

Supporting Information

For

Location and Freedom of Single and Double Guest in Dye-Doped Polymer Nanoparticles

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Description of ET calculations:

Förster fluorescence resonance energy transfer (FRET) is a non-radiative process whereby the energy is transferred from an excited-state donor (D, usually a fluorophore) to a neighbouring ground-state acceptor (A) through a long-range dipole-dipole interaction between the two chromophores. This process happens by resonance interaction between both chromophores, over distances considerably greater than the interatomic ones, without conversion to thermal energy, and without kinetic collision of D and A. The D molecules are the species that initially absorbs the exciting-photon energy, and further transfer the exciton energy towards the consecutive acceptor dye molecules. The efficiency (E) of energy transfer from D to A is related to the distance (R) between the involved chromophores, according to the equation:

$$E = 1 - \left(\frac{\Phi}{\Phi_0} \right) = 1 - \left(\frac{F}{F_0} \right) \quad (1)$$

$$E = \frac{R_0^6}{(R_0^6 + R^6)} \quad (2)$$

where Φ_0 and Φ (or F and F_0) are the fluorescence quantum yields (or emission intensity) of D in absence and presence of an equal amount of A, respectively. R_0 is the Förster critical distance between the involved chromophores at which 50% of the excitation energy in D is transferred to A. R_0 can be obtained from the equation 3:¹

$$R_0^6 = \left(\frac{9000(\ln 10)\phi_D\kappa^2}{128\pi^5 N_A n^4} \right) J(\lambda) \quad (3)$$

where Φ_D is the fluorescence quantum yield of D in absence of A ($\Phi_D = 0.2$ for C153 and 0.1 NR)^{2, 3}, n is the refractive index of the solution ($n = 1.696$)² and κ is the orientation factor, commonly taken as 2/3, assuming a relatively random orientation of both D and A chromophores. The spectral overlap $J(\lambda)$ between the emission spectrum of D and absorption one of A is given by equation 4:

$$J = \frac{\int_0^\infty F(\lambda)\varepsilon(\lambda)\lambda^4 d\lambda}{\int_0^\infty F(\lambda)d\lambda} \quad (4)$$

where $F(\lambda)$ accounts for the emission intensity of D at a wavelength λ , and $\varepsilon(\lambda)$ is the molar absorption coefficient of A at λ .

According to Förster's theory, the rate constant of such process is given by:¹

$$k_{ET} = \frac{1}{\tau_D} \left(\frac{R_0}{R} \right)^6 \quad (5)$$

where τ_D is the mean fluorescence lifetime of the D.

Combining equations 5 and 1 we get the efficiency of energy transfer (eq. 6):

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

Considering a possible homo-FRET (between the same chromophores) the values of the spectral overlap integral (Eq. 4) ($J/10^{14} \text{ M}^{-1}\text{cm}^{-1}\text{nm}^4$) are 0.76 and 7.43 for C153 and NR, respectively. Following equation 3, the obtained R_0 values are 2.18 and 2.84 nm for C153 and NR, respectively.

To calculate the interchromophoric distances in the PVK nanoparticles we assume that the dyes are homogeneously distributed inside of the inner volume of a perfect sphere of 60 nm in diameter (volume = $1.13 \times 10^5 \text{ nm}^3$). The number of dye molecules inside the NP was calculated following a model described elsewhere,⁴ and the obtained values are 7600 for C153 and 4100 for NR for wt% of 2.6 and 1.6, respectively. The ratio between the number of dye molecules and the volume give us the available volume for each dye molecule inside the NP and therefore the distance between them assuming that all the molecules are distributed homogeneously through the entire volume of the NP. According to that, the R is 3.05 and 3.75 nm for 2.7 % wt C153 and 1.6 % wt NR doped NP, respectively. The calculated homo-energy transfer (homo - ET) efficiencies are 11 % for C153 (2.7 % wt C153) and 15% for PVK:NR (1.6 % wt C153).

Description of Wobbling-in-a-Cone Model:

The functions were used to extract the WIC parameters:^{5, 6}

$$r(t) = r_0 [a \exp(-t/\tau_{slow}) + (1-a) \exp(-t/\tau_{fast})] \quad (7)$$

Here, τ_{slow} and τ_{fast} are the two reorientation times associated with the slow and fast motions of the dye molecules in the polymer nanoparticles, respectively. a is the pre-exponential factor giving the relative contributions of the two rotational decays to the total anisotropy signal. r_0 is the limiting anisotropy, which describes the inherent depolarization for a given molecule.

Assuming that the slow and the fast molecular motions in the nanoparticle's interior are separable, we can apply the following relationships:

$$\frac{1}{\tau_{fast}} = \frac{1}{\tau_R} + \frac{1}{\tau_{slow}} \quad (8)$$

$$\frac{1}{\tau_{slow}} = \frac{1}{\tau_D} + \frac{1}{\tau_M} \quad (9)$$

In Equations 8 and 9, τ_R and τ_D are the fast wobbling motion and the slow lateral diffusion of the encapsulated molecule inside the polymer nanoparticle's domain and along side its surface, respectively. These two molecular motions are joined with the overall rotation of the polymer nanosphere in aqueous suspensions, which we call τ_M .

The latter is the time constant for the overall rotation of the nanoparticle and can be estimated from the Stokes-Einstein-Debye (SDE) equation under stick boundary conditions:

$$\tau_M = \frac{4\pi\eta r_M^3}{3k_B T} \quad (10)$$

Here, η is the viscosity of the medium, k_B is the Boltzmann constant, T is the temperature, and r_M is the hydrodynamic radius of the polymer nanoparticle. In our case, r_M (30 nm) is determined from the average size of the polymer NP (50-70 nm), which is constant for all the systems, as it has been demonstrated in previous studies.⁷

The τ_M value is 14.2 μ s for the studied dye-doped PVK nanoparticle systems. As τ_M resides in the microsecond region, it has a negligible effect on the lateral diffusion phenomena. According to the WIC model, the internal motion of each trapped molecule wobbling inside a cone can be described in terms of cone semi-angle (θ_0) and wobbling diffusion coefficient (D_w). The θ_0 value defines the order parameter S as in Equation 11:

$$S = 0.5 \cos \theta_0 (1 + \cos \theta_0) \quad (11)$$

The order parameter is also related with the amplitude of the slower component of anisotropy decay by:

$$S = \sqrt{a} \quad (12)$$

The diffusion coefficient for wobbling motion D_w is calculated by using Equation 6:

$$D_w = \frac{\cos^2 \theta (1 + \cos \theta)^2}{2(\cos \theta - 1)(1 - S^2) \tau_R} \left\{ \ln \left(\frac{1 + \cos \theta}{2} \right) + \frac{(1 - \cos \theta)}{2} \right\} + \frac{(1 - \cos \theta)}{24(1 - S^2) \tau_R} (6 + 8 \cos \theta - \cos^2 \theta - 12 \cos^3 \theta - 7 \cos^4 \theta) \quad (13)$$

On the other hand, the translational diffusion constant (D_L) is related to the lateral diffusion time τ_D by the Stokes-Einstein (SE) relationship:

$$D_L = \frac{r_M^2}{6\tau_D} \quad (14)$$

In Equation 8, r_M is the radius of the polymer NP where the molecular rotation takes place.

For the above model, the anisotropy decay function due to the wobbling and translation motion could be written as:

$$r(t) = r_0 [S^2 + (1 - S^2) \exp(-t/\tau_R)] \exp(-t/\tau_D) \quad (15)$$

Determination of the Errors on the WIC Parameters

The estimated errors for τ_{slow} , τ_{fast} , are 10-15 % and those have been used to calculate the associated errors to the WIC parameters, τ_R , τ_D , S^2 , and θ_0 using equation 8, 9, 11 and 12, applying the concept of first derivative:

$$dy/dx = f'(x) \quad (16)$$

Therefore, the associated error, Δy is given by:⁸

$$\Delta y = |f'(x)| \Delta x \quad (17)$$

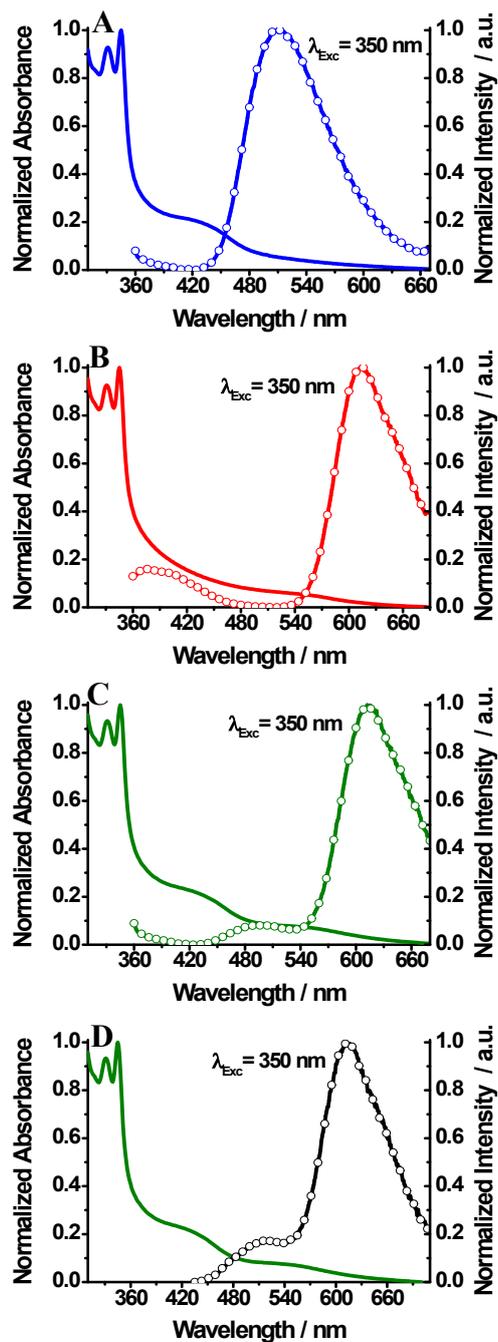


Figure 1S. Normalized (to their maximum of intensity) UV-visible absorption and emission spectra of water suspensions containing pure and doped-PVK polymer NPs: A) PVK:C153(2.72 wt%) NPs, $\lambda_{\text{exc}} = 350$ nm; B) PVK:NR(1.60 wt%) NPs, $\lambda_{\text{exc}} = 350$ nm; C) PVK:C153(2.72 wt%):NR(1.60 wt%) NPs, $\lambda_{\text{exc}} = 350$ nm; D) PVK:C153(2.72 wt%):NR(1.60 wt%) NPs, $\lambda_{\text{exc}} = 410$ nm. The solid lines represent the absorbance spectra, while the emission spectra are drawn as dots and lines.

Table 1S. Values of anisotropic decay parameters (rotational time constants, ϕ_i ; normalized (to 100) pre-exponential factors, A_i ; fundamental anisotropy, r_0) for (A) PVK:C153(0.22-2.72 wt%), (B) PVK:NR(0.63-1.60 wt%), (C) PVK:C153(0-2.70 wt%):NR(1.60 wt%), and (D) PVK:C153(2.72 wt%):NR(0-1.60 wt%).

A

PVK:C153			
wt%	ϕ_1 / ns	ϕ_2 / ns	r_0
C153	(A_1%)	(A_2%)	
0.22	0.19 (38)	4.63 (62)	0.12
0.54	0.18 (46)	3.43 (54)	0.16
1.08	0.17 (53)	2.42 (47)	0.18
2.18	0.14 (63)	1.78 (37)	0.19
2.72	0.13 (67)	1.57 (33)	0.19

B

PVK:NR				
wt%	ϕ_1 / ps	ϕ_2 / ns	ϕ_3 / ns	r_0
NR	(A_1%)	(A_2%)	(A_3%)	
0.63	15 (75)	0.30 (8)	12.2 (17)	0.17
0.95	15 (77)	0.30 (9)	8.01 (14)	0.17
1.27	19 (77)	0.30 (10)	4.41 (13)	0.17
1.60	16 (78)	0.27 (11)	3.09 (11)	0.17

C

PVK:C153:NR (wt% NR fixed to 1.60)				
wt%	ϕ_1 / ps	ϕ_2 / ns	ϕ_3 / ns	r₀
C153	(A₁%)	(A₂%)	(A₃%)	
0	16 (78)	0.27 (11)	3.09 (11)	0.17
0.14	22 (79)	0.31 (12)	3.97 (9)	0.19
0.54	22 (78)	0.28 (15)	4.38 (7)	0.20
1.09	22 (77)	0.29 (15)	5.12 (8)	0.21
1.63	22 (74)	0.31 (16)	5.96 (10)	0.22
2.18	22 (72)	0.32 (17)	6.93 (11)	0.22
2.70	22 (71)	0.46 (18)	7.00 (11)	0.22

D

PVK:C153:NR (wt% C153 fixed to 2.72)			
wt%	ϕ_1 / ns	ϕ_2 / ns	r₀
NR	(A₁%)	(A₂%)	
0	0.13 (67)	1.57 (33)	0.19
0.08	0.12 (70)	1.34 (30)	0.22
0.15	0.11 (73)	1.22 (27)	0.23
0.32	0.058 (77)	0.90 (23)	0.27
0.63	0.043 (82)	0.78 (18)	0.30
0.96	0.030 (84)	0.70 (16)	0.36
1.60	0.030 (84)	0.69 (16)	0.38

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