Supplementary Information

Spin statistics for triplet-triplet annihilation upconversion: exchange coupling, intermolecular orientation and reverse intersystem crossing

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1 Further analysis of transient absorption data

We confirm our assignments (to singlet or triplet states) of spectral features in our transient absorption data by comparing the dynamics.

Fig. S1a shows singlet and triplet PIA spectra in the visible spectral region extracted using multivariate curve resolution alternating least squares (MCR-ALS)\(^1\)\(^2\). Reference spectra used as the starting point of the deconvolution were obtained by time-averaging the data from 0.5–1 ps and 3–7 ns. The concentrations were constrained to be non-negative. The spectra resulting from the MCR-ALS procedure agree well with reported singlet\(^3\) and triplet\(^4\) absorption spectra for rubrene in solution.

The singlet and triplet dynamics extracted using MCR-ALS (Fig. S1b) are characteristic of singlet fission\(^5\). The triplet population rises with a time constant of approximately 3 ps, accompanied by a 50% reduction in the singlet population with a similar time constant. This suggests that singlet fission \(S_1 \rightarrow ^1(TT)\) and triplet-pair fusion \(^1(TT) \rightarrow S_1\) occur simultaneously with a time constant of \(2 \times 3 \text{ ps} = 6 \text{ ps} \sim 10 \text{ ps}\).

In Fig. S1c, we show that the PIA bands at 680 nm and 1170 nm match the singlet dynamics, although an additional fast component is present at 1170 nm. Fig. S1d shows the dynamics at 850 nm and 960 nm, each with the dynamics at 1170 nm, weighted by the absorbance difference between the two wavelengths, subtracted. This removes the singlet component, yielding the residual triplet dynamics, which match those extracted in the visible region by MCR-ALS. This confirms that the peaks at 850 nm and 960 nm arise from triplet excited states.

Figure S1. Transient absorption dynamics. (a) Singlet and triplet PIA spectra extracted in the visible region using MCR-ALS\(^1\)\(^2\). The spectra match previously reported singlet\(^3\) and triplet\(^4\) spectra for rubrene in solution. (b) Extracted singlet and triplet dynamics. (c) Comparison of singlet PIA dynamics. (d) Comparison of triplet PIA dynamics. The singlet component has been removed from the dynamics at 850 nm and 960 nm by subtracting the (suitably scaled) dynamics at 1170 nm.


2 Pump-push-probe spectroscopy of a polycrystalline rubrene film

Figure S2. Evaporated polycrystalline rubrene film. (a) Absorption spectrum of the polycrystalline rubrene film. (b) Microscope image of the film surface, showing micron-scale crystalline texture.

Figure S3. Pump-push-probe spectroscopy at different probe wavelengths. Pump-push-probe spectroscopy for probe wavelengths of 460 nm (a) and 650 nm (b) show no discernable push-induced effects, in contrast to the data at 510 nm (Fig. 7b, main text).

2.1 Alternative explanations for the pump-push-probe data

We find that the effect of our 800 nm push pulses is to enhance the T1 to T3 photo-induced absorption (PIA) when the 400 nm pump is present. In this section we investigate the predicted change in triplet PIA for three possible scenarios and show that only the proposed HL-RISC can give rise to an enhancement.

Let the triplet PIA signal $X$ induced by the 400 nm pump have magnitude $A$ at some arbitrary delay time. Then we have

$$X_{0,0} = 0$$  \hspace{1cm} (S1)  

$$X_{1,0} = A,$$  \hspace{1cm} (S2)

where $X_{i,j}$ denotes the signal with the pump on ($i = 1$), pump off ($i = 0$), push on ($j = 1$) or push off ($j = 0$).
Then, for example, the pump-probe signal is given by:

\[ X_{\text{pump-probe}} = X_{1,0} - X_{0,0} = A - 0 = A. \]  

(S3)

2.1.1 The push acts as a second pump

The first case we consider is that the push pulse acts as a pump from S\(_0\) to S\(_N\) (for example through two-photon absorption) or even from S\(_0\) to T\(_1\). Let the triplet PIA signal induced by the push alone have magnitude \( B \) at the same arbitrary delay time:

\[ X_{0,1} = B. \]  

(S4)

When the push is preceded by the 400 nm pump pulse, some of the ground state has already been depleted by the first pump pulse. As a result, the magnitude of the push-induced triplet PIA will be less than \( B \), by an amount \( \delta_1 \), giving

\[ X_{1,1} = X_{1,0} + X_{0,1} - \delta_1 = A + B - \delta_1. \]  

(S5)

The pump-push-probe signal in this case is

\[ X_{\text{pump-push-probe}} = X_{1,1} - X_{0,1} = A + B - \delta_1 - B = A - \delta_1, \]  

(S6)

and so even if the push pulse acts as a second pump, the effect is to reduce the pump-push-probe signal rather than enhance it.

2.1.2 Internal conversion from T\(_2\) to T\(_1\)

The second case to consider is that the push pulse excites the T\(_1\) to T\(_2\) transition but that T\(_2\) undergoes internal conversion to T\(_1\). In this case, the push pulse has no effect in the absence of the pump:

\[ X_{0,1} = 0, \]  

(S7)

but causes a reduction \( \delta_2 \) in the pump-induced PIA due to depletion of the T\(_1\) state:

\[ X_{1,1} = X_{1,0} - \delta_2 = A - \delta_2, \]  

(S8)

and therefore again resulting in a reduced pump-push-probe signal

\[ X_{\text{pump-push-probe}} = X_{1,1} - X_{0,1} = A - \delta_2 - 0 = A - \delta_2, \]  

(S9)

where the magnitude \( \delta_2 \) of the signal reduction would decrease to zero as the T\(_1\) state is repopulated by internal conversion from T\(_2\).

2.1.3 HL-RISC from T\(_2\) to S\(_1\)

In this case, the push pulse excites the T\(_1\) to T\(_2\) transition and T\(_2\) undergoes rapid HL-RISC to form S\(_1\). S\(_1\) then undergoes singlet fission, forming T\(_1\)+T\(_1\). In the absence of the pump, the push pulse has no effect:

\[ X_{0,1} = 0. \]  

(S10)

When the pump pulse is present, T\(_1\) is again depleted by amount \( \delta_3 \). However, since each S\(_1\) state formed by the subsequent HL-RISC produces two T\(_1\) states through singlet fission, the triplet PIA is enhanced by an amount \( 2\delta_3 \), giving

\[ X_{1,1} = X_{1,0} - \delta_3 + 2\delta_3 = A + \delta_3, \]  

(S11)
and hence a pump-push-probe signal of

\[ X_{\text{pump-push-probe}} = X_{1,1} - X_{0,1} = A + \delta_3 - 0 = A + \delta_3. \]  

Thus, HL-RISC is predicted to produce an enhancement of the triplet PIA, and the dynamics of the enhancement should match the pump-probe singlet fission dynamics.

### 3 Rate equations and constants for the extended kinetic scheme

The rate equations for model 2 (Fig. 7 in the main text) can be written as follows:

\[
\frac{d[T_1]}{dt} = G_T + 2k_D \sum_{l=1}^{9} |(T...T)^l| + k_{IC1} \sum_{m=x,y,z} |C_{TF}^l|^2 \langle TT \rangle_m + k_{IC21}[T_2] - 2k_{TTA}[T_1] \tag{S13}
\]

\[
\frac{d[(T...T)^l]}{dt} = \frac{1}{9} k_{TTA} [T_1] - k_D [(T...T)^l] - k_{TF} \left[ |C_S^l|^2 + |C_T^l|^2 + |C_Q^l|^2 \right] \langle T...T \rangle^l
\]

\[ + k_{TS} \left[ |C_S^l|^2 \langle TT \rangle + \sum_{m=x,y,z} |C_{TM}^l|^2 \langle TT \rangle_m + \sum_{m=a,b,x,y,z} |C_{QM}^l|^2 \langle TT \rangle_m \right] \tag{S14}
\]

\[
\frac{d^5(TT)_m}{dt} = k_{TF} \sum_{l=1}^{9} |C_{QM}^l|^2 \langle T...T \rangle^l - k_{TS} \left( \sum_{l=1}^{9} |C_{QM}^l|^2 \right) \langle TT \rangle_m \tag{S15}
\]

\[
\frac{d^3(TT)_m}{dt} = k_{TF} \sum_{l=1}^{9} |C_{TM}^l|^2 \langle T...T \rangle^l - k_{TS} \left( \sum_{l=1}^{9} |C_{TM}^l|^2 \right) \langle TT \rangle_m - (k_{IC1} + k_{IC2}) |C_{TM}^l|^2 \langle TT \rangle_m \tag{S16}
\]

\[
\frac{d^1(TT)}{dt} = k_{TF} \sum_{l=1}^{9} |C_S^l|^2 \langle T...T \rangle^l - k_{TS} \left( \sum_{l=1}^{9} |C_S^l|^2 \right) \langle TT \rangle_m + k_{SF}[S_1] - k_{SF} \langle TT \rangle_m \tag{S17}
\]

\[
\frac{d[S_1]}{dt} = G_S + k_{SF} \langle TT \rangle_m - k_{SF} [S_1] - k_{SF} [S_1] + k_{RISC}[T_2] \tag{S18}
\]

\[
\frac{d[T_2]}{dt} = k_{IC2} \sum_{m=x,y,z} |C_T^l|^2 \langle TT \rangle_m - (k_{IC21} + k_{RISC})[T_2]. \tag{S19}
\]

Since we assumed an effective linear annihilation rate constant \(k_{TTA}'\), the equations were solved numerically using linear algebra. Definitions of rate constants and overlap factors are given in the main text. Table S1 gives the values of the rate constants used in the simulations and indicates the source of each one. Fig. S4 shows the sensitivity of the model to different rate constants.

### Table S1. Values and sources of the main rate constants.

| Rate       | Value (ns\(^{-1}\)) | Source               |
|------------|----------------------|----------------------|
| \(k_S\)    | 0.0625               | Refs. 6,7            |
| \(k_{SF}\) | 100                  | Approximated from TA data (Fig. S1) |
| \(k_{-SF}\)| 100                  | Approximated from TA data (Fig. S1) |
| \(k_{TS}\) | 10                   | Lower bound on triplet hopping rate, estimated from the TTA rate constant in Ref. 8, larger values have no effect (Fig. S4) |
| \(k_{TF}\) | 5                    | \(= k_{TS}/2\) for 1D diffusion |
| \(k_D\)    | 0.1                  | Approximate, estimated from onset of bimolecular TTA in Fig. 4 |
| \(k_{IC1}\)| 17                   | Energy gap law (Fig. 6) |
| \(k_{IC2}\)| 12                   | Energy gap law (Fig. 6) |
| \(k_{IC21}\)| 8                    | Energy gap law (Fig. 6) |
| \(k_{RISC}\)| 5000                 | Approximate instrument response of pump-push-probe |
Figure S4. Sensitivity of model 2 to different rate constants. Each rate constant was varied by ±3 orders of magnitude about its original value and the effect on η monitored. In particular, we highlight that the value of η does not depend on $k_{SF}$ or $k'_{TTA}$ and that increasing the triplet hopping rates further also has little impact. Note that $k_{IC}$ is the sum of $K_{IC1}$ and $k_{IC2}$. 
4 Literature values of spin statistical factors and energy levels

Supplementary Tables S2 and S3 give non-exhaustive experimental literature values for the spin statistical factor of diphenylanthracene (DPA) and rubrene and the $T_2$ energy in rubrene. These values were used to indicate the spread of reported experimental values shown on Fig. 9d of the main text.

**Table S2.** Experimental values of the spin statistical factor for rubrene and DPA.

| Annihilator | System          | $\eta$ (%) | Reference |
|-------------|-----------------|------------|-----------|
| DPA         | thin film       | 37         | 9         |
| DPA         | solution        | 44         | 10        |
| DPA         | solution        | 36         | 11        |
| DPA         | solution        | 45         | 12        |
| DPA         | solution        | 48         | 14        |
| DPA         | solution        | 52         | 15        |
| rubrene     | solid           | 72         | 16        |
| rubrene     | solution        | 61(5)      | 17,18     |
| rubrene     | solution        | 15         | 19        |

$^a$The value given is the upconversion quantum yield, which is very close to $\eta$ since the other efficiencies are near unity.
$^b$The value and error are taken from the measurements in Ref. 17. Very similar values were reported in Ref. 18.
$^c$It is unclear why the values reported in Ref. 19 are so much lower than the others.

**Table S3.** Experimental values of the $T_2$ energy level in rubrene. Note that only near-infrared (NIR) transient absorption (TA) data is included: some authors report the $T_1 \rightarrow T_2$ transition at 800 nm$^{20,21}$, giving a $T_2$ energy of 2.69 eV however their probe spectra do not extend far enough into the NIR to determine the true transition energy. ISC stands for intersystem crossing.

| System     | Method                  | $T_2$ energy (eV) | Reference |
|------------|-------------------------|-------------------|-----------|
| solution   | thermally activated ISC | 2.38-2.40         | 22        |
| thin film  | NIR TA                  | 2.40              | 23        |
| nanoparticle film | NIR TA   | 2.43              | This work |
| crystal    | NIR TA                  | 2.55              | 24        |
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