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Single and Multistep Energy Transfer Processes within Doped Polymer Nanoparticles

Cristina Martin¹, Santanu Bhattacharyya², Amitava Patra^{*2} and Abderrazzak Douhal^{*1}

¹ *Departamento de Química Física, Facultad de Ciencias del Medio Ambiente y Bioquímica e INAMOL, Universidad de Castilla-La Mancha, Avda. Carlos III, S.N., 45071 Toledo, Spain.*

² *Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata 700 032, India.*

* corresponding author: Amitava Patra, email: msap@iacs.res.in

* corresponding author: Abderrazzak Douhal, email: abderrazzak.douhal@uclm.es

Abstract

Herein, we demonstrate the design of multiple fluorophores Coumarin 153 (C153) and Nile Red (NR) encapsulated semiconducting Poly[N-vinylcarbazole] (PVK) polymer nanoparticles (50-70 nm in diameter) by simple re-precipitation technique, and understand their photophysical properties by using steady-state and picosecond (ps) time resolved emission spectroscopy. It is interesting to note that multistep cascaded energy transfer occurs from the excited host PVK molecules to NR dye molecules through C153. The energy transfer time constants are found to be 180 ps for PVK→C153, 360 ps for PVK→NR, and 140 ps for the overall energy transfer process from PVK to NR through C153 dye molecules. The multistep energy transfer allows tuning the wide range emission from 350 nm to 700 nm by changing the relative concentrations of the encapsulated dye molecules. Bright, stable, and white light emission of the dye doped polymer nanoparticles with a quantum yield of 14 % is achieved at a particular concentration ratio of C153:NR dye. The generation of “cool” white emission in suspension and in solid state film opens up new possibilities in white light OLED based on single nanoparticle.

Keywords: Energy transfer, polymer nanoparticles, time-resolved fluorescence, Nile Red, Coumarin 153.

1. Introduction

The research of designing novel fluorescent nanomaterials with tunable emission has been paid a great attention to find out potential applications in photonic and biophotonic areas.¹⁻³ There are several classes of materials used as fluorescence emitters, but many of these do not present important requirements for brightness, such as high molar excitation coefficient, high fluorescence quantum yield and photo/thermal stability. For example, most of the organic dye molecules undergo fast fluorescence photobleaching, display low fluorescence quantum yield and sometimes being susceptible to irreversible photodestruction.⁴

To address these problems, fluorescent nanoparticles have been proposed as an alternative.⁵⁻⁷ One example is provided by the inorganic semiconductor quantum dots (QDs),⁸ because of its size-tunable absorption/emission properties and high photostability.^{9, 10} However, the poor solubility, blinking behavior, and heavy metal toxicity are some disadvantages of their use as efficient fluorescent materials, in particular for biological applications.¹¹ Silica based nanomaterials with different core-shell architectures (Cdots)¹² have presented an attractive alternative to the semiconductor crystals. These nanoparticles are easy to prepare, susceptible to surface modification and labelling.¹³ Nevertheless, they also present a number of limitations such as, limited dye loading¹⁴ and dye-dye interactions.¹⁵

Recently, a novel class of fluorescent nanoprobe based on π -conjugated polymer nanoparticles (CPNs) have emerged as a promising alternative to the conventional ones.¹⁶⁻¹⁹ Nowadays, conjugated polymers are widely used in organic light emitting diodes (OLED),²⁰ photovoltaic devices,^{21, 22} and as chemical sensors.^{23, 24} Conjugated polymer nanoparticles have several advantages like, easy synthesis, tunable properties, less toxicity and better biocompatibility which make them suitable for potential applications in photonic and electronic devices,^{25, 26} sensing, and imaging.^{27, 28} Furthermore, it has been demonstrated that blended polymers or CPN can be formed starting from these materials.²⁹⁻³¹ The most commonly used conjugated polymers (having high absorption coefficient and fluorescence quantum yield) for the formation of nanoparticles are based on polyaniline,³² polypyrrole,³³ polyacetylene,³⁴ and polythiophenes derivatives.³⁵

In addition to that, non-conjugated semiconducting polymers like [Poly(*n*-vinylcarbazole) (PVK)] can be used as photoconductors or charge transport materials. PVK polymer exhibits some potential advantages e.g. easy availability, high thermal and photochemical stability, and notably high charge carriers mobility³⁶ which are

suitable for light-emitting diodes and photovoltaic devices. Moreover, the efficient energy transfer (ET) processes from the polymer chromophores to the guest has been recently observed.^{37, 38} The ET process between the polymer chromophores and the guest molecules represents a key factor for these systems emitting in a broad range of the visible light. In addition to that, PVK can form stable and bright polymer nanoparticles using the same preparation method used for the conjugated polymer nanoparticles, and it is capable to incorporate hydrophobic luminescent dyes.^{39, 40} A recent study of PVK nanotubes containing Coumarin 6 and Nile Red as dopants, demonstrated the possibility to get a large colour display from these materials.⁴¹ However, the formation of this type of systems requires the use of porous alumina template using wetting technique and multiple purification cycles is needed to obtain the separate discrete tubes.⁴² Furthermore, there is no study on the possibility of cascade ET for these systems.. Based on these considerations, we have used the PVK polymer nanoparticles as host materials proving easy preparation and no purification is required to get the doped systems. To the best of our knowledge, there is no detail on the multiple ET processes in the two different dye-encapsulated PVK nanoparticles by using ps-time resolved spectroscopy.

In the present study, we have fabricated aqueous dispersed PVK polymer nanoparticles doped with C153 and NR dye molecules and try to understand the multistep cascade ET processes from the host polymer to the multiple fluorophore (C153 and NR) guest molecules by using steady-state and time resolved spectroscopy. The obtained information is very important to understand and control the photophysical processes occurring in the excited state. In particular, we want to address some important issues: a) What is the pathway of the ET processes? b) Is the excess of energy transferred from PVK to C153 to NR directly from PVK to NR? And c) What is the overall ET rate? Of particular interest to our research program is to generate white light by changing the concentration ratio of C153 and NR with the hope that such knowledge will enable us to construct efficient fluorescent polymer nanoparticles for bio-imaging applications and OLED's devices.

2. Experimental Part

All the chemicals were purchased from Sigma-Aldrich. Poly(9-vinylcarbazole) (PVK, M.W. 25000-50000), Coumarin 153 (99%), Nile Red (99%), and

tetrahydrofuran (THF, spectroscopic grade >99.5 %) were used as received. We used Poly(vinyl alcohol) (PVA, M.W. 89000-98000) for the preparation of the film.

2.1. Synthesis of the Polymer Nanoparticles

The PVK polymer nanoparticles were prepared by a typical reprecipitation method described elsewhere.¹⁶⁻¹⁸ The Supporting Information gives a brief description of the synthesis procedure and preparation of the nanoparticles.

2.2. Characterization Methods

The morphological characterization of doped and undoped PVK nanoparticles has been done using field emission scanning electron microscopy (FE-SEM). UV-visible steady-state absorption and emission spectra were recorded using JASCO V-670 and Jovin Yvon Fluoromax 4 spectrophotometers, respectively. Emission lifetimes were measured using a time-correlated single-photon counting picosecond (ps) spectrophotometer (Fluotime 200, PicoQuant) previously described.⁴³ The sample was excited with a femtosecond (fs) pulse from a Ti:sapphire oscillator (Mai Tai HP, Spectra Physics) coupled to a second harmonic generator. The pulses (100 fs, 40 MHz, 1 mW) were centered at selected wavelengths (350, 410 and 510 nm) and the emission wavelength was collected at the magic angle (54.7°). We choose these excitation wavelengths because at 350 nm the PVK chromophore are mainly excited, while at 410 and 510 nm we predominately excite the C153 and the NR dyes, respectively (Figure 1A). The instrument response function (IRF) was typically from 30-60 ps depending on the excitation wavelength. In doing so, we can get times as short as 10-15 ps. The emission decays were deconvoluted to the IRF and fitted to a multi-exponential function using Fluofit package (PicoQuant). To understand the tunable colour emission and as well as proper white light emission, the emission spectra are projected on two dimensional 1931 Commission Internationale de L'Eclairaged (CIE) chromaticity diagram. All experiments were done at 293 K.

3. Results and Discussion

3.1. Polymer Nanoparticles Characterization

FE-SEM technique, UV-visible absorption, and fluorescence emission studies have been used to understand the morphology, size, and doping yield of nanoparticles. The chromophores are introduced during the NP formation process. Comparison between the emission spectra of different dye-encapsulated PVK NPs before and after a 0.2-micron membrane filtration (diameter less than 100 nm) suggests that, the preparation yield of the dye-doped NPis above 90% in each case. It suggests that almost 90 % of PVK polymer chains are converted into (< 100 nm) NPs. After three days from

the NPs preparation, the optical density of the initial suspension showed that almost 98% of the dye molecules are still encapsulated, indicating a non significant dye leakage within that period. The FE-SEM image (Figure 1SA) shows that PVK polymer NPs are monodispersed with an average diameter of 50-70 nm. The average size of the polymer NPs remains unaltered when they contain C153 or NR (Figure 1SB).

3.2. Steady-State Study

3.2.1. UV-Visible Absorption Spectra

Figure 1A shows the UV-visible absorption spectra of the pure and dye-doped PVK NPs dispersed in aqueous solutions (2.7 % wt of C153 and 1.6 % wt of NR). For PVK NPs, the absorption intensity maximum is at 345 nm and is assigned to the $\pi \rightarrow \pi^*$ electronic transition.⁴⁴ We also observe a red tail up to 700 nm, which is arising from scatter light due to the NPs size. Upon encapsulation of C153 and/or NR, in addition to the band around 345 nm due to the PVK chromophore, we observe two relatively weak intensity absorption bands at 420 and 525 nm, corresponding to the dyes (C153 and NR, respectively) inside the PVK NPs. These results indicate that the presence of the trapped dye molecules does not affect the electronic energy levels (S_0 and S_1 states) of the PVK chromophore in case of dye-doped NP.

3.2.2. Photoluminescence Study

Figure 1B exhibits normalised (to one) photoluminescence spectra of undoped and doped NPs in water suspensions and upon excitation at 350 nm (where the absorption originates mainly from the PVK chromophore). For the undoped NP, the emission intensity is broad and red shifted by 30 nm with respect to its single chromophore (pure molecular state), for which the maximum is at 350 nm. This behavior is due to the formation of two different conformers of excimers, formed from different π -stacking of carbazole chromophores. The emission at ~ 380 nm (high energy excimer) is attributed to incompletely overlapped carbazole units while the emission at ~ 405 nm (low energy excimer) is due to full overlapping.^{44, 45} The emission spectrum of PVK NPs shows that the intensity at 380 nm is lower than that at 405 nm. However when the PVK is dissolved in toluene (not nanoparticles), the trend is different, the emission intensity at 370 nm is higher than at 415 nm.⁴⁵ Therefore, the excimers emission of the PVK NPs is coming mostly from the full overlapped excimers suggesting strong interactions between the carbazole units in the PVK NPs than in the toluene solution. Upon encapsulation of C153 (2.72 wt %) inside de PVK nanodomain, the emission of PVK is efficiently quenched (by 97% at the maximum of emission intensity), while the broad emission mainly comes from the trapped C153 (intensity

maximum at 510 nm and no vibronic structure).⁴⁶ The broad emission band $\sim 3700 \text{ cm}^{-1}$ (510 cm^{-1} more than C153 in THF) suggests that the encapsulated C153 is interacting with a heterogeneous inner environment,⁴⁷ consisting of sites having different polarities, H-bonding abilities and dielectric nature. Therefore, we can distinguish at least two different populations of trapped C153 molecules: a) molecules interacting with more hydrophobic non-polar environment and b) molecules interacting with more polar environment including trapped water molecules inside the NPs. On the other hand, the emission of PVK is not entirely quenched, when 1.7 wt % of NR are encapsulated, but concomitant with a prominent emission (maximum intensity at 605 nm) arising from trapped NR molecules. The broad NR emission maximum further supports the heterogeneous environment inside the PVK NPs. In presence of both dyes within the NPs (2.7 % wt of C153 and 1.7 % of NR), we observed an efficient (98%) photoluminescence quenching of PVK and a drastic quenching of emission from C153 dye (observing at 510 nm).

Figure 2S shows the spectral overlap between the emission spectrum of PVK NPs and the absorption one of both dyes, and between the emission spectrum of C153 with the absorption of NR. The observed spectral overlaps suggest a possible occurrence of an ET between PVK and both dyes, and between excited C153 and NR, when they are in favourable positions. To further examine the fluorescence behavior of these nanosystems, the emission spectra upon excitation at others wavelengths were recorded. Figure 1C shows the photoluminescence spectra of undoped and dye-doped polymer NPs after excitation at 410 nm. The photoluminescence bands at 510 nm and 605 nm are obtained from PVK:C153 and PVK:NR systems, respectively. A significant fluorescence quenching of C153 and an enhanced emission of NR are observed for PVK:C153:NR system. Note that at 410 nm the absorbance of C153 is 0.1 while NR dye has a small absorption (<0.002). Therefore the C153 is the main excited chromophore at 410 nm. The emission quantum yield of C153 in PVK NPs and NR in PVK NPs are 26 % and 6 %, respectively. When doping PVK NPs by both dyes, the emission quantum yield of NR in PVK NPs exciting at 410 nm reaches 8 %, indicating the occurrence of the ET from C153 dye to NR in PVK NP.

In order to know the type of interactions between PVK and trapped dyes, we collected the excitation spectra observing at 650 nm (Figure 3S). The spectra have their maxima of intensity at 345 nm, coinciding with the absorption maximum of pure PVK, and the two additional weak bands (420 and 525 nm) due to C153 and NR absorptions, respectively, are still present. This result indicates the existence of intra-particle ET

processes from the PVK host to the trapped dyes. For PVK:C153:NR, there are a sequential ET processes that start from the excited PVK to C153 and end at NR. One can argue that the observed emission quenching of PVK NPs and growing up of trapped C153 and NR emission bands is only due to a photons re-absorption phenomenon. To clarify this point, we have recorded the emission and excitation spectra of PVK with C153 and NR in THF solutions using the same concentration of the C153 (1.9×10^{-4} M) and NR (1.0×10^{-4} M) with respect to that of PVK NPs. Figure 4S shows: (i) PVK and C153, (ii) PVK and NR, and (iii) PVK, C153 and NR. Note that PVK chains in THF do not form NPs. Upon excitation at 350 nm, the PVK chains fluorescence intensity is not quenched by adding the dyes to the THF solution. Moreover, the emission intensity of C153 does not change upon addition of NR to the PVK+C153 THF sample. These results show that the change in emission intensities of PVK NPs containing C153 and NR (shown in Figure 1B and 1C) are due to ET processes within the particles, and not to auto-absorption of the emitted photons. Furthermore, the results from the excitation spectra of the above THF solutions support the absence of ET when the PVK NPs are not formed (Figure 4SB).

To understand the emission quenching phenomena and the related ET processes, we investigate the concentration-dependent fluorescence intensity of these nanosystems. Figures 2A and 2B show the emission intensity change upon variation of C153 and NR concentrations. Figures 2C and 2D exhibit the effect of NR and C153 concentrations in the emission intensity of PVK:C153 and PVK:NR systems, respectively. For PVK:C153 NPs upon addition of C153 (up to 2.7 % wt), the intensity of PVK NPs emission decreases, and the intensity of C153 increases. A similar behavior is observed for PVK:NR (up 1.6 %wt) (Figure 2B). However, in this case, the PVK NPs emission is less quenched than in PVK:C153 indicating a moderate ET. Furthermore, we have studied the ET process upon co-doping the polymer NP with the two dyes simultaneously. When the amount of C153 is fixed at 2.72 % wt and that of NR is increased up to 1.6 % wt, no emission from the PVK NPs is observed, while the emission from C153 is quenched and that of NR increases. On the other hand, when the content of NR is fixed in the doped NP, and the content of C153 is varied from 0 to 2.72 % wt, we obtained different photophysical behaviors. Initially, the intensities of PVK and NR decrease, and a new band at 490 nm appears due to the C153 emission. After further increasing the concentration of C153 dye, the emission intensities of both C153 and NR increase, and that from PVK is efficiently quenched. These relative changes in the intensities are due to the presence of different competitive ET pathways in the

system. Firstly, in absence of C153, the excited PVK chromophores transfer their energy to NR. On the other hand, in presence of C153, the PVK chromophores transfer their energy to C153 because of a better spectral overlap. However the emission intensity of C153 in PVK:C153:NR system is lower than that observed for PVK:C153 NPs, and this behavior correlates with that of the enhanced emission intensity of NR. Both systems (Figure 2 C and Figure 2 D) exhibit a strong interaction between excited C153 and NR, a result which is in agreement with the proposed cascaded ET process: PVK→C153→NR. Therefore, the C153 molecules act as a molecular antenna which enhances the ET efficiency from the excited PVK host to the trapped NR. Scheme 1 illustrates possible pathways of the different ET processes.

3.3. Time-Resolved Spectroscopic Study

Picosecond (ps) time-correlated single-photon counting experiments at different excitation and observation wavelengths have been carried out to investigate the details of the excited-state behavior, and related ET phenomena. To exclude the annihilation processes in this kind of systems, we have performed picosecond experiments using different energy power excitations (from 0.008 to 0.13 nJ / pulse). We have observed no change in the fluorescence decays for all the used power excitations independently on the excitation wavelength. The result indicates that the annihilation process is not present in these nanosystems under the used experimental conditions. Figures 3 A and 3 B show the normalized emission decays of doped PVK NPs at two selected wavelengths of observation corresponding to the signals of emission maximum of C153 (510 nm) and NR (610 nm) upon excitation at 350 nm. Figure 3 C exhibits the emission decays of PVK NPs containing 2.7 % wt of C153 and 1.6 % wt of NR, when exciting at 410 nm and recording at 610 nm. The decay curves are fitted with multi-exponential functions. The results are depicted in Table 1.

3.3.1. PVK: C153 case

Upon excitation of PVK NPs containing 2.7 % wt of C153 in water solutions at 350 nm and observation at 430 nm, where the signal mainly comes from the polymer matrix, the fit gives time constants of 180 ps, 690 ps and 2.88 ns. The emission decay of undoped PVK NPs shows longer lifetimes (3.31 and 16.32 ns) as it has been reported (3.24 and 16.36 ns)^{39, 45, 48} In these reports, the shortest component is assigned to high energy excimers while the longest one to the low energy ones.^{45, 46} The reduction in the lifetimes from the undoped and doped PVK NPs are due to a possible ET processes between the two PVK excimers and C153 that acts as a quencher of PVK emission.

For the emission of C153 (510 nm observation wavelength), the signals fit to a three-exponential function having a rise-time of ~ 180 ps and two decays of 1.23 ns and 5.01 ns (Table 1). The rise-time at 510 nm corresponds to one of the decay (180 ps) of the polymer NPs at the blue part of the spectrum (430 nm). According to the steady-state spectra (Figure 1B), and taking into account that there is no ET when C153 is dissolved in THF with PVK chromophores (keeping constant the ratio like in the case of PVK:C153 NPs) (Figure 4SA), we assign the 180 ps-component to main component of the ET process from excited PVK NPs to the encapsulated C153 molecules. The contribution of this component in the decay signal (59 %) at a specific wavelength does not reflect the amount of PVK emission quenching by C153, as it depends on the two other components related to the emission lifetimes of C153 and PVK. Comparable values of lifetimes in PVK conjugated polymer NPs have been reported and assigned to the ET from the polymer to the guest molecules.³⁹ The 1.23 and 5.01 ns lifetimes of the trapped C153 molecules reflect the effect of different environments around C153 inside the polymer NPs matrix. It is well known that the C153 emission lifetime depends on solvent properties.⁴⁹ For example, in toluene (a hydrophobic solvent with a low polarity) the lifetime is ~ 5.2 ns, which is comparable to the longest time observed in our measurements (5.0 ns). Hence, we suggest that this value corresponds to C153 molecules in a more hydrophobic local environment inside the PVK NP. On the other hand, the C153 fluorescence lifetimes in water are ~ 250 ps and 1.8 ns.⁵⁰ The ns-value is not very different from the 1.23 ns, observed in PVK:C153 NP. We suggest that it comes from a co-population of trapped C153 molecules within an environment allowing H-bonding interactions with the surrounding caged water molecules. However, we can not exclude the possibility of C153 molecules located close to the NPs surface where they can be affected by the solvent water molecules.

To further explore the complexity of the emission of C153, Table 1B shows the results obtained from multi-exponential fit of the emission decays collected at several wavelengths of observation and upon excitation at 410 nm, where > 95 % of the absorption is due to trapped C153 molecules. At the blue part of the emission spectrum (500 nm), we obtain 220 ps, 1.38 ns and 4.91 ns. At 610 nm, the pre-exponential factor of the ps-component disappears, while that of the 4.91 ns become the major one and it increases up to 94%. The changes in the pre-exponential factors of the three components indicate the presence of different environments surrounding C153 inside the PVK NP. In order to understand the effect of the environment on C153 photobehavior, we recorded ps-emission decays of C153 in THF/H₂O mixtures at different water contents.

Table 1S gives the lifetime values obtained from the multi-exponential fit. In pure THF solution the lifetime is ~ 5 ns, however when the water content is increased, two additional components appear, ~ 250 ps and ~ 1.8 ns. These new components are assigned to the interactions between the C153 and the water molecules through H-bonding interactions. These results are in agreement with previous studies in MeOH/H₂O mixtures where the short component was assigned to a fast solvent reorganization and the second one to the fluorescence lifetime of C153.⁵⁰ The observed 180 ps-rising component in PVK:C153 NPs upon excitation at 350 nm is not observed when we excited at 410 nm. However, we obtain 220 ps time constant due to H-bonding interactions of C153 with water molecules, as explained above.

It is worthy to note that the heterogeneity of the system may lead to a distribution of the fluorescent lifetimes of encapsulated C153 molecules. Single molecule fluorescence microscopy can be used as a tool to explore the heterogeneity of the lifetime distribution and ET within these polymer NPs.^{51, 52} For example, using mesoporous material containing fluorescent dyes, we have shown the existence of different populations of the same guest having different lifetimes and their dependence on sample preparation.^{15, 53, 54}

3.3.2. PVK:NR case

For 1.6 % wt NR-doped PVK NPs, the signals obtained at the host emission (430 nm) upon excitation at 350 nm also reveal a multi-exponential decay with time constants of 360 ps, 1.44 ns and 7.72 ns (Table 1A). As it has been observed in the PVK:C153 NPs, the lifetimes of the PVK in the PVK:NR NPs are reduced due a ET from the PVK to NR. However, in this case, the shortening in the lifetimes is lower than that observed using PVK:C153 due to a less efficient ET. When NR emission is monitored at 610 nm and upon the same excitation wavelength, the fit of the decay also needs three components giving a rise time of ~ 360 ps, and two decays of 1.21 ns and 4.04 ns (Table 1A). The rising component (360 ps) reflects the existence of an ET from PVK to NR, and the ns-components at 610 nm are due to NR fluorescence lifetimes. As it has been said in PVK:C153 NPs, we can not connect the amplitude of the 360 ps decay to the amount of PVK emission quenching using steady-state spectra in presence of NR. Upon direct excitation of NR at 510 nm (where the main absorption comes from NR), the decay components are 0.28 ns, 1.33 and 3.73 ns. This result of NR suggests heterogeneous interactions of the dye with the local environment inside the PVK NPs. The 3.73 ns component reflects the lifetime of one population of NR molecules located in a more hydrophobic environment.⁵⁵ The presence of water molecules inside the PVK

NPs leads to populations of NR having a lifetimes of 1.33 ns (the emission lifetime in methanol is 1.01 ns)⁵⁵ and 280 ps which is not very different from the value obtained in pure water (420 ps).⁵⁶ As described for the PVK:C153 system, the short component (excitation at 510 nm) reflects H-bonding interactions with water molecules, and it is not related with any ET processes (supported also by the steady state experiments).

3.3.3. PVK:C153:NR case

Figure 3 A shows the normalized emission decay of PVK:C153 (2.72 % wt) and PVK:C153:NR (2.72 % wt : 1.6 % wt) NPs upon 350 nm excitation (absorbance of PVK) and observed at 510 nm (C153 emission). Table 1A gives the obtained time constants from multi-exponential fits of the signal. In PVK:C153 system, the observed rise time 180 ps which is not presented in PVK:C153:NR system. The pre-exponential factor of this ps-component reaches 70%. The value of the longest lifetime decreases from 5.01 to 2.89 ns. These results confirm the existence of an interaction between excited C153 and NR, where the later can act as an ET quencher of C153 emission. Figure 3 B shows the 610 nm emission decays of PVK:NR (1.6 % wt) and PVK:C153:NR (2.72 % wt : 1.6 % wt) upon 350 nm excitation. The fit of the PVK:C153:NR signal yields a rising component of 140 ps, and decays of 1.15 ns and 3.14 ns. Here, the ps-time decay component is due to an ET process from PVK host to trapped C153 and NR.

Figure 3 C shows the 610 nm emission decays of PVK:C153 (2.72 % wt) and PVK:C153:NR (2.72 % wt : 1.6 % wt) upon excitation at 410 nm (C153 absorption). The obtained times from the multi-exponential fit of PVK:C153:NR are a rise of 70 ps, and three decays of 0.33, 1.12 ns and 2.9 ns. The rising component corresponds to a decaying one at 510 nm of observation without the presence of NR (under identical excitation conditions), and reflects an ET from excited C153 to NR. This ET process is much faster than any of the other involved processes, including ET in the same system after a direct excitation of PVK (350 nm). The reason behind this fast process is due to the close proximity between the two encapsulated entities, as well as to a better spectral overlap between the donor (C153) and the acceptor (NR) emission and absorption spectra, respectively.

Figure 5S shows a comparison of the emission decays (upon excitation at 410 nm, and observation at 610 nm) of PVK:C153:NR NPs and THF solution containing PVK, C153 and NR (where the formation of NPs is not possible). Note that the concentration of C153 (1.9×10^{-4} M) and NR (1.0×10^{-4} M) in PVK THF solutions and in the PVK NPs are the same. The absence of the ps-risetime in THF supports the assignment of 70

ps to an ET process from C153 to NR in the PVK:C153:NR (both trapped by PVK NPs).

Regarding the time constants for the ET process observed within the nanosystems and PVK NPs as host, the above data and analysis suggest the following values: 180 ps for rise time for PVK→C153, 360 ps for PVK→NR, 70 ps for C153→NR, and 140 ps for the global process in PVK→C153→NR. The analysis suggests that PVK NPs act as an efficient host matrix and the green emitting C153 makes the overall ET process faster from PVK to red emitting encapsulated NR molecules. This allows to generate white light emission. It is worth to note, that these time constant energy transfer values could not be assigned only to a Förster energy transfer process, as the excited donor energy could migrate/diffuse through the polymer chains following the exciton diffusion channel.²⁹ Detail analyses taking into account the diffusion between the PVK chains and Förster type energy transfer is needed in order to determine the specific related rate constants.

3.4. Tunable and White Light Generation

Based on the observed cascaded ET phenomena, we produced tunable photoemission from aqueous dispersed dyes-encapsulated PVK NPs by simply varying the relative concentration of the dopant molecules. Figure 4 A exhibits the colour of the emission and quantum yields of these samples under UV light excitation. It is to be noted that blue (a), cyan (b) and magenta (c) emissions are coming from host PVK, encapsulated C153 and NR within PVK NPs, respectively. Salmon pink emission appears at (2.7:1.6) ratio of both C153 and NR contents (d). Furthermore, tunable color emission in a relatively wide visible range by a single wavelength excitation has been achieved by varying the relative concentrations of C153 and NR inside the PVK NPs: For example, concentrations ratio of 2.7:0.96 gives pink emission (h), 2.7:0.64 shows light pink (f), and white light color is at 2.7:0.32 (g). Figure 4 B shows the CIE (1931 Commission international de L' Eclairaged (CIE)) x-y chromaticity diagram the map of emitting multiple dye doped PVK polymer nanoparticles by varying C153:NR ratio (using the same wt % for the samples in the photographs) on a two dimensional projection. We got efficient bright white emission at a particular C153:NR wt % ratios (2.7:0.32) in water suspension (Figure 4B) and in solid state film (Figure 4C). The colour coordinate at this point is X=0.33 and Y=0.39 in the chromaticity diagram (CIE coordinate).

3.5. Cascade Energy Transfer in Solid Film

Figure 5A shows a comparison between the normalized emission intensities of PVK:C153:NR (2.7 % wt of C153 and 1.7 % of NR) NPs in water suspensions, in a PVA-water suspension and in a PVA-solid film. PVA was added to the PVK doped NPs to get a solution of a higher viscosity, and serves as an intermediate step in the fabrication of the film. This one was made by drop-casting method, and it was dried under vacuum. Small differences were observed between the water, the PVA-water suspensions, and the PVA-solid film samples emission upon 350 nm excitation. These differences are explained in terms of changes in the environment due to a reduction in the number of the caged water molecules, which increases the hydrophobicity of the environment. As a consequence, different interactions between the doping dye molecules and the NPs occur, thus influencing the ET efficiency and fluorescence lifetimes. On the other hand, interparticles interaction in the polymer film can occur as it has been observed in other system with polymer matrix.⁵⁷ Upon 350 nm excitation of the PVA-solid film NPs, the emission of PVK is not completely quenched, which suggests that the ET from its excited chromophores to C153 or NR is less efficient than in water suspensions. However, the excitation spectra collected at 650 nm indicate that the existence of intra-particle efficient ET from the host to the trapped dyes is still present in PVA-solid film (Figure 6S).

To get information about the photobehavior of the PVK:C153:NR NPs dispersed in the PVA-solid film, we also measured the ps-time-resolved emission spectroscopy (Figure 5B). The emission signals for trapped C153 and NR upon excitation of PVK NPs at 350 nm were recorded. The signals were fitted using multi-exponential functions, and the results are given in Table 2. Gating at 510 nm (C153 emission) we got lifetimes of 430 ps, 1.24 ns and 3.85 ns. While observing at 610 nm (NR fluorescence) we obtained a lifetime of 3.85 ns and a rising component of 240 ps. The rise-time reflects the energy transfer process, in a way not very different from the one in water suspension samples. On the other hand, the increase of the trapped dyes lifetime (compared with the water suspension results) agrees with a more hydrophobic nature of environment due to the reduction of water content in the dried sample.

Therefore, in solid state as in suspensions, we observed cascaded ET events, in which the C153 molecules inside PVK polymer NPs can act as a molecular antenna, enhancing the ET efficiency from the excited PVK to the trapped NR, and therefore leading to a tunable and white light emission.

Classically, white light generation is based on the ET between multiple layers mixing the three primary colours (red, green and blue).⁵⁸ Recent approach to improve

the devices efficiency is based on using a single-layer white-light emitter to reduce the charge separation between layers in the classical devices.⁵⁹ One adopted solution is the use of light emitting semiconductor polymers doped with small dyes, which allows obtaining white light with a single layer.⁶⁰ However, this kind of devices presents some limitations as the morphology depends on film preparation (concentration, solvent, treatment after deposition, etc.).⁶¹⁻⁶³ Figure 7S shows that PVK-solid film prepared by using PVK+C153+NR mixture in THF (keeping constant the concentrations and the ratio between the dyes, 2.7:0.32 for C153:NR wt %) does not exhibit white light emission, indicating a less efficient ET from C153 and NR when both dyes are not encapsulated in the PVK NPs. On the other hand, if we prepare the PVA-solid film from the PVK:C153:NR NPs water suspension, we could generate white light emission. In addition to this, the PVA-solid film shows only small differences in the emission spectrum between the fresh PVK:C153:NR (2.7:1.6 for C153:NR wt %) and the same sample 40-days old, independently on the excitation wavelength (Figure 8S). These results indicate a good stability of the system in dark. Further work will be done to check the photostability (under continuous irradiation) of the film.

Thus, semiconductor doped polymer NPs were presented as a promising alternative to obtain white light generation from a single layer in which the morphology may be easily controlled.¹⁶

4. Conclusion

We have fabricated by means of simple precipitation method 50-70 nm (in diameter) NPs of Poly[N-vinylcarbazole (PVK) containing one or two kind of organic dyes (C153 and NR), and studied their photobehavior under different experimental conditions using steady-state and picosecond (ps) time resolved emission spectroscopy. We observed multistep cascaded ET from the excited host PVK molecules to NR through C153, a process allowing to get a tunable emission from 350 to 700 nm at a single wavelength of excitation. The time resolved experiments gave the time of the elementary ET processes between the host (PVK) and guest (C153 or NR), and between the trapped two guest. For example, exciting PVK:C153:NR NPs dispersed in a water solution, the ET time constants are: 180 ps for PVK→C153, 360 ps for PVK→NR, and 140 ps for the global PVK→C153→NR and PVK→NR transfers. These ET time constant values are a combination between the Förster ET process and the migration or diffusion of the excited donor through the polymer chains.

At a particular concentration of both dyes, we obtained bright, stable, and white light emission with a quantum yield of 14 %. The NPs exhibit “cool” white emission both in suspension and in solid film, showing the possibility to get a white light LED based on single nanoparticle NP.

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Supporting Information: Table 1S and Figures 1S-7S and experimental parts of dye encapsulated of PVK NPs. Table 1S contains the lifetimes of C153 in THF/H₂O mixture upon 370 nm excitation. Figure 1S presents electron microscopy image of doped and undoped PVK polymer nanoparticles. Figure 2S shows the spectral overlap between the acceptor absorption and the donor emission bands. Figure 3S shows excitation emission spectra of doped PVK NPs. Figure 4S exhibits the emission and excitation spectra of PVK, C153 and NR mixtures in THF. Figure 5S is a comparison between the normalized emission decay curves of PVK:C153:NR in a THF solution and in PVK NPs water solution. Figure 6S presents a comparison of the excitation spectra in water suspension, PVA-water suspension and in PVA-solid state. Figure 7S shows a comparison between the PVK:C153:NR NPS in film and PVK+C153+NR mixed film. Figure 8S presents the stability on time of the emission spectra of PVK:C153:NR in solid film.