Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Supporting Information for:

Energy and electron transfer processes in polymeric nanoparticles

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Table 1-ESI: Relative reagent's molar ratios used for the synthesis of the studied polymeric nanoparticles.

	A	D	MMA	EGDMA
PAD0	1	0	93	53
PAD25	1	23	70	53
PAD75	1	70	23	53
PD25	0	23	70	53
PS75	0	70	23	53

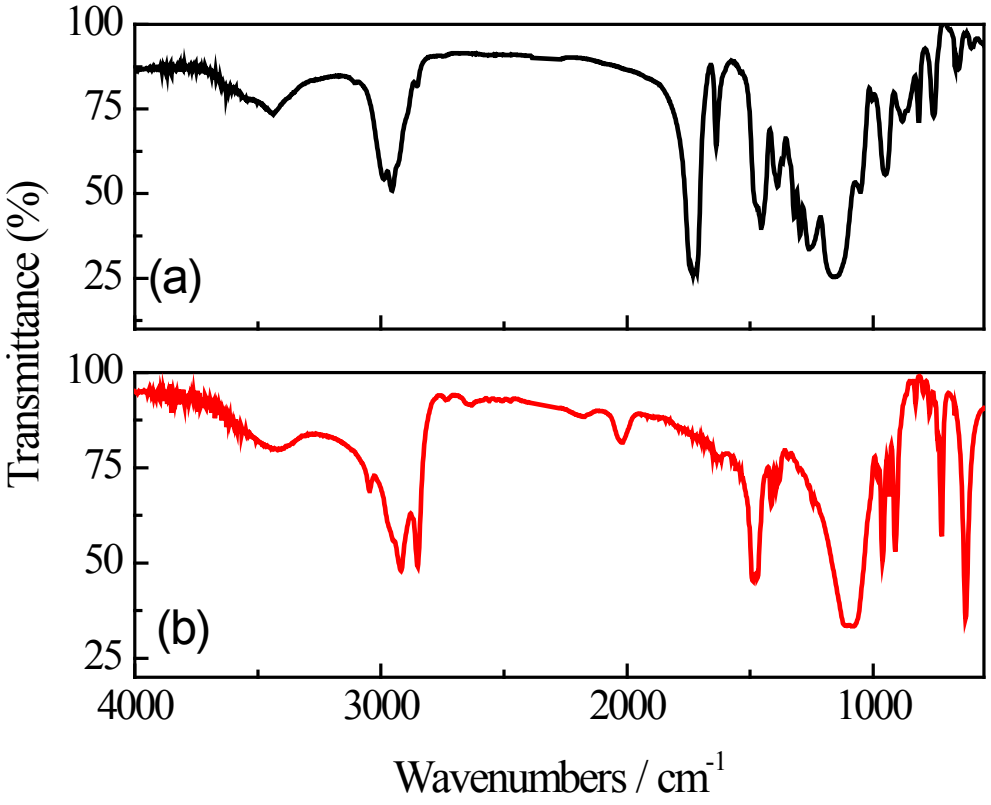

Figure 1-ESI FT-IR of **(a)** PAD0 and **(b)** $CTAClO_4$, both disperse in KBr.

Table 2-ESI: Values obtained from DLS experiments for the NPs studied in DCM

D_h: hidrodinamic diameter; δ: distribition width, P.I.: Polydispersity Index

	D_h (nm)	δ (nm)	P.I.
PAD0	7	3	0.27
PAD25	6	4	0.24
PAD75	9	4	0.40
PD25	8	7	0.37
PD75	9	7	0.40

Table 3-ESI: Lifetime (τ_i) and preexponential factor (a_i) obtained from the fitting of the fluorescence decay profiles of the anthracenyl fluorophore (A) in the different polymeric nanoparticles (excitation wavelength 378 nm).

	τ_1 / ns	a_1	τ_2 / ns	a_2	τ_3 / ns	a_3	τ_M/ ns
PAD0	4.32	0.046	9.53	0.046	-	-	6.92
PAD25	1.13	0.052	4.63	0.052	11.4	0.009	3.41
PAD75	0.88	0.111	3.25	0.039	11.9	0.003	1.70

The mean lifetime is calculated according to equation 1 (main text): $\tau_M = \frac{\sum_i a_i \tau_i}{\sum_i a_i}$

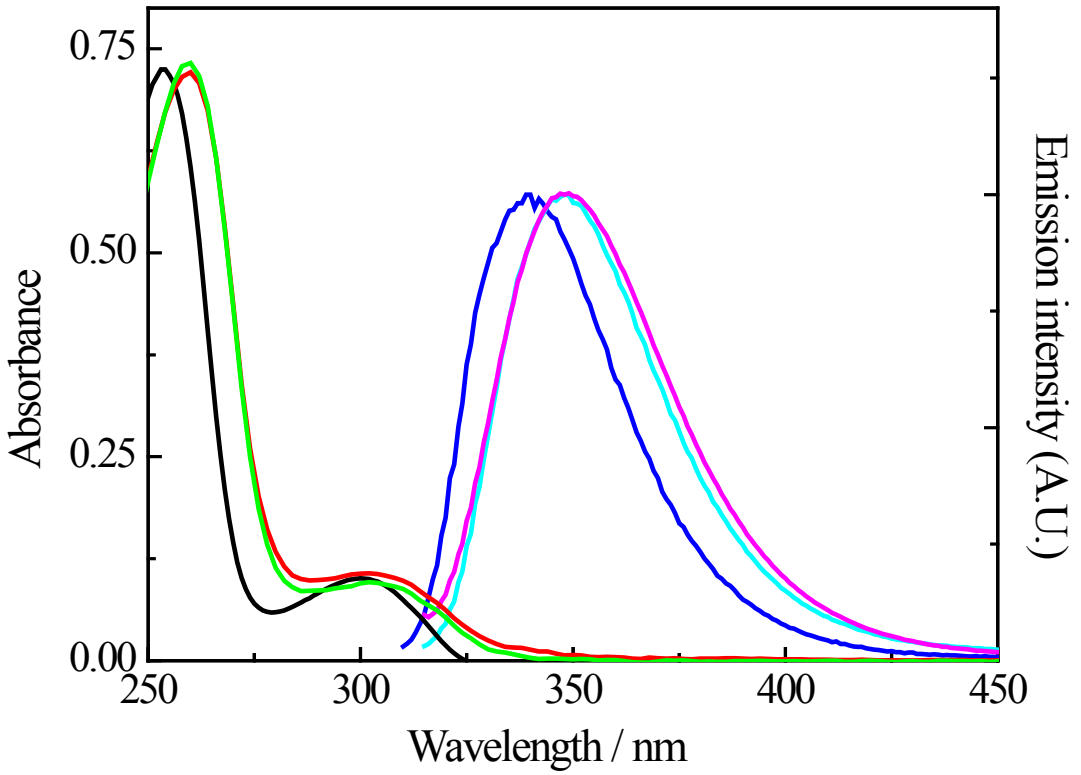

Figure 2-ESI: Absorption spectra of DMA (black line), PD25 (red line) and PD75 (green line) in THF. Emission spectra obtained by excitation at 306 nm of DMA (blue line), PD25 (light blue line) and PD75 (magenta line) in the same solvent.

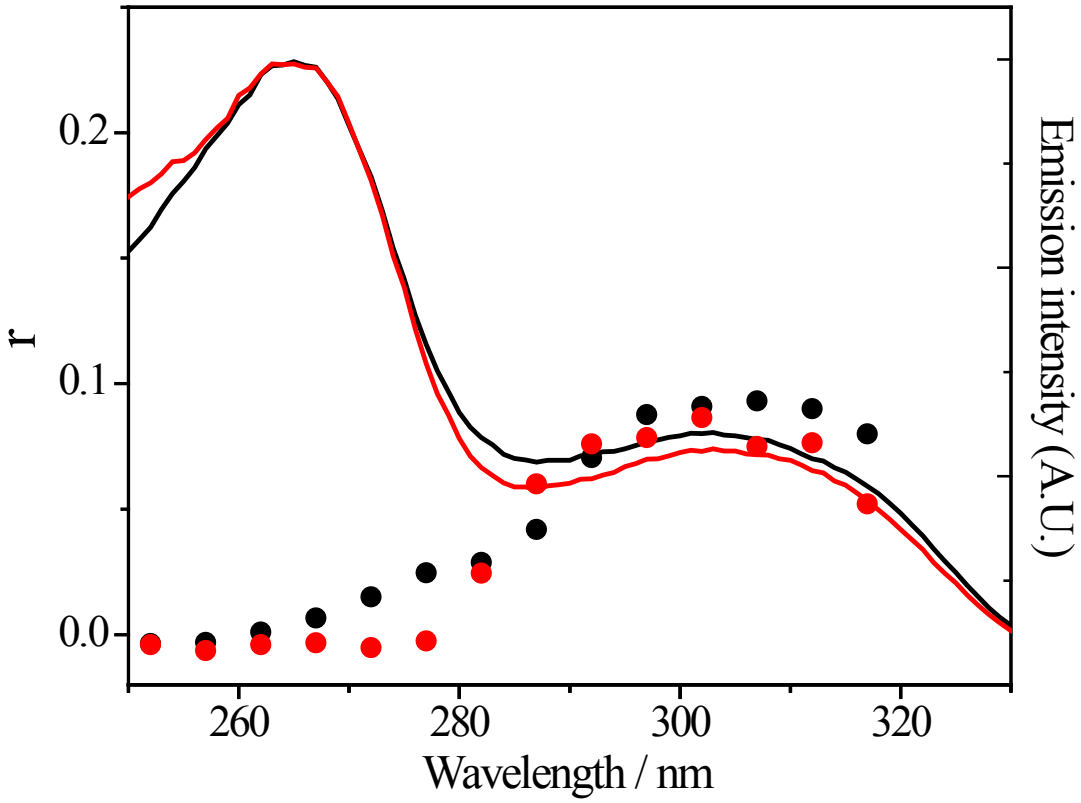

Figure 3-ESI: Excitation spectra of a dispersion of PD75 0.02 mg/ml (black) and PAD75 0.03 mg/ml (red) in THF. Emission wavelength: 350 nm. The excitation steady-state anisotropy (r) spectra are represented by the solid circles of the corresponding colors. The actual values of r are shown in the left axis of the plot.

Table 4-ESI: Quenching of the singlet excited state of 9MA by DMA in different media.

Solvent	ε	n	k_q/ M^{-1} s^{-1}	ΔG^*_{et}/ (kJ/mol)	$h\upsilon_e^{max}$/ kJ	τ_e/ ns
Hexane	1.88	1.375	$1.5\ 10^{10}$	-36.9	252.1	8.1
c-hexane	2.02	1.426	-	-37.8	250.9	-
Butyl ether	3.08	1.399	-	-42.7	243.9	12.6
Ethyl ether	4.02	1.352	$1.4\ 10^{10}$	-45.1	237.6	23.8
Ethyl acetate	6.02	1.372	-	-47.9	229.8	-
THF	7.58	1.407	$1.4\ 10^{10}$	-49.1	228.7	17.1
Dichloromethane	9.08	1.445	$1.6\ 10^{10}$	-50.4	226.3	23.4
Acetonitrile	35.7	1.339	$1.5\ 10^{10}$	-50.4	-	-

ΔG^*_{et} where calculated from the redox potential of D (E_{ox} = 0.81 V) and A (E_{red} = -1.93 V) measured versus SCE in acetonitrile[1] and the E_{00} energy of the anthracenyl fluorophore (values are reported in the main text) following the procedure already published. [2]

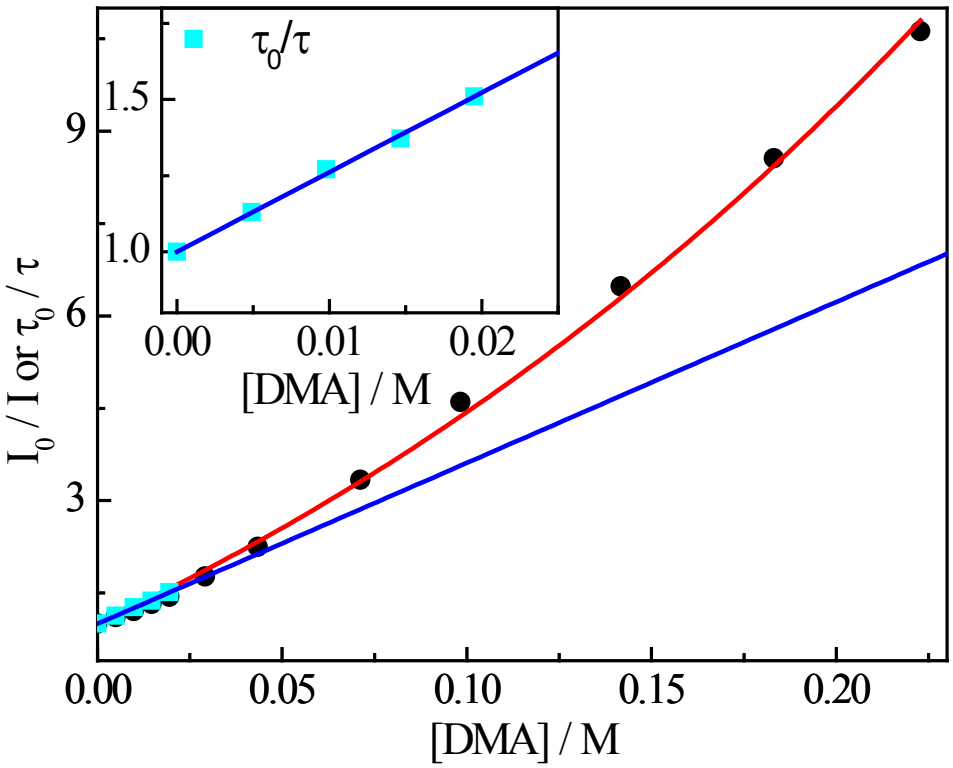

Figure 4-ESI: Quenching of 9MA emission by DMA in DCM studied by steady-state (black circles) and time resolved (blue squares) spectroscopic methods

The Stern-Volmer ($k_q\tau_0 \sim$ 26.1 M^{-1}) constant for the dynamic quenching was calculated from the slope of the τ_0/τ plot show in the insert of figure 4-ESI, and the I_0/I data was fitted to equation 6 (main text-red line) taking R_{AD} as the only adjustable parameter.

$$\frac{I_0}{I} = \left(1 + k_q\tau_0[Q]\right) exp^{\left(\frac{4\pi N_A[Q]}{3R_{AD}^3}\right)}$$

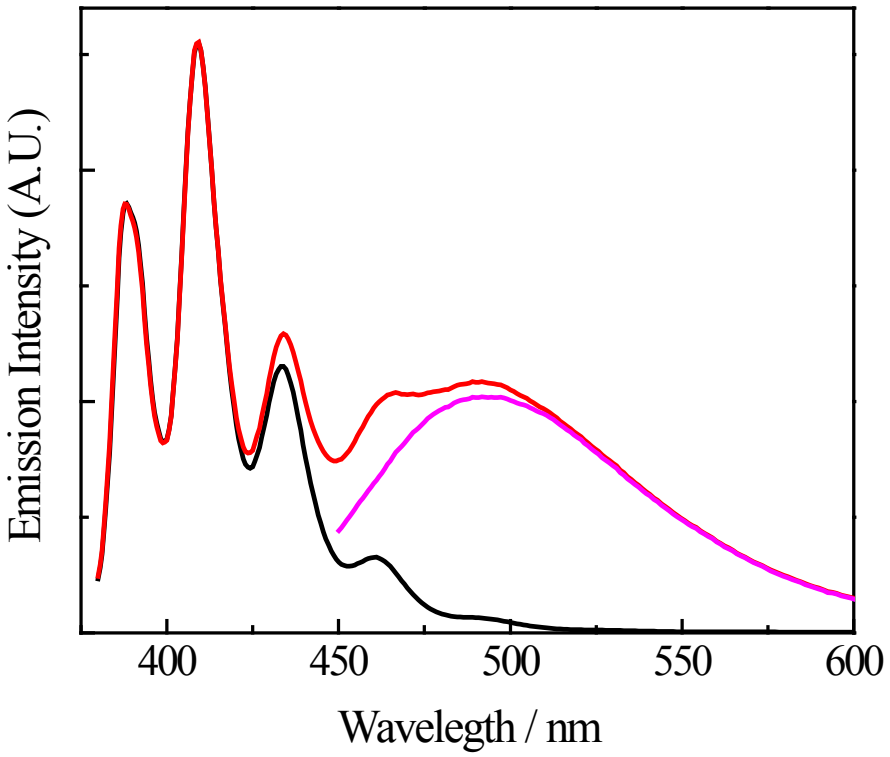

Figure 5-ESI: Emission spectra of 9MA in ethyl ether in the absence (black) and in the presence of DMA 0.1 M (red). Both spectra were normalized at 415 nm. The emission spectrum of the intramolecular exciplex (magenta) was obtained by subtracting the black spectrum from the red spectrum.

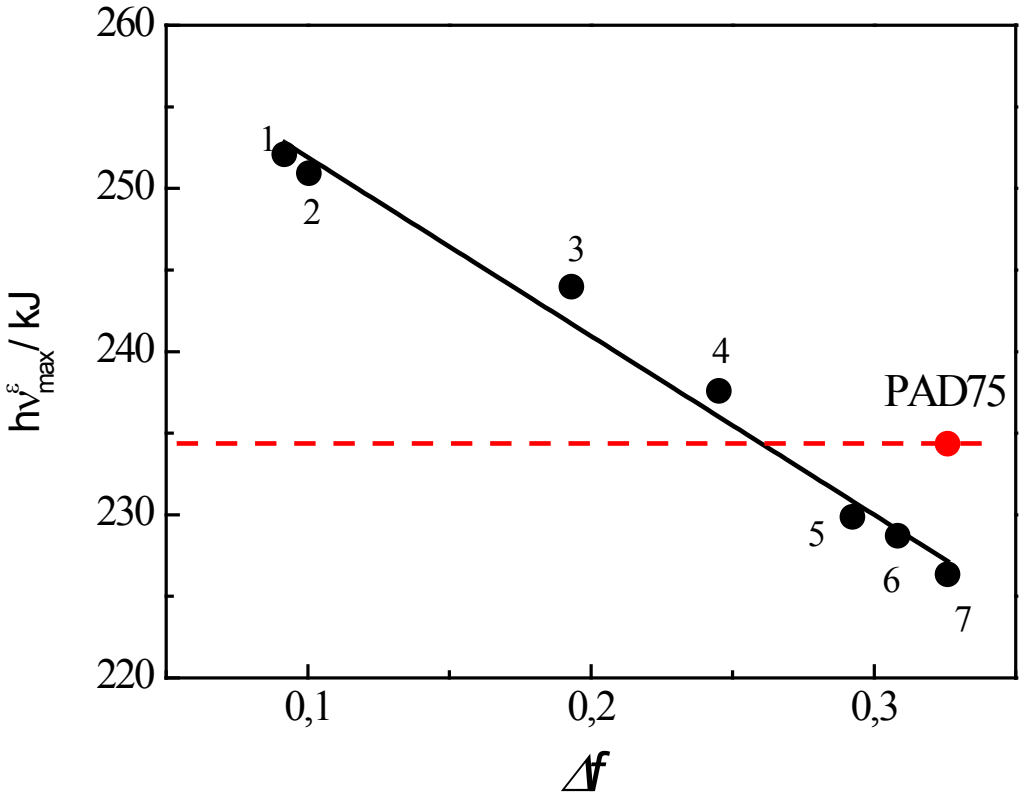

Figure 6-ESI: Lippert-Mataga plot for the intermolecular 9MA/DMA exciplex (black solid circles) and the corresponding emission energy of the (intra-particle) exciplex formed by PAD75 in DCM (red dashed line). Solvents: n-hexane (1), c-hexane (2), butyl ether (3), ethyl ether (4), ethyl acetate (5), THF (6) and DCM (7).

The Lippert-Mataga expression is given by:

$$h\upsilon_{max}^{\varepsilon} = h\upsilon_{max}^{\varepsilon_0} - \frac{2\mu_e^2}{4\pi\epsilon_0\rho^3}\Delta f$$

where: $\Delta f = f_\varepsilon - \frac{1}{2}f_{n^2}$, with $f_\varepsilon = \frac{\epsilon-1}{2\epsilon+1}$ and $f_{n^2} = \frac{n^2-1}{2n^2+1}$. The values of the static dielectric constant (ε) and refractive index (n^2) of the solvents are collected in table 4-SI. From the slope of the plot in Figure 5-SI, the ratio: $\frac{\mu_e^2}{4\pi\epsilon_0\rho^3}$ ~ 55 kJ/mol was calculated. In turn, this values is used to estimate the $\Delta G_{et}^{*\varepsilon}$ as described above. Values of relative permittivities (ε_r) and refraction index (n_D) of pure solvents were obtained from literature. [3,4,5].

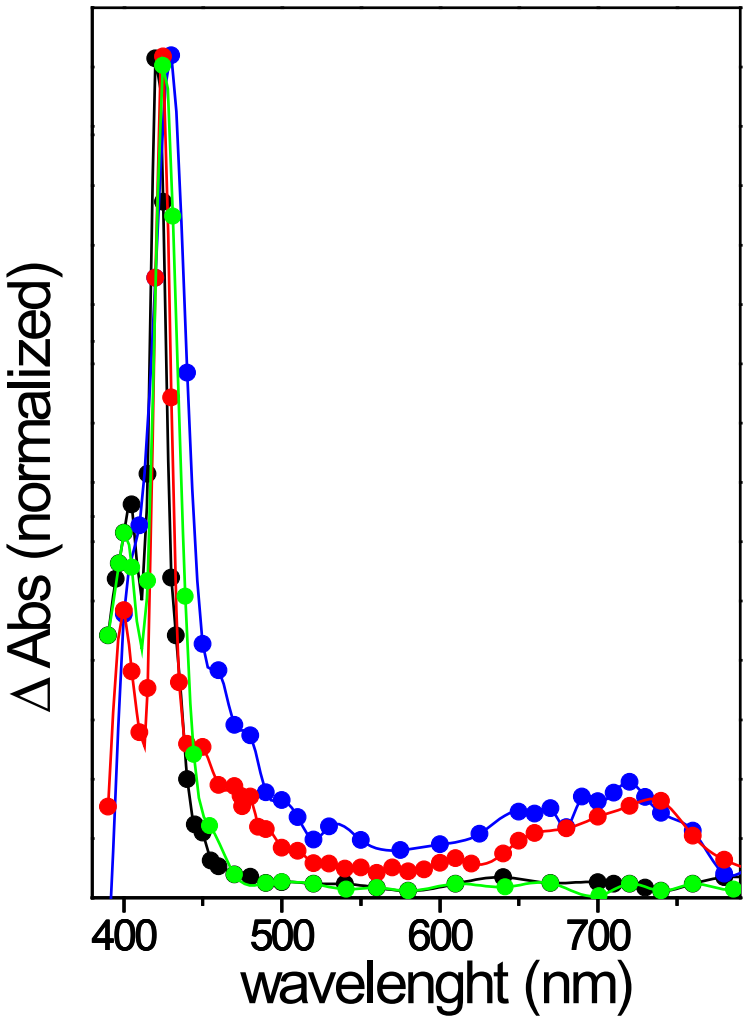

Figure 7-ESI: Normalized transient absorption spectra obtained 5 μsec after laser excitation (355 nm) for 9MA in acetonitrile (black), 9MA+ DMA 0.40 M in acetonitrile (blue), 9MA+ DMA 0.40 M in DCM (green) and a dispersion of PAD0 2.5 mgr/ml + DMA 0.40 (red). Samples were deaerated.

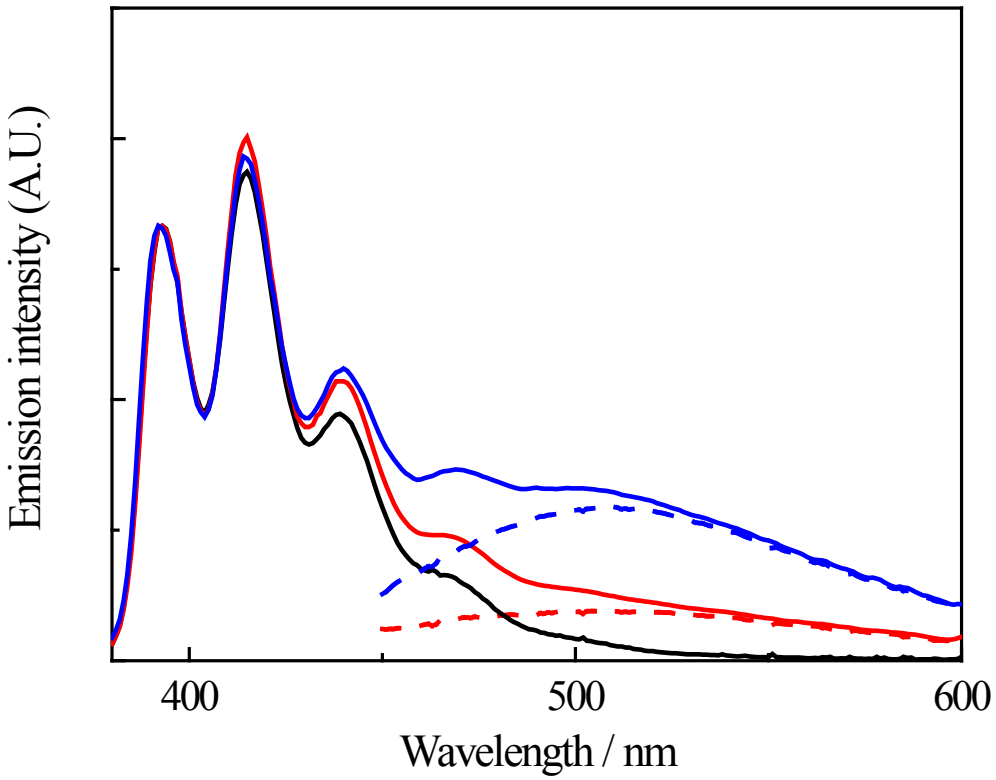

Figure 8-ESI: Emission spectra of PDA0 (black continuous line), PDA25 (red) and PDA75 (blue) in DCM. All spectra were normalized at 490 nm. The dashed lines show the emission of the intra-NP exciplex obtained by subtraction.

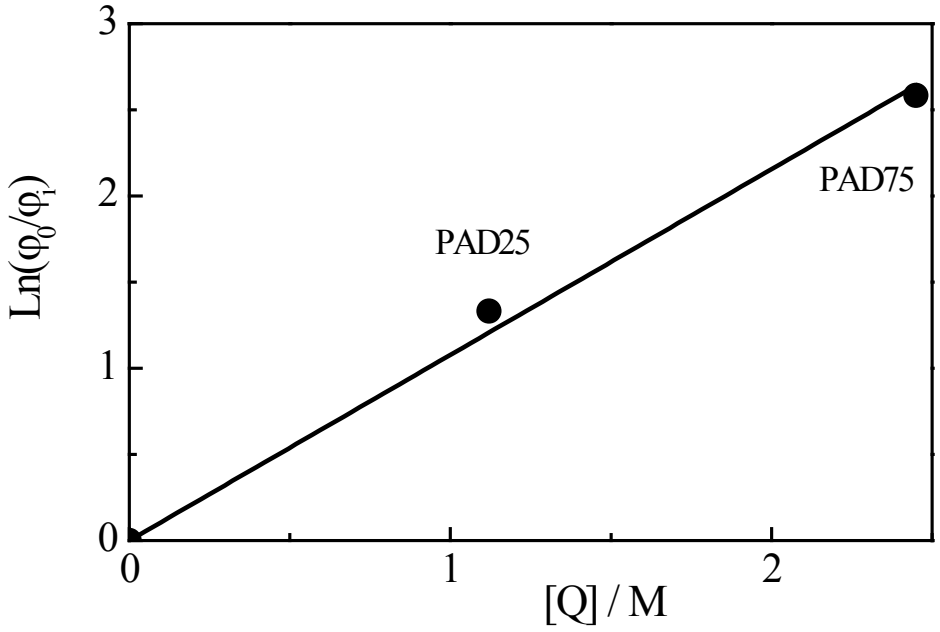

Figure 9-ESI: Perrin plot for the "overall" intra-NPs eT quenching of the anthracenyl fluorophore as a function of D concentration.

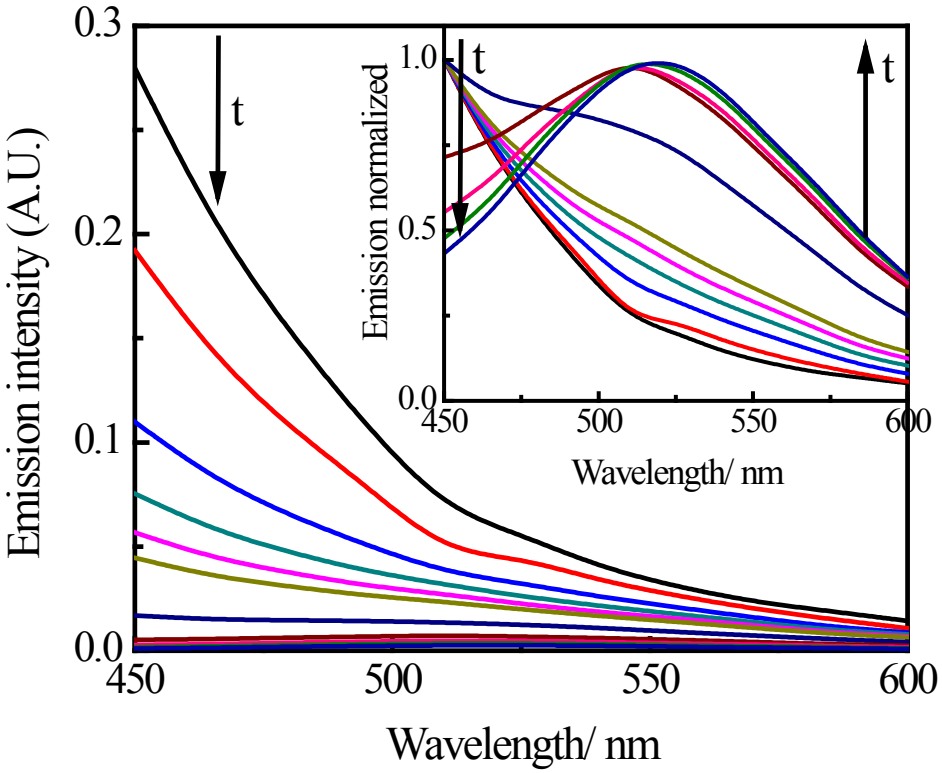

Figure 10-SI: Time resolved emission spectrum (TRES) obtained for a dispersion of PAD75 (2.5 mg/ml) in DCM. Excitation wavelength: 378 nm. The emission spectra correspond to 0.5, 1, 2, 3, 4, 5, 10, 20, 30, 40 and 50 ns after pulsed excitation.

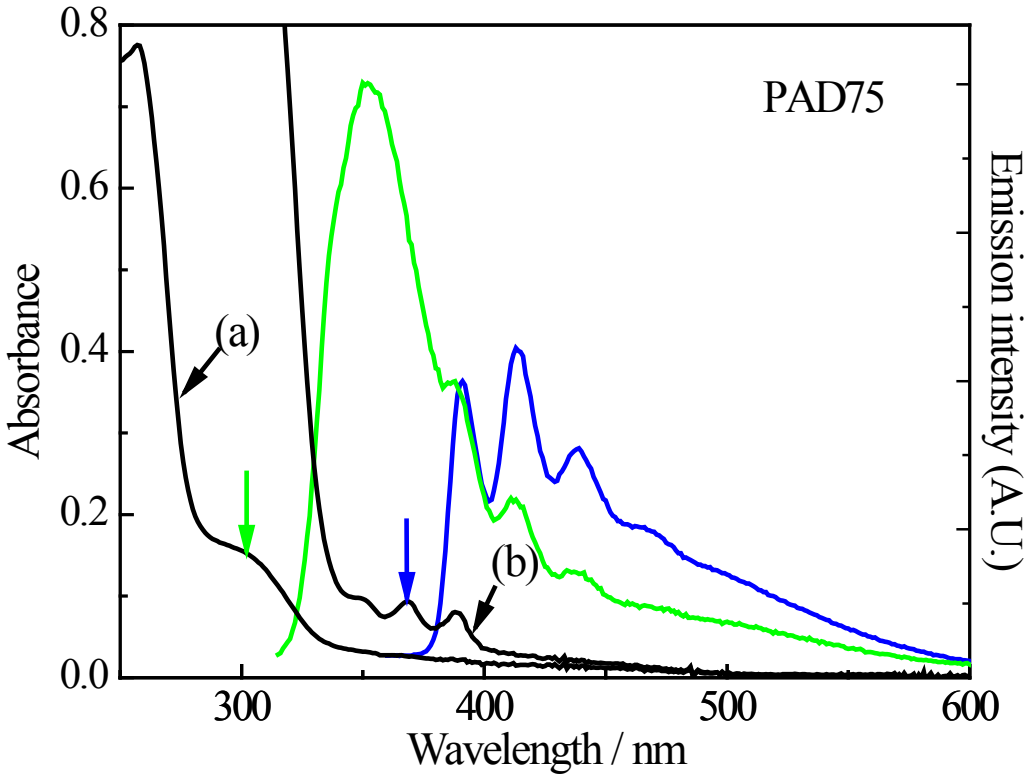

Figure 11-ESI: (a) absorption spectrum of a dispersion of PAD75 (0.02 mg/ml) in THF and (b) absorption spectrum of a dispersion of PAD75 (1.2 mg/ml) in the same solvent. Emission spectra obtained by excitation of the dispersions at 368 nm (blue line) and 306 nm (green line) of a dispersion of PAD75 (0.02 mg/ml) in THF.

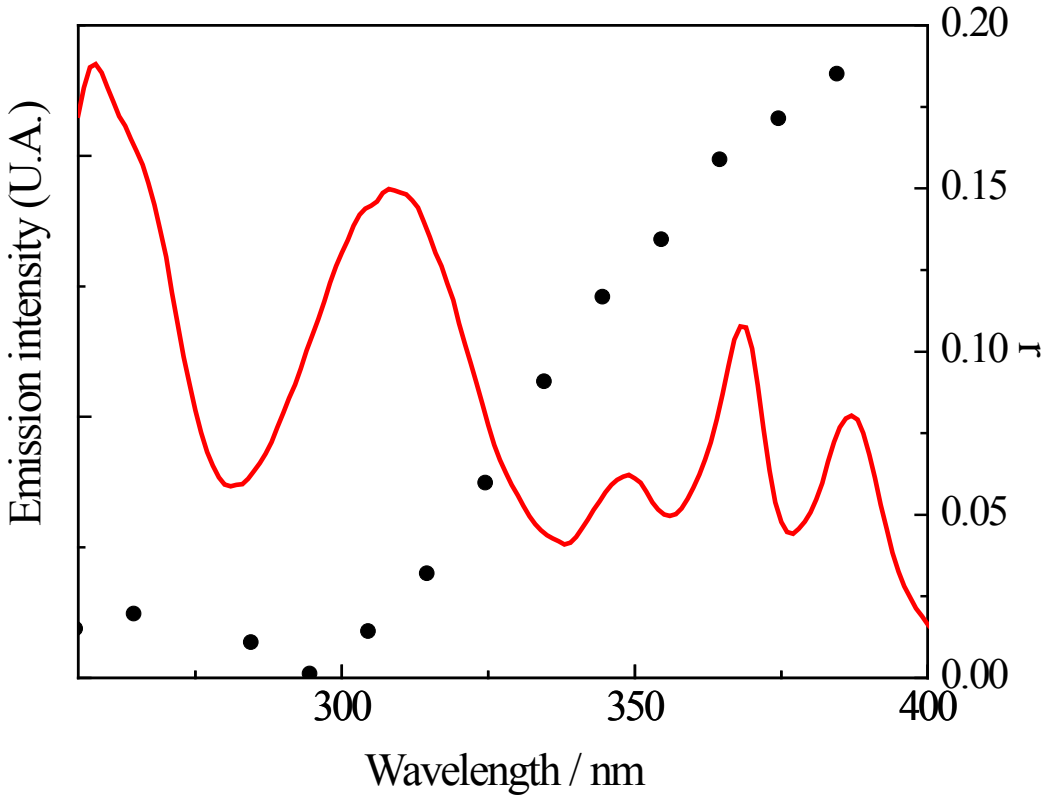

Figure 12-ESI: Excitation spectrum of a diluted dispersion of PAD75 (0.04 mg/ml) in THF. Emission wavelength: 440 nm. The excitation steady-state anisotropy (r) spectrum is represented by the solid circles. The actual values of r are shown in the right axis of the plot.

References

1 -M. Mac, J. Najbar, J. Wirz, Chem. Phys. Lett., 235 (1995) 187-194.

2 - C. Solis, V. Grosso, N. Faggioli, G.Cosa, M. Romero, C. Previtali, H. Montejano and C. Chesta; *Photochem.Photobiol. Sc.,* 2010, 9, 675.; b) G. Cosa and C. A. Chesta. *J. Phys. Chem.* 1997, *101*, 4922.

3- S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, 2nd. ed. New York, 1993.

4- Y. Marcus, Chem. Soc. Rev. 409 (1993) 409.

5- J.J. Michels, J.G. Dorsey, J. Chromatogr. 457 (1988) 85.