# **Supplementary Information**

# Singlet energy collection competes with triplet-pair separation, not singlet fission, in rubrene-based nanoparticles for photon upconversion

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## 1 Supplementary methods

#### Preparation of DBP-doped polycrystalline films

Rubrene was dissolved in anhydrous toluene at a concentration of  $11.3 \text{ mg ml}^{-1}$ , shaken until no solids remained visible and then passed through a  $0.2 \mu \text{m}$  pore size PTFE filter. DBP was dissolved in anhydrous toluene at a concentration of  $0.83 \text{ mg ml}^{-1}$ , then shaken and filtered in the same way. The rubrene and DBP solutions were combined in a 10:1 ratio, producing a  $10 \text{ mg ml}^{-1}$  solution of rubrene containing 0.5 mol% DBP. Samples containing 0.1 mol% DBP were also prepared by diluting the DBP solution five-fold before mixing. Films were then prepared and encapsulated in the same way as for neat polycrystalline rubrene films.

#### Steady-state PL comparison of rubrene NPs and polycrystalline rubrene films

Excitation was provided by a 532 nm continuous wave laser diode (CPS532, Thorlabs). PL was collected via optical fibre and detected with a CCD spectrometer (AvaSpec, Avantes). The excitation intensity was  $\sim 1 \,\mathrm{W \, cm^{-2}}$ . A 532 nm notch filter was used to reduce laser scatter in the measured spectra.

### 2 Picosecond dynamics of rubrene nanoparticles

Fig. S1 and Fig. S2 show that anisotropy changes and peak shifts, which are characteristic signatures of exciton migration in transient absorption<sup>1</sup>, occur faster than, or on a similar timescale to, initial singlet fission. We note that monitoring the singlet excited state absorption (ESA) peak wavelength beyond 200 ps is impossible due to spectral overlap with the triplet ESA. Interestingly, the timescale of the singlet ESA shift is similar to the timescale of the first singlet fission step, suggesting that exciton migration to fission sites, resulting in <sup>1</sup>(TT) formation, may be occurring within the first 10 ps.

Beyond 20 ps however, both the singlet ESA peak position and the anisotropy are constant, suggesting that the ~100 ps secondary rise time that we observe for the triplet signal in transient absorption is not due to exciton migration to fission sites. Instead, the fission dynamics are consistent with the formation of a ~50:50 equilibrium between S<sub>1</sub> and triplet-pair states within 10 ps. Although we cannot with certainty say whether the initial triplet-pair states are strongly interacting <sup>1</sup>(TT) states or, as has been recently suggested<sup>2</sup>, weakly interacting <sup>1</sup>(T...T) states, we believe that the former is more likely in this case for several reasons. Firstly, S<sub>1</sub>  $\rightarrow$  <sup>1</sup>(TT)  $\rightarrow$  <sup>1</sup>(T...T) is the generally accepted pathway for singlet fission<sup>3,4</sup>, including in rubrene<sup>5–7</sup>. Secondly, as shown in Section 4, we would expect a triplet hopping rate of around 100 ps based on the annihilation rate constant; this is consistent with the second time constant of the triplet dynamics, suggesting that the first (10 ps) component reflects the formation of <sup>1</sup>(TT). Lastly, our sequential model is consistent with the model in Ref. 8, which the authors use to predict the same power law photoluminescence dynamics that we measure (Figure 3a, main text).



**Figure S1. Formation of a** ~**50:50 equilibrium between S**<sub>1</sub> **and** <sup>1</sup>**(TT).** (A) The singlet population decays to approximately half its initial value mono-exponentially with a time constant of 5 ps. (B) The triplet population rises mono-exponentially with the same time constant. This represents the expected behaviour for the creation of a 50:50 equilibrium between S<sub>1</sub> and <sup>1</sup>(TT) with a singlet fission (and triplet-pair fusion) rate of 10 ps.



Figure S2. Signatures of exciton migration occur on a similar timescale to initial singlet fission dynamics. (A) The slight redshift of the singlet excited state absorption (ESA) feature that occurs after photo-excitation has a time constant of approximately 4 ps. (B) The initial change in anisotropy has a smaller 1 ps time constant. These timescales are considerably faster than the ~100 ps secondary rise in the triplet-pair population that we observe in transient absorption.



Figure S3. Isosbestic point during singlet fission in rubrene NP films. The presence of an isosbestic point between the singlet and triplet excited state absorptions suggests that the singlet fission yield is high in the rubrene NP films. Data is shown for an excitation density of  $41 \mu J \text{ cm}^{-2}$ .

## 3 Sample-to-sample variations

We find that the absolute PLQY values are slightly sensitive to the sample preparation conditions, and that they decrease over time. Table 1 summarises the sample-to-sample variation in measured PLQY. For DBP-doped rubrene NPs, we quote the value of 61% since we were able to reproduce this number reliably in freshly-prepared samples. We observe only small changes to the measured excited state dynamics, as shown in Figs. S4 and S5.

Sample	Time between preparation and PLQY measurement	PLQY (%)
Rub	<1 month	7.6, 5.9, 4.2
Rub	18 months	3.6, 2.9
Rub/DBP	<1 month	59, 63, 64, 61
Rub/DBP	18 months	46, 44

 Table 1. Measured values of absolute PLQY for different samples.



**Figure S4. Picosecond photophysics are similar for fresh and aged samples.** Although a direct comparison is impossible owing to the different pump wavelength and excitation density, we measure similar photophysics for both freshly prepared samples and samples kept in a glovebox for one year.



**Figure S5. TCSPC decays are similar for fresh and aged samples.** (A) For pure rubrene NPs, the initial decay is slightly faster (and the PLQY correspondingly slightly lower) than for samples stored longer. The behaviour on longer timescales is very similar. (B) For DBP-doped rubrene NPs, there is very little observable change in the PL decay between fresh and stored samples, although we find that the absolute PLQY decreases from 61% to 46%.

### 4 Estimation of the triplet hopping rate in rubrene

The bimolecular triplet-triplet annihilation rate constant  $\gamma$  is related to the triplet diffusivity *D* in three dimensions through<sup>9</sup>

$$\gamma = 4\pi D R_a \tag{S1}$$

where  $R_a$  is the annihilation radius. The diffusion constant can be written in terms of the triplet hopping rate k and the hopping distance R. In three dimensions<sup>10</sup>

$$D = \frac{kR^2}{6}.$$
 (S2)

For simplicity we will assume that the annihilation radius is equal to the hopping distance since triplets are fairly localised in rubrene<sup>11</sup>. This gives us a simple relationship between the annihilation constant and time constant for triplet hopping:

$$\tau = \frac{1}{k} \approx \frac{2\pi R^3}{3\gamma} \tag{S3}$$

Taking R = 7.18 Å, the b-axis lattice constant of orthorhombic rubrene<sup>12</sup> and using the measured value of  $\gamma = 5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  for rubrene single crystals<sup>13</sup> gives a hopping time of  $\tau \approx 150 \text{ ps}$ .

We can also estimate a lower bound for the annihilation constant on our rubrene nanoparticles from the excitation density dependent triplet dynamics of the rubrene NPs, shown in Fig. 3b of the main text. In the simplest case we can assume that the triplet population dynamics T(t) are governed by only triplet decay and bimolecular annihilation, giving <sup>14</sup>

$$\frac{dT(t)}{dt} = -k_T T(t) - \gamma T^2(t), \tag{S4}$$

where  $k_T$  is the inverse of the triplet lifetime. The solution of this rate equation can be linearised<sup>15</sup>,

$$\frac{1}{T(t)} = \left(\frac{1}{T(0)} + \frac{\gamma}{k_T}\right) \exp\left(k_T t\right) - \frac{\gamma}{k_T},\tag{S5}$$

where T(0) is the triplet population at t = 0. From the simulation presented in Fig. 4b of the main

text, we obtained the ratio of singlet and triplet populations a few ns following excitation, giving us a conversion factor from measured pulse energy at 532 nm in units of  $\mu$ J cm<sup>-2</sup> to triplet excitation density in units of cm<sup>-3</sup>. The conversion factor was then multiplied by two since there are two triplets per triplet-pair state. This procedure gave us a conversion factor of  $9.2 \times 10^{17} \mu$ J<sup>-1</sup> cm<sup>-1</sup>, which we used to convert our measured triplet TA signal at 510 nm into a population density. The inverse of these populations are plotted in Fig. S6 against exp ( $k_T t$ ), where we have taken  $k_T = 10^{-5}$  ns<sup>-1</sup> (ref.<sup>16</sup>).



**Figure S6. Triplet-triplet annihilation in rubrene nanoparticles.** The triplet annihilation dynamics cannot be described by a single annihilation rate constant as suggested by equations (S4) and (S5). This is because the interplay with other excited states, such as triplet-pair states, is not considered. Nevertheless, we can extract order-of-magnitude values for the annihilation rate constant that are similar to that measured for single crystal rubrene.

Applying equation (S5) to the linearised data in Fig. S6 was not possible for a single value of  $\gamma$ . This is in part because the simple rate model in equation (S4) assumes that triplet-triplet annihilation is a loss channel when in fact it can efficiently form triplet-pair states which also contribute to the measured triplet signal<sup>13</sup>. Nevertheless, as shown in Fig. S6, we find that the annihilation rate constants obtained using this over-simplified model are a similar order of magnitude to that measured for rubrene single crystals<sup>13</sup>.

## 5 Ultrafast TA of DBP monomers in solution



**Figure S7. Ultrafast TA of DBP monomers in solution.** (A) Ultrafast TA of DBP dissolved in anhydrous THF at a concentration of  $10^{-4}$ M. We observed a single spectral feature that decayed uniformly with time and is assigned to the S<sub>1</sub> state. (B) TA spectrum associated with the S<sub>1</sub> state of DBP obtained by averaging the TA data from 10 ps onwards. (C) Normalised TA dynamics at 587 nm give the approximately exponential decay of the S<sub>1</sub> state of DBP monomers. The lifetime is ~4 ns.

### 6 Deconvolution of ultrafast TA data

#### 6.1 MCR-ALS procedures

We extracted the spectra and dynamics of the different excited state species from our ultrafast TA data using Multivariate Curve Resolution Alternating Least Squares (MCR-ALS)<sup>17,18</sup>. We generated reference spectra, used to act as starting points for the fitting procedure, in the following ways. We obtained the rubrene singlet spectrum from the measurement of rubrene monomers in solution, by averaging the data from 10 ps onwards. This is the spectrum plotted in Fig. 2b(i) of the main text. This spectrum was then redshifted in energy by 32.7 meV such that the peak coincided with the maximum of the S<sub>1</sub> spectral feature in the solid samples. We obtained the DBP singlet spectrum in an exactly analogous way from the measurement of DBP monomers in solution (Fig. S7b). In this case the required redshift was 55.9 meV. We estimated the rubrene triplet spectrum for the nanoparticle (NP) samples by averaging the pure rubrene NP TA data ( $18 \mu J \text{ cm}^{-2}$ ) from 5 ns onwards. Beyond 5 ns the spectral shape remained unchanged because the singlet component had decayed, thus we judged the remaining spectral features to be representative of excited triplet species. We used the same procedure to obtain a starting spectrum for the triplets in the polycrystalline films.

Next, we grouped all of our ultrafast TA measurements by sample type. For the nanoparticle (NP) samples, this gave six datasets in total: rubrene NPs with and without the 0.5 mol% DBP additive, measured with pump intensities of  $8\mu$ J cm<sup>-2</sup>,  $18\mu$ J cm<sup>-2</sup> and  $41\mu$ J cm<sup>-2</sup>. For the polycrystalline films, we had three datasets: films with 0, 0.1 and 0.5 mol% DBP measured with pump intensities of  $41\mu$ J cm<sup>-2</sup>.

We ran the MCR-ALS algorithm only once for each group of datasets, since the spectral components are common to all samples. Note that the DBP component was excluded for samples of pure rubrene. Grouping the datasets in this way provides a much more tightly constrained deconvolution. We used the reference spectra as described above for the initial point of the fitting procedure. The algorithm was run until convergence was achieved.



**Figure S8.** MCR-ALS residuals. We evaluated the quality of the MCR-ALS reconstructions by plotting the residuals between fitted and measured data. The residuals r are normalised to the maximum TA signal  $\Delta A_{max}$  for each dataset. The residuals are small in all cases, except around t = 0 where coherent artefacts are present in the data, and in the vicinity of the pump scatter.

## 7 Polycrystalline rubrene films



**Figure S9. Polycrystalline rubrene films.** (A) Absorption spectrum of a 50 nm thick spin-coated polycrystalline rubrene film. (B) Optical micrograph of the film showing spherulite crystal structures and visible micron-scale crystalline domains.



**Figure S10.** Triplet losses dramatically reduce the PLQY of rubrene. (A) Triplet and singlet dynamics of rubrene NPs measured by TA (at 510 nm) and TRPL (wavelength integrated) respectively. (B) Triplet and singlet dynamics of a polycrystalline rubrene film. The triplet decay is more rapid, reflecting increased triplet trapping and/or quenching compared to the NPs. This is reflected in the PL dynamics, which also decay more quickly, particularly on microsecond timescales. (C) This results in a dramatic reduction in the steady-state PL of the rubrene film compared to the nanoparticles (the spectra have been normalised to account for differences in absorbed light). The key to obtaining high PLQY in rubrene is therefore to encourage efficient singlet formation through triplet recombination following singlet fission.



**Figure S11.** Addition of DBP does not suppress initial singlet fission in polycrystalline films. (A) Falsecolour map of the transient absorption of a polycrystalline rubrene film containing 0.5 mol% DBP. The triplet signal at 510 nm is very pronounced. (B) MCR-ALS spectra corresonding to the rubrene singlet (orange) rubrene triplet species (blue) and DBP singlet (red). (C) The singlet and triplet dynamics are unchanged despite the addition of DBP. There is only a small amount of energy transfer to DBP, evidenced by the slight rise in the DBP population during the first few tens of picoseconds. Some DBP molecules were photo-excited by the 532 nm pump pulses. (D) despite the apparent lack of energy transfer to DBP occurring on picosecond timescales, and no evidence of singlet fission suppression, most of the photoluminescence comes from DBP rather than rubrene, and it is considerably brighter than the pure rubrene film. This highlights an important point: DBP does not suppress initial singlet fission, instead it reduces the probability of encountering losses associated with triplets and provides a more effective radiative sink for singlet energy (see main text).

#### 8 Kinetic simulations

We modelled the ultrafast TA data using the simple kinetic scheme shown in Fig. 4a of the main text. The rate equations governing the populations of the singlet  $[S_1]$ , strongly-exchange coupled singlet triplet-pair  $[^1(TT)]$ , weakly exchange-coupled singlet triplet-pair  $[^1(T...T)]$ , mixed spin triplet-pairs [(T...T)] and singlet energy collector DBP  $[S_{1c}]$  are given by equations (S6)-(S10).

$$\frac{d[\mathbf{S}_1]}{dt} = -\left(k_r + k_{fret} + k_{sf}\right)[\mathbf{S}_1] - k_{ssa}[\mathbf{S}_1]^2 + k_{tf}[^1(\mathbf{TT})]$$
(S6)

$$\frac{d[^{1}(\mathrm{TT})]}{dt} = k_{sf}[\mathbf{S}_{1}] - (k_{hop} + k_{tf})[^{1}(\mathrm{TT})] + k_{-hop}[^{1}(\mathrm{T}...\mathrm{T})]$$
(S7)

$$\frac{d[^{1}(T...T)]}{dt} = k_{hop}[^{1}(TT)] - (k_{-hop} + k_{spin} + k_{t})[^{1}(T...T)]$$
(S8)

$$\frac{d[(T...T)]}{dt} = k_{spin}[^{1}(T...T)] - k_{t}[(T...T)]$$
(S9)

$$\frac{d[\mathbf{S}_{1c}]}{dt} = k_{fret}[\mathbf{S}_1] - k_{rc}[\mathbf{S}_{1c}]$$
(S10)

#### 8.1 Implementation of the model

The definitions and values of the rate constants are given in Table 2. The values of the rate constants are well constrained by the measured TA data and the optimisation procedure (global least squares fitting to the excitation density dependent singlet and triplet dynamics) was performed principally for cosmetic reasons. We note that values of  $k_{hop}$  and  $k_{-hop}$  were checked against the expected values based on diffusion mediated triplet hopping in the rubrene nanoparticles (see Section 4 and the main text.)

For simulations of pure rubrene samples, we set  $k_{fret} = 0$ . The initial population of the photoexcited singlet state was estimated from the measured power *P*, spot radius at sample position *r* and known repetition rate *f* and wavelength  $\lambda$  of the excitation laser of each experimental setup using

$$N_0 \approx \frac{P}{f\pi r^2} \frac{\lambda}{hc} \frac{1}{d} \left( 1 - 10^{-OD} \right), \tag{S11}$$

where the absorbing sample thickness d was estimated from the measured optical density (*OD*) and known molar absorptivity<sup>19</sup>. A precise measurement of absorbing thickness was impossible since the samples comprised nanoparticles dispersed in a PVA matrix, rather than a continuous film.

We obtained the simulated excited state dynamics corresponding to different experimental measurements by integrating equations (S6)-(S10) using custom-made python code. Note that triplet transient absorption signals were assumed to be proportional to  $[^{1}(TT)]+[^{1}(T...T)]+[(T...T)]$ . The simulated populations were convolved with a Gaussian function with a FWHM of 100 fs to mimic the instrument response of the experimental setup. Since the TA cross sections are unknown for our samples, the triplet and DBP populations were scaled by constant factors to match the experimental data. Residuals are shown in Fig. S12.

#### 8.2 Modelling the inclusion of DBP

To model the inclusion of the singlet energy collector DBP, we initially set  $k_{fret} = 20 \text{ ns}^{-1}$ . Note that since DBP molecules also absorbed the 532 nm pump pulses, we split the initial photoexcitation between S<sub>1</sub> and S<sub>1c</sub> in the ratio 10:1. The mole fraction (0.5%) of DBP in the sample and the ratio of

Rate constant	Description	Value	Source
$k_{sf}$	singlet fission rate $S_1 \rightarrow {}^1(TT)$	$104{\rm ns}^{-1}$	TA data, then optimised
$k_{tf}$	triplet fusion rate $^1(TT) \rightarrow S_1$	$118\mathrm{ns}^{-1}$	TA data, then optimised
$k_{hop}$	triplet hopping rate $^{1}(TT) \rightarrow ^{1}(TT)$	$7\mathrm{ns}^{-1}$	TA data, then optimised
$k_{-hop}$	triplet hopping fusion rate ${}^{1}(TT) \rightarrow {}^{1}(TT)$	$1.2{\rm ns}^{-1}$	optimised, subject to constraint
$k_{spin}$	spin evolution rate $^{1}(TT) \rightarrow (TT)$	$0.25\mathrm{ns}^{-1}$	MFE data, Ref. <sup>20</sup> , fixed
$k_{fret}$	rate of energy transfer to DBP $S_1 \rightarrow S_{1c}$	$20\mathrm{ns}^{-1}$	TA data, fixed
$k_{ssa}$	bimolecular singlet-singlet annihilation rate	$3\times 10^{-17}\text{cm}^3\text{ns}^{-1}$	manually adjusted, then fixed
$k_r$	radiative decay rate of rubrene	$0.0625{\rm ns}^{-1}$	TA data, fixed
$k_{rc}$	radiative decay rate of DBP	$0.25\mathrm{ns}^{-1}$	TA data, fixed
$k_t$	decay rate of rubrene triplets	$10^{-5}  \mathrm{ns}^{-1}$	Ref. <sup>16</sup> , fixed

**Table 2.** Definitions, values and sources of the rate constants used in the model. Note that the optimisation procedure was largely cosmetic: the values of the rate constants are well constrained by the measured TA data.



**Figure S12. Residuals from the simulation of pure rubrene NP film dynamics.** The excited species and excitation density are indicated for each trace. Note that the singlet population was normalised to 1 for the data and simulation.

molar absorptivity at the excitation wavelength (1:10)<sup>19,21</sup> give a ratio of 20:1. We found that 10:1 better reproduced the data, though we note that the model does not reproduce the large effect of singlet-singlet annihilation on the DBP population dynamics so there is some uncertainty in this ratio.

Simply assuming that all of the rubrene singlet states could undergo FRET to DBP yielded the simulation shown in Fig. S13a. In this case, we find that the model underestimates the effect of singlet-singlet annihilation on the DBP population dynamics, but overestimates the depletion of the rubrene

singlet and triplet populations. As discussed in the text, it is likely that the less mobile singlets are not able to find DBP molecules, whilst the more mobile ones that can are particularly susceptible to singlet-singlet annihilation.

We can there assume instead that (arbitrarily) only 50% of the singlet excitons in rubrene can undergo FRET to DBP. To model this we take the average of two simulations, one with  $k_{fret} = 0$ and one with  $k_{fret} = 20 \text{ ns}^{-1}$ . In this case we can reproduce the singlet, triplet and DBP dynamics reasonably well as shown in Fig. S13b, though again, the excitation density dependence of the DBP dynamics is still not captured. This is to be expected since the model does not include diffusion processes.



**Figure S13. Modelling the inclusion of DBP in rubrene NPs.** (A) If all the rubrene singlets are able to undergo FRET to DBP, the depletion of the singlet and triplet populations is overestimated. (B) If instead only half of the rubrene singlets are able to undergo FRET to DBP, the dynamics are reasonably well described. In both cases the effect of singlet-singlet annihilation on the DBP dynamics is underestimated. We suggest that this is because the same mobile singlets that preferentially undergo FRET are also most affected by singlet-singlet annihilation.



**Figure S14. Residuals from the simulation of DBP-doped rubrene NP film dynamics.** The excited species and excitation density are indicated for each trace. Note that the singlet population was normalised to 1 for the data and simulation. The left hand side corresponds to the simulation in Fig. S13a and the right hand side to the simulation in Fig. S13b. Note the difference in the y-axis scales.

# 9 Temperature-dependent PL of rubrene/DBP nanoparticles



**Figure S15. Temperature dependence of steady-state PL.** (A) PL spectra of rubrene NPs at temperatures between 80 K and room temperature. (B) PL spectra of rubrene/DBP NPs.

### 10 Timescales of singlet-singlet annihilation

Fig. S16 shows the effect of normalisation choice on the apparent timescales of singlet-singlet annihilation. In reality, singlet-singlet annihilation affects the dynamics most strongly within the first ten picoseconds, but this is less clear when normalising to the signal maximum.



**Figure S16. Timescales of singlet-singlet annihilation.** Singlet population at three different excitation densities normalised to the signal maximum (left) and to the signal at 200 ps (right). The effect of singlet-singlet annihilation is most pronounced during the first 10 ps, but this is obscured somewhat when normalising to the maximum signal.

#### 11 Estimations of FRET rates

The rate of Förster resonance energy transfer (FRET) between a donor D and acceptor A is given by<sup>19</sup>

$$k = \frac{1}{\tau} \left(\frac{R_F}{R}\right)^6 \tag{S12}$$

where  $\tau$  is the radiative lifetime of the donor, in this case the 16 ns radiative lifetime of rubrene singlet excitons<sup>22,23</sup>, R is the intermolecular distance and the Förster radius  $R_F$  is given by<sup>19</sup>

$$R_F = 0.2108 \left[ \frac{\kappa^2 \Phi_D}{n^4} \int_0^\infty I_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \right]^{\frac{1}{6}}$$
(S13)

where  $\kappa$  is an orientational factor,  $\Phi_D$  is the fluorescence quantum yield of the (isolated) donor, *n* is refractive index,  $I_D$  is the normalised fluorescence spectrum of the donor and  $\epsilon_A$  is the molar absorption coefficient of the acceptor.

Fig. S17 shows the molar absorption coefficients of rubrene and DBP, measured in Refs. 19 and 21 respectively alongside the fluorescence spectrum of rubrene taken from Ref. 19. From the spectral overlaps, we estimate that the rubrene-to-DBP FRET rate is approximately 50 times greater than the rubrene-to-rubrene FRET rate, if all other parameters are equal. This difference can be attributed to the much greater oscillator strength and spectral overlap of DBP.



**Figure S17. Spectral overlap between rubrene and DBP.** Molar absorption coefficients of rubrene and DBP are shown together with their overlap with the rubrene photoluminescence spectrum. From the spectral overlaps, we estimate rubrene-to-DBP FRET to be approximately 50 times faster than rubrene self-FRET.

The Förster radius has been previously calculated as 4.7 nm for the rubrene-DBP pair in solid systems<sup>24</sup>. Based on the relative spectral overlap integrals, we estimate the rubrene-rubrene Förster radius to be 2.5 nm. Taking the smallest intermolecular centre-of-mass separation of 7.2 Å in orthorhombic rubrene<sup>25</sup> as a lower bound for R, we estimate a rubrene-rubrene FRET rate of 10 ps, similar to the singlet fission rate.

We do not know how rubrene molecules pack around DBP molecules, but a centre-of-mass distance of 1 nm would seem reasonable, given the significantly larger size of the DBP molecule. This results in an estimated rubrene-DBP FRET rate of 1.5 ps. At 2 nm separation, this rises to 95 ps.

Photo-excited singlet excitons generated on rubrene molecules directly adjacent to a DBP molecule

are therefore expected to transfer their energy to DBP before singlet fission takes place. However, since the concentration of DBP molecules is low (1 in 200), most photo-generated rubrene singlets are not nearest neighbours with DBP sites. These excitons must therefore diffuse by rubrene-rubrene FRET in order to get close enough to a DBP molecule to transfer their energy.

Whilst a kinetic Monte Carlo simulation, or similar, would be needed to quantitatively determine the likelihood of a randomly generated exciton transferring its energy to DBP via FRET rather than undergoing singlet fission, we can get a sense of how unlikely this is from simple calculations.

In a time t after photo-excitation, a singlet exciton diffusing via rubrene-rubrene FRET has an average mean-squared displacement of

$$\langle r^2 \rangle \approx k a^2 t$$
 (S14)

where k is the rubrene-rubrene FRET rate and a is the distance of a single hop. Let us take the time t when a fraction f of initially generated excitons have undergone singlet fission:

$$1 - f = e^{-k_s f t}.$$
 (S15)

Rearranging for t and inserting into our expression for the mean square displacement, we find

$$\langle r^2 \rangle \approx a^2 \frac{k}{k_{sf}} \ln\left(\frac{1}{1-f}\right).$$
 (S16)

Since we estimate the rubrene-rubrene FRET rate to be approximately equal to the singlet fission rate, the root mean square displacement is approximately

$$r_{rms} \sim a \sqrt{\ln\left(\frac{1}{1-f}\right)}.$$
 (S17)

Again taking *a* to be 7.2 Å, we find that by the time 99% of excitons have undergone singlet fission (f = 0.99) the root mean square displacement of a typical exciton is only around 1.5 nm, or just over two intermolecular separations. Thus we would expect singlet fission to outcompete rubrene-DBP FRET fairly comprehensively and indeed the experiments presented in this work clearly demonstrate that this is the case.

To cross-check this analysis, we estimate the root mean square displacement of rubrene singlet excitons when the elapsed time t corresponds instead to the 16 ns radiative lifetime of rubrene. In this case, we obtain a value of 29 nm, in very close agreement with the reported singlet exciton diffusion length of  $(35 \pm 2)$  nm for disordered, solid rubrene<sup>24</sup>.

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