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Supplementary Information

Inter-ligand energy transfer in dye chromophores attached to high bandgap SiO^2 nanoparticles.

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Experimental Details

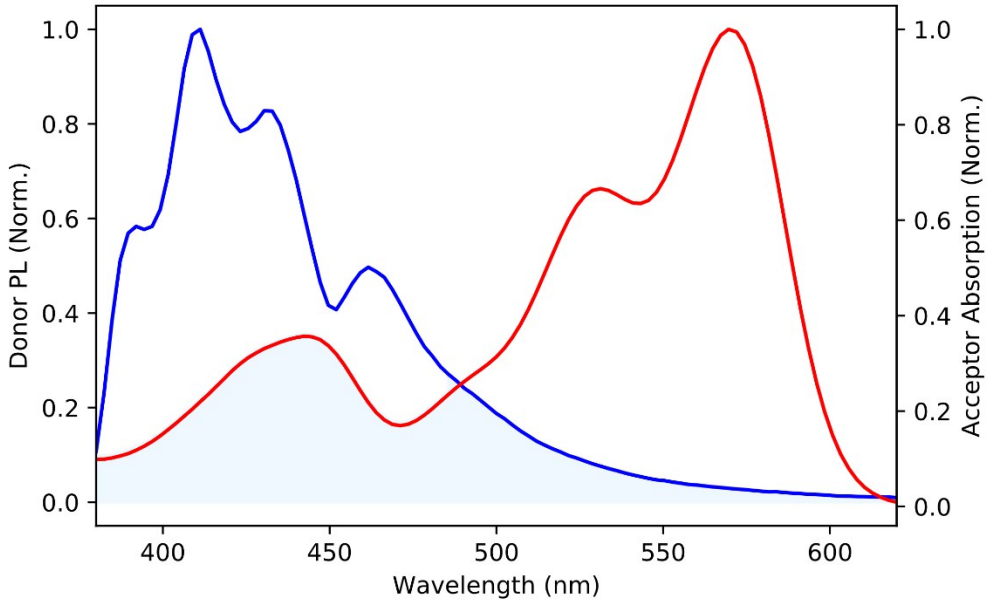
All chemicals were purchased from Sigma Aldrich and used as received.

Synthesis: Perylene diimides were synthesised previously18,29
Attachment of chromophores to silicon dioxide nanoparticles: The surface of the silicon dioxide nanoparticles (nanopowder, 10-20 nm particle size) were initially treated with (3-Aminopropyl)triethoxysilane (APTES) 5% with 20 mg ml 1 nanoparticles in toluene. The solution was left over night and the nanoparticles were washed via flocculation with acetone and centrifugation. The attachment of the perylene diimides to the aminated silicon dioxide nanoparticles was performed in chloroform with 1.1 × molar equivalents of (2-(1H-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate) (HBUT) and 1 × molar equivalents of N, N-Diisopropylethylamine (DIPEA) compared to the perylene diimides. The solution was left over night and the nanoparticles were washed via flocculation with acetone and centrifugation.

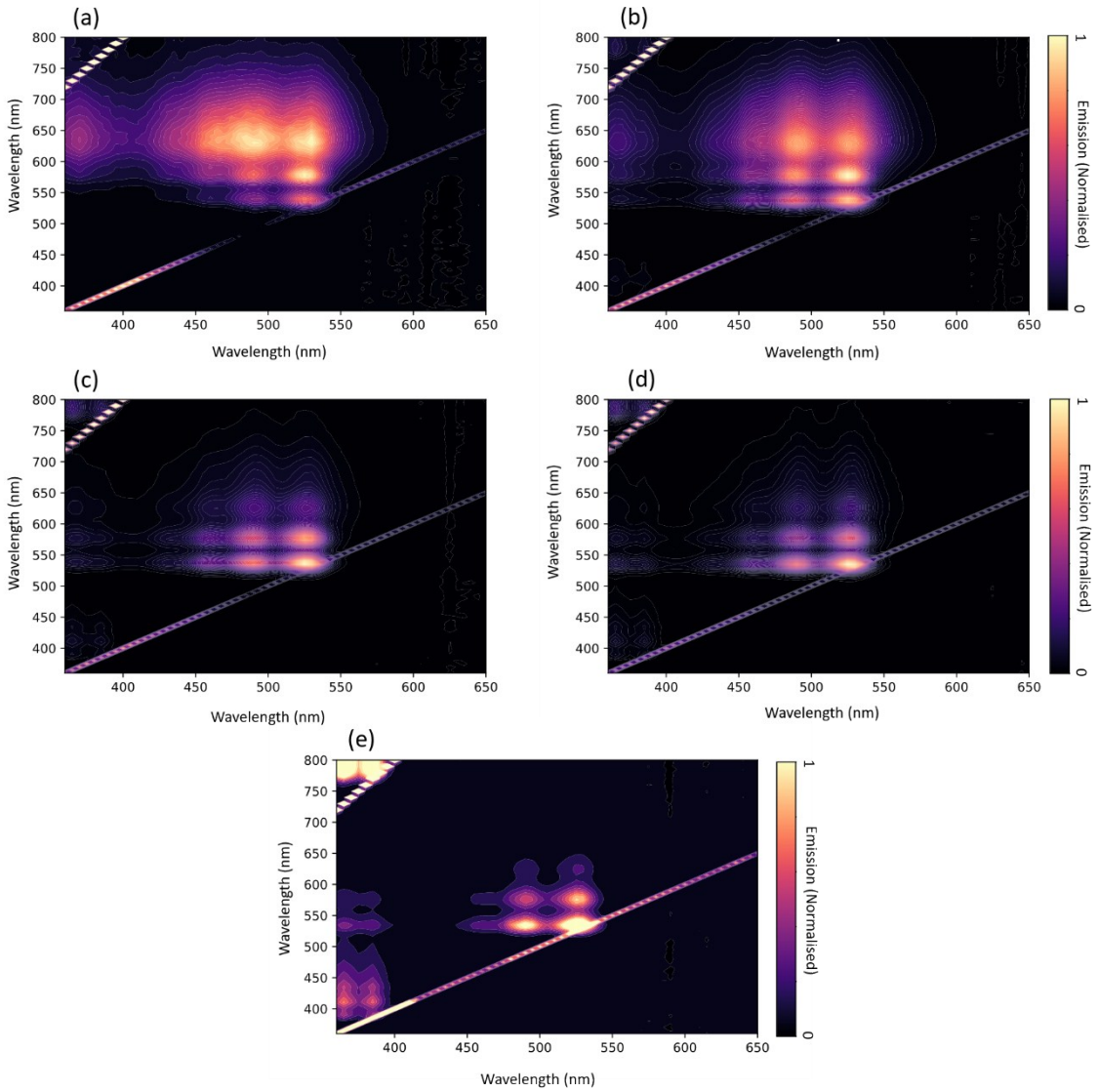
Steady-state spectral measurements: Absorption spectra were measured using a HP 8453 spectrophotometer. Dye-nanoparticle solutions were dispersed in chloroform at a concentration of ~ 1 mg/ml and a 1 cm path length was used. Photoluminescence measurements (1 mg in chloroform in a 1 mm cuvette) and two-dimensional scans were measured on an Edinburgh Instruments FLS90 fluorimeter.

PLQE measurements: Samples in 10 mm cuvettes were placed in an integrating sphere and were photo-excited using a Xenon lamp via a monochromotor. The lamp and the emission signals were measured and quantified using an Edinburgh Instruments FLS90 fluorimeter. PLQE was calculated as per de Mello, et al.[1]

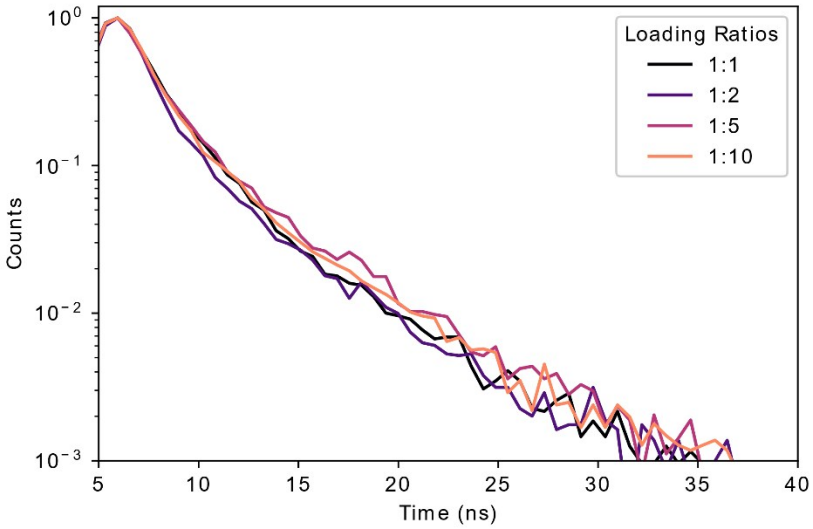
Transient Photoluminescence: Time-correlated single photon counting (TCSPC) was performed on an Edinburgh Instruments FLS90 fluorimeter. Samples were excited with a pulsed laser (PicoQuant LDH400 40 MHz) at 375 nm. The instrument response was determined by scattering excitation light into the detector using a piece of frosted glass. Transient grating photoluminescence spectroscopy (TGPL) was performed as described by Chen et al[2]. A Ti:Sapphire amplifier system (Spitfire Ace) operating at 3kH and generating 200 fs pulses was split into two part One part was converted to 400 nm using an optical parametric amplifier (TOPAS, Light Conversion) and focused to a 70 μm spot to excite the sample. The sample was loaded in a cuvette with 1 mm optical path length and continuously stirred with a magnetic stir bar. The second part of the fundamental 800 nm output was split using a 50:50 beam splitter and focused on the fused silica with a crossing angle of 5°. The interfering beams creating an instantaneous gate which is used to temporally resolve the decay over a broad wavelength range. The scatter of the excitation beam was suppressed using a 435 nm long-pass filter and data is averaged over 30000 shots for every time delay.



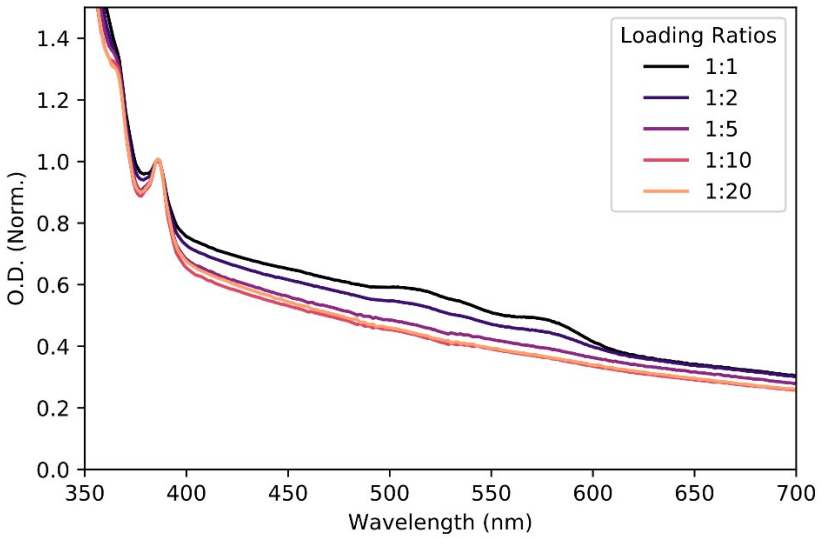
Supplementary Figure 1. Normalised emission spectra of Blue anthracene carboxylic acid, and absorption of Red Perylene Diimide. Red dye absorption is shown with a red line. Blue dye emission is shown with a blue line. The shaded light blue area illustrates the overlap between the two spectra. We calculate, based on the Red absorption coefficient, and assuming an orientation factor based on randomly orientated rigid dipoles, a Förster radius between the molecules of r_0 = 0.6 nm.



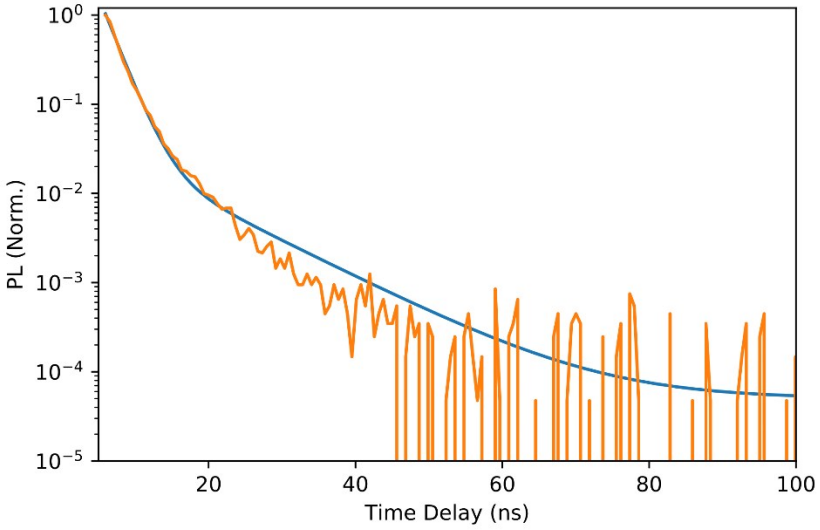
Supplementary Figure 2. Normalised 2-dimensional excitation-emission scans of solutions of Blue-Orange dyes attached to SiO_2 with different dye ratios. (a) shows a 1:1 Orange to Blue dye ratio. **(b)** 1:2 Orange:Blue, **(c)** 1:5 Orange:Blue, **(d)** 1:10 Orange:Blue, **(e)** 1:20 Orange:Blue



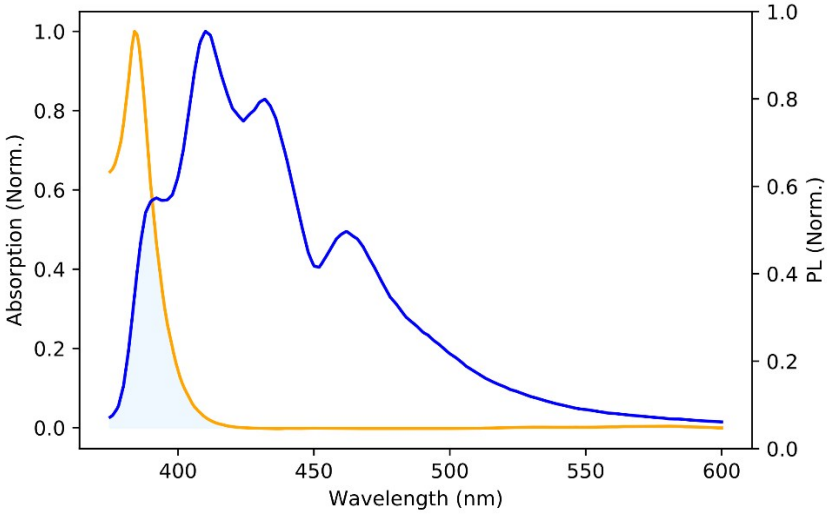
Supplementary Figure 3. Time-correlated single photon counting lifetimes of Blue-Red dyes on SiO_2. Photoluminescence decays of the Blue donor molecule, measured at 415 nm, for different loading ratios of Red:Blue dyes attached to nanoparticles. Excited with 375 nm laser pulses. No significant difference is seen between the different decays, indicating a lack of energy transfer.



Supplementary Figure 4. Normalised absorption of Blue-Red dyes attached to SiO_2 with different Blue to Red ratios. The spectra is normalised to the 0-0 singlet peak of the Blue anthracene. There is some scattering present in the absoprtion spectra. The different loading densities of the Red dye can be seen in the expected peak positions, with the Red contribution decreasing as the Red proportion is decreased, but the Red absorption is weak compared to the comparable Orange absorption system.



Supplementary Figure 5. Time-correlated single photon counting lifetimes of Blue dye on SiO_2 with biexponential fit. Photoluminescence decays of the Blue donor molecule (coloured as orange), measured at 415 nm, excited with 375 nm laser pulses. The blue line is a biexponential fit to the normalised data with a fast time constant component of 2 ns, and slower 10 ns component.



Supplementary Figure 6. Normalised absorption and emission spectra of Blue anthracene carboxylic acid. Blue anthracene absorption is shown by an orange line. Blue anthracene emission is shown by a solid blue line. The shaded blue region illustrates the self-Förster overlap region. The self-Förster radius is calculated with assumptions as described in the main text[3], giving r_0 = 0.5 nm. And from this, we calculate a diffusion length based on self-Förster transport[3] of L_D = 0.6 nm, compared to L_D = 2.2 nm calculated from our Stern-Vomer plot, in Figure 4 of the main text.

References

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