Supporting Information

Nanoscale triplet exciton diffusion via imaging of upconversion emission from single hybrid nanoparticles in molecular crystals

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Contents:

Two-dimensional convolution function for image fitting.

In the actual CCD camera images, the UC emission intensity distribution $I_{uc}(x)$ in the emission spot is a convolution of the density of singlet excitons $n_s(x)$ with the microscope point spread function (PSF):

$$I_{uc}(x) = n_s(x) * f_{PSF}(x), \qquad \text{(S1)}$$

where $f_{PSF}(x)$ is the PSF. Assuming a Gaussian profile of the $f_{PSF}(x)$ with σ_{PSF}^2 its variance, and using

$$n_s(x) \sim S_0 \exp\left(-{}^{x}/_{L_{uc}}\right) \qquad \text{(S2)}$$

for $n_s(x)$, the eqn. (S1) can be written as

$$I_{uc}(x) = exp\left({}^{x}/_{L_{UC}}\right) \times erfc\left(\frac{{}^{\sigma_{PSF}^2}/_{L_{UC}} + x}{\sqrt{2}\sigma_{PSF}}\right) + exp({}^{-x}/_{L_{UC}}) \times erfc\left(\frac{{}^{\sigma_{PSF}^2}/_{L_{UC}} - x}{\sqrt{2}\sigma_{PSF}}\right)$$

(S3)

where erfc is the complementary error function.

For the UC emission image fitting we used a two-dimensional convolution function expressed as

$$I_{uc}(x,y) = \left[\exp\left({}^{x}/_{L_{UCx}}\right) \times erfc\left(\frac{{}^{\sigma_{PSF}^{2}}/_{L_{UCx}} + x}{\sqrt{2}\sigma_{PSF}}\right) + exp({}^{-x}/_{L_{UCx}}) \times erfc\left(\frac{{}^{\sigma_{PSF}^{2}}/_{L_{UCx}} - x}{\sqrt{2}\sigma_{PSF}}\right) \right] \quad \text{(S4)}$$

The values of ${\sigma_{PSF}}^{2}$ are obtained from 2D Gaussian fitting of the fluorescence images of the fluorescence dyes FD1 attached to the HDP (Fig. 3a and e). The fluorescence image spot is actually a convolution of the microscopic PSF with the HDP physical size but because the HDP size is much smaller than the PSF it can be neglected in the further treatment. We denote σ_{PSF}^{D} as the variance of the PSF at the peak emission wavelength of FD1. The size of microscopic PSF is directly related to the wavelength of light λ via:

$$\epsilon = 0.61 \times \frac{\lambda}{NA}, \quad \text{(S5)}$$

where NA is the numerical aperture of the objective lens. Therefore, the value of σ_{PSF}^{D} cannot be directly used as σ_{PSF} in the eqn. (S4) because of the different spectral region of the UC emission. To correct for the different emission wavelengths, using the eqn. (S5) gives the following relationship between σ_{PSF}^{D} and σ_{PSF}:

$$\sigma_{PSF} = \frac{\lambda_{UC}}{\lambda_{D}} \sigma_{PSF}^{D}, \quad \text{(S6)}$$

where λ_{UC} is the UC emission peak wavelength and λ_{D} the FD1 fluorescence peak wavelength. These values were determined from the Fig. S6. For the AC acceptor, $\lambda_{UC}$and λ_{D} were 438 nm and 625 nm, respectively, for the DPA acceptor these values were 444 nm and 626 nm, respectively.

Analysis of the lifetime measurements

Analysis of the UC decay curves in Fig. 4b was done using multi-exponential fitting. The longest three lifetime components were further used to calculate average decay times τ_{UC} of 7.4 × 10^{-5} s and 1.8 × 10^{-4} s for the AC and DPA, respectively. Using these values in the equations (5) and (6), the L_T of AC and DPA were estimated as 50 nm and 4.9 nm, respectively. The average values were used in order to estimate the maximum possible value of triplet exciton diffusion length.

In literature [29], the longest lifetime component instead of an average is often used to estimate the L_T values. The longest lifetime components obtained from the fitting were 8.3 × 10^{-5} s and 2.2 × 10^{-4} s for the AC and DPA, respectively. Using again these values in the equations (5) and (6), the L_T of AC and DPA were estimated as 47 nm and 4.4 nm, respectively. It is clear that while the longest components yield shorter diffusion lengths L_T, the overall scale of the results has not changed.

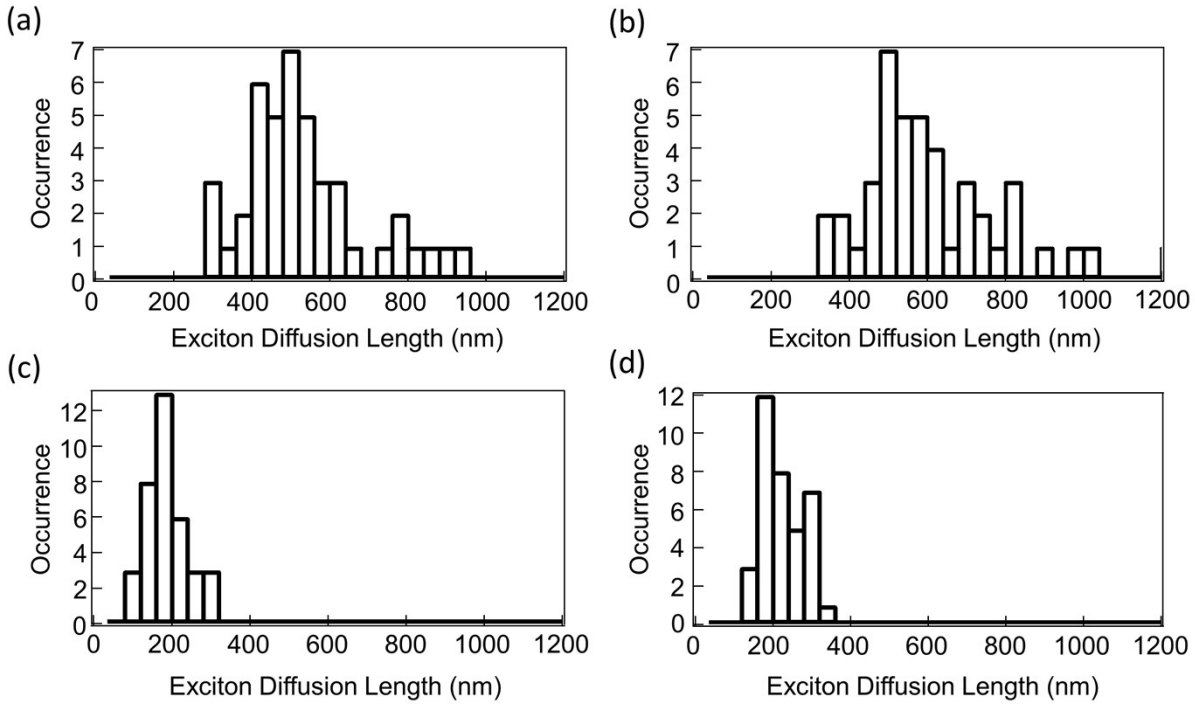

Figure S1. Histograms of L_T along two orthogonal directions for AC (a,b) and DPA (c,d). (a,c) Histograms regarding smaller values. (b,d) Histograms regarding larger values.

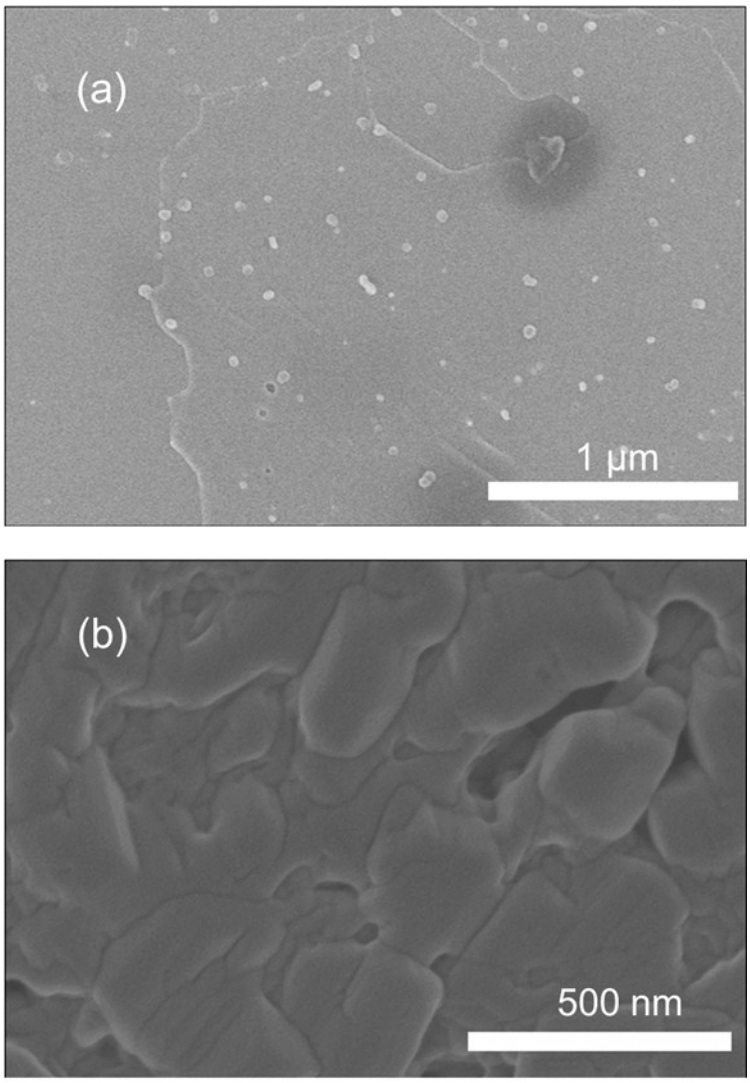

Figure S2. Scanning electron microscope images of (a) AC and (b) DPA acceptor crystalline films.

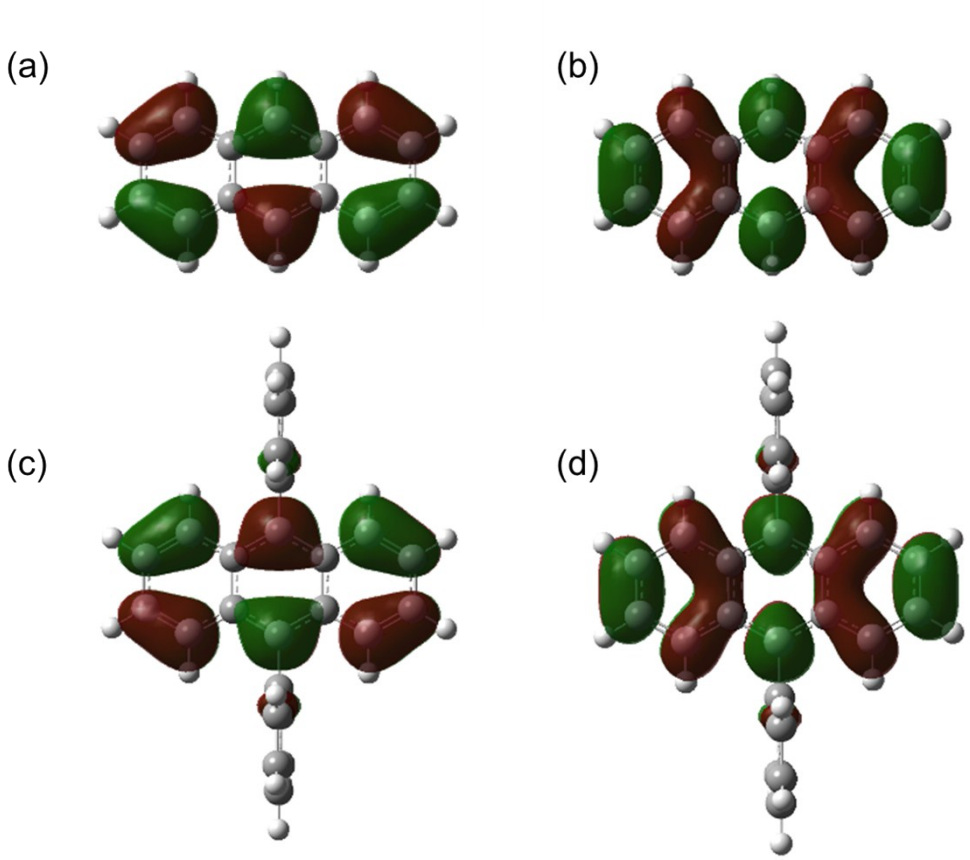

Figure S3. (a, c) Lowest unoccupied molecular orbital of (a) AC and (c) DPA. (b, d) Highest occupied molecular orbital of (b) AC and (d) DPA. Calculation were performed using density functional theory (Gaussian 09, B3LYP functional, 6-31G(d,p) basis set) using conformation optimized at T_1.

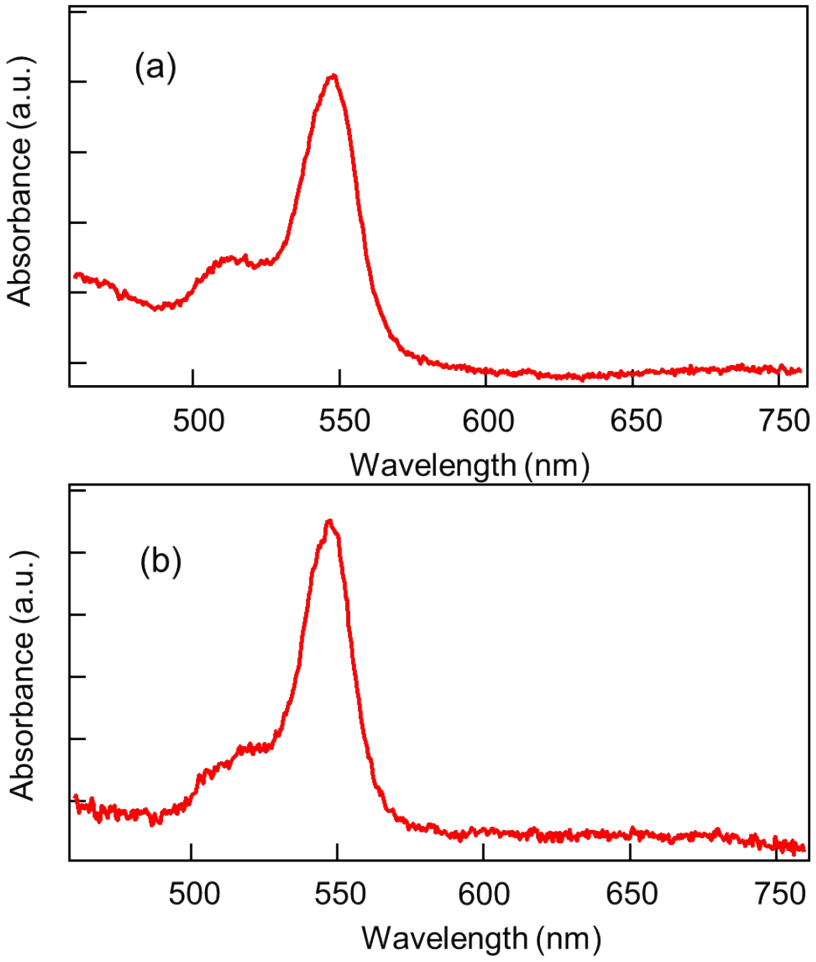

Figure S4. Absorption spectrum of D1 doped in polycrystalline film of (a) AC and (b) DPA. Samples were made by drop-casting.

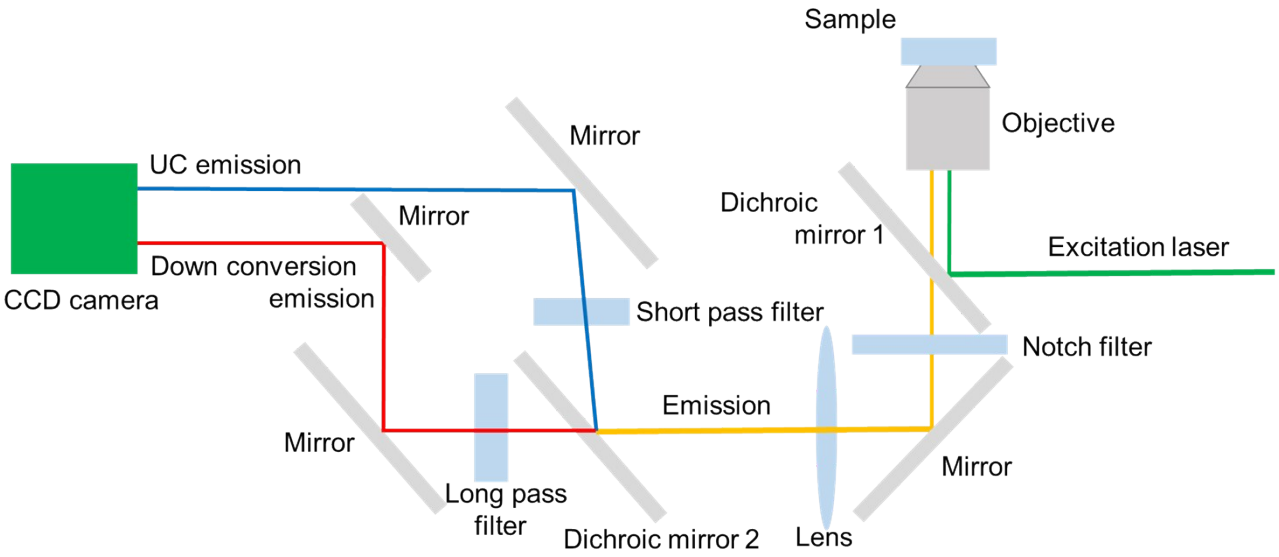

Figure S5. Experimental setup for the microscopic UC emission imaging.

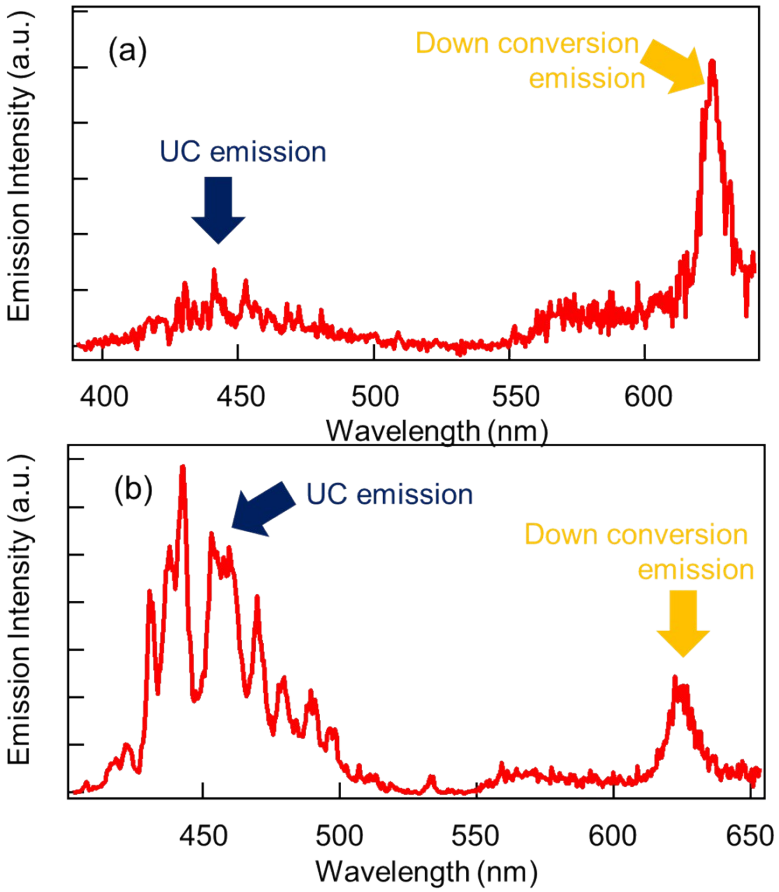

Figure S6. Emission spectrum of (a) AC at the vicinity of HDP and (b) DPA at the point of HDP.