Supporting Information for

Exciton-Exciton Annihilation Is Coherently

Suppressed in H-Aggregates,

but Not in J-Aggregates

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Nonperturbative calculations

In the main manuscript, the resonant coupling between the $S_1 - S_n$ and $S_0 - S_1$ transitions ($V_{m_1,m_2}$) is treated perturbatively, assuming this coupling to be small compared to the phonon-assisted relaxation rate of $S_n$. In this section, we substantiate the findings presented in the manuscript for cases where this condition is not satisfied, by showing that the admixture of $S_n$ states of the lowest-energy two-exciton eigenstates is suppressed for H-aggregates, but not in J-aggregates, when these states are explicitly included in the Hamiltonian diagonalization. Accordingly, the Hamiltonian is given by

$$ H = \sum_m \epsilon_1(m) b_1^\dagger(m) b_1(m) + \sum_{m_1,m_2} J_{m_1,m_2} b_{1(m_1)}^\dagger b_1(m_2) $$

$$ + \sum_m \epsilon_n(m) b_n^\dagger(m) b_n(m) + \left( \sum_{m_1,m_2} V_{m_1,m_2} b_{n(m_1)}^\dagger b_1(m_1) b_1(m_2) + \text{H.c.} \right), $$

where $\epsilon_1(m)$ and $\epsilon_n(m)$ represent the $S_0 - S_1$ and $S_0 - S_n$ transition energies at site $m$, respectively. As in the main manuscript, we consider cyclic aggregates, and take $V_{m_1,m_2}$ to be equal to $J_{m_1,m_2}$ and of point-dipolar form assuming parallel dipoles, and with a nearest-neighbor strength of 1000 cm$^{-1}$. For simplicity, we consider the disorder-free case, and we locate the $S_0 - S_n$ transition energy above twice the $S_0 - S_1$ transition energy. The latter allows to conveniently assess the $S_n$ admixture of the lowest-energy two-exciton eigenstates, which we define as

$$ A_{J/H} = \sum_m |\langle S_n(m) | \Psi_{J/H} \rangle|^2, $$

where $\Psi_{J/H}$ denotes the band-bottom eigenstate for the J/H-aggregate case. We apply a small splitting between the two-exciton and $S_n$ energies in order to assure being outside the perturbative regime, $\epsilon_n(m) = 2\epsilon_1(m) + 100$ cm$^{-1}$, while noting that the results obtained here are found to be retained for larger splittings.

Shown in Fig. S1 is the ratio of the $S_n$ admixtures of H- and J-aggregates, $A_H/A_J$. 

S2
Figure S1: Ratio of the $S_n$ admixtures in the band-bottom eigenstates of H- and J-aggregates as a function of the number of molecules constituting the aggregate. This figure clearly reflects the trend resulting from the perturbative treatment of $V_{m_1,m_2}$ in the main manuscript, namely that the admixture of $S_n$ is strongly suppressed in H-aggregates when compared to J-aggregates. Note that, similarly to the low-temperature annihilation ratio shown in Fig. 4 in the absence of disorder, the admixture ratio diverges with increasing aggregate length. These observations offer an interesting prospect for future research focusing on exciton-exciton annihilation in this nonperturbative regime.

**Analytical derivation**

This section contains an analytical derivation of the zero-temperature exciton-exciton annihilation rates for disorder-free, periodic J- and H-aggregates with nearest-neighbor couplings between the $S_0 - S_1$ transitions and point-dipolar couplings between parallel $S_0 - S_1$ and $S_1 - S_n$ transitions, taken in the long-aggregate limit. It demonstrates that under these conditions, $\Gamma^J \approx 4\Gamma^H$.

Adopting a center-of-mass representation, the two-exciton eigenstates of the Hamiltonian (Eq. 4 of the main text) are expanded as

$$|\Psi_{K,q}\rangle = \sum_{m_1 > m_2} c_{m_1,m_2}^K |m_1,m_2\rangle.$$  \hspace{1cm} (S4)
Disregarding disorder (setting $\epsilon_m = 0$ for all $m$), and assuming periodic boundary conditions and nearest-neighbor couplings between the $S_0 - S_1$ transitions ($J_{m_1,m_2} = J_{\text{NN}} \delta_{m_1,m_2 \pm 1}$), the wavefunction coefficients are given by

$$c_{m_1,m_2}^{K,q} = \frac{2}{M} e^{iK \pi (m_1 + m_2)/M} \sin \left( q \pi \frac{m_1 - m_2}{M} \right), \quad (S5)$$

with the corresponding eigenenergies

$$\omega_{K,q} = 4J_{\text{NN}} \cos \left( \frac{K \pi}{M} \right) \cos \left( \frac{q \pi}{M} \right), \quad (S6)$$

where $M$ denotes the number of molecules, and under the constraint that $K = 0, 2, \ldots, 2M - 2$ and $q = 1, 3, \ldots, M - 2$. At $T = 0$ K, the annihilation rate is given by

$$\Gamma = \frac{2\pi}{\hbar} \rho(E_f) \sum_{m_1=1}^{M} |\langle S_n(m) | H_a | \Psi_{K_0,q_0} \rangle|^2, \quad (S7)$$

where $\Psi_{K_0,q_0}$ represents the band-bottom eigenstate. Setting $\rho(E_f) = 1/\gamma$, and with substitution of Eq. 3 (of the main text) and Eq. S5, this expression can be recast as

$$\Gamma = \frac{2\pi}{\hbar} \rho(E_f) \sum_{m_1=1}^{M} \left| \sum_{m_2=1}^{M-1} V_{m_1,m_2} c_{m_1,m_2}^{K_0,q_0} + \sum_{m_2=m_1+1}^{M} V_{m_1,m_2} c_{m_1,m_2}^{K_0,q_0} \right|^2$$

$$= \frac{2\pi}{\hbar\gamma} \sum_{m_1=1}^{M} \left| \sum_{m_2=1}^{M} V_{m_1,m_2} d_{m_1,m_2}^{K_0,q_0} \right|^2, \quad (S8)$$

with $d_{m_1,m_2}^{K_0,q_0} \equiv \Theta(m_1 - m_2)c_{m_1,m_2}^{K_0,q_0} + \Theta(m_2 - m_1)c_{m_2,m_1}^{K_0,q_0}$ representing the symmetrized wavefunction coefficients (see main text), and $V_{m_1,m_2} \equiv V_{\text{NN}}/|m_1 - m_2|^3$ taken in the point-dipole approximation. Making use of the translational symmetry of the linear, periodic, and disorder-free aggregate, we can further reformulate the result as

$$\Gamma = \frac{2\pi V_{\text{NN}}^2}{\hbar\gamma} \sum_{m_1=1}^{M} \left| \sum_{r=-M/2+1}^{M/2} d_{m_1,m+r}^{K_0,q_0} \right|^2, \quad (S9)$$
while imposing \( r \neq 0 \), and taking \( M \) to be an even number. For J-aggregates, the band-bottom eigenstate corresponds to \( K_0 = 0 \) and \( q_0 = 1 \), so that

\[
J_{m_1, m_2}^{J_0, 1} = \frac{2}{M} \sin \left( \frac{m_1 - m_2}{M} \right),
\]

(S10)

and

\[
d_{m_1, m_2}^{J_0} = \frac{2}{M} \sin \left( \frac{|m_1 - m_2|}{M} \right).
\]

(S11)

Consequently,

\[
\Gamma_J = \frac{8 \pi V_{\text{NN}}^2}{\hbar \gamma M} \sum_{r=-M/2+1}^{M/2} \sin \left( \frac{\pi |r|}{M} \right) \left| \frac{r}{3} \right|^3.
\]

(S12)

The summation over \( r \) can then be rewritten as

\[
\sum_{r=-M/2+1}^{M/2} \sin \left( \frac{\pi |r|}{M} \right) \frac{\sin(\pi r/M)}{|r|^3} = 2 \sum_{r=1}^{M/2} \frac{\sin(\pi r/M)}{r^3} - \left( \frac{2}{M} \right)^3.
\]

(S13)

Upon taking the large-aggregate limit, \( M \to \infty \), the second term vanishes. Further assuming \( M \) to be the square of some integer value, we obtain for the first term

\[
2 \sum_{r=1}^{M/2} \frac{\sin(\pi r/M)}{r^3} = 2 \sum_{r=1}^{\sqrt{M}} \frac{\pi r/M + \mathcal{O}(r^3/M^3)}{r^3} + 2 \sum_{r=\sqrt{M}+1}^{M/2} \frac{\sin(\pi r/M)}{r^3}.
\]

(S14)

The second term satisfies

\[
\left| 2 \sum_{r=\sqrt{M}+1}^{M/2} \frac{\sin(r \pi/M)}{r^3} \right| < 2 \sum_{r=\sqrt{M}+1}^{M/2} \frac{1}{r^3} < \frac{M - 2\sqrt{M} - 2}{(\sqrt{M} + 1)^3} < \frac{1}{\sqrt{M}},
\]

(S15)
which also vanishes with $M \to \infty$. This leaves

$$
2 \sum_{r=1}^{M/2} \frac{\sin(r\pi/M)}{r^3} \approx \frac{2\pi}{M} \sum_{r=1}^{\sqrt{M}} \frac{1}{r^2} \approx \frac{\pi^3}{3M},
$$

yielding for the annihilation rate

$$
\Gamma^J \approx \frac{8\pi^7 V_{NN}^2}{9\hbar\gamma M^3}.
$$

Note that we find the same $\Gamma \propto 1/M^3$ scaling as was found in Ref. 2 for two-exciton states within a coherent domain. For H-aggregates, the band-bottom eigenstate corresponds to $K_0 = M$ and $q_0 = 1$, yielding

$$
c_H^{m_1, m_2} \equiv c_{m_1, m_2}^M = \frac{2}{M} (-1)^{(m_1 + m_2)} \sin \left( \frac{m_1 - m_2}{M} \pi \right)
= (-1)^{(m_1 + m_2)} c_J^{m_1, m_2},
$$

and also

$$
d_H^{m_1, m_2} = (-1)^{(m_1 + m_2)} d_J^{m_1, m_2}.
$$

As a consequence,

$$
\Gamma^J = \frac{8\pi V_{NN}^2}{\hbar\gamma M} \left| \sum_{r=-M/2+1}^{M/2} (-1)^r \frac{\sin(\pi |r|/M)}{|r|^3} \right|^2.
$$

Analogously to the J-aggregate case, the summation can be approximated as

$$
\sum_{r=-M/2+1}^{M/2} (-1)^r \frac{\sin(\pi |r|/M)}{|r|^3} \approx \frac{2\pi}{M} \sum_{r=1}^{\sqrt{M}} \frac{(-1)^r}{r^2} \approx \frac{\pi^3}{6M}.
$$
so that the annihilation rate is given by

$$\Gamma^H \approx \frac{2\pi^7 V_{\text{NN}}^2}{9\hbar^2 \gamma M^3}. \quad (S22)$$

Comparing Eqs. S17 and S22, it follows that $\Gamma^J \approx 4\Gamma^H$.

References

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(2) Malyshev, V.; Glaeske, H.; Feller, K.-H. Exciton–exciton annihilation in linear molecular aggregates at low temperature. *Chem. Phys. Lett.* **1999**, *305*, 117 – 122.