Machine learning photodynamics beyond the Frenkel exciton model: Intermolecular vibrations trigger ultrafast singlet fission in pentacene crystal

Zhengdong Li,^{a†} Federico J. Hernández,^{b†} Christian Salguero,^c Steven A. Lopez,^{c,*} Rachel Crespo-Otero,^{b,*} and Jingbai Li^{a,*}

^a Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic University, Shenzhen, 518055, People's Republic of China

^b Department of Chemistry, University of College London, London, WC1H0AJ, U.K.

^c Department of Chemistry and Chemical Biology, Northeastern University, Boston, 02115, U.S.A.

†These authors contributed to this work equally

* Correspondence to lijingbai@szpu.edu.cn r.crespo-otero@ucl.ac.uk s.lopez@northeastern.edu

Abstract

Crystalline pentacene is a model solid-state light-harvesting material because its quantum efficiencies exceed 100% via ultrafast singlet fission (SF). The SF mechanism in pentacene crystals is unresolved due to insufficient electronic information in time-resolved experiments and intractable quantum mechanical calculations for simulating realistic crystal dynamics. We combine multiscale multiconfigurational approach and machine learning (ML) photodynamics to understand SF in pentacene crystals. Our simulations identify two competing SF channels in the herringbone and parallel dimers, underpinning the high efficiency of SF in pentacene crystal. The predicted SF time constants (61 and 33 fs) are in excellent agreement with experiments (78 and 35 fs). The trajectories highlight the essential role of intermolecular stretching between monomers in generating the multi-exciton state. The ML-photodynamics resolved the elusive interplay between electronic structure and vibrational relations in the SF dynamics, enabling fully atomistic excited-state dynamics for the solid state with multiconfigurational quantum mechanical calculations.

Introduction

The discovery of singlet fission (SF) has triggered the rapid development of organic photovoltaic materials to achieve higher solar conversion efficiencies than those observed for conventional semiconductor solar cells¹⁻⁶. SF is a spin-conserving process that converts a high-energy singlet exciton into two low-energy triplet excitons⁷⁻⁹. It provides an ideal tool to harvest the excess light energy higher than the band gap of solar cells. Many works have studied the SF process in a wide range of organic molecules, such as perylene¹⁰, terrylenediimide dimer¹¹, diphenylisobenzofuran¹², quinoidal thiophenes¹³⁻¹⁴, aza-cibalackrot¹⁵, carotenoids¹⁶, tetracene¹⁷, pentacenes¹⁸⁻²⁰, and hexacene²¹. They showed that SF can take place in subpicoseconds, but the mechanistic origin of such an ultrafast process is not fully resolved. The lack of understanding of this fundamental process and missing mechanisms substantially limit progress toward new materials for SF-based devices. Studying the SF mechanism will contribute to a deeper understanding of how to control the rate and quantum yields of SF in devices, helping maximize the energy efficiency of SF solar cells.

Crystalline pentacene is especially attractive because it generates triplet excitons in 80 fs²². The pentacene crystal contains five types of dimers (Figure 1a), and the maximum electronic overlap is in the herringbone and parallel forms (Figure 1b). The transient absorption (TA) spectrum of pentacene crystals observed two decay time constants (78 and 35 fs)²³, suggesting two unique SF channels. The polarized TA microscopy showed the quantum decoherence rate along the parallel direction is 2.5-fold faster than along the herringbone direction²⁴, suggesting that SF in the parallel dimer is faster than in the herringbone dimer. A recent time-resolved photoemission study observed a mixed nature of local excitation and charge transfer in SF²⁵. Quantum chemical calculations performed by Deng *et al.* suggest the anisotropic vibronic coupling of the pentacene tetramer in the crystal is responsible for the distinct SF channels²⁴. However, the role of molecular vibrations is elusive, which has prevented a holistic understanding of the role of dimer morphology in controlling the SF rates.



Figure 1. (a) The crystal structure of pentacene with five types of dimers. (b) The geometries of the herringbone and parallel dimers optimized with ω B97XD/def2-TZVP. The intermolecular distances are defined by the carbon atoms in each central ring. (c) The semi-localized active space of the herringbone (*top*) and parallel (*bottom*) dimers, computed with the SA6-

CASSCF(4,4)/cc-pVDZ method. The occupations are averaged over 6 states. (d) Schematic representations for the main excited-state electronic configurations observed in the S₁ and S₂ states, computed with the SA6-CASSCF(4,4)/cc-pVDZ methods on the basis of the semilocalized active orbitals in panel (c).

To date, most theoretical studies have employed exciton models (i.e., Frenkel's model²⁶⁻²⁸) to explain the SF mechanism in the pentacene crystal²⁹⁻³¹. Static quantum mechanical (QM) calculations based on the exciton model have revealed essential roles of the charge-transfer (CT) states³²⁻³³, doubly excited (DE) states³⁴, and multi-excition (ME) states³⁵⁻³⁶. in pentacene crystal. The excited-state potential energy calculations suggest that increasing the intermolecular distances (Figure 1b) changes the nature of the S₁ state of the pentacene dimer from CT to DE with ME character and promotes SF³⁷. This finding implies that the elongation of the intermolecular distance may help disentangle the elusive SF mechanism in the excitedstate dynamics of the pentacene crystal. Exciton models have recently been implemented for the nonadiabatic dynamics simulations of these systems³⁸⁻³⁹, but the high computational cost of the excited-state calculations for pentacene dimers in crystalline environments has prevented full-atomistic, on-the-fly nonadiabatic dynamics simulations from being combined with multiconfigurational calculations. Wang et al. 40 simulated the excited dynamics of the pentacene dimers using the trajectories surface hopping method with classical path approximation, which predicted an SF time constant of 700 fs. Zheng et al.⁴¹ and Peng et al.⁴² performed the multi-configuration time-dependent Hartree method with selected vibrational modes, respectively. Although the predicted SF time constants were improved to 70–120 fs. their results only showed an 80% SF yield. The discrepancy between the computations and experiments resulted from the lack of multiconfigurational calculations and full-dimensional nuclear dynamics.

We have overcome previous theoretical limitations with complete active space self-consistent field (CASSCF) calculations (Figure 1c) to fully describe the electronic configuration interactions in the pentacene dimer (Figure 1d). We trained neural networks (NNs) to accelerate the CASSCF calculations for computing the excited-state dynamics of pentacene dimers in crystals in the multiscale machine learning (ML) photodynamics simulations⁴³ in an electrostatic embedding ONIOM scheme⁴⁴. Our simulations showed two unique SF channels in the pentacene crystal via the herringbone and parallel dimers. The predicted SF time constants are in excellent agreement with the experiments. The trajectories reveal the intermolecular stretching in the pentacene dimer during the SF process, which provides new insights into the SF mechanisms in pentacene crystal.

Results and Discussion

Pentacene crystal models.

The pentacene crystal models comprise a photoexcited dimer inside a rigid crystal environment generated from the 3x3x3 supercell. The herringbone (Figure 2a) and parallel (Figure 2b) dimers have 81 and 82 pentacene molecules in their rigid crystal environment, respectively. We compute the excitation energies of the dimers with electrostatic embedding (ee) six-state averaged (SA6) CASSCF(4,4)/cc-pVDZ calculations. This method was previously benchmarked against multireference methods with second-order perturbative corrections, which showed essentially the same topology in the excited-state potential energy surfaces (PES) for the pentacene dimer⁴⁵. The restrained electrostatic potential (RESP) charges of surrounding molecules are embedded to account for the polarization from the

crystal environments to the photoexcitation of pentacene dimers. The total energy combines the ee-SA6-CASSCF(4,4)/cc-pVDZ and GFN2-xTB calculations in a two-layer ONIOM scheme^{44, 46} and details are provided in the Computational Method.

Photodynamics of pentacene dimer in crystals.

We use ML-photodynamics⁴³ simulations to investigate the SF mechanism in pentacene dimers. The NN training data includes the energies and gradients of 6 singlet states of the dimers, including the ground state, computed with the ee-SA6-CASSCF(4,4)/cc-pVDZ calculations. We ignore the NACs between the non-adjacent states and approximate the NACs between adjacent states with the curvature-driven time-dependent couplings (κ TDC)⁴⁷⁻⁴⁸, derived from the Baeck-An approximation⁴⁹. A recent benchmark showed excellent agreement between κ TDC and ground-truth NACs, especially when the energy gap is small (<0.1eV)⁵⁰⁻⁵¹. Thus, we use the NN-predicted energies to compute the κ TDC in the ML-photodynamics simulations when the energy gap < 0.1 eV.

The initial training sets include 1000 Wigner-sampled structures of the pentacene dimers at the zero-point energy level. We expand the training sets with another 2000 structures by rescaling the atomic displacements in all vibrational modes to 90% and 80% with the Wigner sampling. A recent report showed this approach is effective in minimizing the NN errors for large molecules with complex molecular structures⁵². The initial training sets are further amended with the adaptive sampling⁵³ to collect the undersampled structures in the ground-and excited-state PESs. The final training sets increase to 4211 and 3455 data points for the herringbone and parallel dimers. Details of the adaptive sampling are provided in Computational Methods.

We launch the photodynamics simulations for the pentacene crystal from the lowest bright state S₂ (Figure S2) and consider the SF process is dominated by the S₂ \rightarrow S₁ transitions. The excited-state decay time constants (35 and 78 fs) measured in the TA spectrum of the pentacene crystal²³ suggests that 90% of the pentacene excited-state population arrives at the S₁ state in 81–180 fs. As such, we set the ML-photodynamics simulation time to 200 fs with a step size of 0.5 fs. The fewest switches surface hopping (FSSH)⁵⁴⁻⁵⁵ with NN-predicted κ TDC is used to compute the non-adiabatic transition probabilities. A single ML-photodynamics trajectory was completed in 5 days due to the computational bottleneck of GFN2-xTB calculations for the pentacene crystal. Nevertheless, the ML-photodynamics accelerate the ee-ONIOM(SA6-CASSCAF(4,4)/cc-pVDZ:GFN2-xTB) calculations 22-fold, where computing the corresponding trajectory requires 110 days. We simulate over 500 trajectories for the herringbone and parallel dimers to obtain statistically sufficient data for investigating the SF mechanisms.



Figure 2. Illustrations of the pentacene crystal models for (a) the herringbone and (b) parallel dimers. State population dynamics of (c) the herringbone and (d) parallel dimers in 200 fs ML-photodynamics simulations. Plots for 100 randomly selected trajectories of (e) the herringbone and (f) parallel dimers. The gray dashed lines indicate the position of R1=5.8Å and R2=3.4Å in (e) and (f), respectively. The black curves show the average trajectory.

Figures 2e and 2f illustrate the state population dynamics of the pentacene dimers in the crystal. The S₂ relaxation undergoes the S₂ \rightarrow S₁ transitions, where 95% of the herringbone dimers and 97% of the parallel dimers land on the S₁ state in 200 fs. The other trajectories remain in the S₂ or hop to the S₃ state. No trajectories are found in the S₀, S₄, or S₅ states. The S₂ populations fit an exponential decay time constant of 61 and 33 fs in the herringbone and parallel dimers.

Figures 2g and 2h plot the trajectories to illustrate the changes in the intermolecular distances during the S₂ relaxation of the pentacene dimer in the crystal. The average value of R1 is 5.84 Å at the S₂-FC points and 5.92 Å at the S₂/S₁ surface hopping points of the herringbone dimers. The trajectories show continuous elongation of R1 when they arrive at the S₁ state, with R1 approaching 6.39 Å. The average value of R2 in the parallel dimer increases from 3.75 Å at the S₂-FC points to 4.24 Å at the S₂/S₁ surface hopping points and reduces to 3.84 Å in the S₁ state. These trajectories indicate two competing SF channels via the herringbone and parallel dimers in the pentacene crystal.

Based on the fitted time constants in Figure 2e and 2f, the SF in the parallel dimer (33 fs) is faster than that in the herringbone dimer (61 fs), in line with the polarized TA microscopy

experiments²⁴. The predicted SF time constants also match with the decay time constants (35 and 75 fs) observed in the TA spectrum of pentacene crystal²³. It suggests that the two excitedstate decays observed in the TA spectrum²³ are attributed to two competing SF channels. The predicted time constant is 1.8 times longer in the herringbone dimer than in the parallel. This ratio is in excellent agreement with the ultrafast polarized transient absorption microscopy experiment, which reported a factor of 2.5 between the SF time constant measured in the herringbone and parallel direction²⁴. Previous experiments also reported a similar anisotropic SF process in the hexacene crystal with a factor of 4²¹. Thus, the computationally elucidated SF mechanisms found in our ML-photodynamics simulations are transferable to understanding the SF process in the crystals of pentacene and hexacene.

In addition to the intermolecular distances, we compute the Distance Matrix (DM) of the pentacene dimers in the trajectories to compare the intermolecular and intramolecular contributions to the structural changes in the S₂ relaxation. The DM includes all pairwise distances between carbon atoms. Figures 3a and 3b illustrate the differential DMs between the S₂-FC and S₂/S₁ surface hopping structures for the herringbone and parallel dimers, respectively. The almost unchanged values in the diagonal blocks suggest little contribution from the intramolecular vibrations to the S₂ \rightarrow S₁ transitions. In contrast, we find significant changes in the diagonal values of the off-diagonal blocks, indicating that SF in the pentacene crystal is mainly associated with the elongation of the intermolecular distance between the monomers.



Figure 3. Differential Distance Matrices of (a) the herringbone and (b) parallel dimers based on the S₂-FC structures and the S₂/S₁ surface hopping structures. The Distance Matrices are defined by the intermolecular distances between the corresponding carbon atoms in the monomers. The atoms 1–22 and 23–44 refer to the carbon in monomers **1** and **2**, respectively. The diagonal blocks (*bottom-left* and *top-right*) describe the intramolecular distances, and the off-diagonal blocks (*bottom-right* and *top-left*) represent the intermolecular distances. Plots for the reduced potential energy distributions in the trajectories of (c) the herringbone and (d) parallel dimers with the two dominant vibrational modes. The 70 cm⁻¹ and 45 cm⁻¹ stretching

of the herringbone dimer follows the x and z-axis; the 29 cm⁻¹ and 50 cm⁻¹ stretching of the parallel dimer follows the y and z-axis. UMAP clusterings of the S_2/S_1 surface hopping structures of (e) the herringbone and (f) parallel dimers. The hopping points are colored from green to yellow following the increasing order of the intermolecular distances. The red stars mark the locations of the optimized S_2/S_1 conical intersections, whereas the darkest red star represents the global minima of the conical intersections. The color bars illustrate the relative energies of the conical intersections and the intermolecular distances in the S_2/S_1 surface hopping points.

We projected the nuclear displacements in the pentacene dimer trajectories to the vibrational mode coordinates to understand the elongation of the intermolecular distances in the pentacene dimers. The potential energy distributions (PED)⁵⁶ show notable vibronic-active low-frequency motions governing the excited-state dynamics in the pentacene crystal, which are at 70 cm⁻¹ and 45 cm⁻¹ in the herringbone (Figure 3c) and 29 cm⁻¹ and 50 cm⁻¹ in the parallel dimers (Figure 3d), respectively. These modes are associated with hindered intermolecular rotations leading to the intermolecular stretching of the monomers in the quasi-orthogonal direction. These results are consistent with previous studies on the essential vibrational modes triggering the SF in the herringbone dimer⁴⁵. Moreover, the combination of the quasi-orthogonal 70 cm⁻¹ and 50 cm⁻¹ modes in the herringbone and parallel dimer matches the cross-axial low-frequency mode reported in the pentacene tetramer, which showed strong vibrational coherence with a 35 cm⁻¹ phonon facilitating the anisotropic SF in the pentacene crystal²⁴. Our findings suggest that the quasi-orthogonal intermolecular stretching of the herringbone (70 cm⁻¹) and parallel dimer (50 cm⁻¹) produce the anisotropic SF phenomena in the pentacene crystal.

According to the wave-packet dynamics by Duan *et al.*, the low-frequency intermolecular vibrations could facilitate the SF of the herringbone dimer by forming the intermolecular conical intersection (CI)⁵⁷. A similar role of the intermolecular CI was also reported in the pentacene derivative⁵⁸ and other molecular aggregates⁵⁹. We optimized the structures of the S₂/S₁ surface hopping points in the trajectories to understand how the crystal environments affect the intermolecular CIs of the pentacene dimers. Our calculations showed several degenerate intermolecular CIs in both herringbone and parallel dimers (Figure S4). Figures 3e and 3f visualize the UMAP of the S₂/S₁ hopping points resembles the state-crossing regions, where most intermolecular CIs are at the edge of the crossing regions. The global minimum CI of the herringbone dimer is associated with a notably shorter intermolecular distance (R1 = 6.18 Å) than the majority of the S₂/S₁ surface hopping points (R1 = 5.92 Å); the parallel dimer shows the global minimum CI (R2 = 3.99 Å) near the center of the S₂/S₁ surface hopping regions (R2 = 3.84 Å). Overall, the wide S₂/S₁ crossing regions are responsible for the efficient S₂→S₁ transitions in the pentacene crystal.

SF mechanisms for the pentacene crystal

We performed rigid scans of the excited-state energies and electronic configurations along with the intermolecular distances to identify the driving force of SF in pentacene crystals. The R1 and R2 values range from 4.8 to 6.8 Å and 2.7 to 4.7 Å, covering the ranges observed in the trajectories of herringbone and parallel dimers.



Figure 4. Plots for the potential energy curves of (a) the herringbone and (b) parallel dimers in the pentacene crystal, computed with the ee-ONIOM(SA6-CASCI(4,4)/cc-pVDZ:GFN2-xTB) method. The scan shows the ground-state local minimum of the herringbone and parallel dimers near 6.1Å and 4.1Å, respectively. These distances are slightly longer than the optimized values with the ω B97XD/Def2-TZVP method due to the lack of dynamical correlation and dispersion corrections in the SA6-CASSCAF(4,4)/cc-pVDZ calculations. Plots for the number of unpaired electrons (*N*_e) and squared norm of the one-electron transition density matrix (Ω_{1TDM}) in the S₁ state of (c) the herringbone and (d) parallel dimers as functions of the intermolecular distances. *N*_e = 2.0 and Ω_{1TDM} = 1.0 in a SE state, and *N*_e = 4.0 and Ω_{1TDM} = 0.0 in a DE state. Plots for the weights of the configuration state wavefunction (CSF) of the local excitation (LE), charge transfer (CT), and multi-exciton (ME) in the S₁ state of (e) the herringbone and (f) parallel dimers as functions of the intermolecular distances. SS and TT refer to the singlet-singlet and triplet-triplet types of ME. The electronic configurations are omitted if their weights are <0.01.

Figures 4a and 4b show the energies for the singlet (S₀, S₁, S₂) and quintet (Q) states, computed with ee-ONIOM(SA6-CASSCAF(4,4)/cc-pVDZ:GFN2-xTB), where the Q state describes the energy level of the triplet pentacene dimers. The R1 and R2 in the optimized ground-state structures, S₀-min, are 5.84 Å and 3.70 Å (Figure 1b). The Q-S₁ gap becomes negative in the herringbone dimer when R1 > 5.1 Å (Figure 4a) and is negative in the parallel dimer at all R2 values (Figure 4b), suggesting the generation of an unbounded T-T biexciton at the S₁-FC region, followed by an exothermic triplet separation⁶⁰.

Since the trajectories showed efficient S₂/S₁ surface hoppings to continue the SF process, our following discussions focus on the electronic configuration of the S₁ state. The plots of S₁ and S₂ energies show similar topology with an average S₂-S₁ gap of 0.24 eV and 0.08 eV in the herringbone (Figure 4a) and parallel dimer (Figure 4b), respectively. The small S₂-S₁ gaps are responsible for the substantial mixing of multiple electronic configurations in S₁. These results explain the presence of the wide S₂/S₁ crossing seam observed in our ML-photodynamics simulation, associated with ultrafast S₂→S₁ population transfer. We quantify the DE character in the S₁ state using the number of unpaired electrons (*N*_e) and the squared norm of the one-electron transition density matrix (Ω_{1TDM}). The herringbone dimer shows *N*_e of 2.6–2.7 and Ω_{1TDM} of 0.7–0.8 when R1 < 5.2 Å, indicating a dominant single exciton (SE) character in S₁

(Figure 4c). The value of N_e immediately increases to 3.9, and Ω_{1TDM} reduces to 0.09 at R1 = 5.8 Å, showing notable DE character in the S₁-FC point (5.84 Å). In the parallel dimer, N_e increases from 3.7 to 4.0, and Ω_{1TDM} decreases from 0.21 to 0.03 when R2 approaches 3.4 Å (Figure 4d). Thus, the S₁-FC point (R=3.70 Å) of the parallel dimer is also a DE state.

The active orbitals are delocalized over the dimer in the potential energy curve calculations (Figure S1). Thus, the triplet configuration of each monomer cannot be explicitly described due to the orbital mixing between the monomers. As such, we performed the ee-SA6-CASCI(4.4)/cc-pVDZ calculations with the localized active orbitals⁶¹ on the monomer (Figure 1c). In Figure 4e, the herringbone dimer shows more than 50% of the $CT_{1\rightarrow 2}$ character from monomer **1** to **2** in the S₁ state when R1 < 5.0 Å. It also associates minor contributions (7%) from local excitations (LE) of monomers **1** and **2**. The population analysis predicts a $CT_{1\rightarrow 2}$ of 0.44e at 5.1 Å (Figure S3b), which decreases to 0.1e near the S₁-FC geometry (5.84 Å). Continuously increasing R1 leads to a rise of the DE state with a TT character up to 67%, which confirms the TT-type DE state favoring the SF process. In addition, we find a competing ME character corresponding to two coupled SE of both monomers, which increases from 0% to 17% along R1. In the parallel dimer, S₁ shows a weak SE character with $CT_{1\rightarrow 2}$ and $CT_{2\rightarrow 1}$ configurations, which decreases from 7% to 0% when R2 increases from 2.7 Å to 3.7 Å (Figure 4f), in line with the absent CT in the charge analysis (Figure S3e). S₁ exhibits TT character from 53% to 67% when increasing R2, accompanied by 17% of the ME character resulting from the coupled SE character at each monomer. These findings agree with the previous gasphase studies on the herringbone³⁷, and parallel³⁵ dimers, where S₁ changed from a CT-type SE to a DE state with increasing intermolecular distances.

Overall, our results show that the S₁ state of the herringbone and parallel dimers form the TT state when R1 > 5.8 Å and R2 > 3.4 Å, respectively. All predicted trajectories explored these intermolecular distances at the end of the simulations (Figures 2g and 2h), which confirm the formation of the TT state. The complete S₂ \rightarrow S₁ transitions suggest a 100% SF yield in both herringbone and parallel dimers. Moreover, the herringbone dimer shows a wider range of R1 (4.9– 6.6 Å) than R2 of the parallel dimer (3.1– 4.5 Å). They resulted in only 54% of the S₁-FC structures of the herringbone dimers being immediately accessible for SF, whereas the ratio for the parallel dimer is 92%. These results explain why the SF in the herringbone dimer is slower than the parallel dimer. The highly accessible SF channels at the S₁-FC regions explain the ultrafast SF process in the pentacene crystal.

Conclusion

We used the ML-accelerated photodynamics simulations based on the neural networks trained with SA6-CASSCAF(4,4)/cc-pVDZ data embedded in a multiscale scheme with GFN2-xTB calculations to investigate the SF mechanism via the herringbone and parallel dimers in the pentacene crystal. This approach allowed us to explore the excited-state dynamics in the pentacene crystal with high-quality theory at the multiconfigurational level in a full-atomistic manner, beyond the Frenkel exciton model. The unprecedented ML photodynamics trajectories provided statistically sufficient samples over a broad range of the excited-state conformational space of the pentacene dimer, presenting high-fidelity structural information to disentangle the elusive intra and intermolecular vibrations involved in the SF mechanism.

The trajectory analysis revealed two competing SF channels in the herringbone and parallel dimers. Their S_2 lifetimes (61 fs and 33 fs) are in excellent agreement with the TA spectra (78

and 35 fs). The analysis of the potential energy distributions in the trajectories uncovered two intermolecular stretching modes (70 cm⁻¹ and 50 cm⁻¹) that separated the monomers in the herringbone and parallel dimers in the crystal. Combining these two modes explains the formation of the cross-axial low-frequency vibration of the pentacene tetramer at 35 cm⁻¹, as reported in previous polarized TA microscopy experiments. The quasi-orthogonal directions of the intermolecular stretchings in the herringbone and parallel dimers also explain the anisotropic SF phenomenon in the pentacene and hexacene crystals observed in the TA experiments.

The PES scans with ee-ONIOM(SA6-CASSCAF(4,4)/cc-pVDZ:GFN2-xTB) calculations showed that the elongation of the intermolecular distances leads to rapid relaxation of the quintet state below the S₁ and S₂ states, favoring an exothermic triplet separation. These results confirmed that the intermolecular stretchings, conducting to the intermolecular CIs, are the driving force behind the SF in the pentacene crystal. Evaluations of the unpaired electron numbers and the norm of the one-electron transition density matrix in the herringbone dimer demonstrated the electronic nature of S₁ changes from a CT state to a TT state with increasing intermolecular distances. All predicted trajectories approached the required intermolecular distances for SF that confirmed the formation of the S₁-FC structures of the herringbone dimer are immediately accessible for SF, whereas the ratio for the parallel dimer is 92%. These findings explain the faster SF in the parallel dimer than that in the herringbone dimer. The different SF rate constants in the herringbone and parallel dimers result in the anisotropic SF phenomenon in the pentacene crystal. Overall, the co-existence of two efficient but competing SF channels highlights the high efficiency of the SF process in the pentacene crystal.

Computational Methods

Multiscale quantum mechanical calculations.

The experimental crystal structure of pentacene (CCDC:114447) was initially optimized using periodic DFT calculations along with the functional PBE-D2 as implemented in Quantum Espresso⁶². A Monkhorst-Pack k-point grid was chosen to match the unit cell parameters (2x2x1) and considered a basis set a cut-off of 60 Ry. Then, we generated the herringbone and parallel cluster models partitioning the crystal models into two layers: the dimer and the surrounding crystal shell, where the dimer includes 2 molecules and the crystal shell compresses 79 and 80 molecules for the herringbone and parallel dimers, respectively. The total energy was expressed using a two-layer ONIOM scheme^{44, 46}:

$E_{\text{total}} = E_{\text{GFN2-xTB,model}} - E_{\text{GFN2-xTB,dimer}} + E_{\text{QM,dimer}}$

where the $E_{\text{GFN-FF,model}}$ term is the energy for the whole crystal model, computed with the GFN2xTB method⁶³. The $E_{\text{GFN2-xTB,dimer}}$, and $E_{\text{QM,dimer}}$ terms correspond to the GFN2-xTB and QM energies of the pentacene dimer, respectively. In our ML-photodynamics simulations, the QM calculations were replaced by NN predictions. The polarizations from the crystal shell to the pentacene dimer were accounted for by embedding the RESP charges of the surrounding molecules into the GFN2-xTB and QM calculations. The gradients were obtained as the firstorder derivatives of the total energy accordingly, where the nuclear positions in the crystal shells were frozen to describe the rigid environment in the lattice. The pentacene dimer structures in the crystal were optimized using the ONIOM approach implemented in *fromage*⁶⁴, where the energies and gradients of the dimers were computed with the ω B97XD/def2-TZVP calculation using the Gaussian16 program⁶⁵. In training data and the PES scan calculations, the pentacene dimers were computed with the SA6-CASSCAF(4,4)/cc-pVDZ calculations using the BAGEL program⁶⁶. The active orbital localization in the SA6-CASCI(4,4)/cc-pVDZ calculations used the Pipek-Mezey method⁶¹. To study how the crystal environment affects the dimer structure, we optimized the gas-phase geometries of pentacene dimers with the PBE0/cc-pVDZ method using the BDF program⁶⁷⁻⁶⁹.

Training data generation and NN training.

The initial training data generation employed the Wigner sampling at the zero-point energy level to produce 1000 non-equilibrium geometries of the pentacene dimer according to the vibrational frequencies and modes computed with ω B97XD/def2-TZVP calculations. Another 2000 structures were obtained by rescaling the atomic displacements in all vibrational modes to 90% and 80% in the Wigner sampling. The training data contain the energies and gradients of the lowest 6 singlet states. The training data were randomly split into training and validation sets in a 9:1 ratio.

We implemented a feed-forward neural network consisting of multiple perceptron layers based on the TensorFlow/Keras API for Python⁷⁰. The NN computes the inverse distance matrix of the input molecule to predict the energies and gradients. The NN employed a leaky softplus activation function. The loss function of the predicted energies and forces is combined with a ratio of 1:1 to ensure their physical relationship. The hyperparameters were optimized by a grid search over 384 NNs.

We used the adaptive sampling approach to explore the under-sampled data in the initial training set. The adaptive sampling propagates 100 trajectories from the S₂ state for 400 fs with a step size of 0.5 fs using a committee model of two independently trained NNs. We considered the standard deviation (STD) in the predicted energy and gradients of the NN committee as the uncertainty of the current prediction. The trajectories were stopped when the STD exceeded the empirical thresholds for energy (0.03 Hartree) or gradients (0.12 Bohr Hartree⁻¹), respectively. The last geometries of the stopped trajectories were recomputed with the SA6-CASSCAF(4,4)/cc-pVDZ calculations, including the charges of the crystal shell. The adaptive sampling retrained the committee model of NNs after adding the recomputed data to the initial training set. It then restarted the trajectories until the number of the out-of-sampled structures reached the minimum value. To speed up the adaptive sampling, the trajectories were propagated in the gas phase with only the charges of the crystal shell. The final training sets increased to 4211 and 3455 data points for the herringbone and parallel dimers. The mean absolute errors in the final NN predicted energies were 0.0336-0.0363 eV and 0.0351-0.0421 eV for the herringbone and parallel dimers. The NN training, adaptive sampling, and ML photodynamics simulations use PyRAI²MD⁴³.

ML-photodynamics simulations.

The ML-photodynamics simulations propagated 1000 trajectories in the microcanonical ensemble (NVE) from the S₂-FC points of the pentacene dimers in 200 fs with a step size of 0.5 fs. The probability of a nonadiabatic electronic transition was computed with Tully's fewest switches surface hopping (FSSH) algorithm⁵⁴⁻⁵⁵, where we used the curvature-approximated time-derivative coupling (*k*TDC) method⁴⁷⁻⁴⁸ to evaluate the NACs based on the NN predicted

energy gaps. The *k*TDC method showed a good accuracy to the ground-truth NAC obtained with QM calculations when the energy gap was sufficiently small (*e.g.*, 0.5 eV)^{50, 71}. Our tested QM photodynamics simulations using the NACs computed at the SA6-CASSCAF(4,4)/cc-pVDZ level show the majority of the S₂/S₁ surface hops occurred with an energy gap <0.1 eV. Thus, we chose a threshold of 0.1 eV for computing the *k*TDC in our ML-photodynamics simulations.

The close-lying S_2 and S_1 energies made NN training difficult because their energy gaps could be one order of magnitude smaller than the NN prediction errors at the S_2/S_1 surface hopping regions. Thus, the errors in the NN-predicted energies could lead to artifacts in the PES curvatures, resulting in incorrect state population transfers in our ML photodynamics simulations. In our trajectory analysis, we removed the trajectories with incorrect state populations, e.g., exceeding 0–1. As a result, we obtained 571 and 544 trajectories for the herringbone and parallel dimers.

We projected the time-resolved nuclear displacements in the trajectories onto the S_1 -state normal modes coordinates to evaluate the reduced potential energy distribution (PED) as follows

$$Q_i(t) = \sum_A m_A \Delta r_A(t) \cdot v_{Ai}$$

where v_{Ai} are the eigenvector matrix elements, $\Delta r_A(t)$ are the nuclear displacements, m_A is the atomic mass, and Q_i are the coordinates in the normal modes basis set. The potential energy in the *i*th mode is therefore calculated as

$$V_i(t) = (2\pi c \bar{\nu}_i Q_i(t))^2$$

where \bar{v}_i is the normal mode's wavenumber and *c* is the speed of light. The potential energy per mode is then integrated along the trajectory. Finally, the PED is averaged across all selected trajectories and divided by \bar{v}_i to yield the unitless reduced PED.

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Author contributions

Z.L. and F.J.H contributed to this work equally. S.A.L, R.C.O. and J. L. conceptualized the project. Z.L. performed the DFT calculations under the supervision of J.L. F.J.H. and C.S. performed the TDDFT and CASSCF calculations under the supervision of R.C.O. and S.A.L. J.L. performed the ML photodynamics simulations. Z.L., F.J.H., C.S. and J.L analyzed the data. J.L. F.J.H. and Z.L. prepared the manuscript. All authors revised the manuscript.

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