Supporting Information

Distinct Routes of Singlet Fission and Triplet Fusion:

A Fluorescence Kinetic Study of Rubrene

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**S1. Excitation density dependence**

In the context of investigating singlet fission dynamics of rubrene, three major processes can be monitored simultaneously with fluorescence (FL) transient behaviors—singlet fission is reflected in initial fluorescence decay upon photoexcitation, geminate triplet fusion is manifested in subsequent delayed fluorescence, and non-geminate fusion of triplet excitons takes place at a much longer time delay—amounting to a multi-exponential decay. Barring these prominent processes, the FL decay data are further complicated by their dependence on photoexcitation intensity. Firstly, dense singlet excitons would undergo exciton-exciton annihilation. Secondly, compact triplet excitons produced would shorten the separation between them, thus facilitating non-geminate triplet fusion and increasing its temporal overlap with geminate triplet fusion. Even with these complications inherent in the portrayed FL decay data, the FL decay curve in previous reports was typically first truncated at a time delay chosen by investigators’ will at which the signal has approximately dropped to $10^{-3}$ of the initial maximum to remove the long delay data—presumptively representative of non-geminate triplet fusion. The abridged data were then fitted with a bi-exponential function to extract the rates of singlet fission and non-geminate triplet fusion. Alternatively, the multi-exponential tail was modelled by a power-law function because non-geminate triplet fusion involving bimolecular encountering probability will give a power law exponent of $-2$. The former data-analysis approach results in non-reproducible results because of the subjective time truncation, while the latter inflict ambiguity, owing to the multiplicity in the processes involved. One simple approach to overcome this obstacle is to decrease the photoexcitation intensity such that the FL decay data are insensitive to it. Under low-enough photoexcitation, excitons are well separated such that the occurrence of both
exciton-exciton annihilation and non-geminate triplet fusion is minimized. As a consequence, the analysis of the FL decay data can be greatly simplified as previously demonstrated in tetracene.

Figure S1 shows the fluorescence decay as a function of excitation densities. The excitation density is estimated from the absorption coefficient of rubrene at 532 nm, \( \alpha = 2.75 \times 10^4 \text{ cm}^{-1} \), and assuming a circular excitation column within the 100-nm film thickness and a 2.15 \( \mu \text{m} \) diffraction limited spot size. The suppression of non-geminate triplet fusion is signified by the invariant prompt and delayed fluorescence below an excitation density of \( 9 \times 10^{15} \text{ cm}^{-3} \) at 300 K. Figure S1b then shows an excitation density of \( 2 \times 10^{17} \text{ cm}^{-3} \) is sufficient to suppress non-geminate triplet fusion at 220 K. Because triplet hopping is thermally activated, such an excitation density is used in all fluorescence dynamics recorded at lower temperatures to improve the signal levels. At 78 K (Figure S1c), when the excitation density increased by a factor of a thousand from \( 10^{16} \) to \( 10^{19} \text{ cm}^{-3} \), the decay dynamic remains invariant. Comparing the \( 10^{19} \text{ cm}^{-3} \) excitation density to the \( 1.3 \times 10^{21} \text{ cm}^{-3} \) rubrene molecular density indicates a singlet existed in every fifth molecule on average. When taking into account the reduced fission rate at 78 K, the probability of singlet fission is \( k_{-2}/(k_{-2} + k_r) = 0.09 \) (\( k_{-2} \) and \( k_r \) are fission and radiative rates given in Table S1) therefore a fission-generated triplet pair existed in every ten molecule. The absence of non-geminate triplet fusion at such high triplet density clearly shows the triplet hopping rate is significantly reduced and it could become uncompetitive against the triplet fusion rate thus inhibited triplet dissociation in amorphous rubrene below certain temperature. Further evidence for negligible non-geminate fusion is shown in Figure S2, the decay tail with power law exponent much smaller than -2 is inconsistent with bimolecular encountering probability of non-geminate fusion. Note that above \( 10^{19} \text{ cm}^{-3} \) excitation density, the increased prompt fluorescence decay rate suggested singlet-singlet annihilation (SSA) begin
to take part; because the excitation density used in this study is much lower thus SSA is not considered further.

Figure S1. Excitation density dependence of fluorescence decay at three temperatures. The instrument response function (IRF) is included in (a) to show the fast prompt fluorescence is not limited by the instrument. The radiative decay (approximated by fluorescence decay in frozen n-hexane at 78 K) is plotted in (c) to show the delayed fluorescence extended long beyond radiative lifetime.
**Figure S2.** The fluorescence decay data shown in Figure 3 in the main text is replotted on a log-log axis. A power law fit to the temperature dependent fluorescence decay tail results in power law exponents that are much smaller than -2. This indicates the origin of the multiexponential decay tail is not due to bimolecular encountering probability of non-geminate triplet fusion.
S2. Possible assignment of emitting species

The multi-exponential fluorescence decay (Figure 3 in main text) is likely due to multiple emitting species in the sample where excimer is one of the possibilities. Previous literatures reported signature of excimers when the dynamics of the triplet pair is confined in covalently linked tetracene dimers or limited by diffusion of TIPS-tetracene molecules in solvent. However, with restricted triplet-pair dissociation at low temperatures, the absorption and FL spectra of our amorphous rubrene film shown in Figure 1 exhibit clearly resolved vibronic features that rules out excimers as a contributing species. The absence of excimer in this case is reasonable due to the lack of molecular proximity and conformational constrains in solid state to induce the strong coupling required upon excitation.

From Figure 1 in the main text, the 300 K FL spectrum peaked at 2.2 eV and the absorption spectrum peaked at 2.34 eV are consistent with an excitation of a dipole along the molecular $M$-axis reported by Irkhin et al on rubrene single crystals [Phys. Rev. B 2012, 86, 085143]. However the red-shifted FL peak ($E_{FL} = 2.15$ eV) at low temperature is too high in energy to be explained by dipole excited along molecular $L$ or $N$ axis ($E_{FL} = 2.04$ eV).

The origin of Species $a_1$ and $a_2$ may arise from the local order of amorphous film arranged in different polymorphic rubrene. The π-stacked molecular pair in orthorhombic unit cell is separated by 3.7 Å and displaced by 6.1 Å along the long-axis of rubrene while the separation in triclinic unit cell is 3.8 Å with 6.0 Å long-axis displacements; no short axis displacement in either unit cells [J. Mater. Chem. 2010, 20 (1), 159-166]. The strongly π-coupled molecular pair explains the two efficient fission sites while their small differences account for the two spectra and different dynamics observed.
S3. Amorphous vs solution fluorescence spectrum

Figure S3. Fluorescence spectrum of rubrene in toluene (black) and rubrene in amorphous thin film at 300 K (red). The spectrum shape of the two samples is similar. The peak shift can be attributed to different dielectric constants of the environment surrounding a rubrene molecule.
S4. Singlet energy transfer at 78 K

Energy selected fluorescence decay plotted in Figure S4b shows an increasing decay rate in the first 0.5 ns as the probed energy shifted towards the blue side of the fluorescence spectrum. On the other hand the decay dynamics probed at the three spectrum peaks on the red side are identical but show a slower rise time in correspondence to the fast dynamics on the blue side. The concurrence of the fast decay and the slow rise time reveals an energy transfer between donor species on the blue side and acceptor species on the red side. According to the assignment in the main text, donor species on the blue side is attributed to lone molecules (Species \(b\)) while the acceptor species on the red side is attributed to fission-capable pairs (Species \(a_1\) and \(a_2\)). The red-shift of the spectrum of the fission-capable species is attributed to the coupling between the molecular pair that lowered the singlet exciton energy. The fastest decay lifetime measured at 2.30 eV is 0.16 ns after accounting for the instrument response while the rise time on the red side (1.82-2.15 eV) is 0.17 ns.
Figure S4. (a) Fluorescence and absorption spectrum recorded at 78 K. (b) Normalized energy selected decay dynamics at 78 K. The probed energies are shown in (a) by vertical arrows.
S5. Fitting procedures

Each of the emitting species contains three temperature dependent kinetic rates therefore there are a total of six free variables. The recorded fluorescence decay dynamics can be separated into three time regimes: The prompt fluorescence (0 to 5 ns) has contributions from all species while the mid- (10 to 330 ns) and long-term (>330 ns) delayed fluorescence has almost independent contribution from species \( a_1 \) and \( a_2 \) respectively. Each of the time segments has characteristic amplitude and decay rate thus add up to a total of six fitting constrains. The procedures described below allowed us to extract a consistent set of solution by global fitting of the six variable to the six constrains.

I. Fixed radiative decay rate, \( k_r \)

The radiative rate \( k_r \) is temperature independent because it depends on the oscillator strength that is intrinsic to the material. However, the experimentally measured fluorescence decay is a summation over \( k_r \) and other temperature dependent non-radiative decay rates \( k_{nr} \). Two major non-radiative decay routes existed in our case and both can be suppressed in solution at low temperature. Namely, singlet fission is not possible for isolated molecules in frozen solution and phonon assisted relaxations are reduced at low temperature. The 15.6 ns fluorescence lifetime measured in frozen n-Hexane at 78 K (Figure S1c) approaches the reported 16 ns radiative lifetime of rubrene, hence \( k_r \) is set to 0.0625 ns\(^{-1}\) in the fitting model.

II. Negligible triplet hopping rate \( k_{1,i} \) at 78 K

As discussed in section S1, negligible triplet diffusion at 78 K signifies a small triplet hopping rate. As the triplet hopping rate becomes uncompetitive against triplet fusion rate, it becomes insignificant in the fitting. Accordingly \( k_{1,i} \) is set to zero at 78 K.
III. Temperature independent offset $y_0$

Figure 2a shows no other species that is spectrally resolved within the 0.3 to 4.8 $\mu$s time window. However, after subtraction of background contribution from detector dark counts, the decay dynamic in Figure 3 still contains a decay tail beyond 2000 ns that is much slower than the dynamics within 500 to 1500 ns window. It may originate from another fission-capable species that is spectrally similar to species $b$ but with an even weaker coupling leading to the slower decay. Owing to its temperature independence and its decay dynamic much longer than the 5 $\mu$s detection time window, it is approximated by a constant offset, $y_0$.

IV. Approximated analytical solutions at high and low temperature limits

For a quadratic equation with roots $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$, if one of the roots is much smaller than the other Vieta’s formula states that $x_1 \approx -\frac{b}{a}$ and $x_2 \approx -\frac{c}{b}$. Hence when one of the rates dominates, the decay constants $\alpha_1$ and $\alpha_2$ for $N_{S1}$ (eq. 5a and 5b in main text) can be reduced by applying Vieta’s formula. Furthermore, by approximating $Q$ (eq. 5f in main text) to the first two terms of a Taylor expansion, the amplitudes $A$ and $B$ for $N_{S1}$ (eq. 5c and 5d in main text) can also be reduced. Accordingly, at the high temperature limit when singlet fission rate $k_2$ dominates, eq 4 becomes,

$$N_{s1} = N_{s1}^0(1 - k_2/k_{-2})e^{-k_{-2}t} + N_{s1}^0(k_2/k_{-2})e^{-(k_2k_r/k_{-2} + k_{-1})t} \quad (S1)$$

and at the low temperature limit when $k_r$ dominates

$$N_{s1} = N_{s1}^0(1 - k_2k_{-2}/k_r^2)e^{-k_r t} + N_{s1}^0(k_2k_{-2}/k_r^2)e^{-k_2 t} \quad (S2)$$

or when $k_2$ dominates

$$N_{s1} = N_{s1}^0(k_{-2}/k_2)e^{-k_2 t} + N_{s1}^0(1 - k_{-2}/k_2)e^{-k_r t} \quad (S3)$$
Equation S3 says that the delayed fluorescence decays like $k_r$. However Figure S1C shows the delayed fluorescence decays much slower than the radiative rate therefore it rules out eq S3. The fluorescence dynamics at the high and low temperature limits can be approximated by eq S1 and S2 respectively.

V. Setting Initial values

Populations of species $a_1$ and $a_2$:

Species $a_1$ and $a_2$ dominates the delayed fluorescence at different time regimes. Hence the populations $N_{a_1}^{o}$ and $N_{a_2}^{o}$ are estimated by the ratio of integrated area, between 10 to 300 ns and 300 to 4500 ns, under the decay curve measured at 78 K.

Singlet fission rates, $k_{2 \rightarrow 1}$:

The prompt fluorescence is dominated by species $a$ because of its larger population. Equation S1 shows the prompt fluorescence decays like $k_2$ therefore $k_{2,a}$ is estimated from the fluorescence decays between 0 and 2 ns.

Triplet fusion rates, $k_{2 \rightarrow 1}$:

Although the energy of $^1\text{TT}$ state is slightly higher than the energy of $S_1$ state according to endothermic singlet fission in rubrene, the reverse triplet fusion may still encounter a small barrier due to molecular reorganization energy. However eq S1 shows the rate of the delayed fluorescence is mutually dependent on $k_2$ and $k_2$, thus it causes problems in the fitting procedure if both are allowed to vary with temperature in the beginning. Since the activation energy for triplet fusion is expected to be small, it is set as temperature independent in the initial fit. Once a reasonable fitting is obtained after varying the other rates, the fusion rates are then allowed to
vary to further optimize the fitting. In an iterative process by sequentially varying the fusion rates and the two other rates a final optimized fitting is obtained. The values of $k_{2,i}$ and $k_{1,i}$ change by less than 20% with or without the varying $k_{2,i}$ rates.

Equation S1 shows the amplitude of the delayed fluorescence varies according to $k_2/k_2$. Because the population of species $a_1$ is much larger than species $a_2$, its dynamics dominates the fluorescence decay at time less than 300 ns. Accordingly $k_{2,a1}$ can be estimated algebraically from the amplitude of the delayed fluorescence at 300 K (amplitude is estimated from the PL intensity at the turning point of the decay curve).

Equation S2 shows the delayed fluorescence decays like $k_2$ at the low temperature limit. Therefore $k_{2,a2}$ is estimated from the fluorescence decay at 78 K between 500 to 1500 ns.

**Triplet hopping rates, $k_{1,i}$:**

At high temperatures when $k_2$ is large, eq S1 shows the delayed fluorescence decays much like $k_{1,i}$. 
S6. Extracted physical rates

Table S1. Parameters for the best-fit curves shown in Figure 2

|   |   | k_{2, a1} (ns\(^{-1}\)) | k_{2, a1} (ns\(^{-1}\)) | k_{1, a1} (ns\(^{-1}\)) | N_{s1, a2}^0 | k_{2, a2} (ns\(^{-1}\)) | k_{2, a2} (ns\(^{-1}\)) | k_{1, a2} (ns\(^{-1}\)) | y_0 (\times 10^{-4}) |
|---|---|-------------------------|-------------------------|-------------------------|---------------|-------------------------|-------------------------|-------------------------|----------------------|
| 300 | 1.033 | 0.070 | 0.136 | 0.574 | 0.0050 | 0.012 |
| 220 | 0.551 | 0.055 | 0.097 | 0.386 | 0.0048 | 0.007 |
| 160 | 0.206 | 0.045 | 0.063 | 0.130 | 0.0046 | 0.005 |
| 140 | 0.75 | 0.113 | 0.042 | 0.046 | 0.25 | 0.093 | 0.0045 | 0.003 | 1.9 |
|   |   |   |   |   |   |   |   |   |   |
| 120 | 0.047 | 0.037 | 0.022 | 0.079 | 0.0044 | 0.002 |
| 100 | 0.033 | 0.032 | 0.010 | 0.030 | 0.0040 | 0.001 |
| 78  | 0.006 | 0.022 | – | 0.015 | 0.0040 | – |

*Note the radiative rate, k_r = 0.0625 ns\(^{-1}\), is treated as temperature independent.