Supporting Information for

"The Intimate Relationship Between Conjugated Polymers and J-aggregates"

Hajime Yamagata and Frank C. Spano*
Department of Chemistry
Temple University
Philadelphia, PA 19122

I. Holstein Hamiltonian

For the calculated energy dispersion curves and spectra appearing in Fig.'s 2-4 we employed the Holstein-style[1] Hamiltonian which includes electron-vibrational (EV) coupling involving the vinyl-stretching vibration with frequency, $\omega_{vib} = 0.175 \; eV/\hbar$. Written in a representation of one-excitons, the Hamiltonian reads:[2]

$$H = \hbar\omega_{vib}\sum_{n} b_n^{\dagger}b_n + \hbar\omega_{vib}\lambda\sum_{n}(b_n^{\dagger}+b_n)\,|\,n><n\,|+$$

$$+J_{nn}\sum_{n}\{|\,n><n+1\,|+|\,n+1><n\,|\}+\hbar D+\hbar\omega_{0-0}+\lambda^2\hbar\omega_{vib} \qquad (S1)$$

The first terms represents the vibrational energy due to the high frequency mode, while the second term represents the linear EV coupling. $b_n^{\dagger}(b_n)$ is the creation (destruction) operator for vibrational quanta within the harmonic ground state (S$_0$) nuclear potential on molecule n. The pure electronic state, $|\,n>$, indicates that the nth molecule is electronically excited to the first optically allowed state (S$_1$), while all other molecules remain in their electronic ground states. The Huang-Rhys (HR) factor λ^2 measures the shift in the equilibrium positions of the ground and excited state nuclear potentials. The excitonic coupling in the third term is mediated by the nearest-neighbor coupling, J_{nn}, which is negative for a J-aggregate. Finally, ω_{0-0} is the gas-phase 0-0 transition frequency and D is the gas-to-crystal frequency shift, with $D<0$. In all calculations

we utilized periodic boundary conditions.

II. Expressions for the Absorption and Emission Spectrum

The expression for the calculated absorption line shape, $A(\omega)$ is,

$$A(\omega) = \mu_0^{-2} \sum_{\alpha} |< G \,|\, \hat{M} \,|\, \psi^{(\alpha)} >|^2 \, W(\omega - \omega_{\alpha}) \ , \qquad (S2)$$

where the sum is over all eigenstates of H, $|G>$ is the electronic and vibrational ground state of the aggregate and $\hat{M}$ is the aggregate transition dipole moment operator,

$$\hat{M} = \mu_0 \sum_{n} \{| g >< n | + | n >< g |\} . \qquad (S3)$$

Here, $|g>$ is the pure electronic ground state (all molecules in S_0). Finally, W is a line shape function, taken here to be Gaussian, $W(\omega) \equiv \exp[-\omega^2 / \Gamma^2]$.

The *reduced* steady-state PL spectrum at T=0K is evaluated from the expression

$$S(\omega) \ = \ \sum_{v_t = 0,1,\ldots} I^{0-v_t} W(\omega - \omega_{em} + v_t \omega_{vib}) \qquad (S4)$$

where $\omega_{em} = E(0) / \hbar$ is the energy of the lowest energy (k=0) exciton in the v=0 band (see Fig. 2 and Eq.1) and the *dimensionless* 0-v_t emission line strength is defined as,

$$I^{0-v_t} = \mu_0^{-2} \sum_{\{v_n\}}{}' |< \psi^{(em)} \,|\, \hat{M} \prod_n | g_n ; v_n >|^2 \qquad (S5)$$

Here, $| \psi^{(em)} >$ is the wave function corresponding to the k=0 exciton and $\prod_n | g_n ; v_n >$ denotes a vibrationally (but not electronically) excited aggregate state with a total of $v_t \equiv \sum_n v_n$ quanta, a constraint indicated by the primes on the summations in (S5). The reduced PL spectrum in

Eq.(S4) omits the cubic frequency dependence and any dependence on the refractive index in order to focus entirely on the line strengths. The 0-0 line strength from Eq.(S5) is simply,

$$I^{0-0} = \mu_0^{-2} |<\psi^{(em)}| \hat{\boldsymbol{M}} | G >|^2 \tag{S6}$$

To obtain the thermally averaged PL spectrum in Eq. 3, Eq.(S5) is averaged over a Boltzmann distribution of emitting excitons,

$$S(\omega) = \sum_{v_t=0,1,...} < I^{0-v_t}(k) \, W(\omega - \omega_{em}(k) + v_t\omega_{vib}) >_T \tag{S7}$$

where we have emphasized the k-dependence of the line strengths and transition energies,

$$I^{0-v_t}(k) = \mu_0^{-2} \sum_{\{v_n\}}{}' |<\psi^{(em)}(k)| \hat{\boldsymbol{M}} \prod_n | g_n; v_n >|^2 \tag{S8}$$

and

$$\omega_{em}(k) = E(k)/\hbar \tag{S9}$$

In Eq.(S8) $|\psi^{(em)}(k)>$ is the kth exciton's wave function. The thermal average of an arbitrary function of k, is,

$$<F(k)>_T \equiv \frac{1}{Z(N,T)} \sum_k F(k) \mathrm{e}^{-[E(k)-E(0)]/k_bT} \tag{S10}$$

where we have restricted the summation to the first ($v=0$) band in Fig. 2, an excellent approximation at room temperature and lower. The partition function in Eq.(S8) is given by,

$$Z(N,T) \equiv \sum_k \mathrm{e}^{-[E(k)-E(0)]/k_bT} . \tag{S11}$$

When $k_bT << \hbar\omega_{vib}$, the reduced PL spectrum can be approximated by

$$S(\omega) \approx \sum_{v_t=0,1,...} < I^{0-v_t}(k) >_T W(\omega - \omega_{em} + v_t\omega_{vib}), \tag{S12}$$

where $\hbar\omega_{em} = E(0)$ is the energy of the $k=0$ exciton in the $v=0$ band (see Fig. 2).

III. Thermally-averaged Line PL strengths

One can understand the temperature dependence of the PL spectra in Fig. 4 from the thermally averaged line strengths,

$$<I_{PL}^{0-v_t}>_T \equiv \frac{1}{Z(N,T)} \sum_k I_{PL}^{0-v_t}(k) e^{-[E(k)-E(0)]/k_bT} \qquad v_t=0,1,2,.. \qquad (S13)$$

Note that by virtue of the $\Delta k=0$ optical selection rule, only the $k=0$ state can emit to the electronic ground state with no vibrational quanta – i.e. the $k=0$ exciton is the only state which can emit 0-0 photons (see Fig. 2). Inserting $I_{PL}^{0-0}(k) = NF\delta_{k,0}$, into Eq.(S13) leads to,

$$<I_{PL}^{0-0}>_T \equiv \frac{NF}{Z(N,T)} \qquad (S14)$$

Increasing temperature leads to an increase in the partition function and therefore a drop in 0-0 emission as observed in Fig.4a. Interestingly, unlike 0-0 emission, 0-1 emission can originate from any exciton, independent of its wave vector. This is because the terminal state can contain a phonon of wave vector q=k needed to maintain the optical selection rule. (The phonons referred to here are based on the intramolecular vibration and are taken to be dispersionless or Einstein phonons). We therefore have, $I_{PL}^{0-1}(k) \approx I_{PL}^{0-1}(k=0) = F\lambda^2$. When inserted into Eq.(S13) we obtain,

$$<I_{PL}^{0-1}>_T \approx \lambda^2 F \qquad (S15)$$

The side band intensity is practically temperature independent as observed in Fig. 4a.

References

(1)   Holstein, T. Polaron motion. I. Molecular-crystal model. *Ann. Phys.* **1959**, *8*, 325-342.
(2)   Scherer, P. O. J.; Fischer, S. F. On the theory of vibronic structure of linear aggregates. Application to pseudoisocyanin (PIC). *Chem. Phys.* **1984**, *86*, 269-283.