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

Supporting Information

Electronic Energy and Electron Transfer Processes in Photoexcited Donor-Acceptor Dyad and Triad Molecular Systems Based on Triphenylene and Perylene Diimide Units

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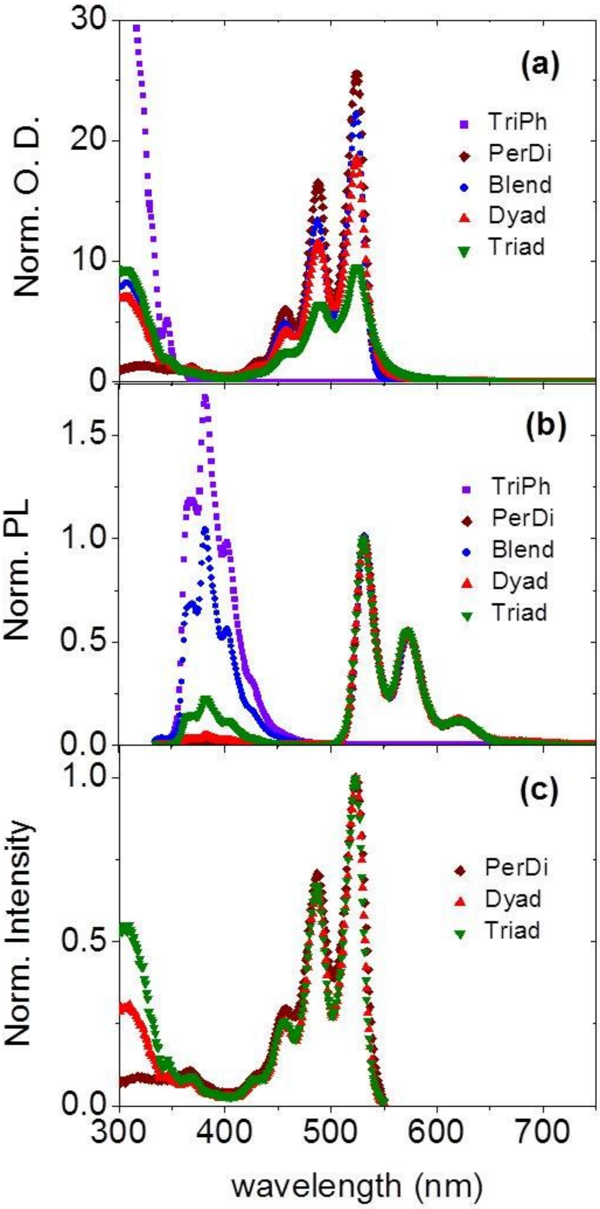

Fig. S1

For TriPh (■), PerDi (♦), TriPh:PerDi blend (●), dyad (▲) and triad (▼) in: (a) absorption spectra normalized at 360 nm, (b) photoluminescence spectra with λ_{ex}= 325 nm and normalized at 520 nm. (c) photoluminescence excitation spectra with λ_{em}= 550 nm and normalized at 520 nm.

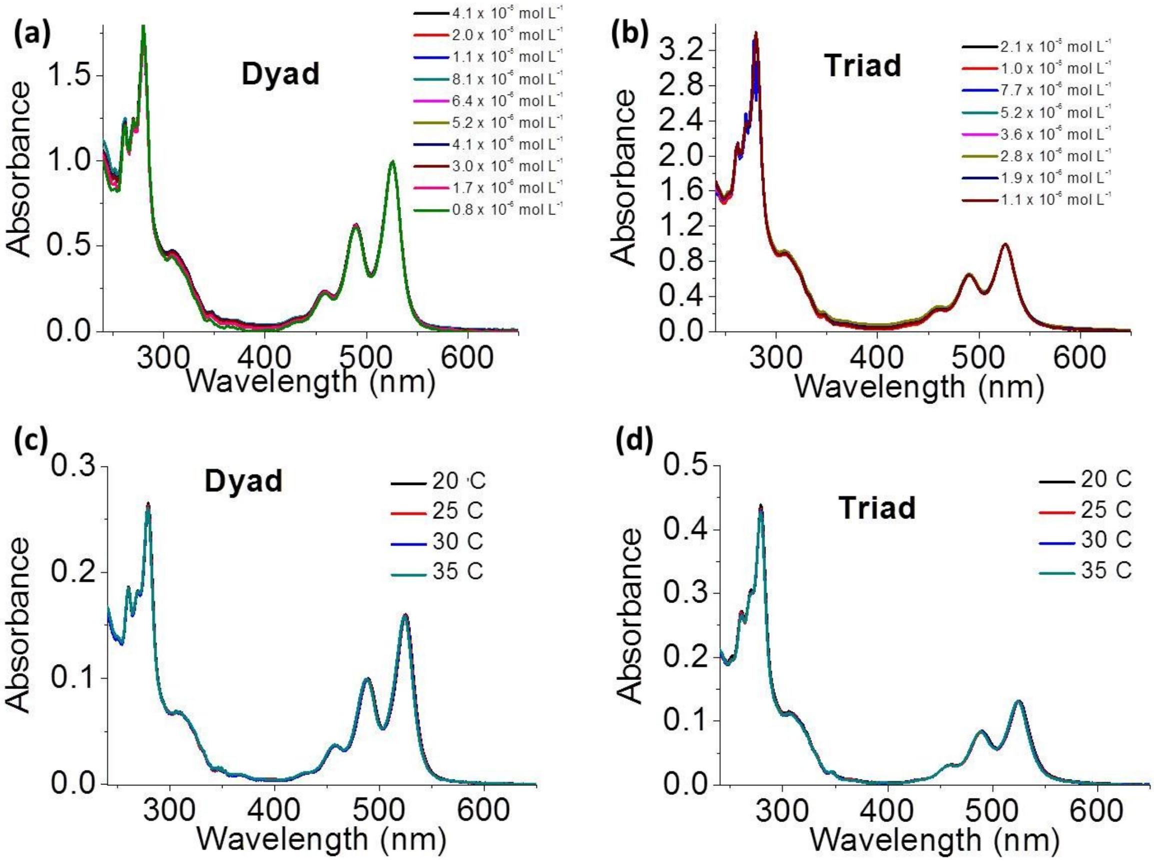

Fig. S2

Concentration dependence of the absorption spectra of the (a) dyad and (b) triad molecules in DCM at room temperature. The spectra were normalized to one at 525 nm, corresponding to the maximum absorption of PerDi moiety. Temperature dependence of the absorption spectra of the (c) dyad and (d) triad molecules in DCM. Concentrations of the dyad and triad solutions were 2.4 x 10^{-6} and 2.7 x 10^{-6} mol·L^{-1}, respectively.

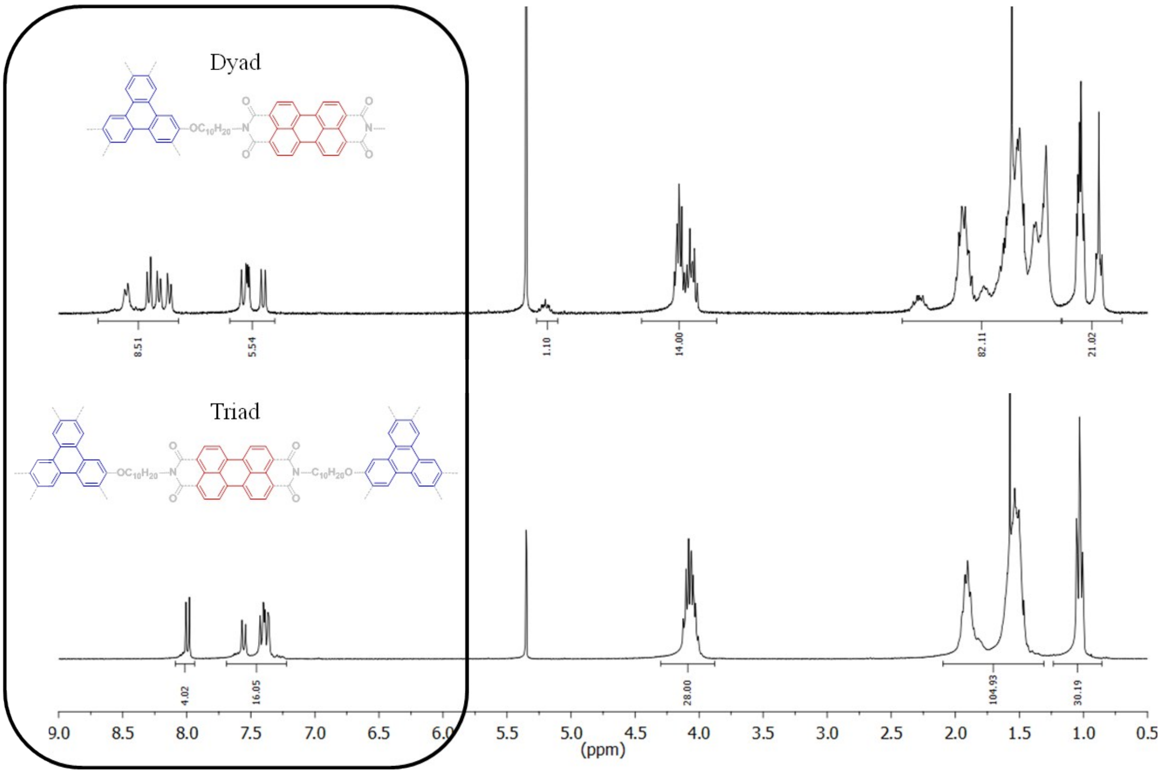

Fig. S3

^{1}H NMR spectra of the dyad and triad molecules in CD_2Cl_2 (Spectrometer 300 MHz). The framed part corresponds to aromatic protons of triphenylene and perylene diimide cores.

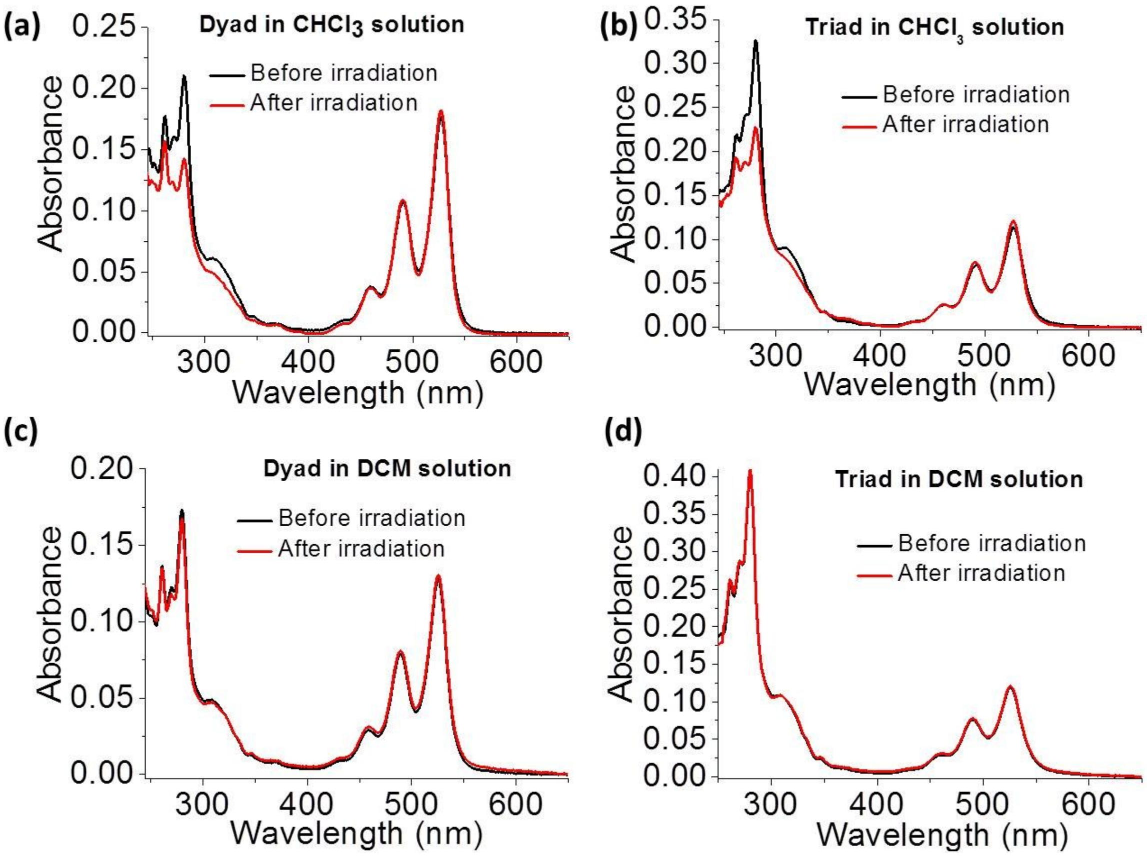

Fig. S4

Absorption spectra of the (a) dyad and (b) triad molecules in chloroform before and after irradiation with a 450 W Xe lamp (irradiation time: 2-3 minutes; wavelength of 325 nm). Same measurements were carried out for (c) dyad and (d) triad molecules diluted in DCM. Concentrations of the solutions were in the range of 1.5 - 2.5 x 10^{-6} mol$\cdot$L^{-1}.

The results show that an UV irradiation leads to a decrease of the absorption from the triphenylene units of the dyad and triad molecules in chloroform solution. This indicates that a photodegradation of the dyad and triad molecules occurs in this solvent. In contrast, the absorption spectra of the dyad and triad molecules are not changed upon UV illumination when using DCM as solvent.

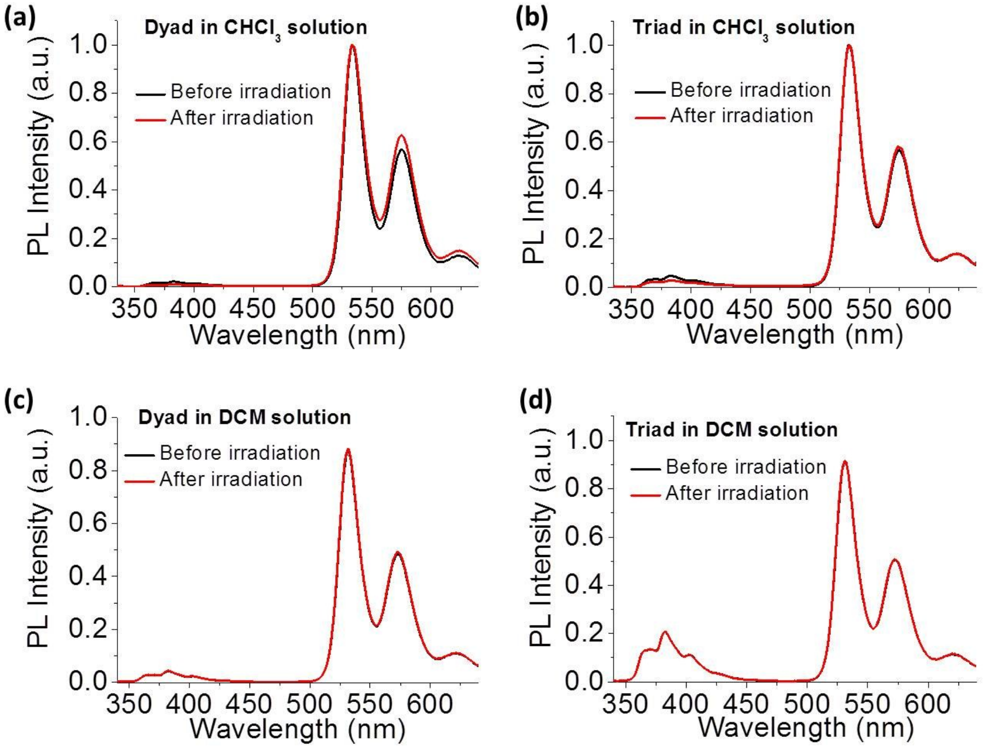

Fig. S5

Photoluminescence spectra of the (a) dyad and (b) triad molecules in chloroform before and after irradiation with a 450 W Xe lamp (irradiation time: 2-3 minutes; wavelength of 325 nm). Same measurements were carried out for (c) dyad and (d) triad molecules diluted in DCM. Concentrations of the solutions were in the range of 1.5 - 2.5 x 10^{-6} mol·L^{-1}. Excitation wavelength was 325 nm where the two units, TriPh and PerDi, absorb light.

These results show the influence of an UV irradiation on the emission spectra of the dyad and triad molecules in chloroform and DCM solutions. In the case of chloroform, the intensity of the emission from TriPh for both dyad and triad molecules is changed, which is a significant problem to determine the energy transfer efficiency. In addition, it can be seen that the ratio of the vibronic peaks of the PerDi emission is changed, this effect being stronger in the dyad case. In contrast, no changes in the emission spectra are observed upon irradiation when the dyad and triad are dissolved in DCM.

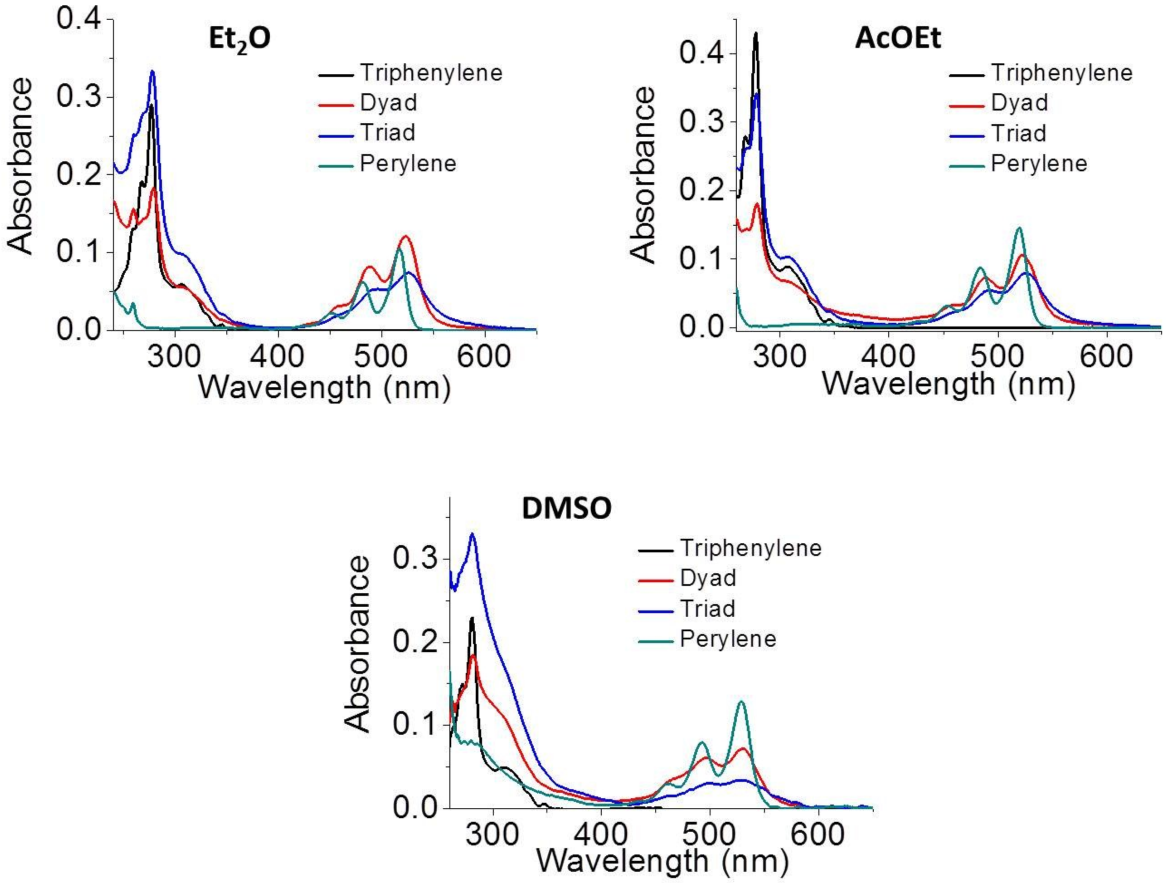

Fig. S6

Absorption spectra of the triphenylene, perylene diimide, dyad and triad molecules in ethyl acetate (AcOEt), diethyl ether (Et$_2$O) and dimethyl sulfoxide (DMSO). Concentration of the solutions were in the range of of 1.5 - 2.5 x 10^{-6} mol·L^{-1}.

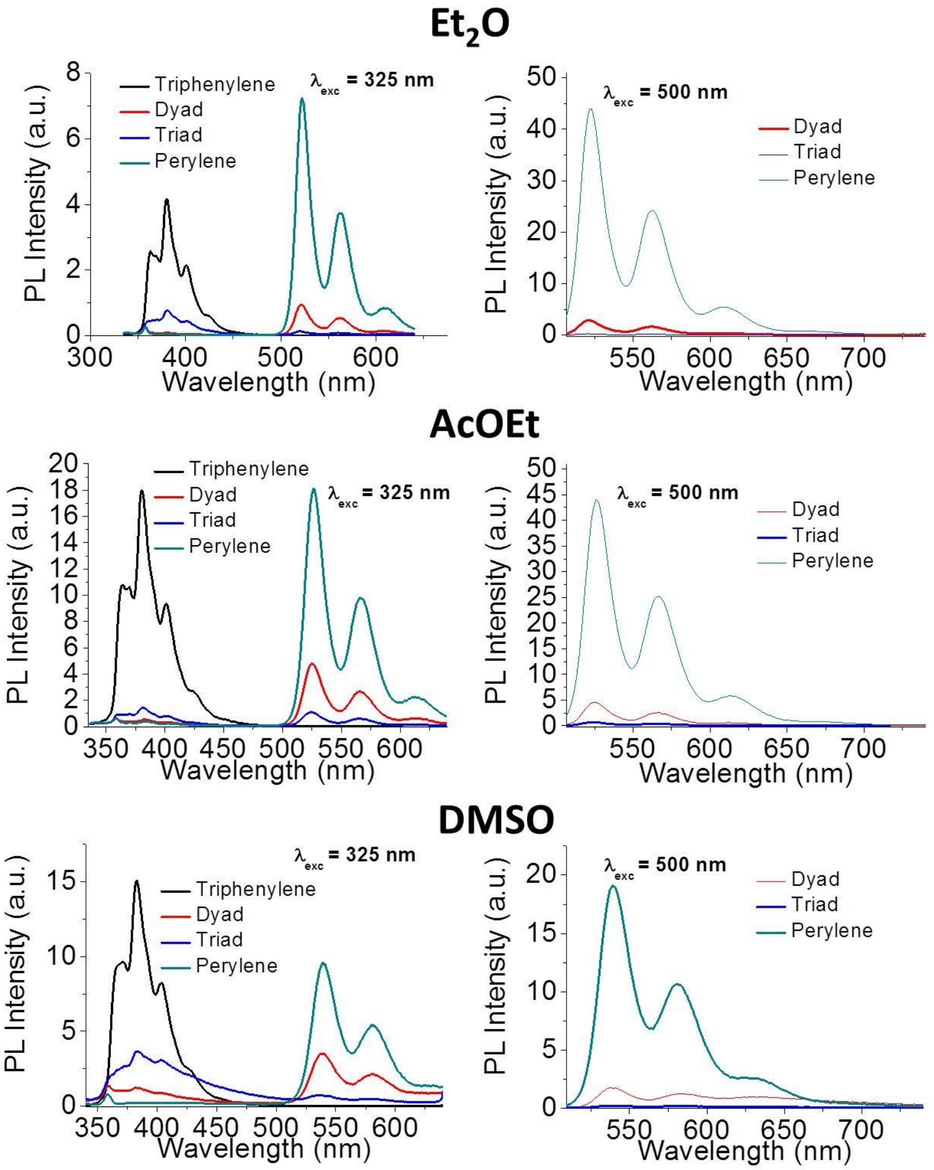

Fig. S7

Photoluminescence spectra of the triphenylene, perylene diimide, dyad and triad molecules in ethyl acetate (AcOEt), diethyl ether (Et_2O) and dimethyl sulfoxide (DMSO). Concentration of the solutions were in the range of 1.5 - 2.5 x 10^{-6} mol·L^{-1}. Excitation wavelengths were 325 nm to excite both TriPh and PerDi units or 500 nm to excite only the PerDi units.

The emission spectra of the dyad and triad molecules in AcOEt and Et_2O exhibit a similar behaviour as that in DCM. Upon photo-excitation at 325 nm, the fluorescence from TriPh is quenched due to energy transfer while there is no increase of the emission of PerDi because of a quenching by photo-induced electron transfer. It is interesting to note however that the larger aggregation in AcOEt and Et_2O results in a more intense emission of the TriPh than PerDi in the triad case. The emission spectra of the PerDi unit in the dyad and triad were also measured using an excitation wavelength of 500 nm. While the optical density of the PerDi, dyad and triad in Et_2O solutions used in these measurements is similar at 500 nm, the PLQY of the PerDi emission decreases by a factor superior to 15 for the dyad and 150 for the triad. Similarly, in AcOEt, the PLQY of the PerDi emission decreases by a factor of about 10 for the dyad and 80 for the triad. In case of the DMSO solutions, the emission spectra of the TriPh and PerDi units in dyad and triad are strongly broadened compared to those of the chromophores alone, which supports our conclusion that intermolecular interactions due to aggregation take place in this solvent. It should also be noticed that, as observed in all other solvents, upon photo-excitation at 500 nm, the emission from PerDi in dyad and triad systems is quenched compared to that of the PerDi alone. Overall, these results demonstrate that energy transfer and photo-induced electron transfer occur in the dyad and triad molecules not only in DCM but also in a range of other solvents with different polarity and viscosity.

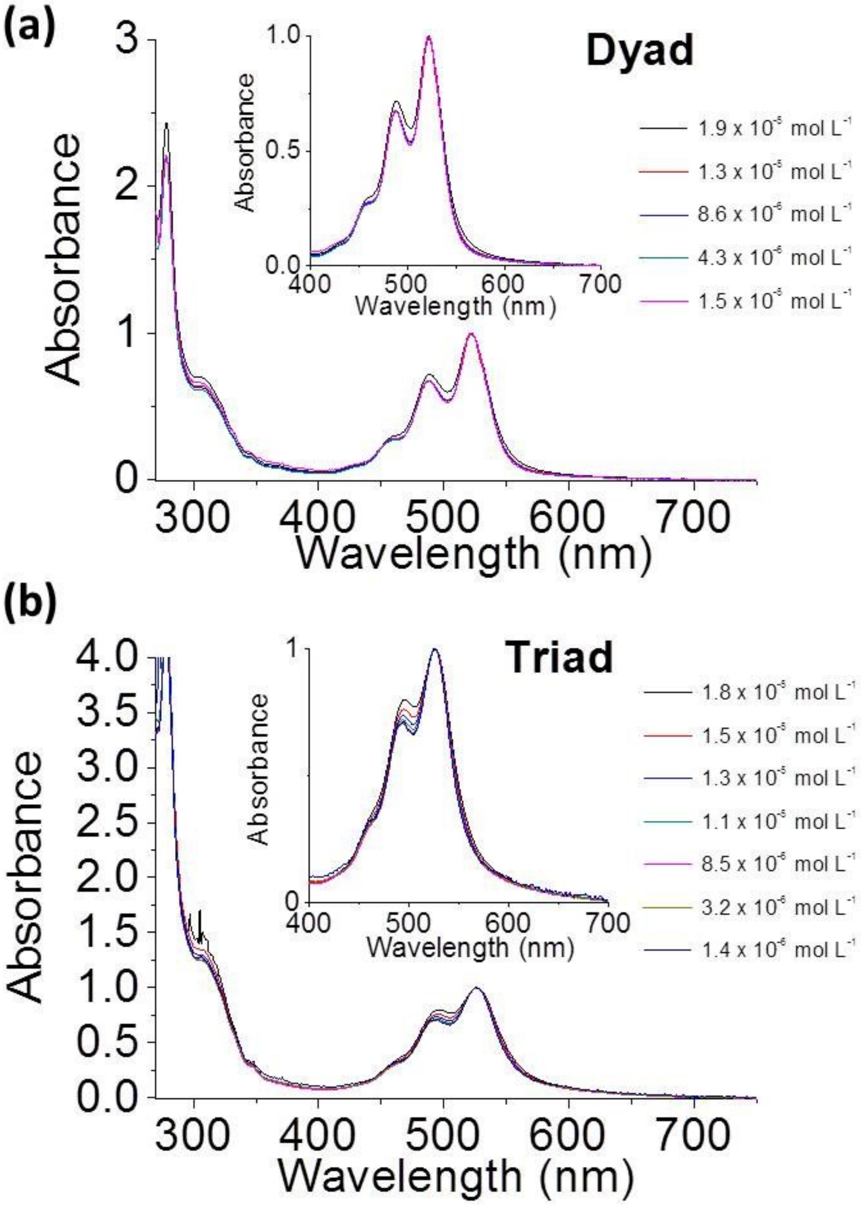

Fig. S8

Concentration dependence of the normalized absorption spectra of the (a) dyad and (b) triad molecules in AcOEt at room temperature.

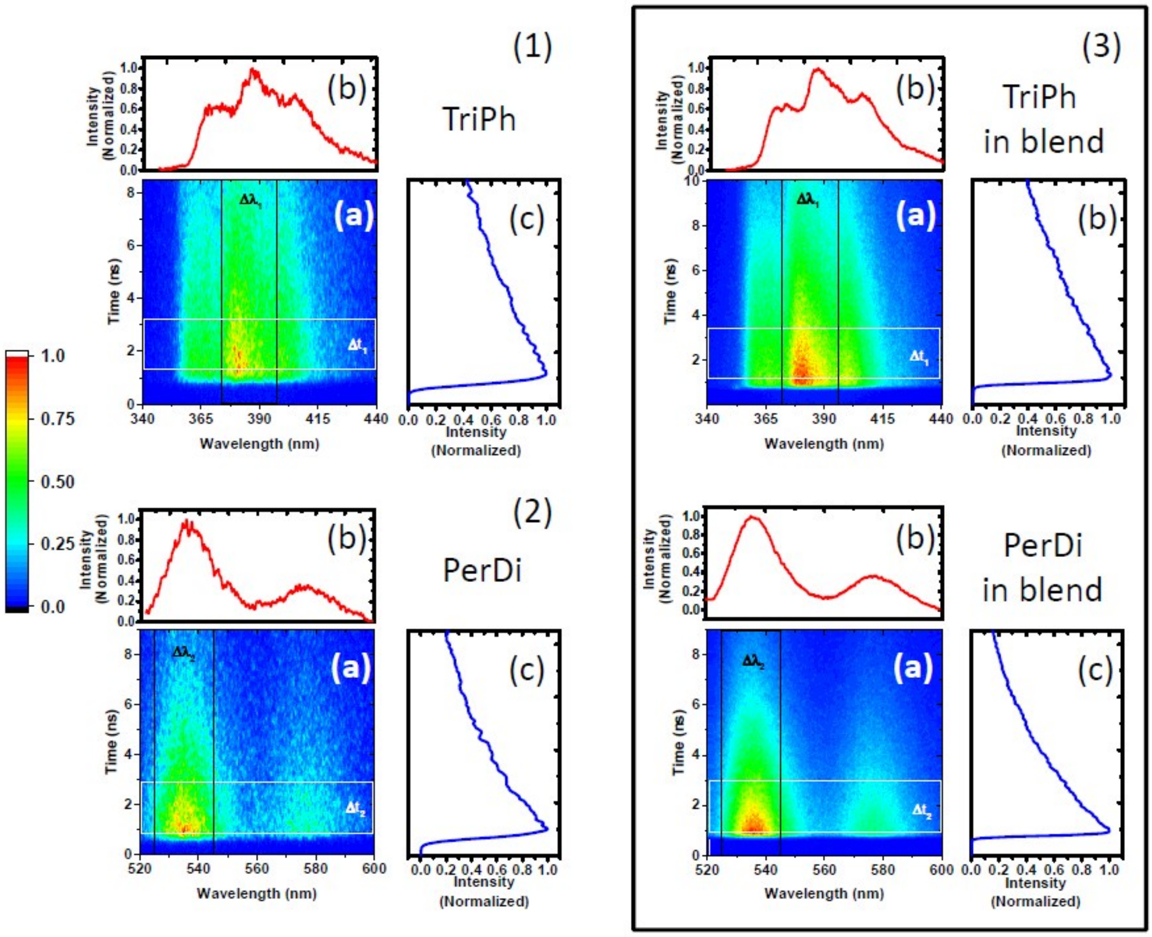

Figure S9

(a) Streak camera images of TriPh (1), PerDi (2) and TriPh:PerDi blend (3) in DCM solution using an excitation wavelength of 325 nm. (b) Integration of the streak camera images of TriPh (1), PerDi (2) and TriPh:PerDi blend (3) along the time axis near the regions marked as Δt_1 and Δt_2 in (a). (c) PL dynamics of TriPh (1), PerDi (2) and TriPh:PerDi blend (3) obtained after integrating the streak camera images along the wavelength axis within the donor and acceptor boxed regions marked in (a).

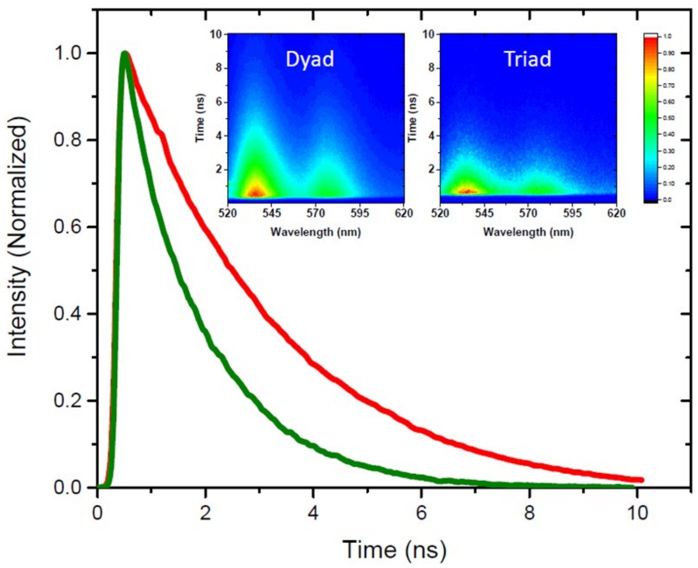

Figure S10

PL decays of the perylene diimide moieties in the dyad (red line) and triad (green line) solutions obtained after integration of the streak camera images in the spectral region of 515-570 nm. The solutions were photo-excited at 515 nm. The corresponding streak camera images are shown in inset.

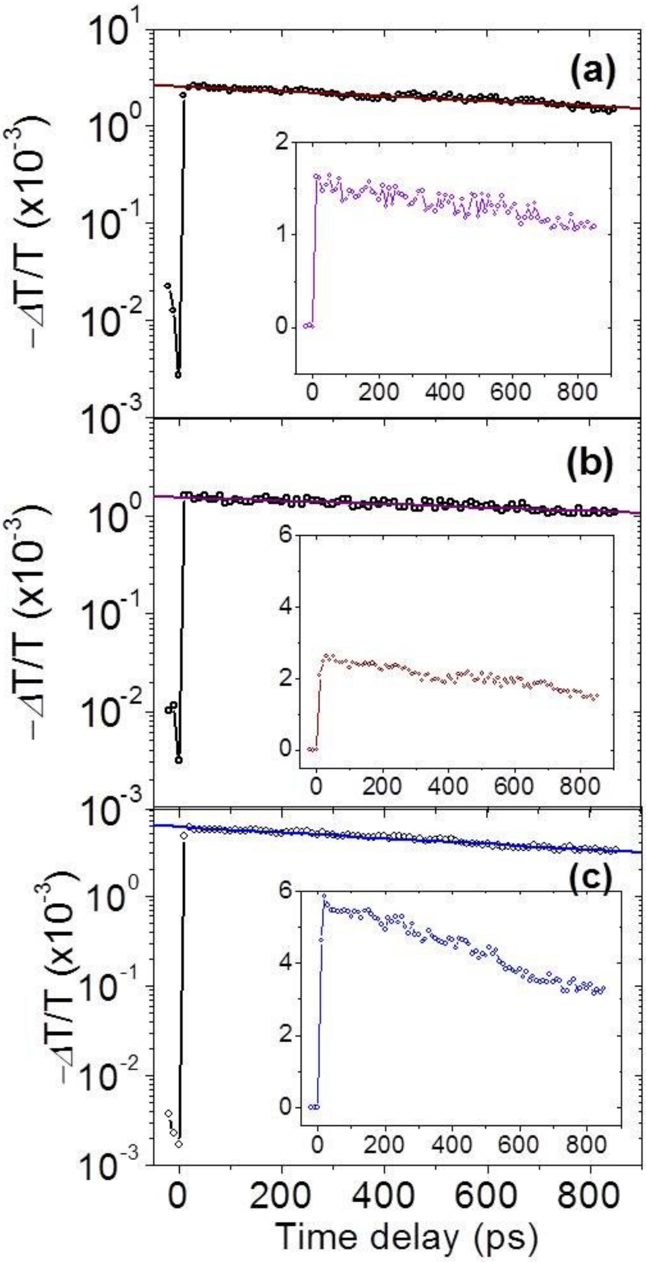

Figure S11

Kinetic curves of *ΔT*/*T* obtained at 725 nm for DCM solutions of TriPh (a), PerDi (b) and TriPh:PerDi blend (c) after subpicosecond excitation pulses at 325 nm.

Kinetic model

- The population of the TriPh and PerDi excited states, noted [T*] and [P*] upon photo-excitation at 325 nm can be described by the following rate equations:

Excitation of the TriPh moieties at 325nm :

$\frac{d[T^*]}{dt} = -(k_T + k_{en} + k_{ee})[T^*]$, which leads to: $[T^*] = [T^*]_0 \exp[-t(k_T + k_{en} + k_{ee})]$.

Direct excitation of P at 325nm:*

$\frac{d[P^*]}{dt} = -(k_P + k'_{ee})[P^*]$, which leads to : $[P^*]_{direct} = [T^*]_{0/direct} \exp[-t(k_P + k'_{ee})]$

Population of P via energy transfer from T:*

$$\frac{d[P^*]}{dt} = -k_{en}[T^*] - (k_p + k'_{ee})[P^*]$$

The solution of this differential equation can be expressed as: $\dot{A}(t)\exp(-\alpha t) - \alpha A(t)\exp(-\alpha t) + \alpha A(t)\exp(-\alpha t) = k_{en}[T^*]_0 \exp(-\beta t)$

with: $\dot{A}(t) = k_{en}[T^*]_0 \exp(\alpha - \beta)t$ and $A(t) = \frac{k_{en}[T^*]_0}{\alpha - \beta}\exp(\alpha - \beta)t + cst$

At t = 0, A(0)=0 → $cst = \frac{k_{en}[T^*]_0}{\alpha - \beta}$

Therefore we can write: $P(t) = [P^*] = \frac{k_{en}[T^*]_0}{\alpha - \beta}\exp(-\beta t) - \exp(-\alpha t)$

With $\alpha = k_T + k_{en} + k_{ee}$ and $\beta = k_p + k'_{ee}$

Taking into account the population of PerDi units produced by direct excitation at 325 nm, the total population of [P*] can be expressed as:

$$[P^*]_{Total} = \frac{k_{en}[T^*]_0}{\alpha - \beta}(\exp(-\beta t) - \exp(-\alpha t)) + [P^*]_{0/direct}\exp(-\alpha t)$$

- The population of PerDi excited state upon selective photo-excitation ($\lambda^{exc} > 400$nm) can be expressed as:

$\frac{d[P^*]}{dt} = -(k_P + k'_{ee})[P^*]$, which leads to: $[P^*] = [P^*]_{0/direct}\exp(-\alpha t)$

→ From this kinetic model, we can conclude that:

- Upon excitation at 325 nm, we should observe a single exponential decay with $\tau = 1/\beta$ for the emission from the TriPh units and a biexponential decay with a rise time $1/\beta$ and a decay $1/\alpha$ for the fluorescence from the PerDi units.

-Upon direct excitation of the PerDi units, a single exponential decay with $\tau = 1/\alpha$ should be obtained.

- As mentioned in the main text of the manuscript, the simple kinetic model described above cannot explain the observed biexponential decay of the emission from the TriPh units upon excitation at 325 nm. This suggests that a more complicated model should be proposed based on a number of different conformers in the ground-state and excited states.

Let us consider the still oversimplified case where two types of conformers, corresponding to the folded and unfolded species, are present in the solution.

- The population of each species can be described by the model above but with different time constants.
- The energy transfer and electron transfer can take place in the folded and unfolded systems.

From these considerations, it can be anticipated that the resolution of such kinetic model would lead to:

- Two exponential decays for the emission from the TriPh units (upon excitation at 325 nm)
- Two exponential decays for the emission from the PerDi units (upon excitation at 500 nm)
- A complicated dynamic behavior with 4 time constants for the emission of PerDi (upon excitation at 325 nm)