

Supporting Information for

Annihilation vs. Excimer Formation by the Triplet Pair in Triplet-Triplet Annihilation Photon Upconversion

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1. Notes

1.1 Chemicals

Sensitizer molecules, PdOEP and PtTBTP, were purchased from PorphyChem. Perylene, cresyl violet and anhydrous solvents with inert gas protection were purchased from Sigma Aldrich. All chemicals were used as received.

1.2 TTA-UC sample preparation

All TTA-UC samples were prepared in an Mbraun glove box having oxygen and water levels less than 1 ppm. Cuvettes were sealed with cap and PTFE septum. Photon upconversion measurements were performed immediately after the preparation.

1.3 Steady state emission

Steady state emission of TTA-UC samples with PtTBTP was measured on an Edinburgh Instruments FLS 1000 spectrofluorometer. A Light Emitting Diode (LED) with collimator and focus lenses was used as a non-coherent excitation source. The LED light source (617 nm), power supply and all the optical units were purchased from Thorlabs (M617L3 mounted LED). The connection and supporting units were home-made from non-fluorescent plastic (PLA) by 3D-printing. Steady state emission measurements of TTA-UC samples with PdOEP were carried out using a Millennia Vs continuous laser from Spectra-Physics Lasers (532 nm) as excitation source and a 533 nm notch filter was used to protect the detector.

1.4 Time-resolved spectroscopy

Phosphorescence quenching was measured on an Edinburgh FLS 1000 spectrofluorometer with a microsecond flash lamp as excitation source. The pulse width of the flash lamp was 1 – 2 μ s and the response width of the PMT-900 detector was 600 ps. The fluorescence lifetime of perylene was measured on the same spectrofluorometer using a microchannel plate photomultiplier tube (MCP-PMT) and a pulsed diode laser (405 nm, 1 MHz) as the excitation source. The laser pulse width was 60 ps and the response width of the MCP-PMT was less than 25 ps. Luminescence decays were fitted using a monoexponential equation:

$$I(t) = I_0 e^{-(t/\tau)}$$

where $I(t)$ is the emission intensity at time t after excitation, I_0 is the emission intensity immediately after excitation and τ is the lifetime. Reconvolution fitting was performed using a script written in origin C.

Transient absorption was measured on an Edinburgh Instrument LP 980 spectrometer. A Spectra-Physics Nd:YAG 532 nm laser (pulse width \sim 7 ns) coupled to a Spectra-Physics primoscan optical parametric oscillator (OPO) was used as pump source ($\lambda_{\text{pump}}=617$ nm). PMT or ICCD detectors were used for recording transient kinetics or spectra, respectively.

1.5 Determination of energy levels of the molecular components

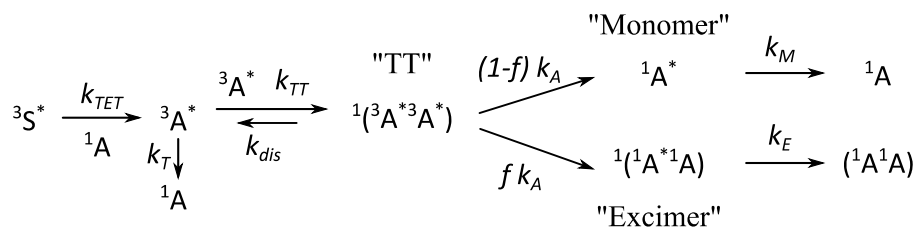
The energy of the first singlet excited state of perylene, PdOEP and PtTBTP were determined from their E_{0-0} values from absorption and emission spectra (Figure 1b). The energy of the first excited triplet state of PdOEP and PtTBTP were determined from the phosphorescence spectra (Figure 1b). Due to the low intersystem crossing quantum yield, the triplet energy of perylene cannot be obtained from the emission spectrum, instead the literature value of 1.53 eV was used.¹

1.6 Kinetic models of the proposed mechanisms.

The descriptions, illustrations, and rate equations for mechanism 1, 2, and 3, are here shown.

1.6.1 Mechanism 1

In mechanism 1, monomers and excimers are both formed from the triplet pair in a parallel fashion. The schematic illustration is shown in Scheme S1.



Scheme S1. The schematic illustration of monomer and excimer formation during TTA by mechanism 1.

Rate equations of mechanism 1:

$$\frac{d[{}^3S^*]}{dt} = G - k_{ph}[{}^3S^*] - k_{TET}[{}^3S^*][{}^1A]$$

$$\frac{d[{}^3A^*]}{dt} = k_{TET}[{}^3S^*][{}^1A] - 2k_{TT}[{}^3A^*]^2 - k_T[{}^3A^*] + 2k_{dis}[({}^3A^*{}^3A^*)]$$

$$\frac{d[(^3A^*3A^*)]}{dt} = k_{TT}[^3A^*]^2 - k_{dis}[(^3A^*3A^*)] - k_A[(^3A^*3A^*)]$$

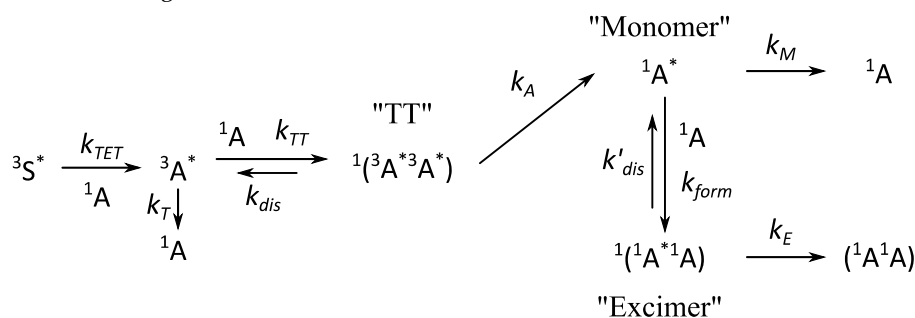
$$\frac{d[^1A^*]}{dt} = (1-f)k_A[(^3A^*3A^*)] - k_M[^1A^*]$$

$$\frac{d[(^1A^*1A)]}{dt} = fk_A[(^3A^*3A^*)] - k_E[(^1A^*1A)]$$

The factors G , k_{ph} , k_{TET} , k_{TT} , k_{dis} , k_A , k_T , k_M and k_E are the generation rate constant of triplet sensitizer, phosphorescence decay rate constant of sensitizer, triplet-triplet energy transfer rate constant, formation rate constant of triplet pair, dissociation rate constant of triplet pair, annihilation rate constant inside the triplet pair, fluorescence rate constant of annihilator monomer, and fluorescence rate constant of annihilator excimer, respectively. Variables $[^3S^*]$, $[^1A]$, $[^3A^*]$, $[(^3A^*3A^*)]$, $[^1A^*]$ and $[(^1A^*1A)]$ are the concentrations of triplet sensitizer, ground state annihilator, triplet annihilator, triplet pair, excited singlet monomer of annihilator, and excimer of annihilator, respectively. Literature values of the dissociative decay lifetime of triplet pairs of aromatic molecules like anthracene or rubrene are usually 10 ~ 100 ns.²⁻⁴ Annihilation inside the triplet pair is fast, and the TTA rate is mainly dependent on the bimolecular triplet pair formation.⁵⁻⁷ The triplet pair can form both singlet monomer and excimer and the fraction of excimer formation is f .

1.6.2 Mechanism 2

In mechanism 2, monomers are formed from the triplet pair and excimers are formed from the diffusion induced association of singlet excited state monomer and ground state monomer. The schematic illustration is shown in Scheme S2.



Scheme S2. The schematic illustration of monomer and excimer formation during TTA in mechanism 2.

Rate equations of mechanism 2:

$$\frac{d[^3S^*]}{dt} = G - k_{ph}[^3S^*] - k_{TET}[^3S^*][^1A]$$

$$\frac{d[^3A^*]}{dt} = k_{TET}[^3S^*][^1A] - 2k_{TT}[^3A^*]^2 - k_T[^3A^*] + 2k_{dis}[(^3A^*3A^*)]$$

$$\frac{d[(^3A^*3A^*)]}{dt} = k_{TT}[^3A^*]^2 - k_{dis}[(^3A^*3A^*)] - k_A[(^3A^*3A^*)]$$

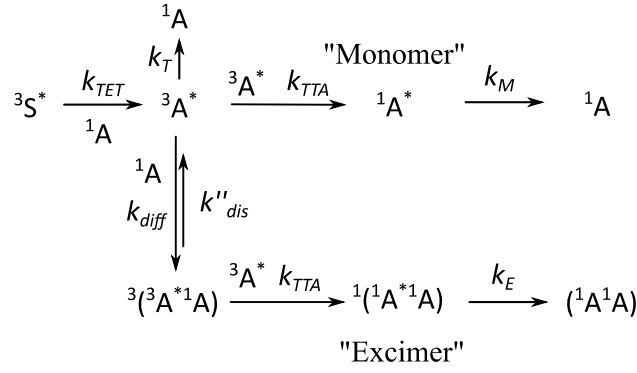
$$\frac{d[^1A^*]}{dt} = k_A[(^3A^*3A^*)] - k_{form}[^1A^*][^1A] + k'_{dis}[(^1A^*1A)] - k_M[^1A^*]$$

$$\frac{d[(^1A^*1A)]}{dt} = k_{form}[^1A^*][^1A] - k'_{dis}[(^1A^*1A)] - k_E[(^1A^*1A)]$$

where k_{form} and k'_{dis} are the rate constants of excimer formation through diffusion and excimer dissociation.

1.6.3 Mechanism 3

In mechanism 3, triplet annihilators can associate with ground state annihilator to form a stable dimer, which readily forms an excimer after annihilation. The schematic illustration is shown in Scheme S3.



Scheme S3. The schematic illustration of monomer and excimer formation during TTA in mechanism 3.

Rate equations of mechanism 3:

$$\frac{d[{}^3S^*]}{dt} = G - k_{ph}[{}^3S^*] - k_{TET}[{}^3S^*][{}^1A]$$

$$\frac{d[{}^3A^*]}{dt} = k_{TET}[{}^3S^*][{}^1A] - 2k_{TTA}[{}^3A^*]^2 - k_T[{}^3A^*] - k_{diff}[{}^3A^*][{}^1A] + k''_{dis}[{}^3A^*{}^1A]$$

$$\frac{d[{}^3A^*{}^1A]}{dt} = k_{diff}[{}^3A^*][{}^1A] - k''_{dis}[{}^3A^*{}^1A] - k_{TTA}[{}^3A^*{}^1A][{}^3A^*]$$

$$\frac{d[{}^1A^*]}{dt} = k_{TTA}[{}^3A^*]^2 - k_M[{}^1A^*]$$

$$\frac{d[{}^1A^*{}^1A]}{dt} = k_{TTA}[{}^3A^*{}^1A][{}^3A^*] - k_E[{}^1A^*{}^1A]$$

where k_{diff} and k''_{dis} are the rate constants of (T_1S_0) formation through diffusion and the dissociation of (T_1S_0), respectively, and k_{TTA} is the rate constant of triplet triplet annihilation.

1.7 Quantum yield calculations

The overall photon upconversion quantum yield (Φ_{UC}) is defined as:

$$\Phi_{UC} = \frac{\text{Photon number emitted}}{\text{Photon number absorbed}}$$

The theoretical limitation of Φ_{UC} for the TTA-UC process is 50% because TTA requires two low energy triplet molecules to form one high energy singlet molecule and one ground state molecule. The quantum yield was determined using the relative method:

$$\Phi_{UC} = \Phi_R \times \frac{\int F_{UC}(\lambda) d\lambda}{\int F_R(\lambda) d\lambda} \times \left(\frac{n_{UC}}{n_R}\right)^2 \times \frac{I_R}{I_{UC}} \times \frac{1 - 10^{A_R}}{1 - 10^{A_{UC}}}$$

where Φ_R is the fluorescence quantum yield of the reference sample, $F_i(\lambda)$ is the emission intensity function, n_i is the refractive index of the solvent, I_i is the excitation intensity and A_i is the absorbance of the sample at the excitation wavelength (617 nm). Cresyl violet was used as emission reference. It has a fluorescence quantum yield in methanol of 0.54.⁸

1.8 Stern-Volmer analysis

The triplet energy transfer rate constant (k_{TET}) was calculated from the Stern-Volmer quenching model as displayed below. Variable $[A]$ is the concentration of annihilator, while τ_0 and τ are the decay lifetimes of the sensitizer phosphorescence in presence and absence of annihilator, respectively.

$$\frac{\tau_0}{\tau} = 1 + k_{TET}\tau_0[A]$$

1.9 Estimation of relative intensities of monomer and excimer emission

For mechanism 2: excimers are formed through diffusion of excited (S_1) and ground state annihilator molecules. Assuming Φ_E is proportional to the rate of excimer formation from singlet monomer $\Phi_E \propto k_{Ex}[{}^1S][{}^1S^*]$, the ratio of Φ_E in low viscosity (Φ_{ELow}) and high viscosity (Φ_{EHigh}) can be written as (note that under our experimental conditions $[{}^1S]$ is assumed to be constant.):

$$\frac{\phi_{ELow}}{\phi_{EHigh}} \propto k_{ExLow}/k_{ExHigh} \cdot [^1S_{Low}^*]/[^1S_{High}^*]$$

According to the viscosity dependence of the diffusion rate constant k_{Ex} the ratio can be rewritten as:

$$\frac{\phi_{ELow}}{\phi_{EHigh}} \propto \eta_{High}/\eta_{Low} \cdot [^1S_{Low}^*]/[^1S_{High}^*]$$

Where η_i is the viscosity of the high and low viscosity solvents. As the singlet population also is proportional to the singlet monomer quantum yield Φ_M we have that:

$$\frac{\phi_{ELow}}{\phi_{EHigh}} \propto \eta_{High}/\eta_{Low} \cdot \phi_{MLow}/\phi_{MHigh}$$

Putting in the viscosities for hexadecane (2.8 cP) and hexane (0.3 cP) and the corresponding ϕ_M values in hexadecane (5%) and hexane (2%), we can conclude that if mechanism 2 was dominating there should be a decrease in excimer emission ϕ_E . We observe an increase of almost a factor 2 supporting a major contribution from mechanism 1 in the low concentration regime.

1.10 Excimer emission in perylene solutions.

Time resolved emission of perylene in different solvents was recorded using 1 mm cuvettes in front face mode (Figure S5). An extra decay component at longer wavelength was observed for perylene solutions at high concentration (Table S1). The extra decay component has longer lifetime and is assigned to the excimer emission of perylene. Lifetimes (τ) of both monomer and excimer increase with solvent viscosity, since the non-radiative decay through molecular motion was restricted. A higher fraction of excimer emission was observed in polar solvents, which is in accordance with the charge transfer character of the perylene excimer.

1.11 Transient absorption and delayed fluorescence in THF

Delayed fluorescence from the annihilator is a result of the excited singlet states formed through TTA. The rate equation of the annihilator in its excited singlet state (neglecting excimer formation and intersystem crossing) can be expressed as:

$$\frac{d[^3A^*]}{dt} = -k_T[^3A^*] - 2k_{TTA}[^3A^*]^2 \quad (\text{eq. 1}) \quad \frac{d[^1A^*]}{dt} = k_{TTA}[^3A^*]^2 - k_F[^1A^*] \quad (\text{eq. 2})$$

where $[^1A^*]$ is the concentration of the annihilator in its singlet excited state and k_F is rate constant of fluorescence. The singlet state of perylene is much shorter than the TTA-UC process (Figure S5), resulting in the emission dynamics mirroring the rate of the singlet excited state formation. Numerical fitting of the delayed fluorescence (Figure S10; Eq 1-2) showed consistent k_{TTA} and k_T values with those obtained from transient absorption data. Figure S10d displays the emission dynamics recorded at 565 nm (excimer emission). The excimer emission occurs at similar timescales as monomer emission, showing that it is a result of TTA.

1.12 Diffusion coefficient and TTA possibility calculations.

Diffusion coefficients (D) in solutions can be calculated by the empirical correlation developed by Wilke Chang.⁹

$$D = 7.4 \times 10^{-8} \frac{(xM)^{0.5}T}{\eta V^{0.6}}$$

where x is the association number of solvent, M is the molecular weight of solute, T is the temperature, η is the viscosity of the solvent, and V is the molecular volume of the solute. The diffusion controlled bi-molecular rate interaction constant k_{diff} at a bi-molecular collision radius r can be calculated from Smoluchowski equation:

$$k_{diff} = 4\pi rND$$

Considering that TTA is a special case of Dexter electron exchange, its typical interaction radius is about 10 Å. The possibility of TTA at that distance can be then calculated by the relative ratio between k_{TTA} and k_{diff} .¹⁰⁻¹¹

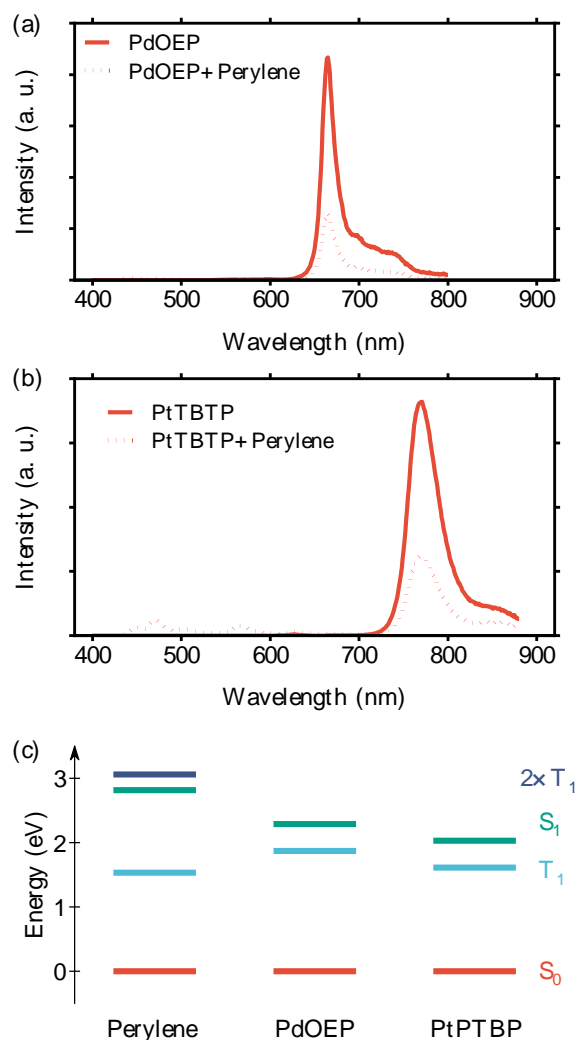


Figure S1. (a), (b) Emission spectra of sensitizer and sensitizer/annihilator solutions excited at 532 nm (PdOEP) or 617 nm (PtTBTP). The concentration of sensitizers were 10 μM and the concentration of perylene was 100 μM (c) The energy diagram of PdOEP, PtTBTP and perylene.

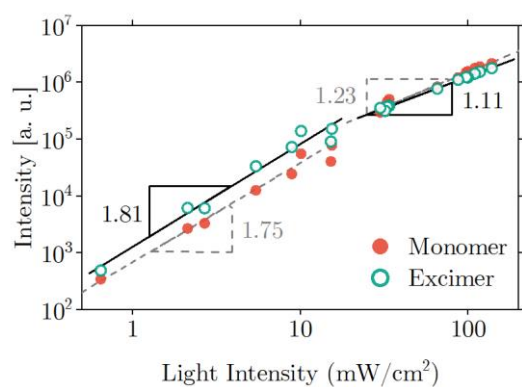


Figure S2. The excitation intensity dependency of TTA-UC in THF solutions (10 μM PtTBTP and 1 mM perylene).

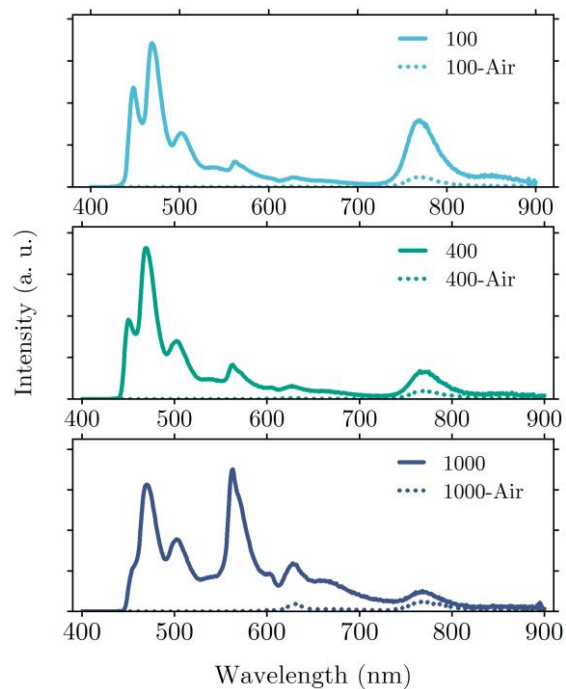


Figure S3. Emission spectra in deoxygenated (solid lines) or ambient (dotted lines) conditions in THF (10 μM PtTBTP and 100, 400 or 1000 μM perylene) when they are excited at 617 nm with 138 mW/cm².

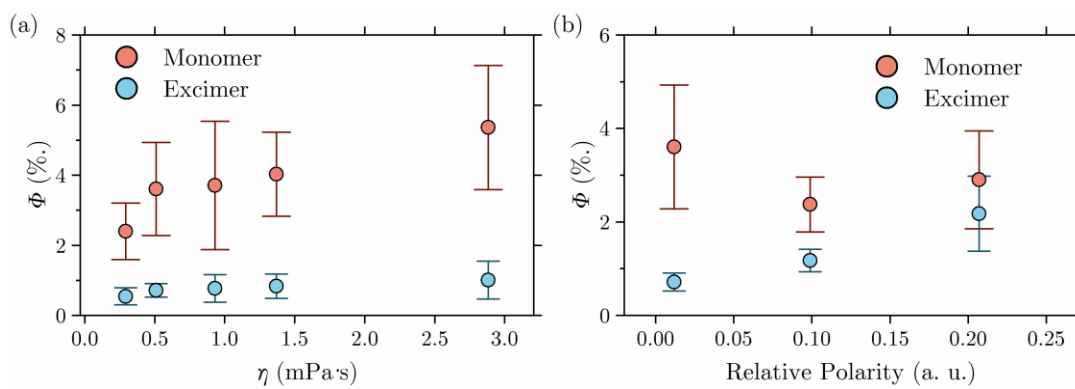


Figure S4. Absolute quantum yield of monomer and excimer emission in TTA-UC vs. (a) solvent viscosity and (b) polarity. Error bar show one standard deviation.

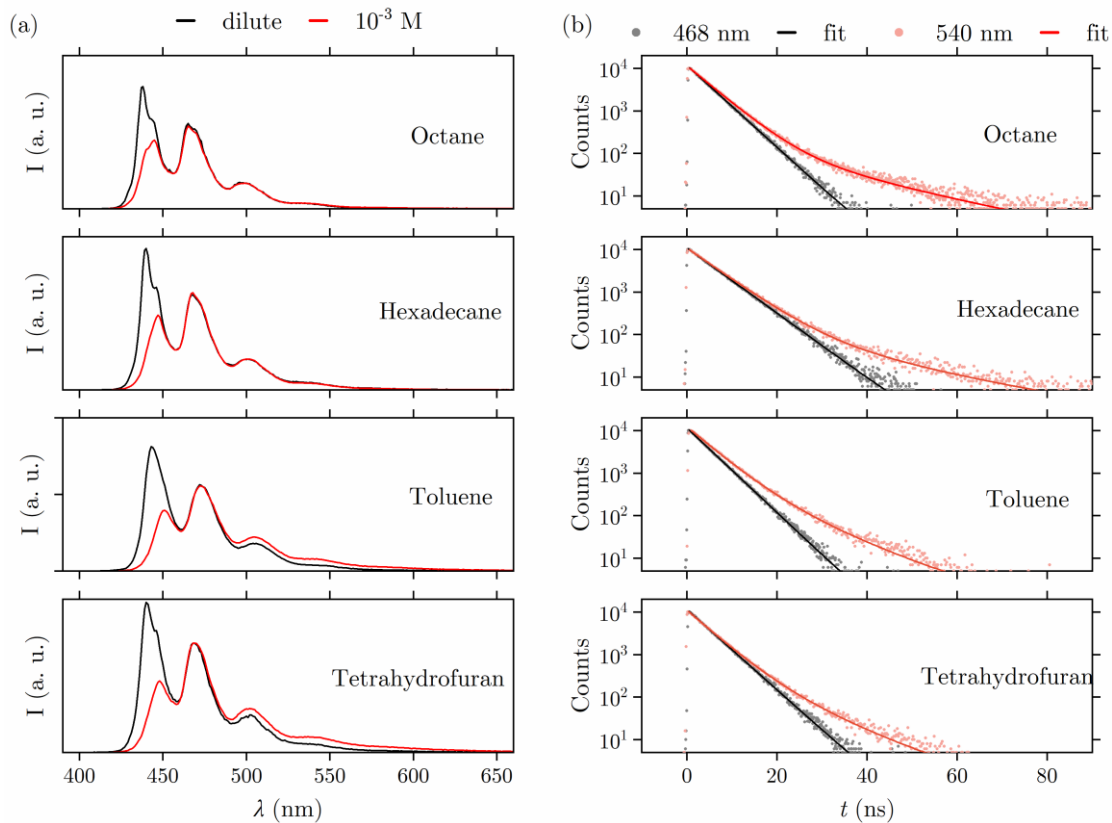


Figure S5. (a) Normalized emission spectra of pure annihilator (excited at 375 nm) in different solvents; (b) Time resolved emission of perylene at 540 nm in different solvents.

Table S1. Fitting results of perylene monomer (M) and excimer (E) emission at 540 nm in different solvents.

Solvent	τ_M (ns)	f_M	τ_E (ns)	f_E
hexane	4.64	95.3%	16.3	4.7%
octane	4.86	92.0%	17.0	8.0%
hexadecane	5.79	92.7%	18.4	7.63%
toluene	4.70	82.2%	10.3	17.8%
tetrahydrofuran	4.54	84.2%	9.87	15.8%

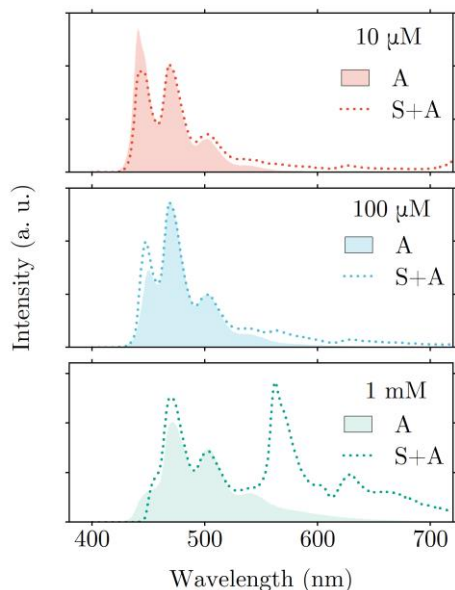


Figure S6. Normalized emission spectra of pure annihilator (excited at 380 nm, 25.8 $\mu\text{W}/\text{cm}^2$) and sensitizer/annihilator (excited at 617 nm, 138 mW/cm^2) solutions in THF (10 μM PtTBTP and 10, 100 or 1000 μM perylene).

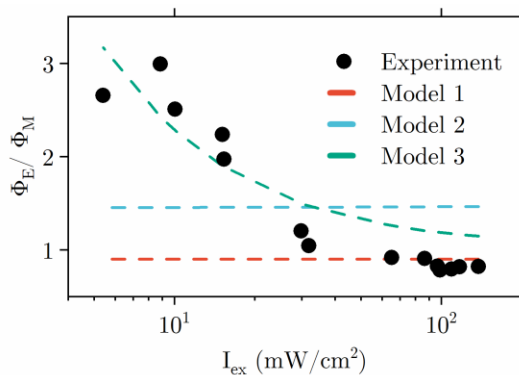


Figure S7. Relative ratio between the quantum yield of monomer and excimer emission of 10 μM PtTBTP and 1 mM perylene in THF, under different intensities of excitation. Simulated curves are shown as lines and are based on mechanism 1-3.

Table S2. Fitting parameters of model 1-3.

paramters	Model 1	Model 2	Model 3
k_{TET} ($\text{M}^{-1}\text{s}^{-1}$)	1.38×10^9	1.38×10^9	1.38×10^9
k_T (s^{-1})	6.56×10^3	6.56×10^3	6.56×10^3
k_{TT} ($\text{M}^{-1}\text{s}^{-1}$)	1.09×10^{10}	1.20×10^{10}	9.51×10^9
k_A (s^{-1})	1.01×10^8	4.13×10^7	4.79×10^8
f	0.143	/	/
k_{form} ($\text{M}^{-1}\text{s}^{-1}$)	/	1.20×10^{10}	/
k'_{dis} (s^{-1})	/	5.21×10^6	/
k_{diff} ($\text{M}^{-1}\text{s}^{-1}$)	/	/	4.55×10^6
k_M (s^{-1})	2.22×10^8	2.22×10^8	2.22×10^8
k_E (s^{-1})	5.68×10^7	5.68×10^7	5.68×10^7

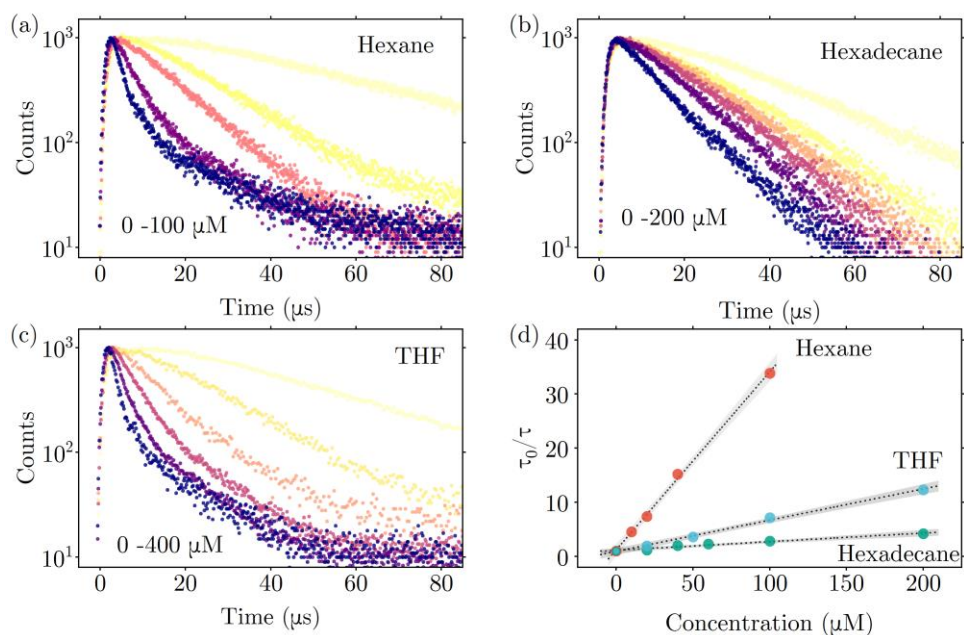


Figure S8. (a-c) Time resolved PtTBTP emission at 770 nm in hexane, hexadecane or THF solutions with a varying concentration of perylene. (d) Stern-Volmer plots for different solvents. The linear fits are shown as dotted lines, and the grey thick lines represent a 95% confidence interval of the fit.

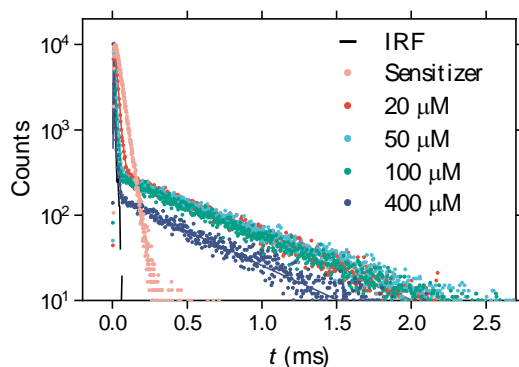


Figure S9. Time resolved phosphorescence decay at 770 nm of solutions containing 10 μM PtTBTP and different concentrations of perylene in THF, when excited at 617 nm.

Table S3. Phosphorescence fitting of TTA-UC samples in THF.

C[perylene] (μM)	τ_1 (μs)	f_1^a	τ_2 (μs)	f_2	Φ_{ph}^b	Φ_{prompt}	Φ_{BET}
20	16.1	74.8%	582	25.2%	22.8%	17.1%	5.74%
40	6.82	53.7%	643	46.3%	13.0%	6.98%	6.02%
100	2.85	37.78%	594	62.22%	7.55%	2.85%	4.70%
400	0.86	20.4%	535	75.5%	3.14%	0.64%	2.37%

a. The factor f is the fractional contribution of the decay component. b. Φ_{ph} , Φ_{prompt} , and Φ_{BET} stands for the quantum yield of overall phosphorescence quantum yield, prompt phosphorescence quantum yield and phosphorescence quantum yield due to back energy transfer, respectively.

Table S4. Fitting results of transient absorption at 485 nm of 2 μM PtTPTB and 1 mM perylene in solvents with different viscosity. The excitation wavelength is 617 nm.

Solvent	η (mPa·s)	k_{TTA} ($\text{M}^{-1}\text{S}^{-1}$)	k_T (s^{-1})	D (m^2s^{-1}) ^a	k_{diff} ^b	γ_{TTA} ^b
Hexane	0.29	9.22×10^9	5.85×10^3	5.06×10^{-9}	3.96×10^{10}	0.233
Octane	0.51	7.48×10^9	4.93×10^3	2.90×10^{-9}	2.27×10^{10}	0.329
Cyclohexane	0.93	4.67×10^9	4.06×10^3	1.59×10^{-9}	1.24×10^{10}	0.375
Dodecane	1.37	3.07×10^9	2.23×10^3	1.08×10^{-9}	8.44×10^9	0.363
Hexadecane	2.88	1.49×10^9	1.15×10^3	5.12×10^{-10}	4.01×10^9	0.372

a. The values of perylene diffusivity (D) in different solvents were calculated from the Wilke Chang correlation.⁹ b. The diffusion rate constant (k_{diff}) was calculated using an assumption that the TTA encounter distance is about 10 Å, due to the Dexter electron exchange mechanism of TTA. The TTA possibility (γ_{TTA}) is then defined as the TTA interaction possibility of triplet perylene when reaching a distance of 10 Å.¹⁰⁻¹¹

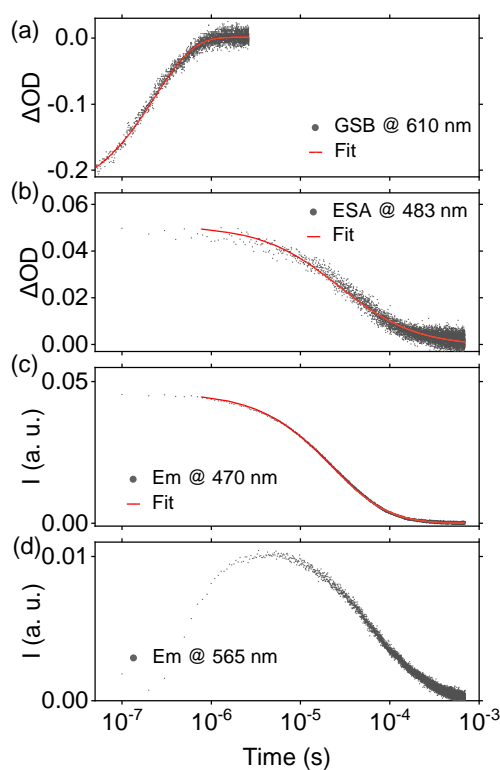


Figure S10. (a-b) Transient absorption decays and (c-d) emission decays of 10 μM PtTBTP and 1 mM perylene in deoxygenated THF after excitation at 617 nm by a short laser pulse. All the decay traces are recorded using the same detector and same laser source.

3. References

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