

Supporting Information

Simultaneous Singlet-Singlet and Triplet-Singlet Förster Resonance Energy Transfer from a Single Donor Material

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Sample Preparation and Experimental

For sample preparation PMMA was dissolved in Anisole at a concentration of 40 mg/ml. NPB and DCJTB were solved each in Anisole using 10 mg/ml. Then a series of different blends was prepared with a fixed amount of 2 wt% NPB (donor) and increasing portion of DCJTB (acceptor): PMMA:NPB:DCJTB (2 wt% : X wt%), with $0 \text{ wt}\% \leq X \leq 2 \text{ wt}\%$ in steps of 0.3 wt%. Additionally, a blend of PMMA:DCJTB (2 wt%) was prepared. The solutions were spin coated onto glass substrates in ambient conditions and rested overnight in nitrogen atmosphere for residual solvent evaporation. Photoluminescence data was taken under nitrogen atmosphere and by illuminating the respective sample with 365 nm UV-LED

(M365L2, $\lambda_{\max} = 365$ nm, Thorlabs). Edge emission spectra (CAS 140CTS, Instrument Systems) and phosphorescence transients (silicon photodetector, PDA100A, Thorlabs) were detected using either CW or triggered (pulse generator: Keysight Agilent Technologies 8114A) excitation mode. Absorption spectra were taken using the spectral photometer UV-3101 (Shimadzu Deutschland) and fluorescence lifetime measurements were performed using a time correlated single photon counting (TCSPC) system (TimeHarp 260 PICO, Picoquant). Photoluminescence quantum yield (PLQY) measurements were performed in a 6" integrating sphere using a LED (M340L4, $\lambda_{\max} = 340$ nm, Thorlabs) as excitation source and the above mentioned spectrometer (CAS 140CTS, Instrument Systems). To distinguish between Φ_S and Φ_T measurements were performed either in ambient air or nitrogen following de Mello's method.¹

Deconvolution of TCSPC Signal

Extracting the signal function $S(t)$ from the measurement data $A(t)$ was done by deconvolution. The experimental data $A(t)$ was first low-pass FFT filtered to reduce the noise level which would induce unwanted oscillations on the deconvolution² and then treated using

$$A(t) = S(t) * \text{IRF}(t) = \int_0^t S(\tau) \cdot \text{IRF}(t - \tau) d\tau, \quad (1)$$

where $\text{IRF}(t)$ denotes the instrument's response function. After deconvolution, $S(t)$ was fitted by a bi-exponential function, which is sufficiently approximating the data. The amplitude-weighted lifetime

$$\langle \tau_{\text{DA}} \rangle = \int_0^{\infty} S(t) dt = \frac{\alpha_1 \tau_1 + \alpha_2 \tau_2}{\alpha_1 + \alpha_2} \quad (2)$$

is used for calculating the transfer efficiency³

$$\Phi_{\text{ET}} = 1 - \frac{F_{\text{DA}}}{F_{\text{D}}} = 1 - \frac{\int S_{\text{DA}}(t)dt}{\int S_{\text{D}}(t)dt} = 1 - \frac{\langle \tau_{\text{DA}} \rangle}{\langle \tau_{\text{D}} \rangle}. \quad (3)$$

Table 1: lifetimes determined from experimental data using eq. (2)

DCJTB concentration	Singlet $\langle \tau_{\text{DA}} \rangle$ [ps]	Triplet $\langle \tau_{\text{DA}} \rangle$ [ms]
0.0	1800	364
0.2	791	322
0.5	256	193
0.8	174	140
1.1	144	99
1.4	105	75
1.7	97	65
2.0	78	47

Rate Model Simulation

For numerical analysis, a virtual cube of 80 nm side length containing about 12 000 donor molecules was considered. Depending on concentration, the respective amount of acceptor molecules was introduced (see fig. 1 as example). All positions were chosen randomly respecting the fact that molecules cannot be placed on top of each other but with their diameter as minimal separation.

The excited state lifetimes were determined from lifetime experiments to be $\tau_{\text{S},i} = 1.8$ ns, $\tau_{\text{T},i} = 364$ ms and $\tau_{\text{S},j} = 1.5$ ns. With $R_{\text{F},\text{S-S}} = 3.6$ nm and $R_{\text{F},\text{T-S}} = 2.5$ nm as calculated above and $k_{\text{D}} = \frac{1}{\langle \tau_{\text{D}} \rangle}$ for both S-S and T-S Förster rate, the excitation probability over time of each distinct donor and acceptor state could be calculated. Considering further each state's PLQY value, those probabilities at each time step n_t could be related to measurable photoluminescence PL. The wavelength filtered donor's TCSPC data was compared to the

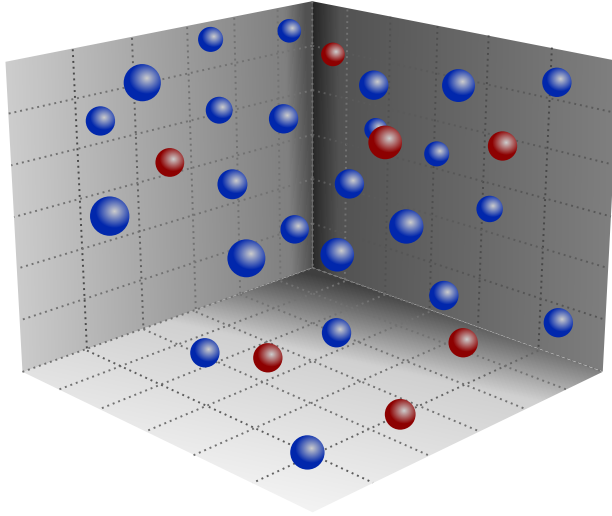


Figure 1: Illustration of donor (blue) and acceptor molecules (red) placed randomly in a virtual cube for numerical simulation.

PL originating from the donor's singlet radiation

$$PL_{S,i}(n_t) = \xi \cdot \Phi_{S,i} \cdot \sum_i ([S_1]_i(n_t) - [S_1]_i(n_t + 1)). \quad (4)$$

On the other hand, the photodetector's signal on millisecond timescale was related to the sum of the donor's triplet and acceptor's singlet emission.

$$PL_{S,j}(n_t) + PL_{T,i}(n_t) = \xi \cdot \Phi_{S,j} \cdot \sum_i \sum_j (k_{\text{FRET},T_i-S_j} \cdot [T_1]_i(n_t)) \quad (5)$$

$$+ \xi \cdot \Phi_{T,i} \cdot \sum_i ([T_1]_i(n_t) - [T_1]_i(n_t + 1)) \quad (6)$$

The factor ξ is the general probability that a generated photon is indeed outcoupled such that it hits the detector. However, as it is considered to be equal for all photons and PL was always normalized for comparison to $PL(n_t = 0)$, it has no further significance. Furthermore, it is assumed that each acceptor singlet (ns lifetime) decays immediately on a triplet-timescale (milliseconds).

References

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