

Supporting Information on
“Intermolecular Packing Effects on Singlet Fission in Oligorylene
Dimers”

Takanori Nagami,[†] Soichi Ito,[†] Takashi Kubo,[§] and Masayoshi Nakano^{*, †, ¶}

[†] Department of Materials Engineering Science, Graduate School of Engineering Science,
Osaka University, Toyonaka, Osaka 560-8531, Japan

[§] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka,
Osaka 560-0043, Japan

[¶] Center for Spintronics Research Network (CSRN), Graduate School of Engineering Science,
Osaka University, Toyonaka, Osaka 560-8531, Japan

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1. Details of the effective electronic coupling for SF rate and the effective Hamiltonian

From Fermi's golden rule, the transition rate from the initial (i) to the final (f) electronic states due to the electronic Hamiltonian H_{el} is given by

$$w_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \langle f | H_{el} | i \rangle \right|^2 \rho(E_0). \quad (S1)$$

Here, $\langle f | H_{el} | i \rangle$ indicates the electronic coupling matrix elements between the initial and final states and $\rho(E_0)$ is the density of the final state when the energy of the final state is equal to that of the initial state. Considering SF in a dimer model, the initial and the final state correspond to singlet excited state (S_1S_0) and double-triplet excited state (T_1T_1), respectively. Thus, the SF rate is proportional to the square of the electronic coupling between the S_1S_0 and T_1T_1 states. By applying the second-order quasi-degenerate perturbation expansion to the indirect coupling term, the SF rate reads:¹⁻³

$$w_{SF} = \frac{2\pi}{\hbar} \left| \langle T_1T_1 | H_{el} | S_1S_0 \rangle + \frac{1}{2} \sum_{\substack{m=AC, CA \\ n=S_1S_0, T_1T_1}} \frac{\langle T_1T_1 | H_{el} | m \rangle \langle m | H_{el} | S_1S_0 \rangle}{E_n - E_m} \right|^2 \rho(E_0). \quad (S2)$$

Here, m indicates charge-transfer (CT) state, where one molecule is a cation and another is an anion (CA) or the reversed (AC). E_n and E_m represent the energies of S_1S_0 or T_1T_1 and CT states, respectively. By neglecting two-electron integrals in the CT-related elements in H_{el} , where two-electron integrals are known to be much smaller than one-electron integrals composed of the Fock matrix elements, the electronic Hamiltonian of SF using the diabatic basis set $\{|T_1T_1\rangle, |S_1S_0\rangle, |S_0S_1\rangle, |CA\rangle, |AC\rangle\}$ is expressed as

$$\begin{pmatrix} \langle T_1T_1 | \\ \langle S_1S_0 | \\ \langle S_0S_1 | \\ \langle CA | \\ \langle AC | \end{pmatrix} \begin{pmatrix} E_{T_1T_1} & & & & \\ V_{2e} & E_{S_1S_0} & & & \\ V_{2e} & J_{ex} & E_{S_0S_1} & & \\ \sqrt{3/2} \langle l_A | F | h_B \rangle & \langle l_A | F | l_B \rangle & -\langle h_A | F | h_B \rangle & E_{CA} & \\ \sqrt{3/2} \langle h_A | F | l_B \rangle & -\langle h_A | F | h_B \rangle & \langle l_A | F | l_B \rangle & 0 & E_{AC} \end{pmatrix}, \quad (S3)$$

where only the lower triangle part is shown because the matrix is symmetric, and where

F denotes the Fock operator, V_{2e} corresponds to the term $\langle T_1 T_1 | H_{el} | S_1 S_0 \rangle$ in eq S2, and J_{ex} is the exciton-exciton coupling $\langle S_1 S_0 | H_{el} | S_0 S_1 \rangle$ in the Frenkel exciton states. Here, we approximately consider the Fock matrix elements using only the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) between the chromophores. Also, the zero differential overlap approximation for the electron repulsion integrals between different chromophores in CT-related coupling matrix elements is adopted. The h_i and l_j denote the HOMO of molecule i and the LUMO of molecule j , respectively. Thus, eq S2 can be simplified as

$$w_{SF} = \frac{2\pi}{\hbar} |V_{eff}|^2 \rho(E_0), \quad (S4a)$$

where

$$V_{eff} = \sqrt{\frac{3}{2}} \frac{\langle l_A | F | h_B \rangle \langle l_A | F | l_B \rangle - \langle h_A | F | h_B \rangle \langle h_A | F | l_B \rangle}{\Delta E_{CT}}, \quad (S4b)$$

and

$$\frac{1}{\Delta E_{CT}} = \frac{1}{2} \left(\frac{1}{E_{S_1 S_0} - E_{CT}} + \frac{1}{E_{T_1 T_1} - E_{CT}} \right). \quad (S4c)$$

For example, when the HOMO of the molecule A ($|h_A\rangle$) is written in a linear combination of an atomic orbital (AO) basis set $\{|\mu\rangle\}$ with coefficients $\{C_\mu^{h_A}\}$ as

$$|h_A\rangle = \sum_\mu C_\mu^{h_A} |\mu\rangle, \text{ and likewise for the LUMO of the molecule B as } |l_B\rangle = \sum_\nu C_\nu^{l_B} |\nu\rangle, \text{ the}$$

element $\langle h_A | F | l_B \rangle$ is expressed by

$$\langle h_A | F | l_B \rangle = \sum_\mu \sum_\nu C_\mu^{h_A} C_\nu^{l_B} \langle \mu | F | \nu \rangle. \quad (S5)$$

The term $\langle \mu | F | \nu \rangle$ corresponds to a Fock matrix element of dimers represented in the AO basis set, and is obtained from density functional theory (DFT) calculation in the ground state of the dimer. The expansion coefficient such as $C_\mu^{h_A}$ is obtained from the calculation of monomer, terrylene or quaterylene in this study. Hereafter, we assume that the energy of CA and AC states, E_{CA} and E_{AC} , respectively, are the same and are labeled by E_{CT} as shown in eq S4c. The charge-transfer state energy E_{CT} is estimated from the equation,

$$E_{CT} = IP - EA + E_{int}, \quad (S6)$$

which states that E_{CT} is composed of the ionization potential (IP) and electron affinity (EA) of the monomer and Coulomb interaction between Müllicken atomic charges of a cation and an anion (E_{int}).

In addition to the SF rate, we investigate the effect of the electronic couplings on the non-perturbed energy levels of the initial (S_1S_0) and final (T_1T_1) states of SF process. As shown in eq S3, it is convenient to consider that the SF electronic Hamiltonian is composed of the set of five diabatic electronic states of dimer, S_1S_0 , S_0S_1 , CA, AC, and T_1T_1 . In order to reveal the effect of the electronic couplings on the energy levels of the initial and final states of SF process, we apply the quasi-degenerate perturbation theory.³ This theory partitions the system into the model space of interest and the complement space of non-interest. In this context, S_1S_0 , S_0S_1 , and T_1T_1 belong to the former, while CT states (CA, AC), the latter. Hence, the SF electronic Hamiltonian of 5x5 matrix in eq S3 is reduced to the effective Hamiltonian H_{eff} , which is the 3x3 matrix expressed as

$$H_{eff} = \begin{pmatrix} E_{T_1T_1} + \Delta E_{T_1T_1} & & \\ V_{eff} & E_{S_1S_0} + \Delta E_{S_1} & \\ -V_{eff} & J_{eff} & E_{S_0S_1} + \Delta E_{S_1} \end{pmatrix}. \quad (S7a)$$

Here, V_{eff} is defined in eq S4b, and other quantities in eq S7a are given by

$$\Delta E_{T_1T_1} = \frac{\frac{3}{2} \left(\langle l_A | F | h_B \rangle^2 + \langle h_A | F | l_B \rangle^2 \right)}{E_{T_1T_1} - E_{CT}}, \quad (S7b)$$

$$\Delta E_{S_1} = \frac{\langle h_A | F | h_B \rangle^2 + \langle l_A | F | l_B \rangle^2}{E_{S_1S_0} - E_{CT}}, \quad (S7c)$$

and

$$J_{eff} = J_{Coul} + J_{CT} = J_{Coul} - \frac{2 \langle h_A | F | h_B \rangle \langle l_A | F | l_B \rangle}{E_{S_1S_0} - E_{CT}}. \quad (S7d)$$

By replacing the electron densities in the evaluation of the Müllicken atomic charges

used for E_{int} with the transition density from the ground state to the lowest singlet excited state in terrylene or quaterrylene calculated using the time-dependent DFT (TDDFT) method, we obtain the Coulomb coupling J_{Coul} , which well reproduces the exciton-exciton coupling J_{ex} in [eq S3](#) since the exchange coupling is usually small and then can be ignored.

2. Fock matrix elements in quaterrylene

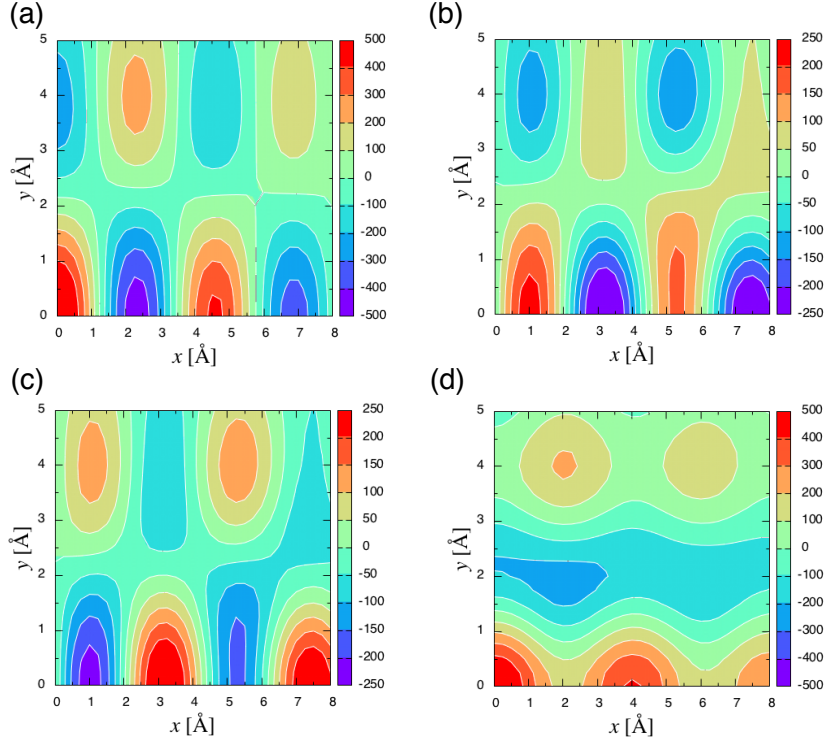


Figure S1. Calculated Fock matrix elements, $\langle h_A | F | h_B \rangle$ (a), $\langle h_A | F | l_B \rangle$ (b), $\langle l_A | F | h_B \rangle$ (c), and $\langle l_A | F | l_B \rangle$ (d), in quaterrylene dimer model defined in Figure 2. All values are given in meV.

3. Effective electronic coupling for the SF rate in quaterrylene

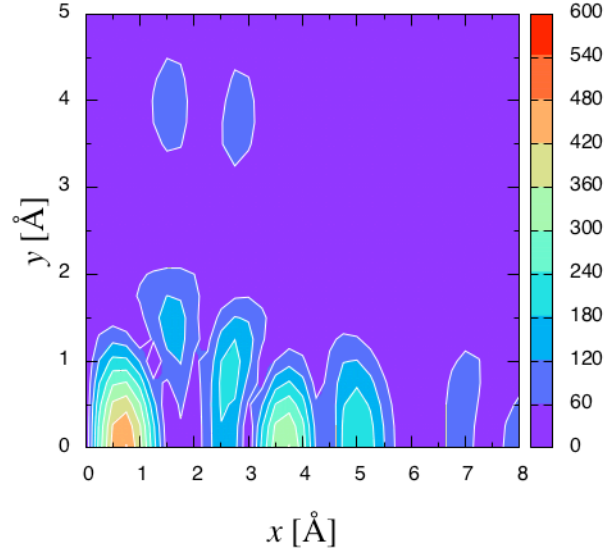


Figure S2. $|V_{\text{eff}}|$ for SF rate in quaterrylene. The values in the color bar are given in meV. It is only shown in $0.0 \leq x \leq 8.0 \text{ \AA}$ because of negligible variation in $x \geq 8.0 \text{ \AA}$.

4. Energies of charge transfer states in terrylene and quaterrylene

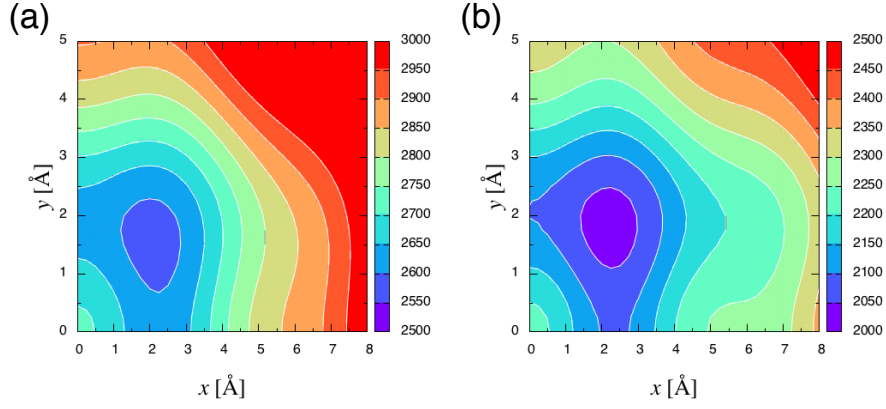


Figure S3. Calculated E_{CT} (using eq 6) of terrylene (a) and quaterrylene (b). All values are given in meV. For quaterrylene, it is only shown in $0.0 \leq x \leq 8.0$ Å, because of negligible variation in $x \geq 8.0$ Å.

5. Diagram of perturbed energy levels for quaterrylene

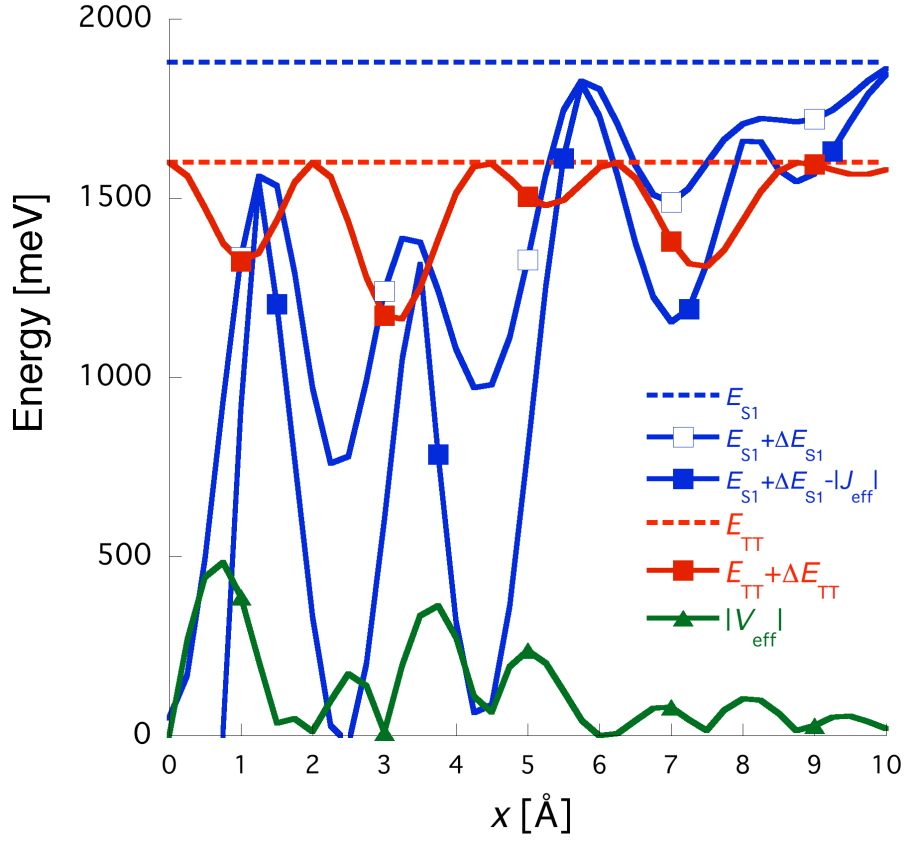


Figure S4. Perturbed energy levels of S_1S_0 (blue-solid line) and T_1T_1 (red-solid line) in the slipped-stack quaterrylene dimer model defined in Figure 2. The value of x [Å] indicates the slip length along the longitudinal axis of the molecular backbone. The dashed horizontal lines denote the non-perturbed energy levels of $E_{S_1S_0}$ (blue-dashed line) and $E_{T_1T_1}$ (red-dashed line), with their values of $E_{S_1S_0} = 1.88$ eV and $E_{T_1T_1} = 1.60$ eV, respectively.⁴ The two blue-solid lines denote the perturbed $E_{S_1S_0}$, $E_{S_1S_0} + \Delta E_{S_1S_0}$ (with white-squares) and the possible lowest split energy of $E_{S_1S_0}$, $E_{S_1S_0} + \Delta E_{S_1S_0} - |J_{\text{eff}}|$ (with blue-squares). The red-solid line denotes the perturbed $E_{T_1T_1}$, $E_{T_1T_1} + \Delta E_{T_1T_1}$. The green-solid line denotes $|V_{\text{eff}}|$ value in the corresponding slipped-stack configuration.

6. Diagram of perturbed energy levels of terrylene with the assumption that E_{CT} is stabilized by 250meV

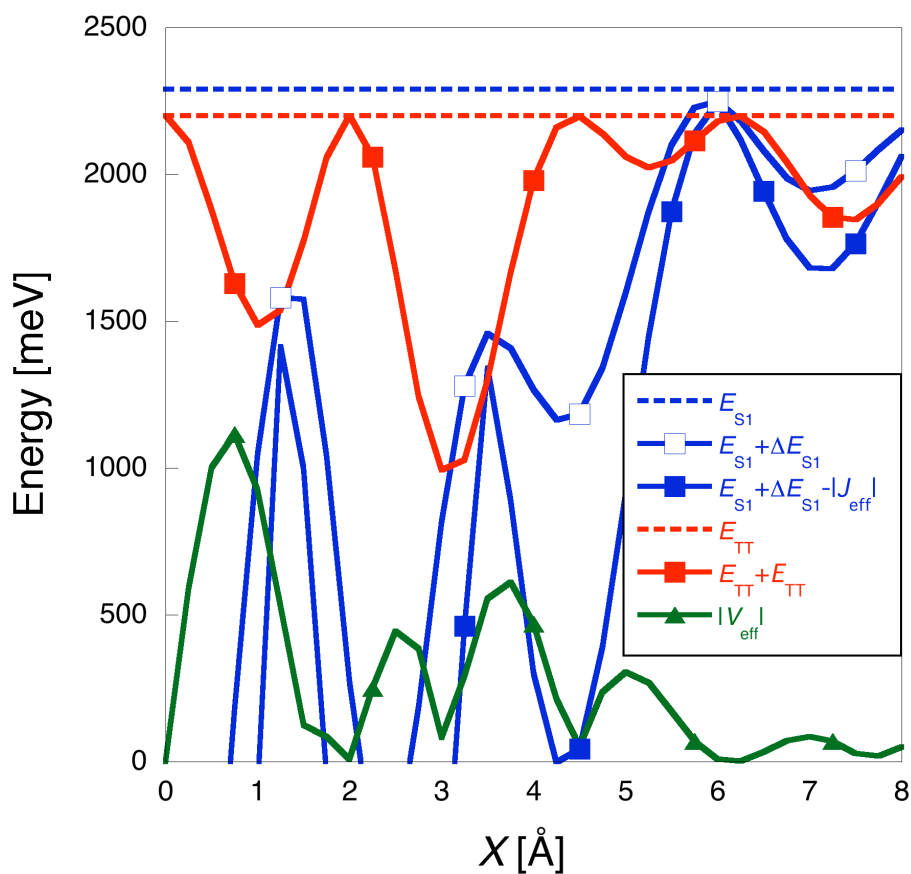


Figure S5. Perturbed energy levels of S_1S_0 (blue-solid line) and T_1T_1 (red-solid line) in the slipped-stack terrylene dimer model defined in Figure 2 and in the same manner as in Figure 7, but the E_{CT} is lowered equally by 250 meV in all x values.

7. Candidate packing for efficient SF in quaterrylene

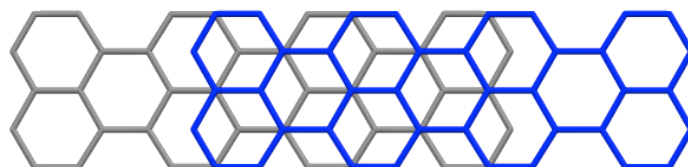


Figure S6. The dimer configuration of quaterrylene in $(x, y) = (5.5, 0.0)$ Å.

8. Crystal packing patterns of terrylene derivatives

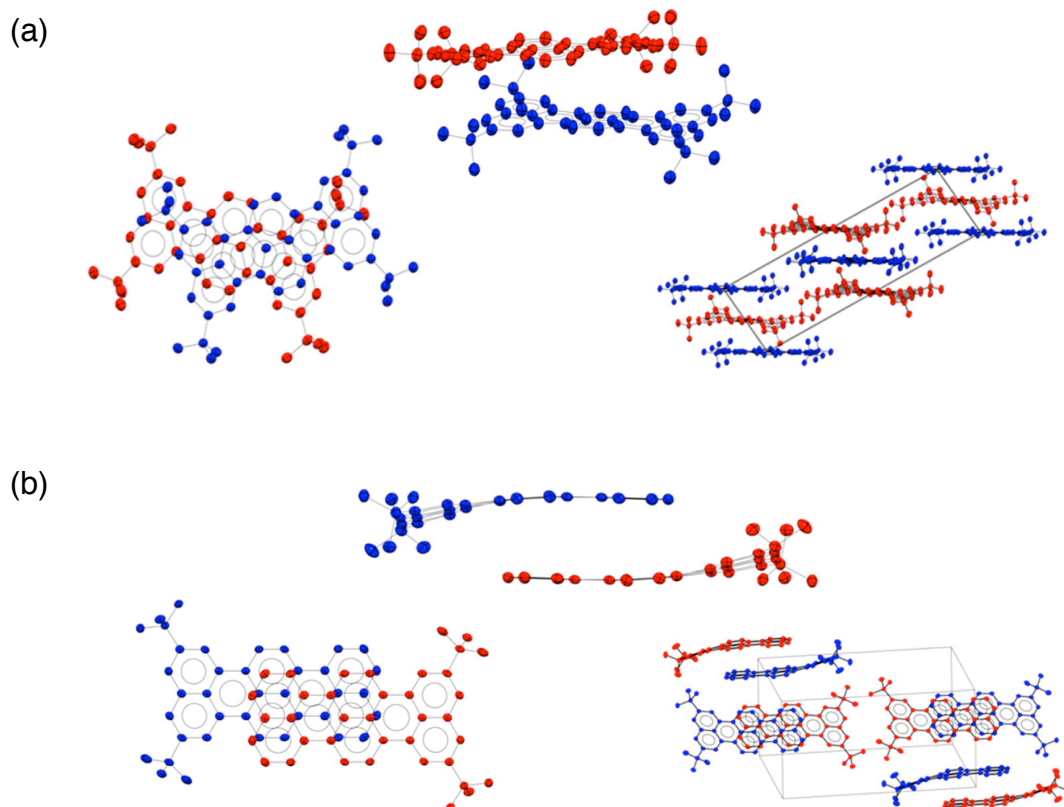


Figure S7. Crystal packing patterns of real terrylene derivatives, 2,5,10,13-tetra(*tert*-butyl)terrylene (a) and 2,5-di(*tert*-butyl)terrylene (b).⁵ In the text, the former is denoted as **1**, and the latter as **2**. The geometry of the displaced monomer in **1** is identified by the shifting parameter x, y, z in the present model with $(x, y, z) = (2.67, 0.35, 3.68) \text{ \AA}$, as well as by the rotational angle around z -axis with 31.7° , while that in **2**, by $(x, y, z) = (4.35, 1.47, 3.31) \text{ \AA}$, as well as by the rotation angle around x -axis with 180° .

9. Non-horizontal couplings in the present model and in 2,5-di(*tert*-butyl)terrylene

From Figure S7(b) with considering the curled edge of terrylene in **2**, the blue-colored monomer in the dimer subset of **2** is found to be displaced and stacked not only as the parallel transition of the red-colored one, but also as the 180° rotation along the molecular short-axis of the red-colored one. As a result, the relationship of molecular orbital interaction between monomers in **2** is different from that in the present model, where the non-horizontal couplings are supposed to have the same sign in any coordinate.

When the monomers are slipped and stacked along the longitudinal or the transverse axis of terrylene, the contribution of intermolecular MO interaction to each Fock matrix element is considered to be simplified as the summation of the atomic orbital (AO) interactions between molecule A and B. Therefore, the sign of each Fock matrix element is determined by the summation of all the intermolecular AO interactions relevant to the interest MO interaction.¹ Figure S8 shows the qualitative description for an example of the MO interactions between C–C bonds of monomers as the smallest unit, in the longitudinal-axis-slip-stack with the half of a C–C bond length. In the case of **2**, the MO phase of the upper molecule for **2** is equivalent to the present model by rotating 180° around the vertical axis to the paper plane. Consequently, the total contribution to the non-horizontal couplings for the present model have the opposite signs, while that for **2** have the same signs with the same amplitude.

As for the stacking of dimers including rotations such as **1**, it is noted that the sign of the Fock matrix elements is varied by the rotational angle even between the non-horizontal couplings, so the consistency of the relationship in signs between the non-horizontal couplings, regardless of the same or the opposite, is not always preserved.⁶

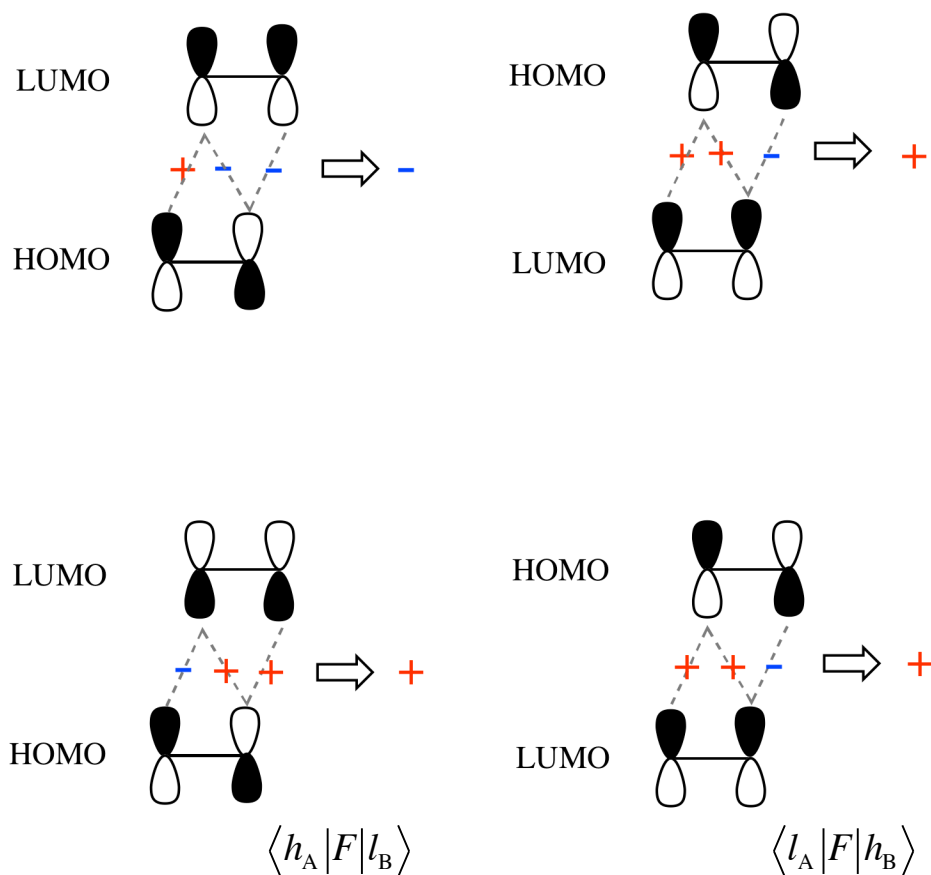


Figure S8. Graphical description for the contribution of MO interactions to the non-horizontal couplings in the C-C bond unit along the longitudinal axis, in the case for the present model (a) and for the packing of **2** (b) from the side view. In each case and each element, molecule A is the lower one and molecule B is the upper one. Dashed lines between molecule A and B denote the possible intermolecular interactions between AOs on molecule A and B. The contribution is defined as minus sign for the interaction of the same AO phase, and as plus sign for the interaction of the opposite AO phase, respectively. The total contribution, which is the summation of all the intermolecular AO contributions and determines the sign of each non-horizontal coupling, is shown in the end point of each arrow.

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