

Supporting information for:

Triplet and singlet exciton diffusion in disordered rubrene films: implications for photon upconversion

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Materials

Sublimation grade Rub and chloranil were purchased from TCI; DBP, PS and toluene were purchased from Merck. The synthesis of triplet sensitizer PdPc was published elsewhere.¹ Chemical structures of the molecules used in this study are depicted in Fig. 1b in the main paper.

Film preparation

Materials were dissolved in toluene at the concentrations of 50 mg/mL (PS), 10 mg/mL (Rub), 1 mg/mL (PdPc), 1 mg/mL (DBP), 1 mg/mL (chloranil) and mixed at appropriate ratios to result in six different sets of films with varying quencher concentration (0 – 1 wt%): i) Rub(80 wt%)/PS films (80 wt% of rubrene in PS); ii) Rub(80 wt%)/PS films with 0.1 wt% of PdPc; iii) Rub(80 wt%)/PS films with 0.1 wt% of PdPc and 0.5 wt% of DPB; iv) neat Rub films; v) neat Rub films with 0.1 wt% of PdPc; vi) neat Rub films with 0.1 wt% of PdPc and 0.5 wt% of DPB. Here wt% is defined as a weight percentage relative to the total weight content of the mixture.

All the films were prepared by spin-coating at 4000 rpm for 1 min on pre-cleaned 1 mm-thick 17x17 mm microscope glass slides as reported by us earlier.² The preparation of the films and solutions was performed in a nitrogen-filled glovebox with O₂ and H₂O concentrations below 0.1 ppm.

The fabricated films were encapsulated using epoxy resin and top-covering glass inside the glovebox before conducting photophysical measurements at ambient conditions. The encapsulation was essential to protect the films from triplet quenching by oxygen as well as to avoid photo-induced Rub degradation.³

Optical microscopy of the films

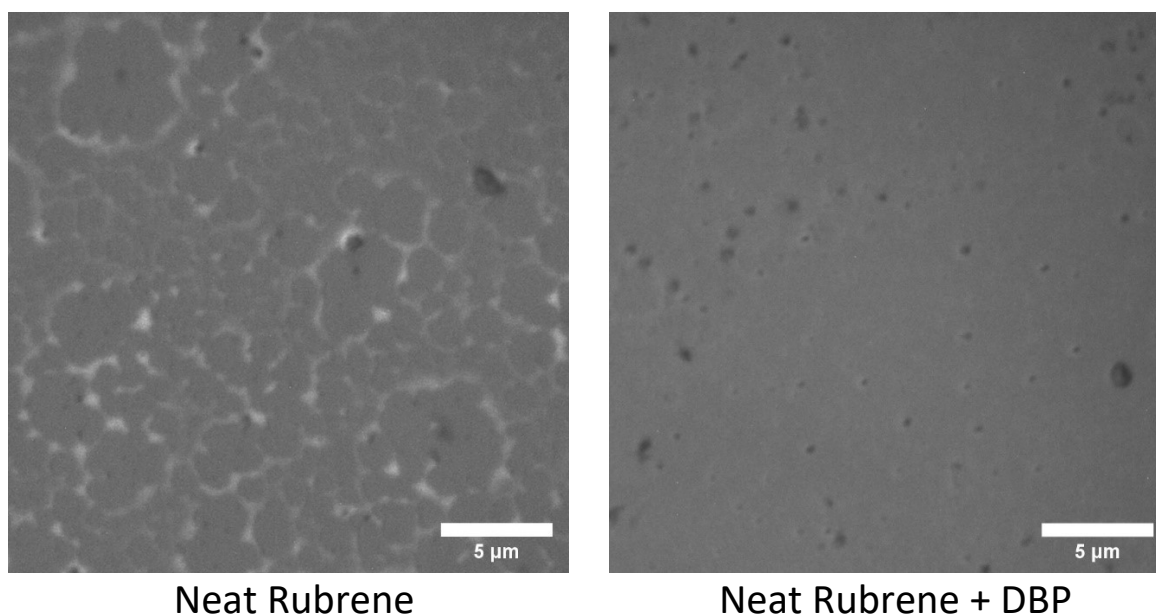


Fig. S1. Optical images displaying different film formation of spin-coated neat films with and without the addition of DBP.

AFM of the films

The spin-coated Rub/PS films were determined to have an average thickness of ~ 54 nm, whereas the neat Rub films were slightly thinner ~ 43 nm (see Fig. S2). The addition of 0.5wt% DBP to the films seems to not cause noticeable changes to the surface roughness (Fig. S3). All the films were rather smooth (RMS ~ 0.3 nm) and looked similar.

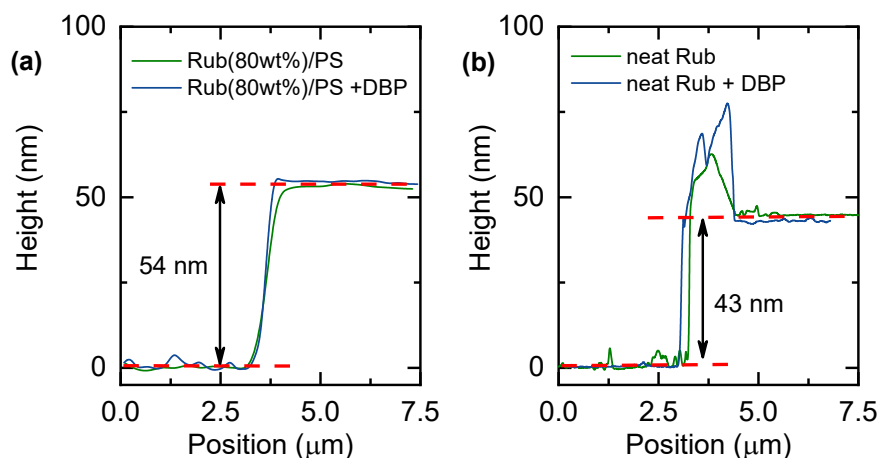


Fig. S2. AFM height profiles for (a) Rub(80 wt%)/PS film with and without 0.5wt% of DBP; (b) neat Rub film with and without 0.5wt% of DBP. The average thickness values, indicated.

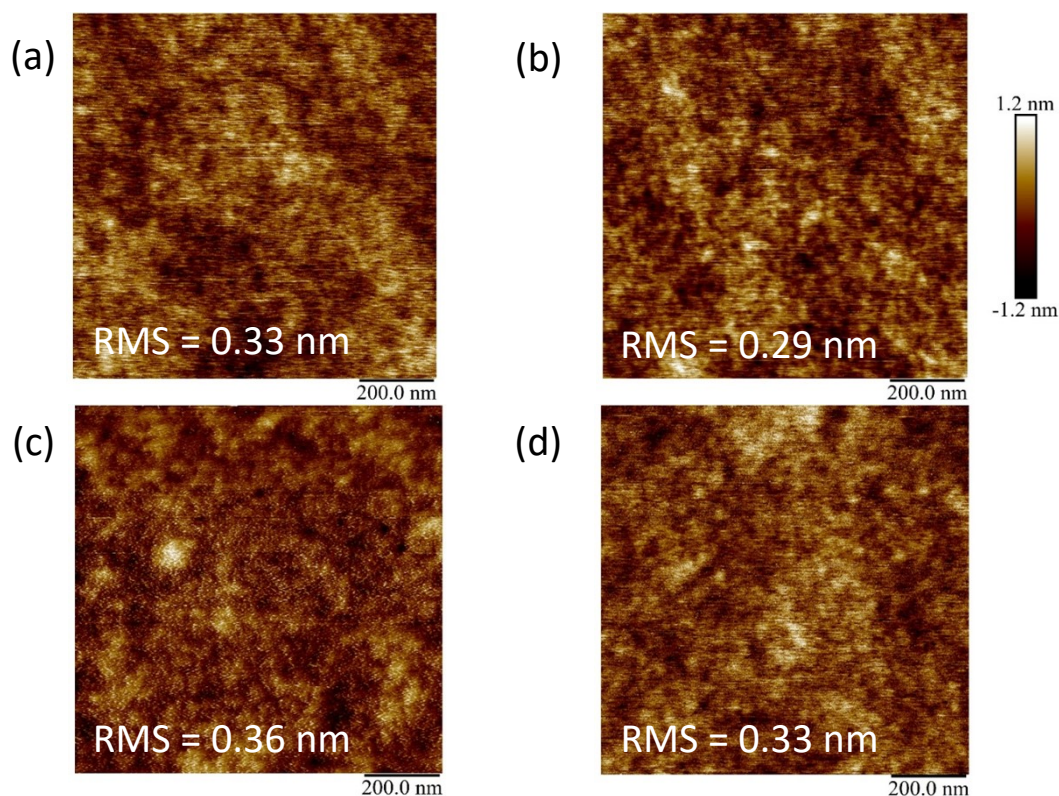


Fig. S3. AFM surface images 1x1 μm of (a) Rub(80 wt%)/PS film, (b) Rub(80 wt%)/PS film doped with 0.5wt% of DBP, (c) neat Rub film and (d) neat Rub film doped with 0.5wt% of DBP. Film RMS values, indicated.

Absorption and emission (PL and UC) spectra of the investigated films

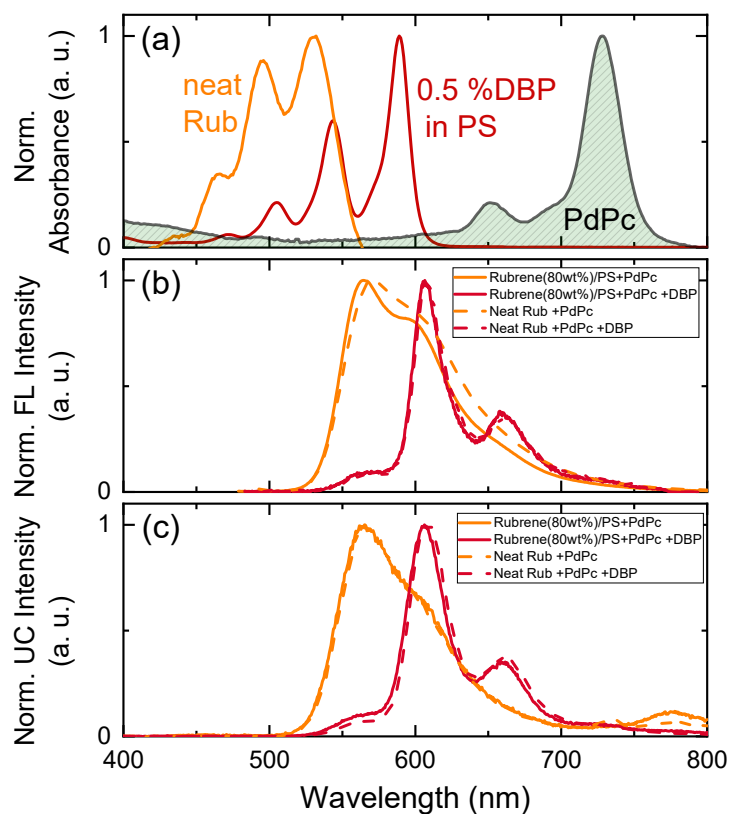


Fig. S4. (a) Absorption spectra of neat Rub film and singlet exciton sink DBP in PS matrix. Absorption spectrum of PdPc sensitizer is displayed for reference. (b) FL spectra of investigated Rub/PS/DBP films (the composition indicated) and (c) UC spectra of the same films. FL and UC excitation, 485 nm and 730 nm, respectively.

PL decay

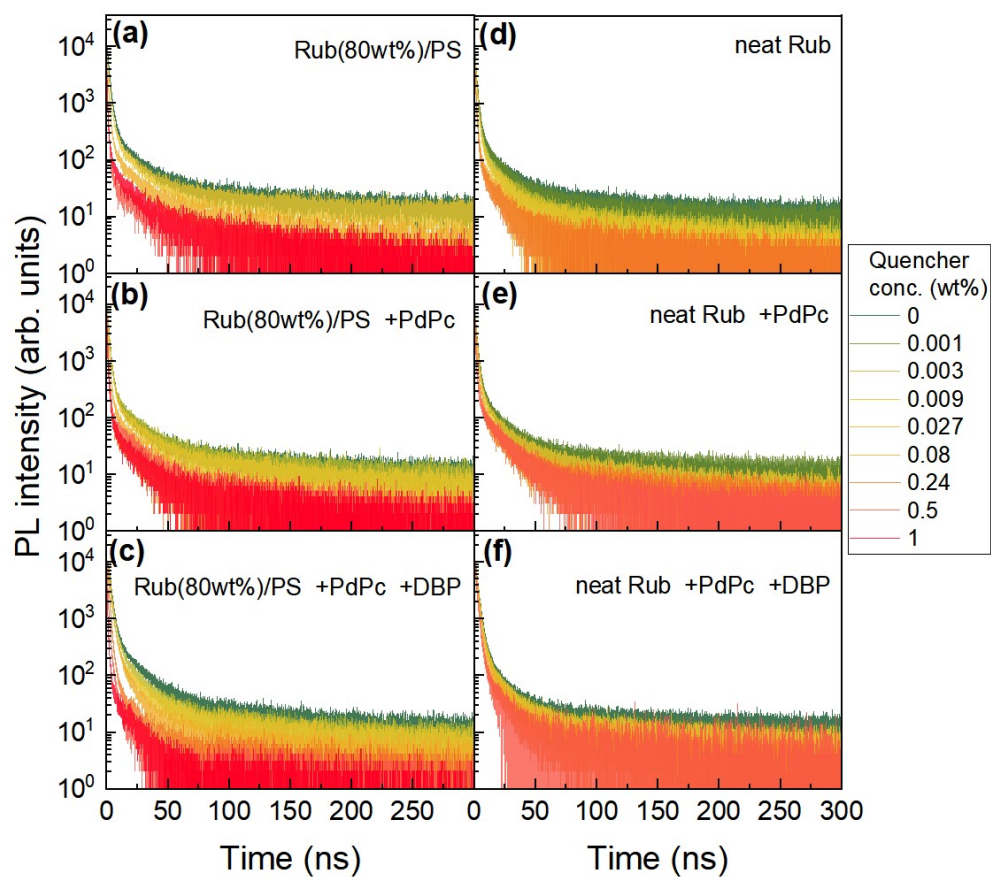


Fig. S5. Full time-range PL transients of the Rub(80 wt%)/PS and neat Rub films (a),(d) undoped; (b),(e) doped with 0.1 wt% PdPc; (c),(f) doped with 0.1 wt% PdPc and 0.5 wt% DBP, at different triplet quencher concentrations from 0 to 1 wt%.

Table S1. The estimated singlet decay fitting parameters for the studied Rub(80 wt%)/PS and neat Rub films used in the quenching experiment.

		Rub(80 wt%)/PS				Neat Rub			
Quencher conc. wt%	τ_1 ns	f_1 %	τ_2 ns	f_2 %	τ_1 ns	f_1 %	τ_2 ns	f_2 %	
0	1.50	74	13.1	26	1.18	77	10.7	23	
0.001	-	-	-	-	1.17	78	10.6	22	
0.003	-	-	-	-	1.04	82	9.46	18	
0.009	1.15	71	10.9	29	0.95	83	8.77	17	
0.027	-	-	-	-	0.56	88	8.29	12	
0.08	0.64	77	10.1	23	0.5	89	8.59	11	
0.24	-	-	-	-	-	-	-	-	
0.5	0.23	90	12.1	10	-	-	-	-	
1	0.13	83	11.7	17	-	-	-	-	
		Rub(80 wt%)/PS+PdPc				Neat Rub/PS+PdPc			
0	1.17	77	12.2	23	1.27	76	11.0	24	
0.001	-	-	-	-	1.15	73	10.6	27	
0.003	1.01	73	11.6	27	-	-	-	-	
0.009	1.15	79	11.4	21	1.15	78	10.2	22	
0.027	-	-	-	-	1.04	83	9.44	17	
0.08	0.66	82	10.4	18	0.77	84	9.47	16	
0.24	0.38	90	11.6	10	0.43	79	11.6	21	
0.5	0.32	84	13.5	16	-	-	-	-	
1	0.17	86	11.6	14	-	-	-	-	
		Rub(80 wt%)/PS+PdPc+DBP				Neat Rub/PS+PdPc+DBP			
0	2.37	78	19.3	22	2.17	84	12.6	16	
0.001	-	-	-	-	2.07	85	11.3	15	
0.003	2.3	82	15.7	18	2.03	86	11.2	14	
0.009	2.04	85	13.9	15	2.02	85	11.3	15	
0.027	1.69	77	7.69	23	1.87	87	11.0	13	
0.08	-	-	-	-	1.59	89	9.54	11	
0.24	1.17	90	7.52	10	1.27	84	8.31	16	
0.5	0.52	79	2.92	21	-	-	-	-	
1	0.23	90	9.1	10	-	-	-	-	

f_i - fractional contribution of each decay time component to the steady state intensity. Concentration of PdPc - 0.1 wt%, DBP - 0.5 wt%.

Photophysical and microscopy measurements

Absorption spectra of the films were recorded using a UV-vis-NIR spectrophotometer Lambda 950 (PerkinElmer). UC transients were recorded using a time-gated intensified CCD camera New iStar DH340T (Andor) coupled with a spectrograph Shamrock SR-303i (Andor), whereas a wavelength-tunable optical parametric amplifier tuned to 730 nm and pumped by a pulsed Nd³⁺:YAG laser NT 200 (Ekspla) (pulse duration – 5 ns, repetition rate – 1 kHz) served as an excitation source. Excitation spot size (of 1.1 mm) was way larger compared to the local film inhomogeneities providing spatially averaged signal. Fluorescence transients of the films were measured by using a time-correlated single-photon counting system PicoHarp 300 (PicoQuant), which utilized a pulsed semiconductor laser diode (repetition rate - 1 MHz, pulse duration - 70 ps, emission wavelength - 485 nm) as an excitation source. Optical microscopy images of the films were obtained using a microscope BX51 (Olympus). Surface roughness and height profiles of the films were measured using atomic force microscope (AFM) Dimension Icon (Bruker).

Evaluation of the exciton diffusion in disordered Rub films

Triplet exciton diffusion

The triplet exciton diffusion in the spin-coated Rub films was evaluated by using the time-resolved PL bulk-quenching technique followed by Stern-Volmer analysis, which was previously demonstrated to be the accurate tool for the determination of exciton diffusion parameters.^{4,5} To this end, a series of Rub films with varying amounts of randomly distributed exciton quenchers were fabricated. Chloranil, exhibiting strong electron accepting properties and causing instant exciton dissociation in contact with excited Rub species, was chosen as a triplet exciton quencher.⁶ In the prepared films with the dispersed quenchers, the excitons are free to diffuse during their lifetime through the Rub network and decay nonradiatively if the quenching site is reached. By measuring UC transients, the quenching efficiency can be evaluated and used to determine Stern-Volmer constant (K_{SV}), and subsequently, the diffusion coefficient (D_T).

Considering that TTA-assisted photon upconversion is a bimolecular process, its intensity (I_{UC}) is proportional to the square of the triplet concentration ($[T]_t$).⁷

$$\frac{d\sqrt{I_{UC}(t)}}{dt} \propto \frac{d[T]_t}{dt} = -k[T]_t - k_{TTA}[T]_t^2 \quad (1)$$

Here k is the first-order decay constant, which accounts for intrinsic triplet exciton lifetime ($k = 1/\tau_T$), whereas k_{TTA} is the second-order decay constant describing the depopulation rate of the triplets via the TTA process. Thus, by measuring UC transients, generally non-emissive triplet excitons in Rub can be probed indirectly. Special care must be taken to ensure that the transients are dominated by spontaneous triplet decay and not TTA (low excitation conditions), as this will allow to probe triplet exciton lifetime, which in turn is affected by the quenchers. Measuring UC transients at low triplet concentrations also eliminates possible deactivation via the singlet-triplet annihilation (STA) channel.

Relative quenching efficiency of the triplets (Q) at a certain quencher concentration ($[Q_c]$) was evaluated by using the following equation:

$$Q = 1 - \frac{\int \sqrt{I_{UC(q)}(t)} dt}{\int \sqrt{I_{UC}(t)} dt} = 1 - \frac{\tau_{T(q)}}{\tau_T} = 1 - \frac{\tau_{UC(q)}}{\tau_{UC}} \quad (2)$$

Here $I_{UC(q)}(t)$ and $I_{UC}(t)$ stand for UC transients of the films with chloranil quenchers present and absent, respectively. $\tau_{T(q)}$ and $\tau_{UC(q)}$ are triplet and UC lifetimes with quenchers present, respectively; τ_T and τ_{UC} are quencher-free triplet and UC lifetimes, respectively. Note that in the regime governed by spontaneous triplet decay, $\tau_T = 2 \times \tau_{UC}$.

K_{SV} was estimated by fitting experimental Q data utilizing "hindered access model"⁵, by which only a fraction (f_a) of the quenchers were accessible to the excitons in emitter molecules due to the possible quencher aggregation.

$$Q = f_a - \frac{f_a}{1 + K_{SV}[Q_c]} \quad (3)$$

Actually, modelling of experimental data revealed f_a to be close to unity implying insignificant agglomeration of the quencher species, and thereby almost complete triplet quenching at the largest

chloranil concentrations of 0.24 wt%. Exciton diffusion coefficient (D) for a given K_{SV} was calculated from the following expression:

$$D = \frac{K_{SV}}{4\pi r P \tau N_A}, \quad (4)$$

where r is reactive radius, which in this case is assumed to be a sum of the radiuses of the spheres (volumes) occupied by emitter and quencher molecules in the solid-state, P is the quenching probability of the exciton upon reaching the quencher (assumed to be =1), N_A is Avogadro's number. Dimensions of the molecules were estimated by taking the cube root of the volume occupied by one mole of that material

$$d = \sqrt[3]{\frac{M}{\rho N_A}}. \quad (5)$$

Here M is a molar mass and ρ is a density of material (density of chloranil $\rho_{ch} = 1.97 \text{ g/cm}^3$, of rubrene $\rho_{Rub} = 1.18 \text{ g/cm}^3$)^{8,9}.

Exciton diffusion length was then calculated from

$$L_D = \sqrt{\tau D}. \quad (6)$$

Singlet exciton diffusion

Singlet exciton diffusion was evaluated employing the same Stern-Volmer analysis as for the triplets, however, instead of the UC signal, fluorescence from the singlet state was measured upon direct excitation of Rub. In this case chloranil served as a singlet exciton quencher. Considering that the singlet emission is directly proportional to the singlet exciton concentration, the part of unquenched excitons can be expressed as the ratio of quenched and unquenched fluorescence lifetimes, $\tau_{FL(q)}$ and τ_{FL} , respectively. Thus, the total quenching efficiency for the singlets can be deduced from:

$$Q = 1 - \frac{\tau_{FL(q)}}{\tau_{FL}}, \quad (7)$$

Thereafter, Stern-Volmer constant as well as important diffusion parameters for the singlets were found from Equations 3, 4 and 6.

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