

Supporting Information

Single and Multistep Energy Transfer Processes within Doped Polymer Nanoparticles

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Synthesis of different dye encapsulated PVK polymer nanoparticles:

A simple method-based reprecipitation technique has been undertaken to prepare fluorophores encapsulated PVK polymer nanoparticles. Three solutions of PVK (0.5 mg/ml), C153 (1.9×10^{-4} M) and NR (1.0×10^{-4} M) were prepared using dried THF. Different amounts of dye solutions were mixed with 1 ml of PVK THF solution and then filled with THF until reaching a fixed volume of 2 ml. For example, in one of the doped systems (PVK:C153 or PVK:NR), we added a volume (from 0 to 500 μ l) of the dye solution to 1 ml of PVK solution, and added an amount of pure THF to keep constant the final volume (2 ml) in all the samples. For tunable colour and white light emission, we controlled the ratio of the relative concentrations of C153 and Nile red in the final stock solution: to 1 ml of PVK THF solution, we added x μ l of C153 and y μ l of NR in THF (x and y being between 0-500 μ l). For each solution, THF was then added in order to keep constant the final volume (2 ml). After that, 500 μ l of each of these stock THF solutions (containing both PVK and dye molecules) were rapidly injected into 10 ml water and brought under vigorous stirring for 15 minutes, followed by ultra-sonication. THF is then partially removed under vacuum evaporation of the obtained suspensions. The solutions were filtered using a 0.2 micron filter to remove PVK aggregates in the microscale region. Pure PVK and doped PVK nearly monodispersed polymer NPs in aqueous suspensions are obtained. To ensure that all the dye molecules are embedded inside the NPs we have checked the optical density (absorption and emission spectra) before and after dialysis using a dialysis membrane having molecular cut-off 12-14 kDa.

The % wt of the dyes were determined as it follows:

$$\% wt = \frac{w_{dye}}{w_{total}} \cdot 100 = \frac{\left(\frac{[stock]V_0}{V_{stock}} \right) \cdot V_{sample} \cdot M}{w_{total}} \cdot 100 \quad \text{Eq. 1S}$$

Where [stock] is the initial concentration of the dye, V_0 is the added volume of what in the 2 ml solution (from 0-500 μ l), V_{stock} is the total volume of the stock solution (2 ml), V_{sample} is the volume of stock solution in water (500 μ l), M is the molecular weight of the dye and w_{total} is the total weight of each sample. Substituting the values of the known volumes we obtain Eq. 2S.

$$\% wt = \frac{\left(\frac{[stock]V_0}{2 \cdot 10^{-3} l} \right) \cdot 500 \cdot 10^{-6} l \cdot M}{w_{total}} \cdot 100 \quad \text{Eq. 2S}$$

Table 1S. Values of time constants (τ_i) and normalized (to 100) pre-exponential factors (A_i) of the multiexponential function used in fitting the emission decays of C153 in different THF-H₂O mixtures. The excitation (λ_{Exc}) and observation (λ_{obs}) wavelengths were 370 and 500 nm, respectively.

V/V of H ₂ O	τ_1 / ns (A_1 %)	τ_2 / ns (A_2 %)	τ_3 / ns (A_3 %)
0	-	-	5.17 (100)
0.03	0.24 (21)	-	5.19 (79)
0.16	0.24 (43)	-	5.19 (57)
0.32	0.21 (47)	1.74 (7)	4.23 (46)
0.96	0.24 (10)	1.74 (44)	4.06 (46)

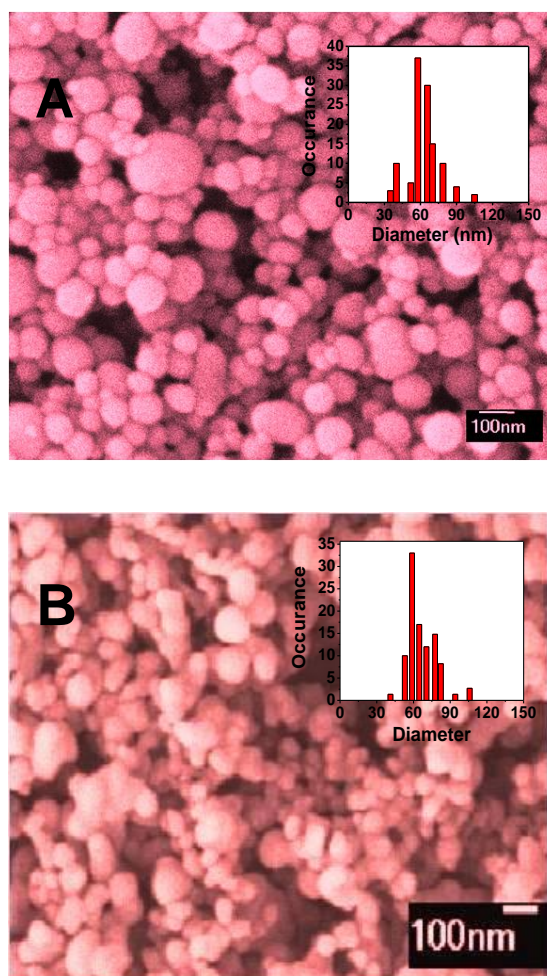


Figure 1S. Scanning electron microscopy image of PVK polymer nanoparticles; (A) without and (B) containing C153 and NR dyes.

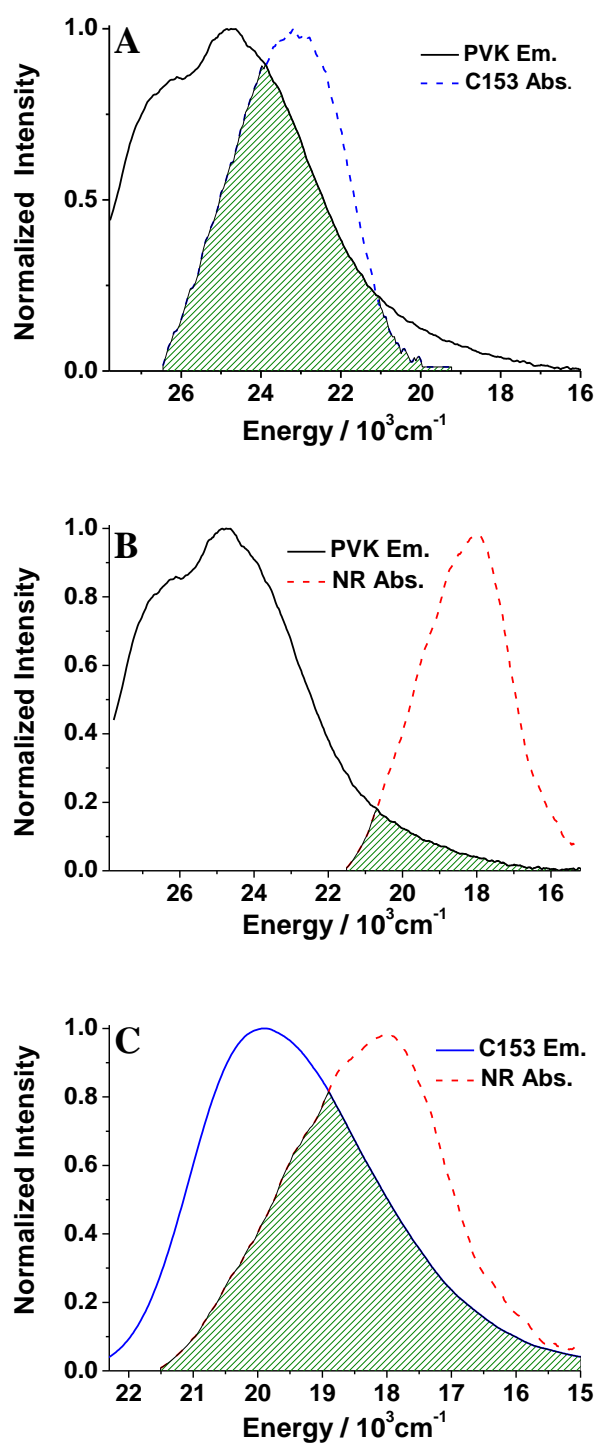


Figure 2S. Spectral overlap (dashed region) between the bands of (A) C153 absorption and PVK emission, (B) NR absorption and PVK emission, and (C) NR absorption and C153 emission in PVK NPs. The spectra are normalized to one at their respective maximum intensity.

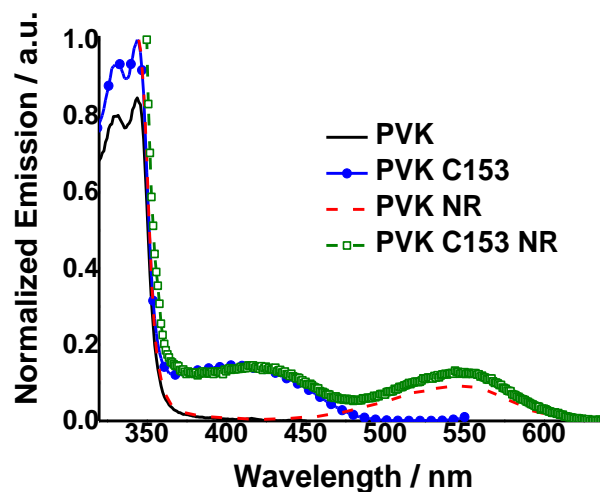


Figure 3S. Excitation spectra of water suspensions containing PVK NPs ($\lambda_{\text{obs}} = 410$ nm), and PVK:C153 NPs ($\lambda_{\text{obs}} = 560$ nm), PVK:NR NPs ($\lambda_{\text{obs}} = 650$ nm) and), PVK:C52:NR NPs ($\lambda_{\text{obs}} = 650$ nm).

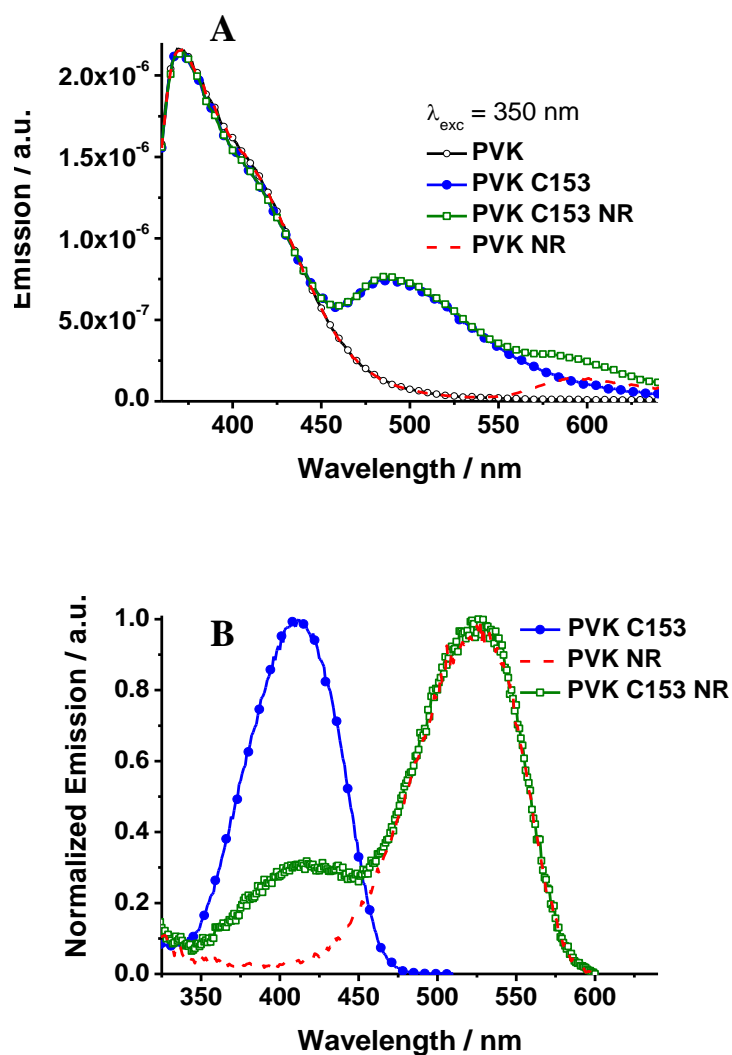


Figure 4S. A) Emission spectra of THF solutions containing PVK, PVK+C153, PVK+NR and PVK+C153+NR. B) Excitation spectra of THF solutions containing

PVK+C153 ($\lambda_{\text{obs}}=520$ nm), PVK+NR ($\lambda_{\text{obs}}=620$ nm) and PVK+C153+NR ($\lambda_{\text{obs}}=620$ nm). Note that the PVK in THF does not form nanoparticles.

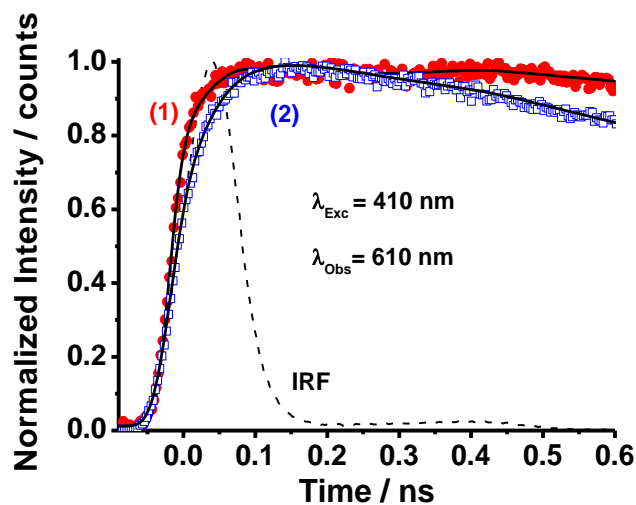


Figure 5S. Normalized emission decay of (1) a THF solution containing PVK, C153 and NR (2) PVK:C153:NR NPs in a water suspension. The inset shows the excitation and observation wavelengths. Note the differences in the rising component absent in (1) and present in (2), indicating the occurrence of energy transfer within the NPs system.

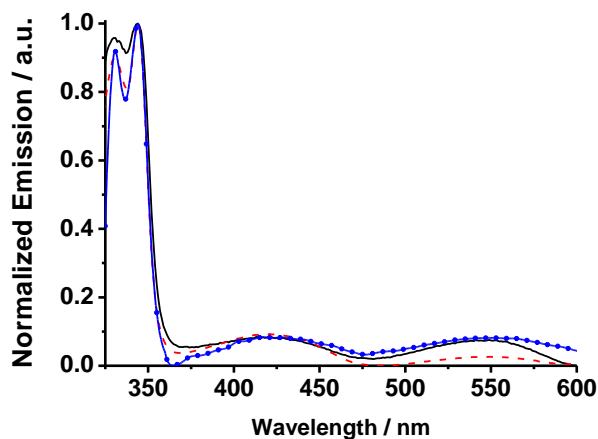
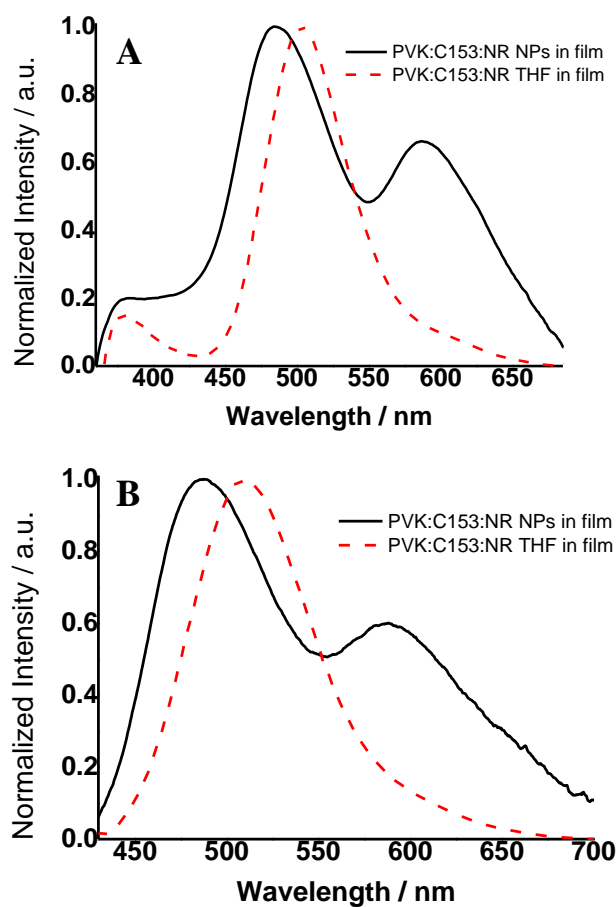


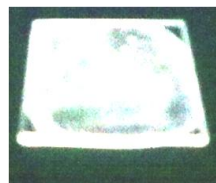
Figure 6S. Excitation emission spectra (observation at 650 nm) of dye-doped PVK NPs in water suspension, PVA-water suspension and in a PVA solid state film.



C



PVK:C153:NR THF in film



PVK:C153:NR NPs in film

Figure 7S. Emission spectra of (solid black line) PVK:C153:NR_(2.7:0.32 %wt for C153:NR) NPs in film and (red dashed line) film of PVK+C153+NR mixture (prepared from THF solution) upon excitation at 350 (A) nm and 410 nm (B), respectively. C) Photograph of the irradiated (340 nm) films containing PVK+C153+NR mixed in film (left, yellow-orange emission) and PVK:C153:NR NPs (right, white light emission) using the same concentrations of PVK, C153 and NR, as in (A) and (B).

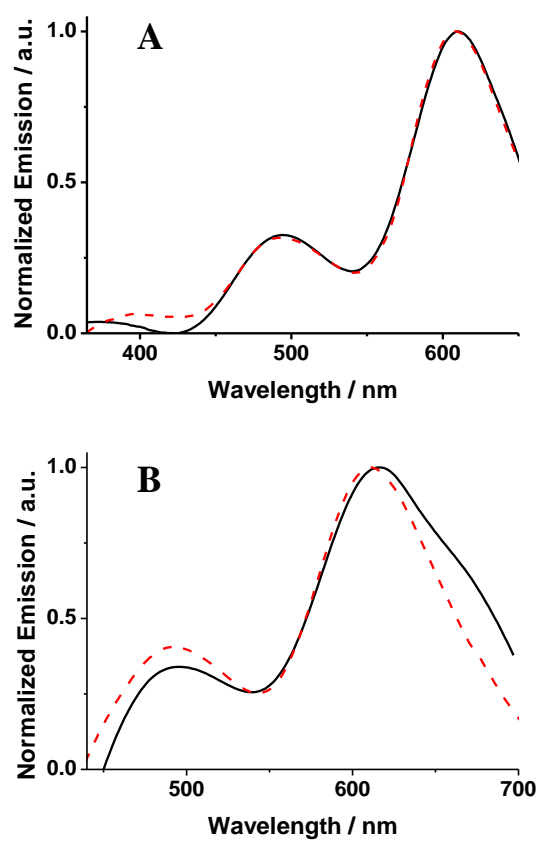


Figure 8S. Emission spectra of PVK:C153:NR (2.7:1.6 %wt for C153:NR) NPs in a PVA film for fresh (solid line) and 40 days old samples (dashed line). The excitation wavelengths were (A) 350 nm and (B) 410 nm.