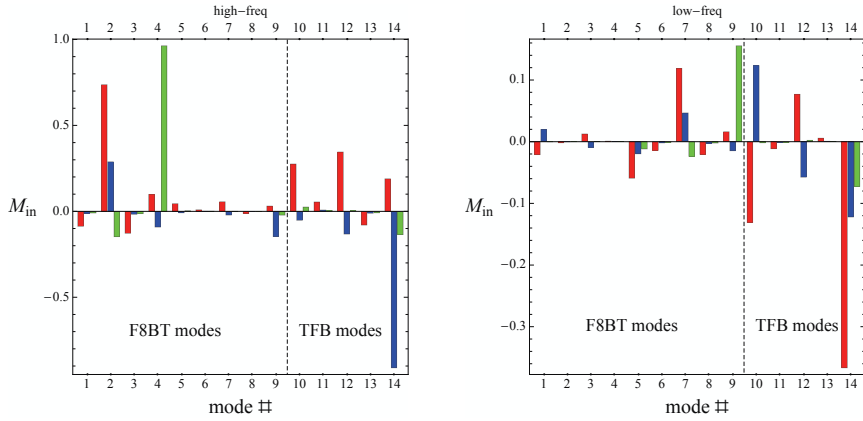


Fig. 7: For the two-state XT-CT model, the projection of the three effective modes (X_1, X_2, X_3) (shown in red, blue, and green, respectively) onto the primitive phonon modes $\{x_i\}$ is illustrated, for a model comprising 14 primitive high-frequency modes and 14 primitive low-frequency modes (i.e., 28 modes overall). Even though the projection involves contributions from both phonon bands, the low-frequency contributions are small, and all three effective modes are of high-frequency type. (Note the change in scale between the l.h.s. and the r.h.s. of the figure.) Furthermore, since the primitive modes are localized on the individual molecular units, the effective modes can be shown to be partially localized as well. Thus, two of the effective modes (shown in blue and green) are dominated by local contributions coming from either the F8BT chain or the TFB chain. The third mode (shown in red) exhibits contributions from both chains. (Reproduced from Ref. [93].)

- dominate the coupling to the electronic subsystem. The next highest order, i.e., $\mathbf{H}_{\text{res}}^{(1)}$ comprising modes (X_4, X_5, X_6), is exclusively composed of low-frequency (ring torsional) modes. The second-order contribution $\mathbf{H}_{\text{res}}^{(2)}$ in turn consists again of high-frequency modes. At higher orders of the hierarchy, high-frequency and low-frequency components start to mix.
- ii. From the branching plane representation of the potential in the (X_1, X_2) coordinates (see Sec. 4.1), one can infer that the system exhibits a conical intersection. However, the Franck-Condon geometry is found to lie significantly below this intersection, and the dynamics evolves in an extended avoided-crossing region in the vicinity of the intersection.
 - iii. Despite the predominance of the high-frequency modes in the electronic coupling, the low-frequency ring-torsional modes which appear at the order $\mathbf{H}_{\text{res}}^{(1)}$ of the mode hierarchy play a key role in the XT-CT transfer.

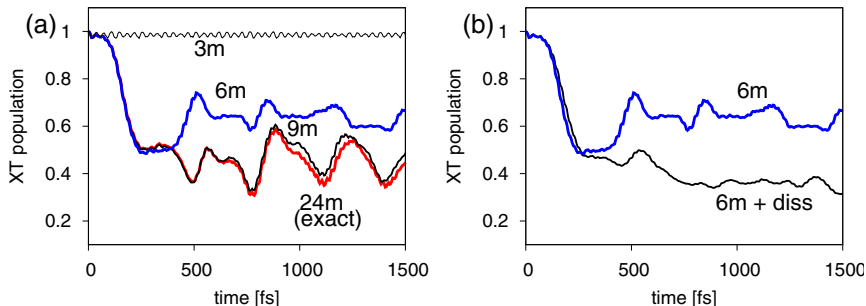


Fig. 8: Time-evolving XT state populations obtained from quantum dynamical (MCTDH) calculations for the 2-state model of Sec. 5.1, for different levels of the HEP hierarchy as compared with the full-dimensional (24-mode) result. Panel (a) shows the $\mathbf{H}^{(0)}$ approximation (3 modes) as compared with the $\mathbf{H}^{(1)}$ approximation (6 modes) and the $\mathbf{H}^{(2)}$ approximation (6 modes). Panel (b) presents a comparison with the $\mathbf{H}_{\text{diss}}^{(1)}$ approximation including a Markovian closure as described in Sec. 4.3. Here, the coherent oscillations are largely damped out (adapted from Refs. [50, 51, 53]).

Indeed, exciton dissociation is observed to be inefficient in the absence of the low-frequency modes.

Figs. 7 and 8 illustrate the HEP analysis for the XT-CT model in more detail. Fig. 7 shows the decomposition of the first three modes of the hierarchy (X_1, X_2, X_3) into the primitive phonon modes [93]. As mentioned above, these modes constituting $\mathbf{H}_{\text{eff}}$, are all of high-frequency type. Two of these effective modes can be seen to be localized on the TFB vs. F8BT moieties, whereas the third mode is delocalized over both chains.

Fig. 8 shows time-dependent state populations as obtained from quantum dynamical (MCTDH) calculations. While the full (here, 24 dimensional) model exhibits an ultrafast XT decay, no net decay is observed for the reduced 3-mode model truncated at the lowest level of the effective mode hierarchy. The dynamics is strongly diabatic if confined to the high-frequency subspace ($\mathbf{H}_{\text{eff}}$) and involves repeated coherent crossings [51]. The dynamical interplay between the high-frequency and low-frequency modes is apparently a central feature of the process. To account for these effects, a treatment at the level of $\mathbf{H}^{(1)}$ is necessary, i.e., a six-mode model including the low-frequency modes. At the level of $\mathbf{H}^{(2)}$, the dynamics is found to be essentially exact. Similar conclusions can be drawn from a non-Markovian master equation approach [92, 93].

A qualitatively correct picture of the dynamics can indeed be obtained from a two effective-mode model – one high-frequency mode plus one low-

frequency mode – similarly to an early analysis by Halperin and Englman who proposed a two-frequency description of the Jahn-Teller coupling in solids [94]. A reduced-dimensional potential surface spanned by two relevant high-frequency vs. low-frequency modes shows that the XT-CT transition is essentially determined by low-frequency motion while the dynamics in the high-frequency direction remains diabatic [53].

An alternative explanation can be given in terms of a vibronic resonance effect, i.e., population transfer occurs due to the fact that the high-frequency subspace is tuned into resonance as a function of the low-frequency motions [88, 96]. This is very similar to resonant vibration-vibration coupling in liquids [95] where the transfer of vibrational excitation between solute species is mediated by low-frequency solvent modes.

Finally, we address the inclusion of dissipative effects in accordance with the discussion of Sec. 4.3. Dissipation is not expected to induce major changes in the dynamics, but its effect could be important in view of the fact that the finite-dimensional model under consideration tends to overemphasize coherent features on intermediate and long time scales. Fig. 8 (panel (b)) illustrates the effects of dissipation included at the level of the Markovian closure addressed in Sec. 4.3. We consider the $\mathbf{H}_{\text{diss}}^{(1)}$ approximation according to Eq. (16), i.e., the HEP hierarchy is carried to the first order (thus including six modes) and the external bath is added so as to close the hierarchy at this order. Here, an explicit bath composed of 15 external modes is included, using an Ohmic spectral density. The bath is resonant with the low-frequency modes of the $\mathbf{H}_{\text{res}}^{(1)}$ subspace, i.e., the bath is itself composed of low-frequency modes distributed according to an Ohmic spectral density. As expected, a pronounced attenuation of the coherent oscillatory behavior is observed. A realistic modeling of the exciton dissociation process is presumably intermediate between the strongly coherent, oscillatory evolution of Fig. 8a) and the partially damped dynamics of Fig. 8b).

5.2 Three-state XT-CT-IS model

While the two-state XT-CT model accounts for some of the essential features of the exciton dissociation process, a more detailed, molecular-level picture should include (i) intermediate electronic states that feature a non-negligible coupling to the XT and/or CT states, (ii) an ensemble of relevant interface configurations, as illustrated in Figs. 3 and 6. In Refs. [52, 53], these two aspects have been addressed. This analysis further allows one to verify whether the conclusions of the two-state analysis are corroborated by a more realistic treatment.

Regarding the role of intermediate states, we have focused on an additional charge transfer state which exhibits a non-negligible coupling to the exciton state and could therefore play a significant role in the exciton dissociation dynamics. Recent experimental studies provide strong indications that such an

intermediate state (here denoted IS) could contribute to photocurrent production [32]. In the semiempirical calculations of Ref. [44] for the same system, the CT state is identified as an exciplex state which remains “pinned” to the interface, while an additional charge transfer state is assigned as a potential photocurrent generating state (see the discussion of Sec. 2.2).

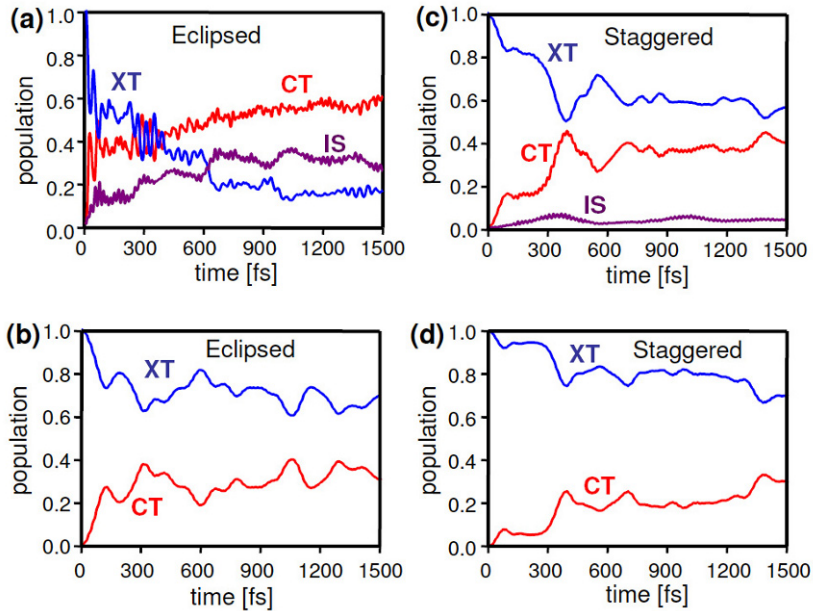


Fig. 9: Time-evolving state populations for the interface configurations of Fig. 3: (a) 3-state 28-mode wavepacket propagation for the E configuration, and (b) a complementary 2-state 28-mode calculation for the E configuration that was restricted to the XT-CT subspace; (c) and (d) are analogous calculations for the S configuration. Reproduced from Ref. [52]. Copyright 2008 by the American Physical Society.

In Refs. [52, 53], we have carried out a series of three-state simulations based on the model Eq. (20), including a comparative analysis of two representative interface structures at the TFB:F8BT heterojunction, i.e., the eclipsed (E) vs. staggered (S) configurations shown in Figs. 3 and 6. As mentioned above, the E vs. S configurations generate significantly different model parametrizations, pertaining to a strong-coupling vs. weak-coupling regime, respectively. As shown in Fig. 9, an ultrafast decay of the photogenerated exciton state is observed for both interface structures, even though the details of the dynamics differ in the two cases. Complementary calculations carried

out for a two-state model comprising the XT and CT states in the absence of the intermediate (IS) state (see panels (b) and (d) of Fig. 9), provide clear evidence that the intermediate “bridge” state plays an important role in accelerating the process.

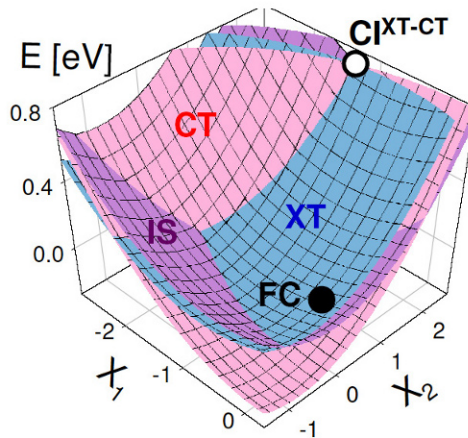


Fig. 10: For the 3-state model of Sec. 5.2., projections of the coupled diabatic XT, CT and IS potential surfaces (E configuration) onto the XT-CT branching plane are shown. The white and black circles indicate the conical intersection and Franck-Condon geometry, respectively. Reproduced from Ref. [52]. Copyright 2008 by the American Physical Society.

In order to obtain a reduced-dimensional picture of the dynamics and identify the roles of the respective phonon branches involved in the process, we again employ the HEP model. The hierarchy of effective modes – now with six modes at each level of $\mathbf{H}_{\text{eff}}$ and $\mathbf{H}_{\text{res}}^{(n)}$, see Eqs. (19)–(20) – again features the high-frequency vs. low-frequency modes in alternation. We therefore expect that the main dynamical features of the previous two-state model carry over to a more realistic treatment. Fig. 10 shows a projection of the diabatic states on the XT-CT branching plane. The inclusion of intermediate states generates a landscape of intersecting surfaces, thus opening various competing decay pathways. As pointed out above, the indirect $\text{XT} \rightarrow \text{IS} \rightarrow \text{CT}$ pathway plays an important role and significantly accelerates the exciton dissociation. The IS state mediates the charge separation while also acting as a competing final state [53].

We conjecture that the dynamical robustness of the ultrafast exciton decay indeed results from the presence of multiple decay pathways. While the trans-

fer efficiency at individual avoided-crossing or conical intersection topologies can depend in a sensitive fashion on the molecular polymer structure, the ensemble of such structures is characterised by an efficient decay. The present approach suggests a systematic procedure by which a molecular-level analysis is carried out for such an ensemble of interface structures.

6 Discussion and Conclusions

In the analysis summarized here, we have attempted a molecular-level description of exciton dissociation at a polymer heterojunction, using a detailed electronic structure and quantum dynamical characterisation of the polymer interface. This study leads to detailed insight into the nature of the electron-phonon coupling mechanism which generates an ultrafast (fs-ps scale) exciton decay. The main ingredients of the analysis are (i) explicit electronic structure calculations (CIS and TD-DFT) for fragments of the polymer interface to determine the relevant electronic states and the Franck-Condon transition energies (Sec. 2), (ii) the construction of a linear vibronic coupling Hamiltonian which is initially set up in a localized site representation and then applied in a delocalized diabatic representation (Sec. 3), (iii) efficient multiconfigurational quantum dynamical techniques as applied to this linear vibronic coupling model, along with variants of the model which use the effective mode transformations described in Sec. 4. This analysis has led to the formulation of two-state and three-state model Hamiltonians involving the photogenerated exciton state and a charge-separated “exciplex” state, along with an additional, intermediate charge transfer state that could be relevant for photocurrent generation. This picture is in general agreement with other studies of the same system [44].

The effective mode decomposition described in Sec. 4 leads to a mechanistic interpretation of the vibronic coupling dynamics which involves both high-frequency (C=C stretch) and low-frequency (ring-torsional) modes. While the electron-phonon coupling is largely dominated by the subset of high-frequency modes, these modes taken by themselves cannot account for the ultrafast decay dynamics. The low-frequency ring-torsional modes which only appear at the second order of the HEP hierarchy (Sec. 5) are thus found to play a crucial role. The dynamical interplay of high- vs. low-frequency modes can be understood in terms of the nonadiabatic dynamics induced by the low-frequency motions via a vibronic resonance effect. The present picture points to the generic nature of the observed dynamical pattern for a two-band phonon distribution (see also Refs. [58,97] which address the spectroscopic signature of both types of phonon modes in phenylene based polymers). A very similar dynamical mechanism could hold in related systems like carbon nanotubes [98].

The bulk heterojunction material exhibits an ensemble of interface configurations, such that spectroscopic observables and measurable photocurrents reflect statistically averaged properties (with the exception of observations

pertaining to single-molecule spectroscopy). Here, we have examined two representative configurations, i.e., the eclipsed (E) vs. staggered (S) configurations described in Sec. 2.2. These configurations differ significantly in the model parametrization, illustrating the importance of inter-chain interactions. The present analysis shows that even though the details of the exciton dissociation dynamics differ between these two configurations, an ultrafast process is observed in both cases. This suggests that the exciton dissociation process is dynamically robust. Given that this observation does not necessarily hold for the simpler two-state model of Sec. 5.1 (where the low-frequency modes do not always match the resonance window which guarantees that an efficient transfer occurs), we conjecture that the presence of intermediate states is of key importance.

The present approach has focused on the exciton dissociation event at the heterojunction, and does not account for exciton migration towards the interface region. This is justified by the fact that the highly filamented bulk heterojunction structure facilitates an immediate decay since the exciton is likely to reach the interface within its short diffusion length (of the order of 10 nm). Experimental observations for related polymer interfaces show that a considerable range of decay time scales can exist, reflecting an ultrafast decay of a subset of excitons, while longer time scales are associated with exciton states that are not localized in the immediate vicinity of the interface [102]. The present study focuses on the former subset of rapidly decaying states. However, site-site transfer could straightforwardly be included by returning to the lattice Hamiltonian of Sec. 3.1.

Further, the present analysis does not give a complete picture of all vibronic coupling pathways available to the system, but is primarily concerned with the intermolecular charge transfer at the heterojunction interface. Even though competing intramolecular internal conversion processes involving the monomer excited states could play a role (see the discussion of Sec. 1), the TD-DFT electronic structure calculations described in Sec. 2 confirm that the lowest-lying charge transfer states are of inter-chain character. The relevant states and their geometry dependence are described in a qualitatively correct way by the model Hamiltonian of Sec. 3, which builds upon a simplified electronic structure description in terms of monoexcited configurations. A more elaborate electronic structure picture for a range of geometries could lead to an even more complex scenario involving both inter- and intramolecular vibronic coupling pathways.

Finally, our analysis focuses on the primary events at the heterojunction and does not yet include a description of photocurrent production and the possible regeneration of excitons at the heterojunction. Both effects require going to longer time scales and accounting for finite temperatures. Exciton regeneration is in fact of crucial importance in the TFB:F8BT blend, since LEDs fabricated from this material have been shown to exhibit a remarkably large photoluminescence efficiency that must originate in secondary exciton formation [26, 32, 42].

The question as to how photocurrent is generated from either the exciplex states – i.e., long-lived charge-transfer excitons pinned to the interface – or from other charge transfer states (e.g., the intermediate state identified in our analysis [52] and related studies [44]) is currently an open issue. Recent experimental observations indicate that the dissociation of interfacial charge-transfer excitons constitutes the bottleneck for photocurrent generation [99–104]. A theoretical description that includes the prediction of photocurrent generation requires the use, e.g., of non-equilibrium Green’s function techniques (see the Chapter by G. Cuniberti and collaborators in this volume) as combined with the vibronic coupling models described here. A detailed understanding of all phases of carrier generation, recombination, and transport is of paramount importance, especially in view of the fact that carrier generation and mobility are still the key limiting factors to device efficiency. The present analysis paves the way for such a complete *ab initio* picture of the processes at polymer junctions.

Acknowledgments

We thank Laura Herz for constructive discussions. This work was supported by the ANR-05-NANO-051-02 and ANR-NT05-3-42315 projects, by NSF grant CHE-0712981, and by the Robert Welch Foundation (E-1337).

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