

Supporting Information

Functionalized Dye Encapsulated Polymer Nanoparticle Attached with a BSA Scaffold as Efficient Antenna Materials for Artificial Light Harvesting

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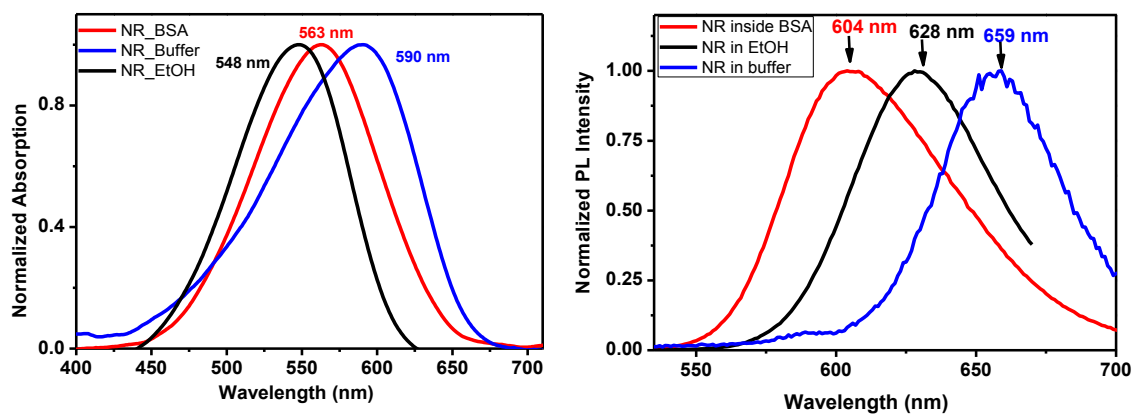


Figure S1: Absorption (Left panel) and emission (Right panel) spectra of NR in different environments.

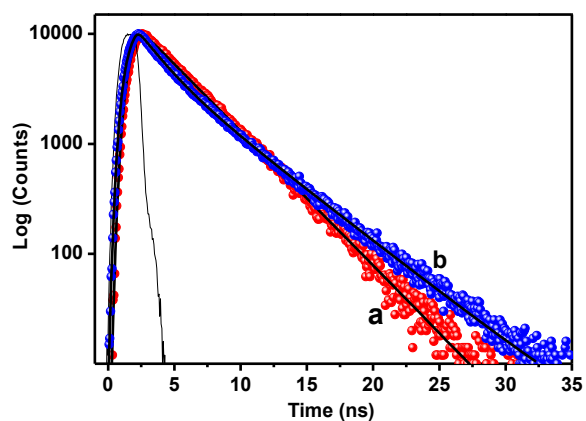


Figure S2: Time resolved emission decay curves of NR in EtOH (a) and encapsulated inside BSA (b) (λ_{ex} : 489 nm, λ_{em} : 628 nm).

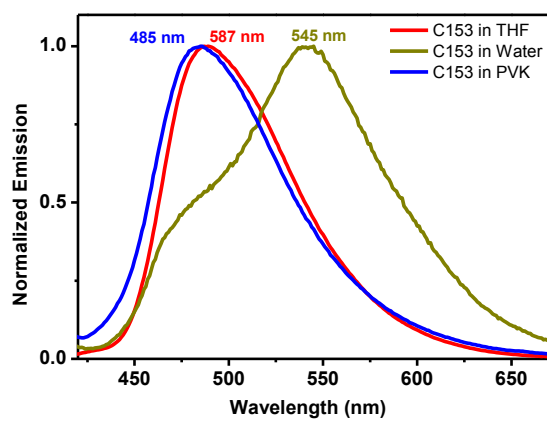


Figure S3: Normalised emission spectra of C153 in different environments (λ_{ex} : 400 nm).

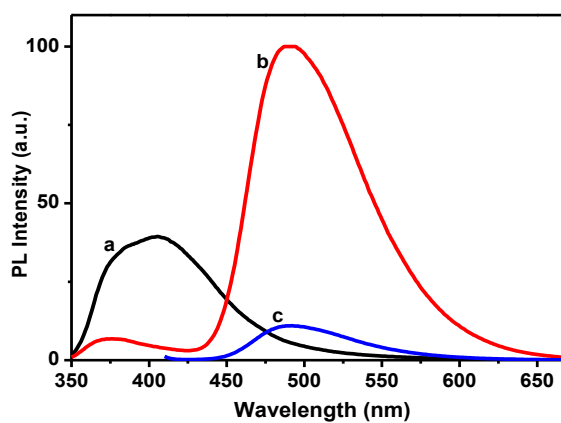


Figure S4: Photoluminescence spectra of PVK nanoparticles (excited at 340 nm) (a), C153 doped PVK nanoparticles (b) excited at 340 nm and excited at 400 nm (c).

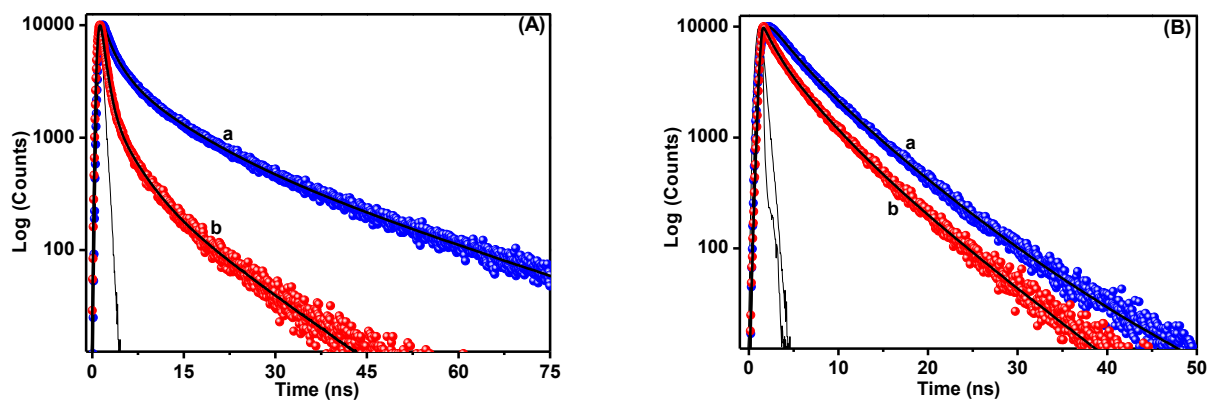


Figure S5: Time resolved emission decay curves of (A) PVK (a) and C153 (1.23 μM) doped PVK (b) polymer nanoparticles at λ_{ex} : 340 nm, λ_{em} : 400 nm and of (B) C153 emission (λ_{em} : 489 nm) at the excitation of 340 nm (a) and 404 nm (b) for C153 doped PVK polymer nanoparticles.

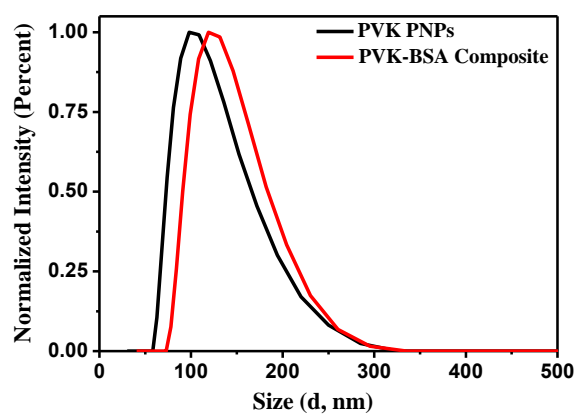


Figure S6: DLS distribution data of PVK polymer nanoparticles and PVK-BSA complex.

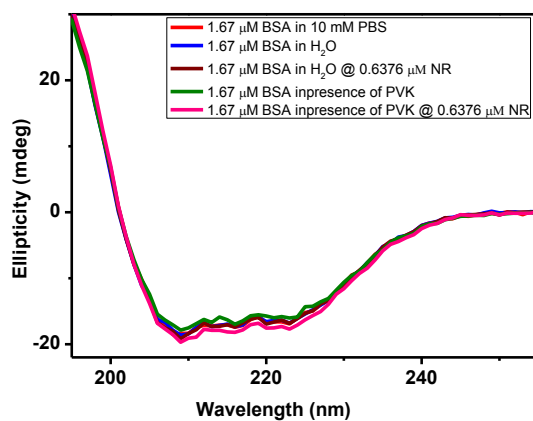


Figure S7: Far-UV circular dichroism spectral profiles of BSA protein in different environments.

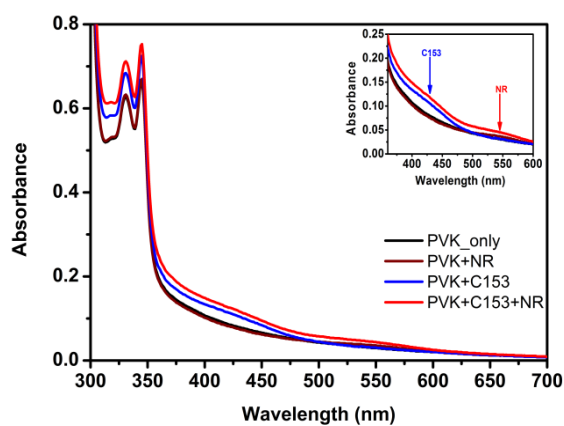


Figure S8: UV-Visible absorption spectra of pure PVK PNPs, C153 doped PVK PNPs and complexes formed with addition of NR dye encapsulated BSA (Inset shows the enlighten view of absorption of C153 and NR).

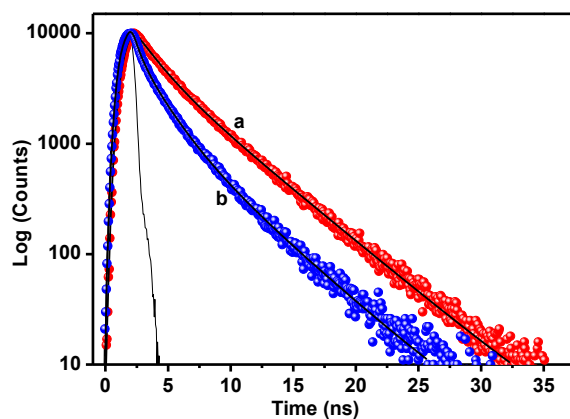


Figure S9: Time resolved emission decay curves of NR encapsulated BSA in absence (a) and presence of PVK polymer nanoparticles (b) (λ_{ex} : 489 nm, λ_{em} : 604 nm).

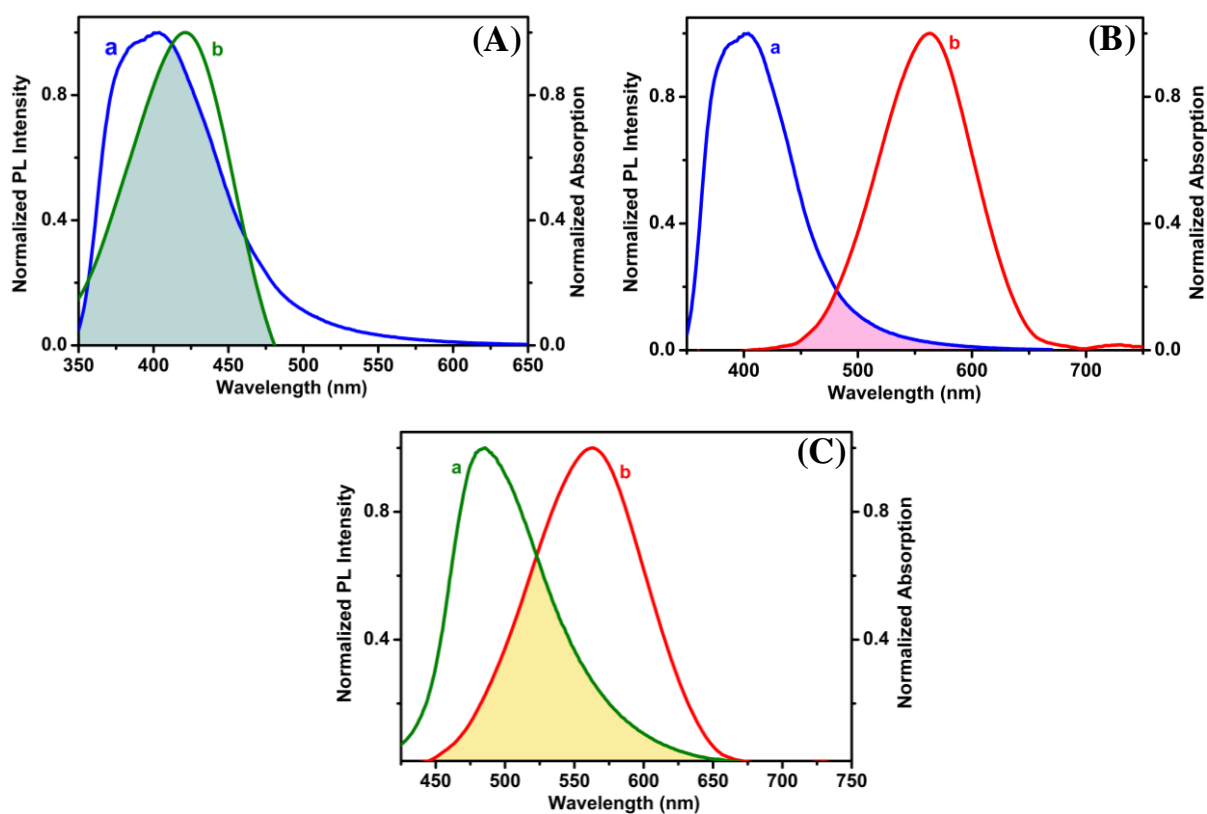


Figure S10: Pictorial representation of spectral overlap between (A) emission spectrum of PVK PNPs (a) and absorption spectrum of C153 (b), (B) emission spectrum of PVK (a) and absorption spectrum of NR (b) and (C) emission spectrum of C153 (a) and absorption spectrum of NR (b).

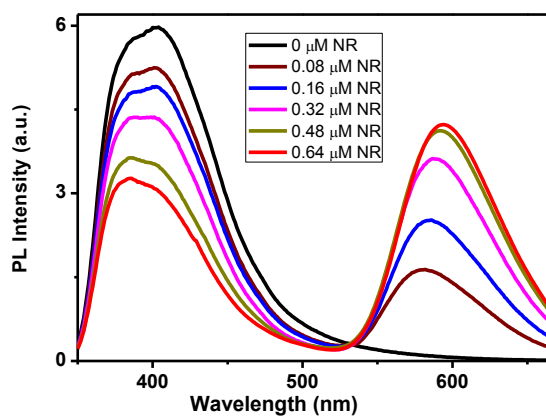


Figure S11: Photoluminescence spectra of PVK as the gradually increased concentration of NR (λ_{ex} : 340 nm).

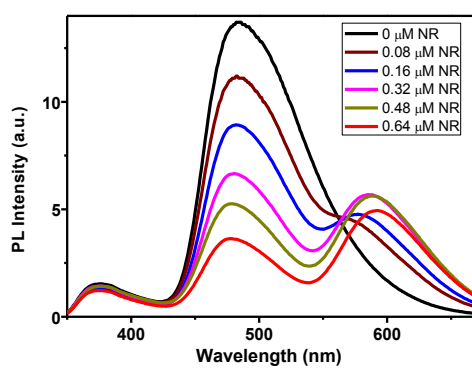


Figure S12: Photoluminescence spectra of C153 (1.23 μM) doped PVK as the gradually increased concentration of NR (λ_{ex} : 340 nm).

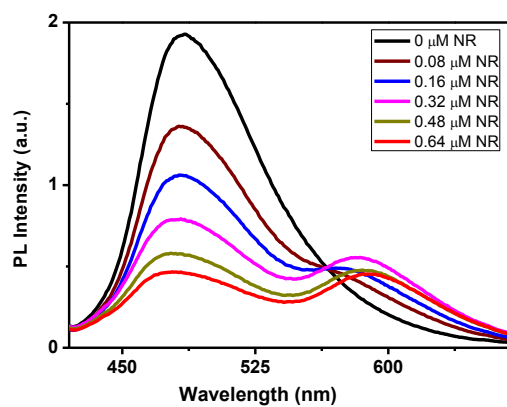


Figure S13: Photoluminescence spectra of C153 (1.23 μM) doped PVK as the gradually increased concentration of NR (λ_{ex} : 400 nm).

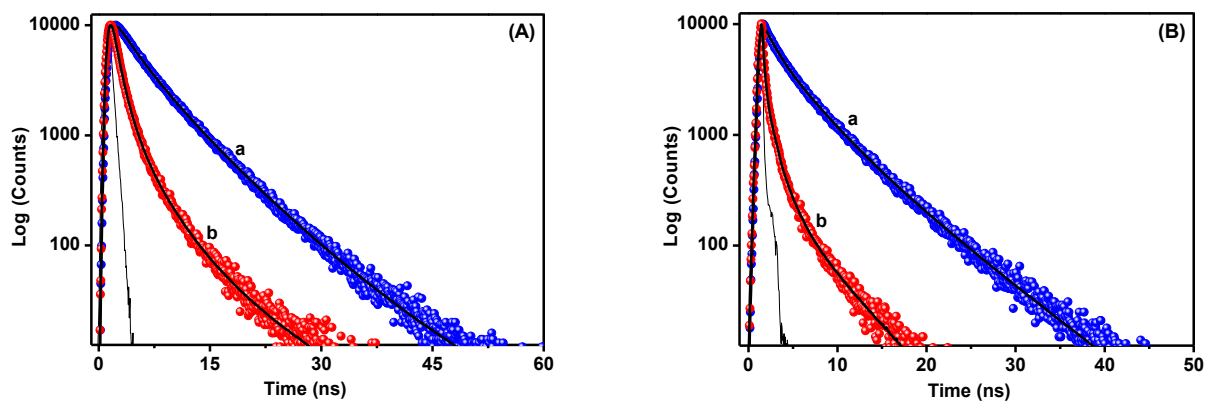


Figure S14: Time resolved emission decay curves of C153 (λ_{em} =489 nm) at the excitation of 340 nm (A) and 404 nm (B) in absence (a) and presence (b) of NR (0.64 μM).

Table S1: Time resolved emission decay data of PVK, C153 (1.23 μM) doped PVK polymer nanoparticles at different excitation wavelengths.

System	λ_{ex} (nm)	λ_{em} (nm)	τ_1 (a_1) [ns]	τ_2 (a_2) [ns]	τ_3 (a_3) [ns]	$\langle\tau\rangle$ [ns]
PVK only	340	400	0.72 (0.62)	4.58 (0.28)	19.6 (0.10)	3.69
C153 doped PVK	340	400	0.24 (0.90)	1.82 (0.08)	7.17 (0.02)	0.51
	404	489	1.03 (0.42)	3.67 (0.41)	7.13 (0.17)	3.15
	340	489	-0.35 (0.52)	3.44 (0.32)	7.47 (0.16)	

Table S2: Time resolved emission decay data of C153 in presence of NR (0.64 μM) encapsulated BSA protein at different excitation wavelengths.

System	λ_{ex} (nm)	λ_{em} (nm)	τ_1 (a_1) [ns]	τ_2 (a_2) [ns]	τ_3 (a_3) [ns]	$\langle\tau\rangle$ [ns]
C153 doped PVK/NR encapsulated BSA	340	489	0.39 (0.74)	1.54 (0.23)	5.51 (0.03)	0.81
	404		0.14 (0.92)	0.85 (0.07)	3.77 (0.01)	0.23

Calculation of number of C153 dyes in one PVK PNP:

Considering PVK nanoparticle as hard sphere, the average volume of 80 nm PVK nanoparticle is $2.68 \times 10^{-16} \text{ cm}^3$. We have calculated the average number of aqueous dispersed PVK nanoparticles using the following relation¹

Number of PVK nanoparticle = Amount of PVK nanoparticle / (Volume of PVK nanoparticle x density of PVK)

We have added 1 ml of stock THF (500 μL of 0.5 mg mL^{-1}) solution in 10 ml water. From the above relation, the calculated numbers of PVK nanoparticles are 7.77×10^{11} in 10 mL water. For C153 doped PVK nanoparticle, stock THF solution contains $14.82 \mu\text{M}$ of C153 dye. Considering the homogenous distribution of C153 dye molecules inside PVK nanoparticle, the number of C153 dyes in 10 ml water is 8.93×10^{15} . Therefore, the number of C153 dyes inside one 80 nm PVK polymer nanoparticle is 1.15×10^4 .

Change in energy transfer efficiency with changing the size of PVK PNPs:

We have synthesized three different sizes of polymer nanoparticles using simple reprecipitation technique. To synthesize polymer nanoparticles, 0.05 mg mL^{-1} , 0.5 mg mL^{-1} and 1.0 mg mL^{-1} PVK in THF stock have been employed for 50 nm, 80 nm and 100 nm polymer nanoparticles respectively. Formation of PVK PNPs is confirmed by SEM image (Fig S15). We used same NR dye concentration ($0.64 \mu\text{M}$) for BSA encapsulation which is then added to three different sizes of PVK polymer nanoparticles and measure the energy transfer efficiency.

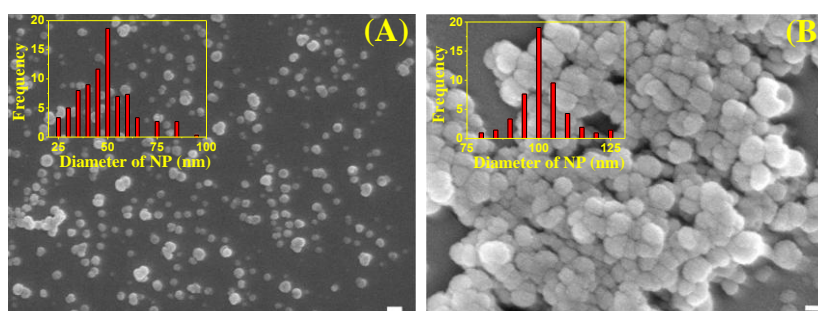


Figure S15: FE-SEM images of 50 nm (A) and 100 nm (B) PVK PNPs [Scale bar in (A) and (B) is 100 nm].

According to Förster theory, the efficiency of energy transfer (E) can be calculated using the following equation.²

$$E = \frac{R_0^6}{R_0^6 + r^6} \quad (1)$$

Where, R_0 and r are the Förster distance and the distance between donor and acceptor. Again R_0 can be estimated using the following equation.²

$$R_0 = 0.211[\kappa^2 \eta^{-4} \theta_D J(\lambda)]^{1/6} \quad (2)$$

In which, κ^2 is the orientation factor between donor and acceptor, η^{-4} is the refractive index of the donor, θ_D is the quantum yield of the donor and $J(\lambda)$ is the overlap integral between normalized donor emission and the acceptor absorption. Here, all the parameters (excluding $J(\lambda)$) are same for different sizes polymer nanoparticle. Normalized emission intensities for three different sizes indicate the same overlap integral value for three different sizes polymer nanoparticles (Shown in Fig S16). It is already reported that spectroscopic properties of polymer nanoparticles will not change when the size of particle is greater than 10 nm.³

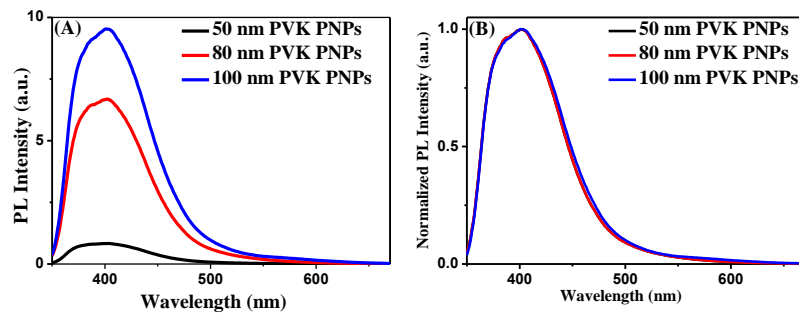


Figure S16: Emission spectra of three different sizes PVK polymer nanoparticles (A) and normalized emission spectra of the different sized polymer nanoparticles (B) excited at 340 nm.

For same concentration of NR dye, the overlap integral ($5.7 \times 10^{13} \text{M}^{-1} \text{cm}^{-1} \text{nm}^4$) is same for all cases as a result the Förster distance in different sized polymer nanoparticles is same for all cases. Hence, the energy transfer efficiency depends only on centre to centre distance between the donor and the acceptor. Assuming, the location of the donor chromospheres in the centre of the nanoparticles as a result larger particle size experiences larger distance from the acceptor with increasing the size of the polymer nanoparticles. Thus, the energy transfer efficiency will be reduced with increasing the size of the donor polymer nanoparticles.

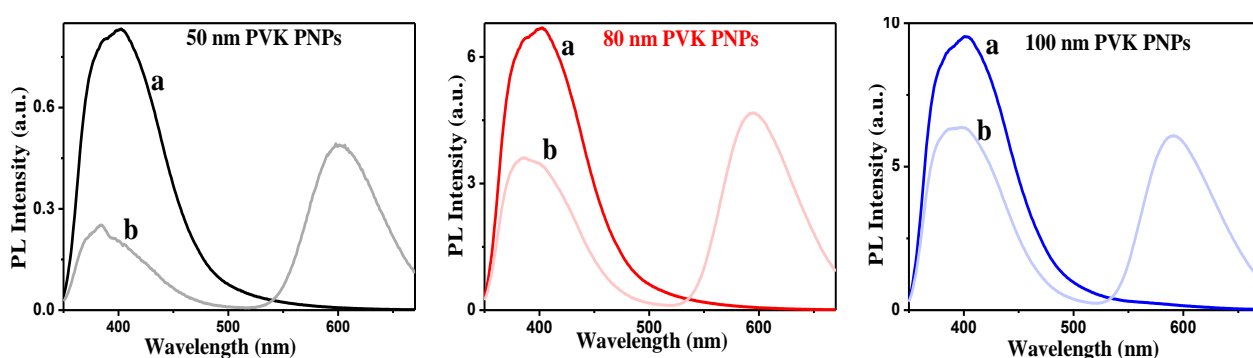


Figure S17: Emission spectra of only PVK polymer nanoparticles (a) and PVK/NR (0.64 μM) encapsulated BSA complex (b) at 340 nm excitation in different sizes nanoparticles system.

The calculated energy transfer efficiencies are 76 %, 49 % and 34 % for 50 nm, 80 nm and 100 nm polymer nanoparticles, respectively (Fig S17) using the following equation from emission quenching in the donor emission.²

$$E = 1 - \frac{F_{DA}}{F_D} \quad (3)$$

Where, F_D and F_{DA} are the fluorescence intensity of PVK in absence and presence of NR respectively. Number of donor chromospheres is also important factor to dictate the amount

of quenching for same concentration of acceptor molecules. Consequently, more quenching in the donor emission is found in smaller particles. We have measured the energy transfer efficiency for different sizes C153 doped PVK. Similar trend of decrease in energy transfer efficiency have also been found with increasing size of PVK nanoparticles.⁴

References:

- 1 S. Bhattacharyya, B. Jana and A. Patra, *ChemPhysChem*, 2015, **16**, 796-804.
- 2 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, 2006, 3rd Edition.
- 3 J. K. Grey, D. Y. Kim, B. C. Norris, W. L. Miller and P. F. Barbara, *J. Phys. Chem. B*, 2006, **110**, 25568-25572.
- 4 S. Bhattacharyya, B. Paramanik and A. Patra, *J. Phys. Chem. C*, 2011, **115**, 20832-20839.