Supporting Information for Publication

Energy Fluctuations Induced Quantum Decoherence and Exciton Localization in Singlet Fission

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I. Fission dynamics

Here we show the simulation results for tetracene dimer modeled by a simplified Hamiltonian (see the text).

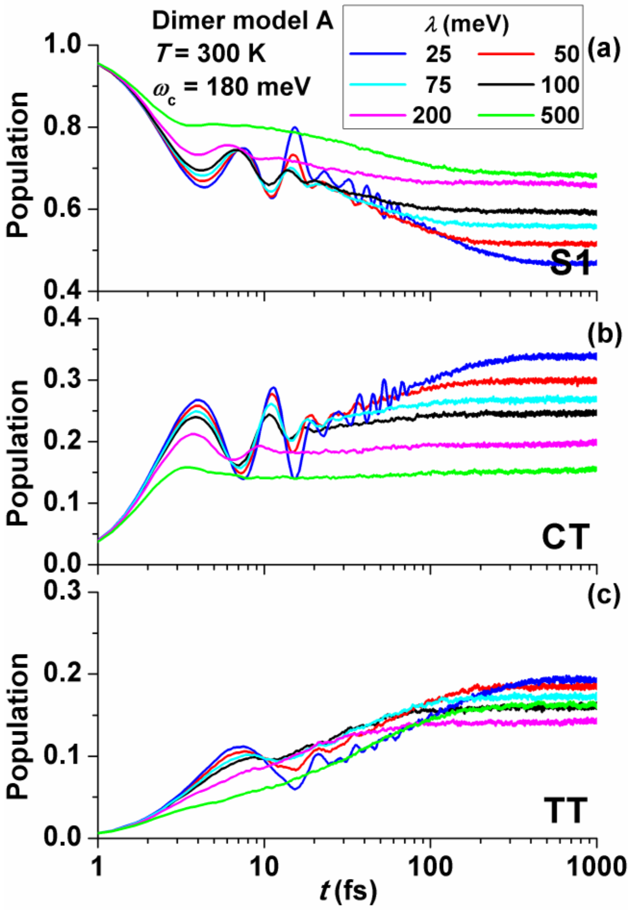

Figure S1. Time dependent state population of the dimer system with various electron-phonon coupling strength. Results are shown for the model A for different types of exciton states: (a) S1; (b) CT; and (c) TT. Each of which is the sum of all individual states in the same type. $T = 300$ K.

Figure S1 displays the time-dependent state population of three types of exciton states for the dimer model A for various values of reorganization energy λ. As the coupling strength increases, the short time coherence diminishes, and the coherence of the S1 and CT states are more pronounced than that of the TT states, the latter of which are almost suppressed at $\lambda = 200$ meV. The long time S1 population increases as the coupling strength increases, and the reverse trend is seen for the CT population. The long time TT population in a little more complicated, firstly decreases and then increases again.

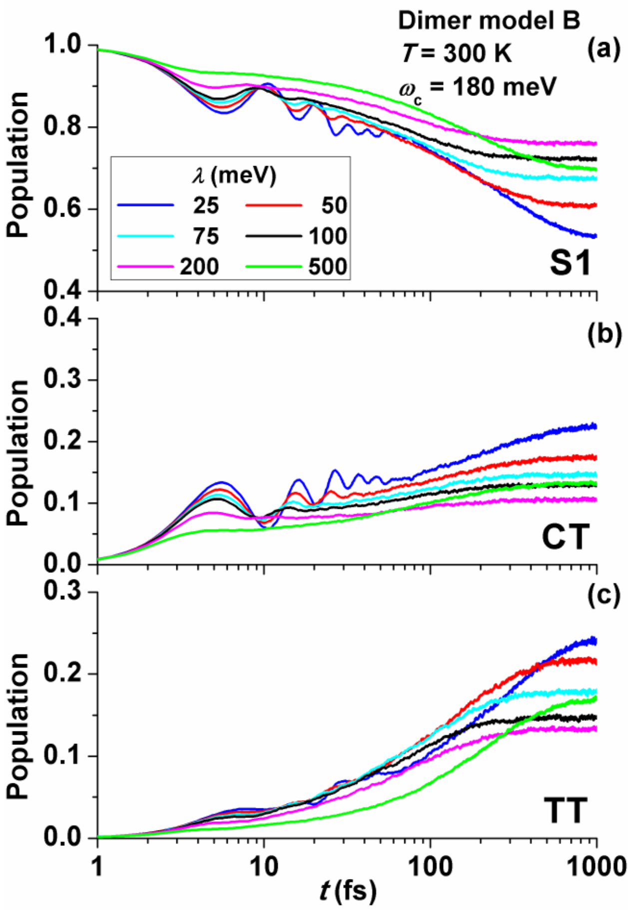

Figure S2. The same as Figure S1 except for the model B.

Figure S2 shows the time-dependent state population of three exciton states for the dimer model B. The dependence on the value of reorganization energy of the exciton population is examined. The results are similar with those for model A in the text. And few different observations are noted. (1) the short time coherence of the state population for model B is less pronounced that that for model A, which implies that the transition from the coherent to the incoherent regime occurs at a smaller coupling strength; and (2) for the largest coupling case, i.e. $\lambda = 500$ meV, the long time S1 population decreases, and both the long time CT and TT population increase again as the coupling strength increases, which shows a reverse trend with respect to smaller coupling cases.

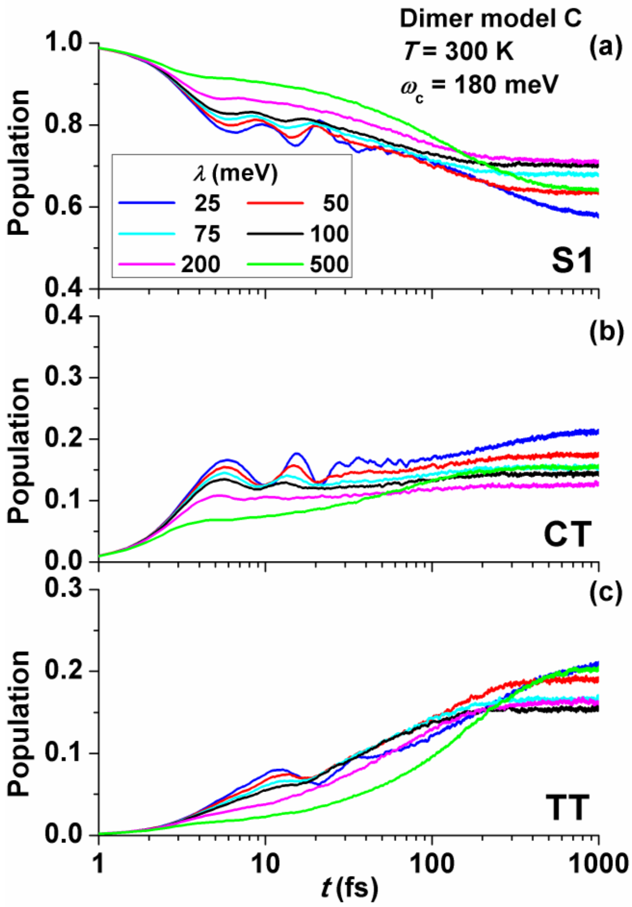

Figure S3. The same as Figure S1 but for the dimer model C.

The results for the dimer model C are shown in Figure S3. By introducing the S1-S1 coupling, the exciton transfer is promoted, and the short time coherence seems also to transfer from the S1 to the TT state, which may be due to the interference between different pathways. Also the effect of the coupling strength on the long time exciton population is less pronounced than that for the model B. The long time TT population shows a reverse trend around $\lambda = 200$ meV.

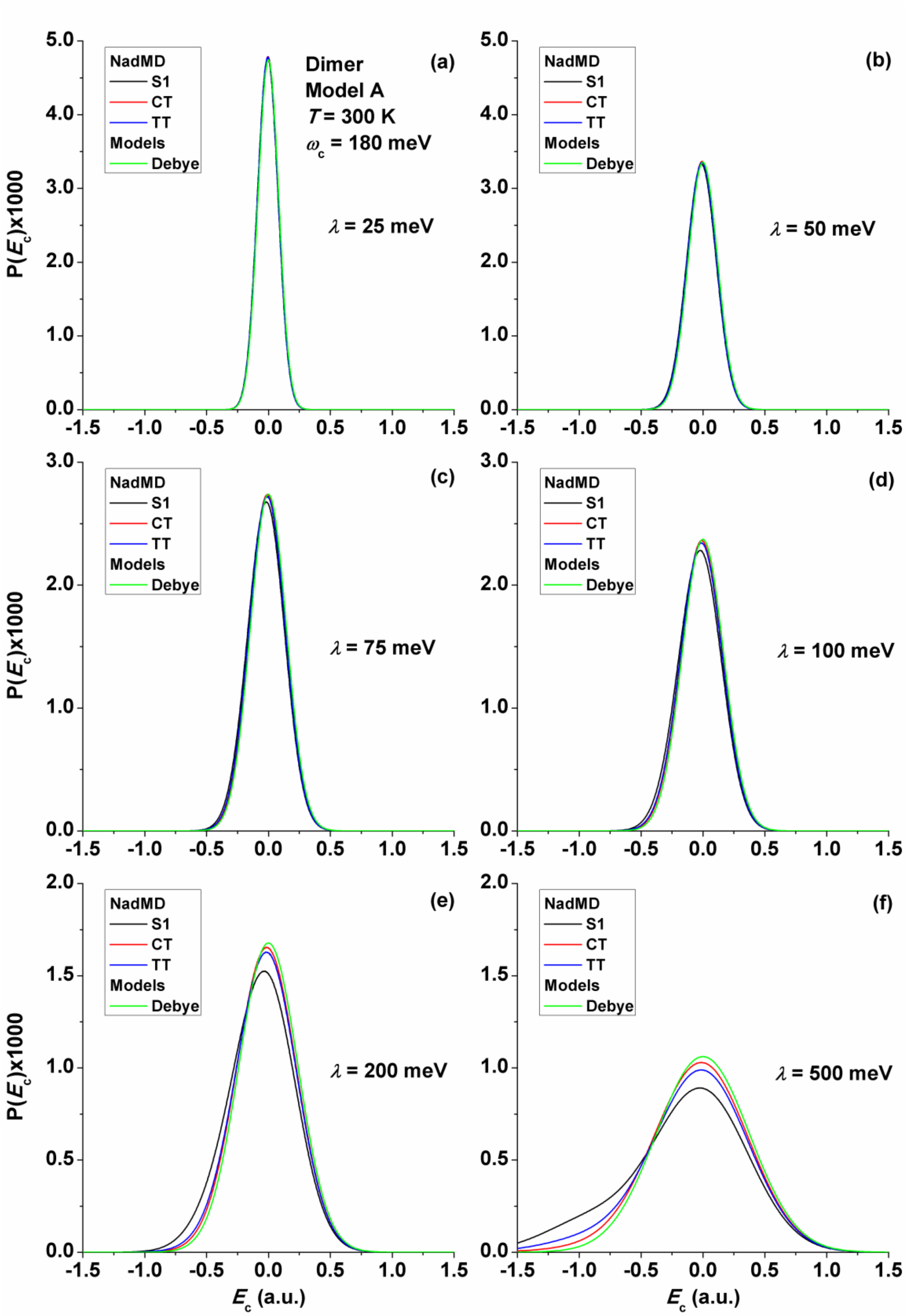

Figure S4. Probability distribution functions of the electron-phonon coupling energy for SF dimer model A with various values of coupling strength. Compared are the results obtained from nonadiabatic MD simulations (NadMD) along with those predicted by the Debye model (Eq. 7), for different λ values, i.e. (a) 25 ; (b) 50;(c) 75 ; (d) 100 ; (e) 200 ; and (f) 500 meV. T = 300 K.

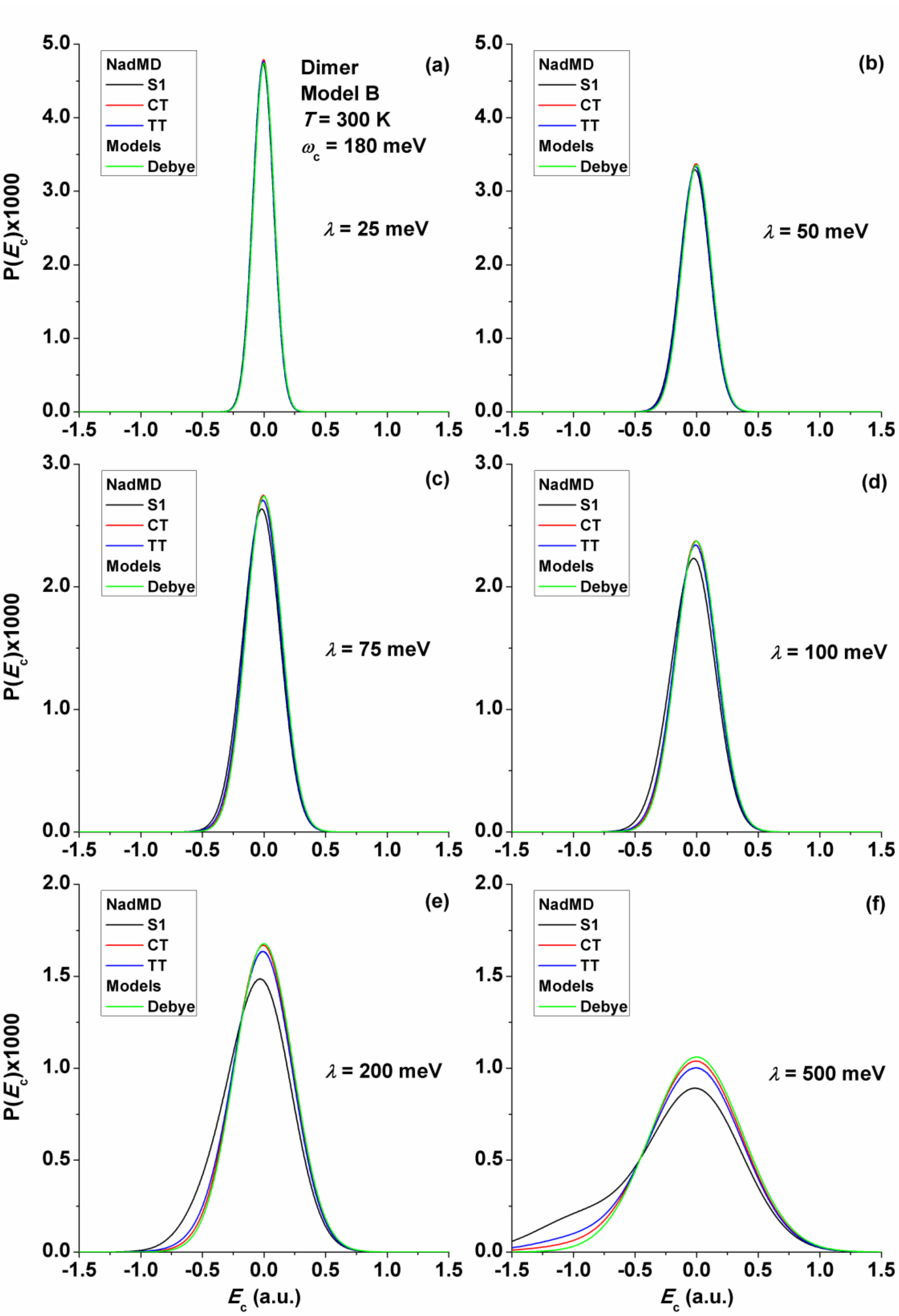

Figure S5. Probability distribution functions of the electron-phonon coupling energy for SF dimer model B with various values of coupling strength. Compared are the results obtained from nonadiabatic MD simulations (NadMD) along with those predicted by the Debye model (Eq. 7), for different λ values, i.e. (a) 25 ; (b) 50;(c) 75 ; (d) 100 ; (e) 200 ; and (f) 500 meV. T = 300 K.

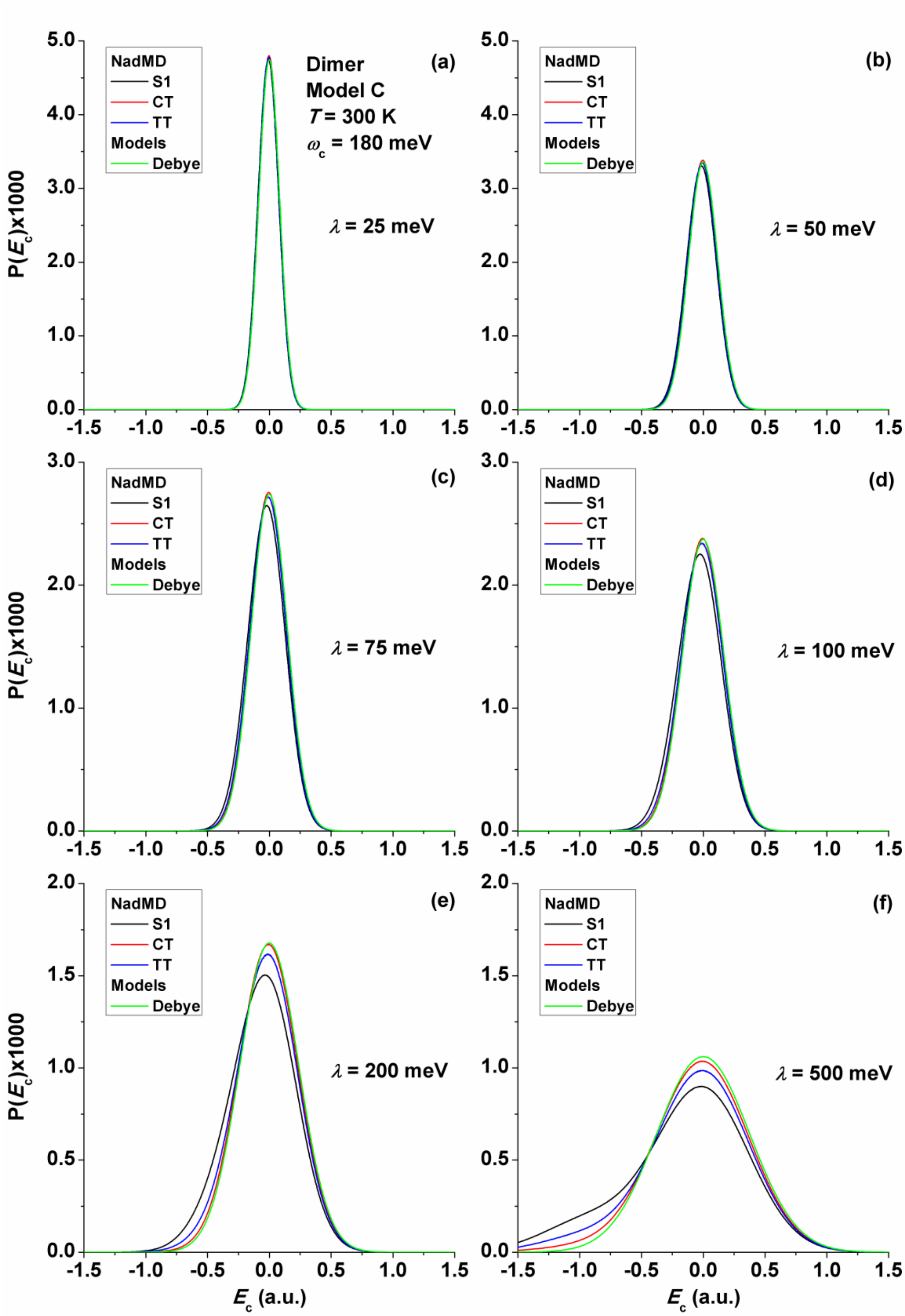

Figure S6. The same as Figure S4 but for the dimer model C.

Figure S4 compares the simulated probability distribution function of the electron-phonon coupling energy $\mathrm{P}(E_c)$ for all exciton states in the dimer model A with the predictions from the characteristic harmonic oscillator model (Eq. 7), for various values of reorganization energy ranging from 25 to 500 meV. The appreciable deviation from the Gaussian distribution seems to start from around 100 meV.

Figure S5 shows the probability distribution function $\mathrm{P}(E_c)$ for the three exciton states in the dimer model B. The deviation of the distribution function from the Gaussian distribution appears at smaller coupling strength (between 50-100 meV) than that for model A because here the interstate coupling is smaller, and the system is more liable for exciton localization. Similar results are obtained for the model C (Figure S6), except for the displacement is a little more pronounced.

II. Fitting process for the QT model

According to our simple QT model, there are three parameters in Eq 11a to be fitted, namely the effective interstate coupling W, the coherent displacement factor c, and the incoherent portion of the localized state A. To simplify Eq 11a, we apply the linear approximation to the E_c on the RHS of Eq 11a, i.e.

$$E_c = -2c\lambda, \quad \text{(S1)}$$

then Eq 11a becomes now

$$E_c(max) = -\frac{2c\lambda e^{-L^2} e^{\frac{4c^2\lambda^2}{\sigma_E^2}} + 2A\lambda\left(1-e^{-L^2}\right) e^{-\frac{4\lambda^2(1-2c)}{\sigma_E^2}}}{e^{-L^2} e^{\frac{4c^2\lambda^2}{\sigma_E^2}} + \left(1-e^{-L^2}\right)\left[1-A\left(1-e^{-\frac{4\lambda^2(1-2c)}{\sigma_E^2}}\right)\right]}. \quad \text{(S2)}$$

And again the two limiting cases are

(1) $E_c(max) = -2c\lambda$, when $\mathrm{L} \to 0$; (S3a)

(2) $$E_c(max) = -\frac{2A\lambda e^{-\frac{4\lambda^2(1-2c)}{\sigma_E^2}}}{1-A\left(1-e^{-\frac{4\lambda^2(1-2c)}{\sigma_E^2}}\right)}$$, when $L \to \infty$. (S3b)

Eq S3b indicates that $E_c(max)$ could reach two local attractors, i.e. $E_c(max) = 0$ for $c < 0.5$ and $A < 1$ or $E_c(max) = -2\lambda$ for c > 0.5 or A = 1. Also when c = 0.5, we have $E_c(max) = -\lambda$, and A = 0.5.

Then the least square fitting is used to obtain the best estimate of parameters. Eq S1 should work well for small L, and the reulsting small values of c (see Table I) indicate that it is also good in the whole range which the data sets span, although we note that the accuracy of Eq. S1 may degrade for large coupling strength. Therefore the fitted parameters should be taken at best to be semiqualitative accurate. However the overall trend of the function of $E_c(max)$ is well predicted, and the coherent to incoherent transition could be quantified by the QT model we proposed. And the refinement of the model would definitely be an interesting topic for future studies.