

Supporting Information for:

**Designing J- and H-Aggregates Through Wave Function Overlap Engineering:
Applications to Poly(3-hexylthiophene)**

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In the S.I. we first present the general Hamiltonian used in describing the electronic properties of a molecular dimer including vibronic coupling and charge transfer. The expressions for the absorption and PL spectral observables used in obtaining Figures 7, 9 and 10 are also included.

Hamiltonian

The Hamiltonian used to describe a dimer consisting of two coupled chromophores can be partitioned as¹,

$$H = H_{FE} + H_{CT} + H_{CTV} \quad (\text{S.1})$$

where the Frenkel Hamiltonian including vibronic coupling is given by,

$$H_{FE} = E_{S_1} + J_{TS} \{ |1\rangle\langle 2| + |2\rangle\langle 1| \} + \hbar\omega_0 \sum_n b_n^\dagger b_n + \hbar\omega_0 \sum_n \left\{ \lambda_0 (b_n^\dagger + b_n) + \lambda_0^2 \right\} |n\rangle\langle n| \quad (\text{S.2})$$

Here, E_{S_1} is the energy of the lowest optically excited state S_1 in a given monomer. $|n\rangle$ is a pure electronic state in which the n th ($n = 1, 2$) molecule is excited to the state S_1 , while the remaining molecule is unexcited (in state S_0). The second term represents excitonic coupling with J_{TS} equal to the intermolecular through-space Coulombic coupling. The last two terms represents the vibrational energy contribution including linear exciton-vibrational coupling. The operator $b_n^\dagger (b_n)$ creates (annihilates) a vibrational excitation on the n th molecule. Finally, the HR factor is λ_0^2 .

Charge transfer is accounted for in the Hamiltonian,

$$\begin{aligned}
 H_{CT} = E_{CT} \{ & |1^+, 2^-\rangle \langle 1^+, 2^-| + |2^+, 1^-\rangle \langle 2^+, 1^-| \} \\
 & + D_e |1\rangle \langle 1^+, 2^-| + D_e |2\rangle \langle 2^+, 1^-| \\
 & + D_h |1\rangle \langle 2^+, 1^-| + D_h |2\rangle \langle 1^+, 2^-| + h.c.
 \end{aligned} \tag{S.3}$$

E_{CT} is the energy of the charge transfer exciton consisting of a nearest-neighbor displacement of charges. The ket $|n^+, (n+1)^-\rangle$ represents the state consisting of a hole on molecule n and an electron on molecule $n+1$. ($n+1=1$ when $n=2$) The coupling between a Frenkel exciton and the CT state formed by transferring an electron (hole) to a neighboring molecule is represented by the dissociation integral D_e (D_h).

Finally, the vibronic coupling with the CT states is governed by,

$$H_{CTV} = \hbar\omega_0 \sum_{n=1,2} \left\{ \lambda_+ (b_n^\dagger + b_n) + \lambda_- (b_{n+1}^\dagger + b_{n+1}) + \lambda_+^2 + \lambda_-^2 \right\} |n^+, (n+1)^-\rangle \langle n^+, (n+1)^-|, \tag{S.4}$$

where $\lambda_+^2(\lambda_-^2)$ is the HR factor for the cation (anion).

Spectral Observables

For the numerical calculations of the spectral observables the Hamiltonian in Eq.(S.1) was expressed in a one- and two-particle basis set as described previously² and then diagonalized numerically to yield all eigenstates and energies. For the absorption spectrum we use the expression,

$$A(\omega) = \frac{1}{N\mu^2} \sum_{\alpha} |\langle G | \hat{M} | \psi^{(\alpha)} \rangle|^2 W_{LS}(\omega - \omega_{\alpha}) \quad (\text{S.5})$$

where $\alpha (=1,2,\dots)$ indexes the eigenstates $|\psi^{(\alpha)}\rangle$ with associated energies $\hbar\omega_{\alpha}$ in order of increasing energy. $|G\rangle$ is the vibrationless ground state and \hat{M} is the transition dipole moment (tdm) operator, obtained by summing over the molecular tdm's:

$$\hat{M} \equiv \sum_{n=1,2} \{ \mu_1 | g \rangle \langle n | + \mu_2 | n \rangle \langle g | \}, \quad (\text{S.6})$$

Here, μ_n is the molecular tdm of molecule n , $|n\rangle$ is defined after Eq.(S.1) and $|g\rangle=|g_1g_2\rangle$ is the pure electronic aggregate ground state of the dimer. Finally, $W_{LS}(\omega - \omega_{\alpha})$ is the lineshape function, taken here to be Gaussian.

In calculating the reduced PL spectrum we use the expression,

$$S(\omega) = \sum_{v_i=0,1,2,\dots} I_{PL}^{(0-v_i)} W_{LS}(\omega - \omega_{\alpha=1} + v_i\omega_0). \quad (\text{S.7})$$

Eq.(S.7) represents a vibronic progression with the 0- ν_t peak sourced by emission terminating on the ground electronic state with ν_t vibrational quanta distributed over the two S_0 nuclear potentials. As written, the expression assumes the low-temperature limit where emission takes place from just the lowest energy exciton (with $\alpha=1$). To treat higher temperatures a Boltzmann distribution of emitting excitons is taken as described in greater detail in Ref. ³. In order to focus entirely on the impact of aggregation on the oscillator strengths we have also neglected in Eq.(18) the cubic frequency dependence found in the Einstein spontaneous emission expression, as well as any influence of a frequency-dependent index of refraction. Hence we refer to the PL spectrum in Eq.(18) as a *reduced* PL spectrum.

Eq.(S.7) contains the dimensionless emission line strength for the 0- ν_t transition given by,

$$I_{PL}^{(0-\nu_t)} \equiv \frac{1}{\mu^2} \sum_{\nu_1, \nu_2=0,1,2,\dots}' | \langle g_1 \nu_1, g_2 \nu_2 | \hat{M} | \psi^{(\alpha=1)} \rangle |^2 \quad (\text{S.8})$$

where the prime on the summation indicates that the total number of vibrational quanta in the terminal state, $| g_1 \nu_1, g_2 \nu_2 \rangle$, satisfies, $\nu_t = \nu_1 + \nu_2$.

References

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- (2) Spano, F. C. *Acc. Chem. Res.* **2010**, *43*, 429-439.
- (3) Yamagata, H.; Spano, F. C. *J. Chem. Phys.* **2011**, *135*, 054906.