Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information: Blue to near-IR energy transfer cascade within a dye-doped polymer matrix, mediated by a photochromic molecular switch

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S1. Experimental procedure.

The 10 mM C314 (Exciton), 10 mM spiropyran (SP, TCI Chemicals), and 1 mM HITC (Sigma Aldrich) dye solutions were prepared in chloroform. A 2.5% w/w poly(methyl methacrylate) (PMMA) polymer (Sigma Aldrich, $M_w \approx 350{,}000$ g/mol, density = 1.17 g/cm^3) solution was prepared in chloroform. Dye-doped PMMA samples were made by mixing together 0.25 ml PMMA solution, 0.01 mL C314 solution, 0.05 mL spiropyran solution, and 0.01 mL HITC solution. The mixed solution was then cast onto a glass slide and left to dry within an enclosed petri dish, so as to slow the rate of evaporation and produce a smooth film. A photo of the C314+SP/MC+HITC sample, before and after UV irradiation, is shown in Figure 1. Dye-doped PMMA samples of the individual dyes were produced in the same way, with pure chloroform used to make the total casting volume constant.

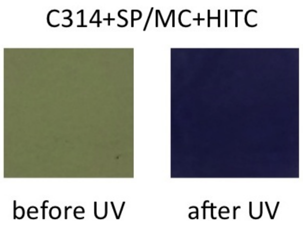

Figure 1: Photos of the C314+SP/MC+HITC PMMA sample before (left) and after (right) UV irradiation.

Absorption spectra of the samples were recorded using a UV/Vis spectrometer (Varian, Cary 50 Bio). For dispersed emission experiments, the samples were excited with a laser beam ($\tau \sim 5$ ns, $f = 10$ Hz, ~ 5 mW/cm^2) from a tunable optical parametric oscillator (Opotek Vibrant), with the emission collected by a F/1 lens and sent to a spectrometer (Jobin Yvon, Triax 552) interfaced with a cooled, 2-dimensional, charge-coupled device detector (Jobin Yvon, Symphony). For the time-correlated single photon counting experiments (TCSPC), two different set-ups were used. To probe the excited state lifetime of the merocyanine (MC) isomer, the sample was excited with a laser beam ($\tau \sim 12$ ps, $f = 82$ MHz, ~ 5 mW/cm^2) from a 532 nm, picosecond, diode-pumped Nd:YAG laser (Time Bandwidth Products, Cheetah-X), with the emission collected by a F/1 lens and passed through a 640-690 nm band pass filter and sent to a cooled photomultiplier tube (Becker and Hickl, PMC-100) connected to a TCSPC card (Becker and Hickl, SPC-630). To probe the excited state lifetime of the C314 dye, the sample was excited with a laser beam ($\tau \sim 100$ fs, $f = 5.4$ MHz, ~ 1 mW/cm^2) from a 435 nm, frequency-doubled, cavity dumped, femtosecond Ti:sapphire laser (Coherent MIRA 900F/APE PulseSwitch), with the emission collected by a F/1 lens and passed through a monochromator (Jobin Yvon H20) set to 470 nm and sent to a microchannel plate photomultiplier (Eldy model EM1-132-1) connected to a TCSPC card (Becker and Hickl SPC-150). To record the instrument response function (IRF), the elastically scattered light was monitored. The time-resolved fluorescence decay curves were fitted using various functions (see S2) convoluted with the IRF (FAST software, Edinburgh Photonics).

UV irradiated samples were exposed to collimated, continuous-wave 365 nm light (~ 20 mW/cm^2) from a light-emitting diode (M365L2-C1, Thorlabs) for 20 sec immediately before the experiments. Although TCSPC experiments monitoring the MC fluorescence before UV irradiation for the C314+SP/MC+HITC sample were attempted, the extremely weak signal and interference from the HITC emission led to unreliable lifetimes.

For the reversible SP $\leftrightarrow$ MC switching experiments, the following cycle was applied: emission collected (435 nm, ~ 5 mW/cm^2, 30 sec), UV irradiation (365 nm, ~ 20 mW/cm^2, 20 sec), emission collected (435 nm, ~5 mW/cm^2, 30 sec), visible irradiation (532 nm, ~50 mW/cm^2, 4 min).

S2. Time-resolved fluorescence decay fitting.

The fluorescence decay curve of the FRET donor in the PMMA matrix, in the absence of the FRET acceptor, can be fitted using a single exponential decay function:

$$I_D(t) = I_0 e^{-(\frac{t}{\tau_D})} \tag{1}$$

where I_0 is the initial intensity and τ_D is the lifetime of the FRET donor in the absence of FRET acceptors.

When introducing the FRET acceptors into the PMMA matrix (randomly distributed in three dimensions), the fluorescence decay of the FRET donor will become faster due to the introduction of the FRET decay channel. In theory, the donor's exponential fluorescence decay will become non-exponential and, assuming three-dimensional energy transfer, can be fitted using the following function:

$$I_{DA}(t) = I_0 \exp[-(\frac{t}{\tau_D}) - 2\gamma(\frac{t}{\tau_D})^{\frac{1}{2}}] \tag{2}$$

$$\gamma = \frac{\Gamma(1/2)}{2} C_A \frac{4}{3} \pi R_0^3$$

where C$_A$ is the acceptor concentration (molecules/nm^3) and R_0 (nm) is the Förster distance, defined as the distance where the FRET quantum yield (Φ) is 0.50.[1] Fitting of the fluorescence decays provides an experimental estimate for R_0. However, as donor→donor homo-FRET is expected to be present in our sample, allowing the excitation energy to migrate from its original position before undergoing FRET to the acceptor, it is not suitable to use Eq. (2). Homo-FRET occurs as the donor dye concentration leads to their separation being on the same order as R_0 (Table 1), together with the acceptor dyes sometimes being in much lower concentration than the donor dyes. As a reference, we still show the parameters obtained when fitting the fluorescence decays using Eq. (2) in Table 2.

Table 1: Estimated concentration parameters for the donor dyes in the dye-doped PMMA samples.

donor	mol/dm^3	ave D$\cdots$D separation (nm)	D+D R_0 theoretical (nm)
C314	1.25×10^{-2}	5.1	3.2
MC[a]	3.91×10^{-2}	3.5	3.2

[a] after UV irradiation

We also have fitted the fluorescence decays using a stretched exponential decay function:

$$I(t) = I_0 e^{-(\frac{t}{\tau_c})^\beta}, \tag{3}$$

where I_0 is the initial intensity, τ_c is the characteristic lifetime, and β is the dispersion parameter. Fitted parameters were used to determine the average lifetime, τ:

$$\tau = \frac{\tau_c}{\beta}\Gamma\left(\frac{1}{\beta}\right)$$

$$\Gamma\left(\frac{1}{\beta}\right) = \int_0^\infty x^{\frac{1}{\beta}-1} e^{-x}\,\mathrm{d}x$$

The stretched exponential function is used because it can fit non-exponential decays with a limited number of variable parameters (the β parameter describes a distribution of first-order decays when it has a value < 1), leading to a reliable and systematic approach for analysing the data. The parameters derived from fitting the fluorescence decays using Eq. (3) are given in Table 3. An estimate of Φ_{FRET} can be made using the integrated areas under the functions fitted to the fluorescence decays (deconvoluted for the IRF):[1]

$$\Phi_{FRET} = 1 - \frac{\int_0^\infty I_{DA}(t)\mathrm{d}t}{\int_0^\infty I_D(t)\mathrm{d}t} \tag{4}$$

Table 2: Parameters for the dye-doped PMMA samples derived from the fluorescence decay curves fitted using Eq. (2).

sample	τ_D (ns)	γ	R_0 experiment (nm)	R_0 theoretical (nm)
C314 fluorescence decay				
C314	3.14			
C314+HITC		0.19	4.1	3.8
C314+SP/MC		1.47^a	2.6	4.1
MC fluorescence decay				
SP/MC	2.24^a			
C314+SP/MC+HITC		0.81^a	6.6	5.5

[a] after UV irradiation

Table 3: Parameters for the dye-doped PMMA samples derived from the fluorescence decay curves fitted using Eq. (3).

sample	τ_D (ns)	β	τ_c (ns)	τ (ns)	Φ_{FRET}
C314 fluorescence decay					
C314	3.14				
C314+HITC		0.85	2.14	2.33	0.26
C314+SP/MC		$0.85^a/0.60^b$	$2.19^a/0.32^b$	$2.38^a/0.48^b$	$0.24^a/0.85^b$
C314+SP/MC+HITC		$0.85^a/0.60^b$	$1.59^a/0.26^b$	$1.73^a/0.39^b$	$0.45^a/0.88^b$
MC fluorescence decay					
SP/MC	2.24^b				
C314+SP/MC+HITC		0.70^b	0.53^b	0.68^b	0.70^b

[a] before UV irradiation

[b] after UV irradiation

S3. Estimation of the SP→MC conversion efficiency.

The SP→MC conversion efficiency is estimate using the C314+SP/MC+HITC absorption spectrum, before and after UV irradiation. By using the molar extinction coefficients reported for C314 (4.70×10^{4} M^{-1}cm^{-1}) and MC (3.68×10^{4} M^{-1}cm^{-1}),[2,3] their absorption band intensities, and the known concentration of C314 (1.25×10^{-2} mol/dm^{3}), we estimate the concentration of MC to be $\sim3.91\times10^{-2}$ mol/dm^{3}. Using the known concentration of spiropyran (6.25×10^{-2} mol/dm^{3}) and assuming before UV irradiation all the population is present as SP, we estimate that UV irradiation results in a conversion of ~60% of SP into MC.

S4. Estimation of the Förster Distance.

A theoretical calculation of R_0 can be made using the parameters that dictate the FRET efficiency for a donor-acceptor pair: the donor's fluorescence quantum yield (Φ_R), the degree of overlap between the donor's emission and acceptor's absorption spectra, i.e., overlap integral (J), the relative alignment of the donor and acceptor's transition dipole moments, i.e., orientation factor (κ^2), and refractive index of the host medium (n):[1]

$$R_0 = 0.0211 \times (n^{-4}\Phi_R J \kappa^2)^{1/6} \tag{5}$$

The overlap integral (J) is calculated by:

$$J = \int_0^{\infty} F_D(\lambda)\,\varepsilon_A(\lambda)\,\lambda^4 \mathrm{d}\lambda$$

where λ is the wavelength of light, $F_D(\lambda)$ is the intensity of the fluorescence spectrum of the donor at that wavelength (when the integral of the donor's fluorescence band is normalised), and $\varepsilon_A(\lambda)$ is the molar extinction coefficient of the acceptor at that wavelength.

Calculation of the Φ_R for a chromophore's excited state can be made from the radiative lifetime (τ_R) and the τ_D, which accounts for relaxation via radiative and non-radiative decay:

$$\Phi_D = \frac{\tau_D}{\tau_R} \tag{6}$$

The τ_R is also affected by the n of the surrounding medium:

$$\frac{1}{\tau_R} = \frac{n^2}{\tau_{R\,(vac)}}$$

where $\tau_{R\,(vac)}$ is τ_R in a vacuum.

Using these equations we can calculate an Φ_R estimate for MC in PMMA. To do this we use the Φ_R and excited state τ_D measured for MC (0.016 and 0.21 ns, respectively)[4,5] in ethanol solution ($n = 1.36$) and the excited state τ_D measured here for MC (2.24 ns) in PMMA ($n = 1.49$). We arrive at an estimate of $\Phi_R = 0.20$ for MC in PMMA. For C314 we use $\Phi_R = 0.83$, as measured by Felorzabihi et al. in PMMA.[6] For the calculation of J the molar extinction coefficients used for MC and HITC are 3.68×10^4 M^{-1}cm^{-1} and 2.15×10^5 M^{-1}cm^{-1}, respectively.[2,3] For κ we use 0.476, recommended for randomly distributed, but static donor-acceptors.[1] The C314+HITC, C314+MC, and MC+HITC pairs are calculated to have $R_0 = 3.8$ nm, 4.1 nm, and 5.5 nm, respectively.

S5. Overall C314 to HITC energy transfer.

From our measured τ_D and Φ_{FRET} values we can estimate an average FRET rate (k_{FRET}) between the donor and acceptors:

$$\Phi_{FRET} = \frac{k_{FRET}}{k_{FRET} + \frac{1}{\tau_D}} \tag{7}$$

The derived values for the dye-doped PMMA samples are shown in Table 4. It should be noted that in our samples the k_{FRET} values are influenced by the extent of donor→donor homo-FRET.

Table 4: FRET parameters for the dye-doped PMMA samples derived from the fluorescence decay curves.

sample	k_{FRET} (ns^{-1})	Φ_{FRET}
C314+HITC		
C314→HITC	0.12	0.26
C314+SP/MC		
C314→MC	$0.10^{a}/1.76^{b}$	$0.24^{a}/0.85^{b}$
C314+SP/MC+HITC		
C314→HITC	0.12^{c}	$0.19^{a}/0.04^{b}$
C314→MC	$0.14^{a}/2.12^{b}$	$0.26^{a}/0.83^{b}$
MC→HITC	1.04^{b}	0.70^{b}
C314 to HITC overall		$0.37^{a}/0.62^{b}$

[a] before UV irradiation

[b] after UV irradiation

[c] fixed

To estimate the overall C314 to HITC energy transfer (i.e., via both C314→HITC and C314→MC→HITC FRET pathways) for the C314+SP/MC+HITC sample, we first assume that the C314→HITC FRET rate is the same as in the C314+HITC sample. This allows us to estimate Φ_{FRET} values for the separate C314→HITC and C314→MC FRET pathways: $\Phi_{FRET} = 0.19$ and 0.26 before UV irradiation, respectively, and $\Phi_{FRET} = 0.04$ and 0.83 after UV irradiation, respectively. By then using $\Phi_{FRET} = 0.70$ for the MC→HITC FRET step, which is assumed to be constant before and after UV irradiation, we estimate the overall C314 to HITC energy transfer quantum yield to be 0.37 and 0.62, before and after UV irradiation, respectively.

Therefore, the overall C314 to HITC energy transfer quantum yield is predicted to increase by ∼70% after UV irradiation increases the MC population. This is significantly below the ∼300% enhancement seen in the HITC emission band's intensity after UV irradiation. Whereas MC→HITC radiative energy transfer may play a role, it can-not entirely account for this difference. The most probable explanation is that the photophysical rates for the donor dyes assumed to be constant in the above calculation are altered between the samples having different combinations of dyes: e.g., when adding HITC to the sample the presence of the Cl^- counter ion may affect the τ_D of C314, the Φ_{FRET} for MC→HITC FRET before UV irradiation may be less than after UV irradiation due to the reduced ability to undergo homo-FRET, or the addition or absence of dyes in the PMMA matrix may slightly influence the average spacing between the chromophores. Nevertheless, the emission and fluorescence decay data show that we can appreciably direct the C314 dye's excitation energy towards being transferred to the HITC dye by treating the SP/MC switch with UV light, with FRET playing a key role.

References

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