Supporting Information

An electron-phonon interaction model for SF in prototypical molecular crystals

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S1  Truncation test of gradient calculation

With data in our recent work about the nonlocal electron-phonon couplings for charge transport in tetracene and rubrene crystal systems, we tested the truncation of gradient calculation to check if we can reduce scanning calculation cost. Here, we compared the final spectral density results between the benchmark results in reference and truncated results by fixing some components of gradient as 0. And the indexes of dimer are displayed in Figure 1 of manuscript.

Considering the chemistry structure and the composition of HOMO and LUMO of tetracene and rubrene, the carbons of conjugated skeleton predominate the gradients for HOMO/HOMO couplings and LUMO/LUMO couplings. Therefore, we test the truncation by setting i) $\nabla_i V = 0$ for all hydrogens in both systems and calculated the spectral density for hole transport (i.e. HOMO/HOMO coupling) and ii) $\nabla_i V = 0$ for all phenyl groups in rubrene systems and computed the spectral densities for hole and electron transport (LUMO/LUMO coupling).

S1.1  Set $\nabla_i V = 0$ for all hydrogens in both systems

First, we fixed all components of hydrogens and calculated the el-ph coupling with respect to the HOMO/HOMO coupling for both systems. The results (a), (c) and (e) in Figure S1 give relatively good results with this truncation approximation while results of (b) and (d) show obvious difference in low and middle region due to the large contribution of hydrogen atoms for phonon modes in this range and the small el-ph coupling for dimer AC of tetracene and dimer AC of rubrene.

Since there are several coupling terms of singlet fission are too small (e.g. couplings between TT state and LE/CT states), we would not apply this approximation in our work.
Figure S1: Spectral density of hole transport for tetracene (a-c): (a) dimer AB, (b) dimer AC, (c) dimer BC and rubrene (d-e): (d) dimer AC and (e) dimer AB. Label ‘standard’ for benchmark results and ‘reduced’ for approximation by fixing $\nabla_i V = 0$ for all hydrogen.
S1.2 Set $\nabla_i V = 0$ for all phenyl groups in rubrene system

The side chains in rubrene, i.e. phenyl groups have very low distribution on the HOMO and LUMO orbitals of rubrene according to the CASSCF calculation of rubrene monomer. Therefore, we set $\nabla_i V = 0$ for all phenyl groups in rubrene system and we calculated gradient of both hole (HOMO/HOMO coupling) and electron (LUMO/LUMO coupling) transport.

The results in Figure S2 shows the validation of this truncation for both HOMO/HOMO coupling and LUMO/LUMO coupling. And we used this approximation in this case.

Figure S2: Spectral density of (a) hole transport and (b) electron transport for rubrene dimer AB. Label ‘standard’ for benchmark results and ‘reduced’ for approximation by fixing $\nabla_i V = 0$ for all phenyl group.
S2  Electronic Hamiltonian elements

In this section, we list the results of electron Hamiltonian calculation for other two dimers of tetracene in Table S3. And the results provide consistent feature with the Hamiltonian matrix of tetracene dimer AB, i.e. SF would occur via superexchange pathway for all dimers of tetracene. And the indirect couplings between LE states and TT state of antisymmetric dimers (dimer AB and BC) are larger than couplings of symmetric dimer (dimer AC) which is in agreement with the calculation results of HOMO/HOMO coupling.

Table S1: Electronic Hamiltonian elements of tetracene dimer AC (unit: eV)

<table>
<thead>
<tr>
<th></th>
<th>$A^*B$</th>
<th>$AB^*$</th>
<th>$A^+B^-$</th>
<th>$A^-B^+$</th>
<th>$A^TB^T$</th>
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</thead>
<tbody>
<tr>
<td>$A^*B$</td>
<td>4.112</td>
<td>0.105</td>
<td>4.112</td>
<td>5.091</td>
<td>4.076</td>
</tr>
<tr>
<td>$AB^*$</td>
<td>-0.009</td>
<td>-0.014</td>
<td>5.091</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>$A^+B^-$</td>
<td>0.014</td>
<td>0.009</td>
<td>0.000</td>
<td>5.091</td>
<td></td>
</tr>
<tr>
<td>$A^-B^+$</td>
<td>0.000</td>
<td>0.000</td>
<td>0.004</td>
<td>0.004</td>
<td>4.076</td>
</tr>
</tbody>
</table>

Table S2: Electronic Hamiltonian elements of tetracene dimer BC (unit: eV)

<table>
<thead>
<tr>
<th></th>
<th>$A^*B$</th>
<th>$AB^*$</th>
<th>$A^+B^-$</th>
<th>$A^-B^+$</th>
<th>$A^TB^T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A^*B$</td>
<td>4.133</td>
<td>0.019</td>
<td>4.140</td>
<td>4.636</td>
<td></td>
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<tr>
<td>$AB^*$</td>
<td>-0.115</td>
<td>-0.028</td>
<td>4.636</td>
<td>0.000</td>
<td>5.049</td>
</tr>
<tr>
<td>$A^+B^-$</td>
<td>0.029</td>
<td>0.119</td>
<td>0.000</td>
<td>5.049</td>
<td></td>
</tr>
<tr>
<td>$A^-B^+$</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.052</td>
<td>-0.083</td>
<td>4.128</td>
</tr>
</tbody>
</table>
S3 Ex-ph couplings

S3.1 Gradient of electronic Hamiltonian

According to the Equation 6 and 7 of manuscript, the phonon mode whose overlap with gradient are large would have a large ex-ph coupling. Additionally, the norm of the gradient could evaluate the influence of ex-ph coupling (e.g. fluctuation of electronic Hamiltonian elements). Therefore, we present the results of gradients in this subsection.

S3.1.1 The gradient of energy parts

The results of $\nabla \varepsilon$ are shown in Figure S3, S4, S5 and S6 for rubrene dimer AB, tetracene dimer AB, tetracene dimer AC and tetracene dimer BC respectively. The gradient of LE state shows local characteristic while components of gradient of CT states and TT state are delocal among all carbons of conjugated skeleton, but all the arrows of these gradients are in the conjugation plane which are making sense by considering the $\pi$ type bond of HOMO/LUMO, and the vibration-like gradients imply the minor distribution of low frequency acoustic modes to local ex-ph couplings. In addition, the longer arrows of TT states indicate larger ex-ph coupling of TT state energy for all dimers.

S3.1.2 The gradient of coupling parts

The results of $\nabla V$ are displayed in Figure S7, S8, S9 and S10 for rubrene dimer AB, tetracene dimer AB, tetracene dimer AC and tetracene dimer BC respectively. And all of the results suggest delocal feature for nonlocal ex-ph couplings. Besides, there are several arrows of gradients for ex-ph couplings point toward out of conjugated skeleton which are different from the gradients for local ex-ph coupling.
Figure S3: The gradient vectors $\nabla \varepsilon$ illustrated by red arrows of (a) LE1 state, (b) CT1 state and (c) TT state for rubrene dimer AB.

Figure S4: The gradient vectors $\nabla \varepsilon$ illustrated by red arrows of (a) LE1 state, (b) CT1 state and (c) TT state for tetracene dimer AB.
Figure S5: The gradient vectors $\nabla \varepsilon$ illustrated by red arrows of (a) LE1 state, (b) CT1 state and (c) TT state for tetracene dimer AC.

Figure S6: The gradient vectors $\nabla \varepsilon$ illustrated by red arrows of (a) LE1 state, (b) CT1 state and (c) TT state for tetracene dimer BC.
Figure S7: The gradient vectors $\nabla V$ illustrated by red arrows of (a) $A^*B-A^B^-$ coupling, (b) $A^*B-A^-B^+$ coupling and (c) $A^+B^-A^TB^T$ coupling for rubrene dimer $AB$.

Figure S8: The gradient vectors $\nabla V$ illustrated by red arrows of (a) $A^*B-A^B^-$ coupling, (b) $A^*B-A^-B^+$ coupling and (c) $A^+B^-A^TB^T$ coupling for tetracene dimer $AB$. 
Figure S9: The gradient vectors $\nabla V$ illustrated by red arrows of (a) $A^*B-A^+B^-$ coupling, (b) $A^*B-A^-B^+$ coupling and (c) $A^+B^-A^TB^T$ coupling for tetracene dimer AC.

Figure S10: The gradient vectors $\nabla V$ illustrated by red arrows of (a) $A^*B-A^+B^-$ coupling, (b) $A^*B-A^-B^+$ coupling and (c) $A^+B^-A^TB^T$ coupling for tetracene dimer BC.
S3.2 Spectral density

The local and nonlocal spectral densities of tetracene dimer AC and dimer BC systems are illustrated in Figure S11 and S12 respectively. The local parts show almost the same results as well as the tetracene dimer AB system because of the local feature. While nonlocal parts present the major contribution of low frequency modes and the detailed difference among spectral densities of three dimers due to the different intermolecular packing.

Figure S11: Spectral densities of local ex-ph couplings for tetracene dimer AC (a-c) with subfigures (a) LE1 (A°B) state, (b) CT1 (A+B) state and (c) TT (ATBT) state, and tetracene dimer BC (d-f) with subfigures of (d) LE1 (A°B) state, (e) CT1 (A+B) state and (f) TT (ATBT) state.
Figure S12: Spectral densities of nonlocal ex-ph couplings for tetracene dimer AC (a-d) and dimer BC (e-h). (a, e). LE1-CT1 ($A^*B-A^+B^-$) coupling term, (b, f). LE1-CT2 ($A^*B-A^-B^+$) coupling term, (c, g). LE1-TT ($A^*B-A^T B^T$) coupling term and (e, h) CT1-TT ($A^+B^-A^T B^T$) coupling term.
S3.3 Important vibration modes

Given the definition of a set of molecular modes \( \{ \mathbf{l}_K^X \} \) localized on molecule \( X \) (A or B) where \( K \) is the index of the molecular mode, it is convenient to decompose the total spectral density into local components via projection methods,

\[
J_{i/ij}(\omega) = \sum_K J^K_{i/ij}(\omega),
\]

where,

\[
J^K_{i/ij}(\omega) = \frac{1}{2\hbar} \sum_I [(\mathbf{Q}_I \cdot \mathbf{l}_K^A)^2 + (\mathbf{Q}_I \cdot \mathbf{l}_K^B)^2] g^{I}_{i/ij} \delta(\omega - \omega_I).
\]

Here, the modes from \( K = 7 \) to \( K = 3N_a \) where \( N_a \) is the number of atoms in a molecule, correspond to the vibrational modes of the molecule in gas phase and were calculated by DFBT+ in this case. while the modes for \( K = 1, 2, 3 \) are the translation modes of the rigid molecule and \( K = 4, 5, 6 \) are the rotation modes of the rigid molecule.

As a consequence, we can find all the important vibration modes which donate large distribution to spectral density and ex-ph couplings. And we displayed some of them below in Figure S13 and S14 for tetracene and rubrene system respectively.
Figure S13: Some important vibration modes which have large ex-ph couplings for SF in tetracene crystal with the frequency values calculated by DFTB+. Mode (b) contributes the largest peaks for spectral densities of all local ex-ph coupling for all tetracene dimers while others have large nonlocal ex-ph couplings for dimer AB ((a), (e) and (f)), dimer AC ((a) and (c-f)) and dimer BC ((a) and (e)).
Figure S14: Some important vibration modes which have large ex-ph couplings for SF in rubrene crystal with the frequency values calculated by DFTB+. Modes (b-h) have large local ex-ph couplings while modes (a), (b), (e) and (g) predominate the high frequency region of spectral densities of nonlocal ex-ph couplings.
S3.4 Fluctuation of electronic Hamiltonian elements

The fluctuations of electronic Hamiltonian elements for tetracene dimer AC and dimer BC are listed in Table S3 and S2 individually by applying Equation 9 in the manuscript. The results are very similar to the results of tetracene dimer AB in Table 3 of the manuscript.

Table S3: Fluctuation $\sigma$ of electronic Hamiltonian elements of tetracene dimer AC at 300 K (unit: meV)

<table>
<thead>
<tr>
<th></th>
<th>$A^*B$</th>
<th>$AB^*$</th>
<th>$A^+B^-$</th>
<th>$A^-B^+$</th>
<th>$A^TB^T$</th>
</tr>
</thead>
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<tr>
<td>$A^*B$</td>
<td>235.0</td>
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<td></td>
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<tr>
<td>$AB^*$</td>
<td>20.2</td>
<td>235.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A^+B^-$</td>
<td>27.2</td>
<td>23.3</td>
<td>221.5</td>
<td></td>
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<tr>
<td>$A^-B^+$</td>
<td>23.3</td>
<td>27.2</td>
<td>0.009</td>
<td>222.0</td>
<td></td>
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<tr>
<td>$A^TB^T$</td>
<td>0.009</td>
<td>0.009</td>
<td>31.3</td>
<td>31.2</td>
<td>439.5</td>
</tr>
</tbody>
</table>

Table S4: Fluctuation $\sigma$ of electronic Hamiltonian elements of tetracene dimer BC at 300 K (unit: meV)

<table>
<thead>
<tr>
<th></th>
<th>$A^*B$</th>
<th>$AB^*$</th>
<th>$A^+B^-$</th>
<th>$A^-B^+$</th>
<th>$A^TB^T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A^*B$</td>
<td>234.8</td>
<td></td>
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<td></td>
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<tr>
<td>$AB^*$</td>
<td>26.8</td>
<td>251.8</td>
<td></td>
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<tr>
<td>$A^+B^-$</td>
<td>38.9</td>
<td>39.9</td>
<td>250.9</td>
<td></td>
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<tr>
<td>$A^-B^+$</td>
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<td>0.029</td>
<td>245.8</td>
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<td>$A^TB^T$</td>
<td>0.026</td>
<td>0.069</td>
<td>43.1</td>
<td>45.3</td>
<td>447.8</td>
</tr>
</tbody>
</table>
S4 Dynamic simulations

Using the master equation combined with frozen-modes approach in manuscript, we simulated the dynamics of tetracene system, and Fig S15 shows the result of tetracene dimer AB with a local initial state (exciton at A, i.e. LE1 state) at 300 K. The population of TT state gives a near exponential evolution (∼500 fs) due to the non-vanish electronic couplings between TT states and other states.

We also performed the master equation for rubrene dimer AB with different initial states at 300 K, which are local initial state ($\psi_0 = \frac{1}{\sqrt{2}}(\psi_{LE1} - \psi_{LE2})$), dark state ($\psi_0 = \psi_{LE1}$) and bright state ($\psi_0 = \frac{1}{\sqrt{2}}(\psi_{LE1} + \psi_{LE2})$). And the result is displayed in Fig S16, which suggests an enhancement effect of phase match.

Figure S15: The dynamics result of tetracene dimer AB with a local initial state within 3 ps at 300 K.
Figure S16: The dynamics results of TT population with different initial states within 3 ps at 300 K, where labels 'bright', 'dark' and 'local' present that initial state is bright, dark and local states respectively. And the insert subfigure shows the dynamics results in the first 500 fs.
References
