Hybrid biexcitons in organic polymer aggregates: A case of Dr. Jekyll meeting Mr. Hyde.

Eric R. Bittner

Department of Chemistry, University of Houston, Houston, Texas 77204, United States

Carlos Silva-Acuna

School of Chemistry and Biochemistry, Georgia Institute of Technology, 901 Atlantic Drive, Atlanta GA 30332, United States; Department of Physics, Georgia Institute of Technology, 771 Ferst Drive NW, Atlanta GA 30332, United States; Departamento de Fisica Aplicada, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, 97310 Mérida, Yucatán, México

(Dated: August 4, 2021)

Frenkel excitons are the primary photoexcitations in organic semiconductors and are ultimately responsible for the optical properties of such materials. They are also predicted to form bound exciton pairs, termed biexcitons, which are consequential intermediates in a wide range of photophysical processes. Generally, we think of bound states as arising from an attractive interaction. However, here we report on our recent theoretical analysis predicting the formation of stable biexciton states in a conjugated polymer material arising from both attractive and repulsive interactions. We show that in J-aggregate systems, JJ-biexciton states can arise from repulsive dipolar interactions with energies $E_{JJ} > 2E_J$ while in H-aggregates, HH-biexciton states $E_{HH} < 2E_H$ corresponding to attractive dipole exciton/exciton interactions. These predictions are corroborated by using ultrafast double-quantum coherence spectroscopy on a PBTTT material that exhibits both J- and H-like excitonic behavior.

I. INTRODUCTION

It is generally understood that the primary photoexcitations in organic semiconducting materials are molecular $\pi-\pi^*$ electronic singlet states $(S_1)$ termed Frenkel excitons [1]. While local in nature, at sufficiently high packing densities, excitons can delocalized over several molecular units and sufficiently higher excitation densities, exciton-exciton interactions begin to dominate the optical properties of such materials [2]. Biexcitons, bound pairs of excitons, are consequential intermediates in a wide range of photophysical processes such as exciton dissociation into electrons $(e^-)$ and holes $(h^+)$ [3],

\[ S_0 + 2\hbar\omega \longrightarrow [2S_1]^\dagger \longrightarrow 2e^- + 2h^+ \]  

(1) bimolecular annihilation [4],

\[ S_1 + S_1 \longrightarrow [2S_1]^\dagger \longrightarrow S_0 + S_0 \]  

(2) singlet fission producing triplet $(T_1)$ states [5]

\[ S_0 + 2\hbar\omega \longrightarrow [2S_1]^\dagger \longrightarrow T_1 + T_1. \]  

(3) Ref. [4] notes that bimolecular annihilation may be mediated both by resonance energy transfer and diffusion-limited exciton-exciton scattering, but in either case we invoke the key intermediate $[2S_1]^\dagger$. Examples of this occur in biological light harvesting complexes where multi-exciton interactions may play important roles [6] in the excitonic transport process; and biexcitons can be crucial in cascade quantum emitters as a source of entangled photons [7]. While ample theoretical work points towards the existence of biexcitons in organic solids [8–14], and in optical lattices [15], there has been only indirect evidence of the dynamic formation of two-quantum exciton bound states in polymeric semiconductors by incoherent, sequential ultrafast excitation [9–15, 17].

Recently, we reported upon the the direct spectroscopic observation of bound Frenkel biexcitons, i.e., bound two-exciton quasiparticles $([2S_1]^\dagger)$, in a model polymeric semiconductor, [poly(2,5-bis(3-hexadecylthiophene-2-yl)thieno[3,2-b]thiophene)] (PBTTT) using coherent two-dimensional ultrafast spectroscopy. [19] The chemical structure of PBTTT is given in Fig. 1(A).

Molecular aggregation in the bulk gives rise to $\pi$-stacking interactions between localized $\pi-\pi^*$ electronic excitations (excitons) that to a good approximation are determined by the relative orientation of the local transition dipole moments between the ground and first singlet excited states. These interactions depend upon the local geometric arrangement of the molecular sites and give rise to exciton states that can be delocalized over multiple units. For example, for a two site system, the excitonic states can be written as

\[ \psi_{\pm} = \frac{1}{\sqrt{2}}(\phi_1 \pm \phi_2) \]  

(4) with energies $\epsilon_{\pm} = \epsilon_o \pm t$ where $t$ is exciton transfer integral and $\epsilon_o$ is the local site energy. Of the two possible eigenstates, only the symmetric state $\psi_+$ carries oscillator strength to the ground state. We shall assume...
the dipoles are parallel and the same plane and write the transfer integral for exchanging an exciton between neighboring sites as

\[ t = -\frac{t_o}{r^3} \left( 3 \cos^2(\theta) - 1 \right) \quad (5) \]

where \( r \) is the separation distance between neighboring sites, \( \theta \) is the angle between the transition moments and a unit vector connecting the two sites, and \( t_o \propto \mu^2 \) is proportional to the product of the transition dipole moments. For \( \theta = 0 \), the transition moments are arranged in a head-to-tail arrangement producing \( t < \pi/4 \). In this case, the bright aggregate state \( (\psi^+) \) is lower in energy than the isolated (non-aggregated) state. This gives rise to a systematic red-shift of the excitonic absorption peak as dye concentration and aggregation is increased.

The “J” refers to E. Jelley who first reported this effect in 1936 in PIC chloride dissolved in ethanol in which he reported that a Stokes shift towards the red with increasing salt concentration. [20] The effect in this system was also reported at about the same time by Scheibe in 1937. [21] On the other hand, for \( \theta > \pi/4 \), the transfer integral \( t > 0 \) and the bright aggregate state is shifted towards higher energies relative to the isolated exciton. System such as this are called H-aggregates (for hypsochromic) corresponding to the systematic blue shift in their absorption/emission peak with increasing aggregation. Theoretical work by Spano and coworkers has produced comprehensive models for H- and J-aggregates taking into account the mixing between vibronic states which allow a direct connection between the local structural morphology and the observed spectral line-shapes. [22-25]

PBTTT is unique in that it supports the formation of both H and J aggregate single exciton states. The experimental observations revealed a correlation between peaks in the single and double quantum spectra the correspond to the formation of HH and JJ biexciton species. This conclusion was supported by both a computational model and theoretical analysis based upon a quasi-one-dimensional continuum model. Here, we shall present an overview of the theoretical model we developed for biexcitons and use it to discuss the possibility of observing biexcitons in related organic polymer materials.

II. THEORETICAL MODEL

A. One-dimensional impurity model

Two excitons become bound when their mutual attraction is sufficient to overcome their kinetic energy. To examine this in the framework of the tight-binding model developed in manuscript, we take a continuum limit and work in a relative coordinate reference frame where \( x = |r_1 - r_2| \) is the separation between two localized excitons. Thus, the Schrödinger equation can be approximated as

\[ t\psi'' + U\delta(x)\psi = E\psi. \quad (6) \]

For bound states, \( \psi(x) \) must vanish as \( x \to \pm \infty \), giving that

\[ \psi(x) = \begin{cases} \sqrt{\kappa}e^{-\kappa x} & x > 0 \\ \sqrt{\kappa}e^{\kappa x} & x < 0 \end{cases} \quad (7) \]

where \( \kappa = U/2t \) is a positive constant and \( E = tn^2 \). In general, we take \( t = -\hbar^2/2\mu_{\text{eff}} \) and \( U < 0 \) for an attractive potential giving rise to a bound state energetically below the continuum for the scattering states.

For molecular aggregates, the transfer integral \( t \) depends upon the relative orientation of the transition moments between the exciton donor and acceptor sites and varies as \( t = |\mu_{\text{ge}}|^2(1 - 3\cos^2(\theta))/R^3 \) where \( \theta \) is the relative orientation of the two transition moments and \( R \) is the separation between the two species (taking \( z \) to be along the direction connecting the two molecular centers). For J-aggregates, \( \theta \approx 0 \) for “head-to-tail” coaxial alignment of transition dipoles giving \( t < 0 \) and \( \mu_{\text{eff}} > 0 \) while for H-aggregates \( \theta \approx \pi/2 \) corresponding to the dipoles being aligned perpendicular to \( z \) in which \( t > 0 \) and hence \( \mu_{\text{eff}} < 0 \). Optically, the bright state for a J-aggregate lies at the bottom of the energy band while the bright state for an H-aggregate lies at the top. This implies that two kinds of bound biexciton species could exist in systems such as PBTTT which is well-known for having both H-like and J-like character.
B. Homogeneous lattice model in 1- and 2-dimensions

To explore the possibility of having multiple species of bound, biexcitons in the same system, we begin by writing a generic lattice model for the system by defining exciton operators \(a_n\) and \(a_n^\dagger\):

\[
a_{nm}^\dagger a_m = (-1)^{\delta_{nm}} a_n = \delta_{nm}. \tag{8}
\]

These operators are Pauli operators that create and remove single excitations on to a site labeled by \(n\). On a given site, they obey the Fermion relation \(a_n a_m + a_m^\dagger a_n = 0\), which enforces Pauli exclusion since \(a_n a_m = a_m^\dagger a_n = 1\), but commute “off-site” with \([a_n, a_m^\dagger] = 0\) when \(n \neq m\). This is different than the usual Fermion algebra where the anti-commutation rule is in force over all sites, giving rise to the exchange interaction. Further, we can write a generic multi-exciton Hamiltonian as

\[
H = \sum_{nm} h_{nm} a_n^\dagger a_m + \frac{1}{2} \sum_{nm} U_{nm} a_n^\dagger a_m^\dagger a_n a_m, \tag{9}
\]

where \(h_{nm}\) describes the single-exciton dynamics and \(U_{nm}\) is the exciton/exciton interaction.

In principle, the parameters entering into the Hamiltonian in Eq. (9) are defined by the system of interest. For the case of excitons, the diagonal elements of the single particle term defines the energy to place an exciton in site \(n\), and we write \(h_{nn} = \epsilon_n\). For a homogeneous lattice, all site energies are the same, and \(\epsilon_n = \epsilon_o\). Similarly, the off-diagonal elements of \(h_{nm}\) correspond to the matrix elements for transferring an excitation from site \(n\) to \(m\). To a good approximation, the single-exciton transfer interaction can be described within the dipole-dipole approximation as described above. However, the exciton/exciton 2-body interaction is more difficult to define. Formally, it arises from the Coulomb interaction between an exciton on one site with an exciton on another site. Formally, a Frenkel exciton corresponds to a single electron/hole excitation on a given site. However, molecules are not point particles and excitons may acquire some intramolecular charge-transfer character. Therefore, we anticipate that \(U_{nm}\) is also dipole-dipole like and reflects the relative orientation of the *static* exciton dipole moments.

For a one-dimensional chain with lattice spacing \(a\), \(n\) is simply an index along the chain such that the site location is given by \(r_n = na\). However, for 2- and 3-dimensional systems, we shall take it as an \(n\)-tuple index specifying the site location. For the single particle term, \(h_{nm}\) is the excitation energy for single site (\(\epsilon_n\)) and \(h_{nm}\) (for \(n \neq m\)) corresponds to the hopping integral between sites. Upon transforming into the reciprocal space, we find

\[
\tilde{a}_k = \frac{1}{\sqrt{N}} \sum_n e^{-ik\cdot n} a_n \tag{10}
\]

one finds the single particle energy dispersion as

\[
(\epsilon(k) - E)e^{ik\cdot n} = \sum_m h_{nm} e^{ik\cdot m}. \tag{11}
\]

To determine the 2-excitons, we begin by writing

\[
|\psi\rangle = \sum_{kk'} c_{kk'} a_k^\dagger a_{k'}^\dagger. \tag{12}
\]

where \(c_{kk'}\) are the expansion coefficients for this state. At this point, there are various approaches one can take to find the general solutions for the Schrödinger equation for the 2-exciton system. Indeed, for a small enough lattice, one can simply directly diagonalize the Hamiltonian in Eq. (9) for a finite sized grid. However, we are not interested in the full solution of this problem. Rather, we are focused upon only solutions corresponding to *bound* exciton pairs, and especially those bound pairs that retain their J- or H-like excitonic character. With this in mind, we develop a analytical solution that naturally extends to the full model.

C. Greens function approach

Exact solutions for the biexciton problem can be obtained for homogeneous 1-, 2-, and 3-dimensional systems in which the hopping integral between nearest neighbors is the same in any direction, all the site-energies are the same, and the exciton/exciton interaction only involves nearest neighbor terms. Employing the Greens function approach developed by Vektaris,[9] those solutions are given by

\[
\phi_K(n) = \sum_m \left( G_{nm} - \frac{G_{nm} G_{0m}}{G_{00}} \right) U_m \phi_K(m) \tag{13}
\]

where \(2K = k + k', 2q = k - k'\) define the center of mass and relative motions,

\[
G_{nm} = \frac{1}{N} \sum_q \frac{e^{-q\cdot(n-m)}}{E - \epsilon(K + q) - \epsilon(K - q)} \tag{14}
\]

is a Greens function, and

\[
\phi_K(n) = \frac{1}{\sqrt{N}} \sum_{k+k'=2n} \exp(iK\cdot(k-K')) \tilde{c}_{kk'} \tag{15}
\]

is the 2-exciton wavefunction written in terms of the coefficients \(\tilde{c}_{kk'}\). Finally, we have assumed the interaction \(U_{nm}\) to be translationally invariant such that

\[
U_{nm} = \sum_{n'} U_n \delta_{n,m+n'}. \tag{16}
\]

Note that \(\phi_K(0) = 0\), which enforces the exclusion principle.

In general, the complete solution of Eq. (13) would produce both bound and unbound bi-exciton states. We are ultimately interested solely in bound exciton pairs. These states necessarily must lie outside of the energy band for the free exciton pairs. That is to say, \(|E - 2\epsilon| \gg 2|t|\) to produce a bound biexciton state. Any 2-exciton state
create and remove excitons with wavevector \( \mathbf{k} \). Similarly, we define operators \( \hat{J}_n \) and \( \hat{H}_n \) which create and remove excitons with wavevector \( \mathbf{k} \) in the \( \pm x \)-direction, but localized to the \( n \)-th column, as sketched in Fig. 2. These can be written in terms of the original lattice operators

\[
\hat{J}_{m,k_x} = \frac{1}{\sqrt{N}} \sum_n e^{i k_x n} a_{(n,m)} \tag{17}
\]

\[
\hat{H}_{n,k_y} = \frac{1}{\sqrt{N}} \sum_m e^{i k_y m} a_{(n,m)}. \tag{18}
\]

Both are equivalent representations and we can choose to use either (but not both) to rewrite the original problem in this new representation.

Thus, we can write

\[
\sum_{nm} \hbar \epsilon_{nm} a^\dagger_{nm} a_m = \sum_{k_x,m} (\epsilon_J(k_x) \delta_{mm'} + t_H (mm') \hat{J}_m^\dagger \hat{J}_{m',k_x} + \epsilon_H(k_y) \delta_{nn'} + t_J (nn') \hat{H}_{n,k_y}^\dagger \hat{H}_{n',k_y} \tag{19}
\]

where in the first line we diagonalized in the \( J \)-direction and in the second, we diagonalized in the \( H \)-direction. This implies that we can think of a \( J \)-exciton state as moving in the \( J \)-direction with hopping integral \( t_H \) and \( H \)-exciton states as moving in the \( H \)-direction with hopping integrals \( t_J \). The dispersion relations are then as usual

\[
\epsilon_J(k_x) = \epsilon_0 + 2t_J \cos(k_x) \tag{20}
\]

\[
\epsilon_H(k_y) = \epsilon_0 + 2t_H \cos(k_y) \tag{21}
\]

where \( t_J < 0 \) is the nearest-neighbor coupling along the \( x \)-direction and \( t_H > 0 \) is the nearest-neighbor coupling taken in the \( y \)-direction. To remind, throughout we are taking the wavevector \( k \in [-\pi, \pi] \).

Since the problem is formally separable between \( x \) and \( y \) directions, the single-particle terms do not mix wavevector components since \( k_x \) and \( k_y \) are “good” quantum numbers for this system. Furthermore, diagonalizing Eq. 12 always returns one to the relation in Eq. 4; however, using the \( J \) and \( H \) operators, we can reduce the 2-particle/2-dimensional problem into a one for pair of particles within a 1 dimensional frame. Fig. 2 is a sketch of the 2D lattice showing the alignment of the transition dipoles for each site. Superimposed over the lattice sites are pairs of \( J \) (in A) and \( H \)-like (in B) exciton states.

If we use the \( J_{k_m} \) (or \( H_{k_n} \)) states as a basis for a given value of \( k \), we can use Eq. 13 to find the biexciton energies as

\[
E_{xx}(k) = 2\epsilon_x + \frac{4t^2}{U} \cos^2(k) + U \tag{22}
\]

where \( \epsilon_x \) is the excitation energy of either the \( J \) or \( H \) single exciton. At \( k = 0 \), the difference between the interacting and localized excitons is the contact energy \( U \), which defines the binding energy for the exciton pair. The binding energy must be at least greater in magnitude than \( 4t \), else the lowest energy interacting state will be still within the band for the freely dissociated pairs. These bands will split from the freely dissociated bands once \( U/t > 1 \). As in the 1D defect model above, bound states can occur only if \( t \) and \( U \) have the same sign.
E. Biexciton stability

Realistic molecular aggregate systems are not homogeneous due to local structural variations. Consequently, one expects a certain variation in either or both the local hopping integrals and site energies. Energetic variation along the direction of exciton motion limit the use of the band model developed above and we shall continue the analysis in real-space. However, we shall assume that the \( J^- \) and \( H^- \) exciton basis remains a valid ansatz allowing us to treat their motion as being quasi-one-dimensional. With this in mind, we write

\[
\hat{H} = E_0 + \Delta \sum_{j=1}^{N} (-1)^j \hat{c}^\dagger_j \hat{c}_j + t \sum_{j=1}^{N} (\hat{c}^\dagger_{j+1} \hat{c}_j) + U \sum_{j=1}^{N} \hat{c}^\dagger_{j} \hat{c}^\dagger_{j+1} \hat{c}_{j+1} \hat{c}_j.
\]

(23)

where the \( \hat{c}_j \) and \( \hat{c}_{j}^\dagger \) operators correspond to the \( J \) or \( H \) exciton operators at a particular value of \( k_x \) or \( k_y \) and \( E_0 \) corresponds to the single exciton energy for the \( J \) or \( H \) state. Here, we introduce \( \Delta \) as a crenelation parameter to account for the periodic energy differences between neighboring subunits. in which odd-numbered sites correspond to sub-unit A and even-numbered sites correspond to sub-unit B. Periodic boundary conditions are such that \( \hat{c}_N = \hat{c}_1 \).

Numerical solutions were determined by directly diagonalizing \( H \) for a given parameterization for sufficiently large lattices to properly capture the relevant states. The non-interacting case \( U = 0 \), can be solved exactly for given values of \( t \) and \( \Delta \) yielding eigenvalues \( \epsilon_\pm(k) = \pm \sqrt{(2t^2 \cos(k/2))^2 + \Delta^2 / 2} \) for free excitons moving on this lattice. Pauli exclusion forces pairs excitons to separate spatial regions and the problem can be approximated using the 1D impurity model in Sec. 1.A. From this we can arrive at a criteria for the stability of the biexciton pairs since the energy of any bound pair must lie below the lowest energy for a pair of unbound excitons. In other words, the coupling must be strong enough to overcome the kinetic energy of the two quasi-particles,

\[
\left( \frac{U}{2t} \right)^2 > 2 \sqrt{(\Delta/t)^2 + 4}
\]

(24)

where on the left side of the inequality is the biexciton binding energy and on the right side of the inequality is the energy of 2 free excitons on the crenelated lattice. In Fig. 4 we compare the results of the analytical approximation to the exact numerical solutions. The blue and orange dashed curves are the results of the analytical model and the points are from the numerical solutions. Except for the transition region, the results are in perfect agreement which confirms our asymptotic analysis.
FIG. 5. Spectral cuts along the two-quantum coherence energy axis, relative to the two-quantum diagonal energy axis ($\hbar \omega_{2Q} = 2\hbar \omega_{1Q}$, $E_{XX}$) at fixed $\hbar \omega_{43} = 2.06$ (H-aggregate resonance, blue), 1.99 (J-aggregate resonance, purple), and 1.94 eV (J-aggregate resonance, red).

### III. COMPARISON TO EXPERIMENTAL MEASUREMENT

We have examined the theoretical concepts by means of two-dimensional coherent excitation spectroscopy on PBTTT, with structure depicted in Fig. 1, which we reported extensively in Ref. 19. In that work, we identified spectral features associated with the 0–0 excitation peak of both the H- and J-aggregate components of the hybrid aggregate, with cross peaks between reflecting spectral correlations due to their shared ground state. The origin of the H-aggregate vibronic progression was centered at 2.06 eV, while a weaker peak at 1.99 eV was assigned to the J-aggregate vibronic origin. By performing two-quantum coherence measurements, we found spectral signatures of both HH and JJ biexcitons. A cross-section of the 2D spectral data is shown in Fig. 5. We found that HH biexcitons displayed attractive biexciton binding with energy $-64 \pm 6$ meV, where as JJ biexcitons displayed repulsive correlations with binding energy $+106 \pm 6$ meV; that is that the energy of the HH-biexciton resonance is lower than twice the H-aggregate resonance energy, while the corresponding energy for the JJ-biexciton resonance is higher.

We rationalized this observation as depicted in Fig. 2: two quantum interactions for excitons dispersed along the polymer backbone (J aggregates) are with $J < 0$, while $J > 0$ for those for between excitons dispersed on several chains (H aggregates). Considering physically reasonable parameters, we concluded that biexcitons in PBTTT are stable by the arguments depicted in Fig. 4.

### IV. CONCLUSIONS

We present here theoretical and experimental evidence supporting the formation of bound Frenkel biexcitons in a molecular aggregate material. In our theoretical analysis, we solved the full 2D interacting model and give the conditions necessary for the formation of stable, stationary states corresponding to bound exciton pairs. The model provides a road-map for developing a bi-exciton materials genome in terms of the properties of the J- and H-excitons. We show that for bound biexcitons, both the exciton-exciton interaction $U$ and the single-particle hopping integral $t$ must have the same sign. Furthermore, $U/t > 2$ so that the exciton/exciton potential interaction is greater than their total kinetic energy. Curiously, we find that while H-like excitons for bound biexcitons with attractive interactions, J-like exciton pairs form bound states arising from a repulsive interaction.

An open question, however, is the nature of the exciton-exciton interaction itself. Here, we introduce it as a parameter into our model with a dipole-dipole like form in that the exciton-exciton coupling in one direction is different from that in a perpendicular direction. It is also important to point out that while this interaction appears to have a dipole-like form, it necessarily must reflect the static dipole of the local Frenkel excitons rather than their transition dipole moments, which are responsible for the single exciton transfer between local sites. Computing these interactions from a first-principle ab initio theory remains a formidable challenge since it necessitates the accurate calculation of doubly excited states with some degree of charge-separation.

**ACKNOWLEDGMENTS**

The work at the University of Houston was funded in part by the National Science Foundation (CHE-2102506, ) and the Robert A. Welch Foundation (E-1337). The work at Georgia Tech was funded by the National Science Foundation (DMR-1904293).

[1] J. Frenkel, On the transformation of light into heat in solids. i, Phys. Rev. 37, 17 (1931).
[2] V. Agranovich and B. Toshich, Collective properties of fenkel excitons, Sov. Phys. JETP 26, 104 (1968).
[3] C. Silva, A. S. Dhoot, D. M. Russell, M. A. Stevens, A. C. Arias, J. D. MacKenzie, N. C. Greenham, R. H. Friend, S. Setayesh, and K. Müllen, Efficient exciton dissociation via two-step photoexcitation in polymeric semiconductors, Phys. Rev. B 64, 125211 (2001).
[4] M. A. Stevens, C. Silva, D. M. Russell, and R. H. Friend, Exciton dissociation mechanisms in the polymeric semiconductors poly (9, 9-dioctyfluorene) and poly (9, 9-dioctyfluorene-co-benzothiadiazole), Phys. Rev. B 63, 165213 (2001).
[5] C. Silva, D. M. Russell, A. S. Dhoot, L. M. Herz, C. Daniel, N. C. Greenham, A. C. Arias, S. Setayesh, K. Müllen, and R. H. Friend, Exciton and polaron dynamics in a step-ladder polymeric semiconductor: the influence of interchain order, J. Phys.: Condens. Matter 14, 9803 (2002).

[6] G. D. Scholes, G. R. Fleming, A. Olaya-Castro, and R. Van Grondelle, Lessons from nature about solar light harvesting, Nat. Chem. 3, 763 (2011).

[7] K. N. Avanaki and G. C. Schatz, Mechanistic understanding of entanglement and heralding in cascade emitters, J. Chem. Phys. 154, 024304 (2021).

[8] F. C. Spano, V. Agranovich, and S. Mukamel, Biexciton states and two-photon absorption in molecular monolayers, J. Chem. Phys. 95, 1400 (1991).

[9] G. Vektaris, A new approach to the molecular biexciton theory, The Journal of Chemical Physics 101, 3031 (1994). https://doi.org/10.1063/1.467616

[10] F. C. Spano, V. Agranovich, and S. Mukamel, Biexciton states and two-photon absorption in molecular monolayers, J. Chem. Phys. 95, 1400 (1991).

[11] F. B. Gallagher and F. C. Spano, Theory of biexcitons in one-dimensional polymers, Phys. Rev. B 53, 3790 (1996).

[12] S. Mazumdar, F. Guo, K. Meissner, B. Fluegel, and N. Peyghambarian, Exciton-to-biexciton transition in quasi-one-dimensional organics, J. Chem. Phys. 104, 9292 (1996).

[13] V. Agranovich, O. Dubovsky, D. Basko, G. La Rocca, and F. Bassani, Kinematic frenkel biexcitons, J. Lumin. 85, 221 (2000).

[14] G. Kun, X. Shi-Jie, L. Yuan, Y. Sun, L. De-Sheng, and Z. Xian, Effect of interchain coupling on a biexciton in organic polymers, Chin. Phys. B 18, 2961 (2009).

[15] P. Xiang, M. Litinskaya, and R. V. Krems, Tunable exciton interactions in optical lattices with polar molecules, Phys. Rev. A 85, 061401 (2012).

[16] A. Chakrabarti, A. Schmidt, V. Valencia, B. Fluegel, S. Mazumdar, N. Armstrong, and N. Peyghambarian, Evidence for exciton-exciton binding in a molecular aggregate, Phys. Rev. B 57, R4206 (1998).

[17] V. I. Klimov, D. McBranch, N. Barashkov, and J. Ferraris, Biexcitons in π-conjugated oligomers: Intensity-dependent femtosecond transient-absorption study, Phys. Rev. B 58, 7654 (1998).

[18] I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, et al., Liquid-crystalline semiconducting polymers with high charge-carrier mobility, Nat. Mater. 5, 328 (2006).

[19] E. G. Meza, R. Malatesta, H. Li, I. Bargigia, A. R. S. Kandada, D. A. Valverde-Chávez, S. Kim, H. Li, N. Stingredients, S. Tretiak, E. R. Bittner, and C. Silva-Acuña, Frenkel biexcitons in hybrid π photophysical aggregates (2021), arXiv:2101.01821 [cond-mat.mtrl-sci]

[20] E. E. Jelley, Spectral absorption and fluorescence of dyes in the molecular state, Nature 138, 1009–1010 (1936)

[21] G. Scheibe, L. Kandler, and H. Ecker, Polymerisation und polymere adsorption als ursache neuartiger absorptionsbanden von organischen farbstoffen, Naturwissenschaften 25, 75 (1937)

[22] F. C. Spano, Modeling disorder in polymer aggregates: The optical spectroscopy of regioregular poly(3-hexylthiophene) thin films, J. Chem. Phys. 122, 234701 (2005).

[23] F. C. Spano, Erratum: “Modeling disorder in polymer aggregates: The optical spectroscopy of regioregular poly(3-hexylthiophene) thin films” [J. Chem. Phys. 122, 234701 (2005)], The Journal of Chemical Physics 126, 159901 (2007). https://doi.org/10.1063/1.2721549

[24] F. C. Spano, J. Clark, C. Silva, and R. H. Friend, Determining exciton coherence from the photoluminescence spectral line shape in poly(3-hexylthiophene) thin films, J. Chem. Phys. 130, 074904 (2009).

[25] F. C. Spano and C. Silva, H- and J-aggregate behavior in polymeric semiconductors., Annu. Rev. Phys. Chem. 65, 477 (2014).