Multi-Conformational Luminescence and Phosphorescence of Few Phenazine 1,2,3-Triazole Molecules

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Abstract

Dropcast films produced from blends solutions of phenazine 1,2,3-triazole molecules in very low concentrations in a 1,3-Bis (N-carbazolyl) benzene (mCP) matrix were investigated at room temperature. The mCP acts as an optically inert matrix, having no influence on the emission properties of the guest molecules. Its conductive properties also ensure that blend films, within a completely organic character, are formed as truly active layers. The fluorescent and phosphorescent emission properties of the phenazine molecules, depending on their conformational states, allowed relatively intense emissions in blue, green, red and also in white, without the need to mix different materials. Although the results of absorption of the blended films have shown no characteristics of the guest molecules, due to their relatively low concentrations, the excitation of them occurs directly by the incident laser beam. The steady-state spectroscopy for the monomer and dimer singlet fluorescence states of respective blue and green emissions of the films were investigated. The analysis of their temporal decays were done using a different approach based on the Exponentially Modified Gaussian (EMG) function. The phosphorescent emissions of the triplet steady-states, occurring in the orange or in the red wavelength regions, were observed to be correlated, respectively, to the formation of guest monomers or to the guest dimers singlet states.

I - Introduction

Simple molecular structures of phenazine have been studied since the 1960s [1–5]. Its relatively weak fluorescence was mainly due to the decay of its singlet levels to triplet levels via an intersystem crossing (ISC). New phenazine derivative structures with relatively intense fluorescent properties have been synthesized and were very useful as probes in a biological environment [6–9]. In this sense, the 1,2,3-triazole phenazine molecule, the same as used in this work, proved to be effective as a selective metal probe, detecting cadmium ions that are extremely harmful to human health [10]. In addition to demonstrate their usefulness as a metal sensor, the 1,2,3-triazole phenazine molecules, also allowed the observation of an intense phosphorescent emission at room temperature.

The possibility of observing emissions of singlet and triplet levels at room temperature from a single material gave rise to a series of studies made in our group considering their optical properties in steady state [11] and using optical techniques resolved in time [12, 13]. In these previous works, blends of 1,2,3-triazole phenazine molecules were made in Zeonex (cycloolefin polymers - ZEON Corporation), an optically inert and insulating matrix used to disperse and give greater rigidity to the probe's organic molecules. Studies of the interaction between few probe molecules in Zeonex, seeking to better understand aggregation processes and their consequences in differentiating the emission of phosphorescent bands were also carried out [14].

In this work, taking a step forward, we will investigate the steady-state and time-resolved emission properties of singlet states of monomers and dimers of few interacting probe molecules dispersed in a (N-carbazolyl) benzene (mCP) matrix, featuring a completely conductive organic layer. The use of a new

conductive mCP matrix it is a way to verify if the optical properties of the phenazine type guest molecules would change or not in a new molecular environment, differently of that using Zeonex.

II – Samples And Experimental Details

The 1,2,3-triazole phenazine molecule, hereinafter called the probe molecule, was synthesized from the natural lapachol product, extracted from the heartwood of *Tabebuia* sp. (Tecoma) [10]. Its molecular structure is shown in Fig. 1a. The mCP molecular structure is shown in Fig. 1b. Tridimensional forms of monomers and dimers of the probe molecule, obtained from Density Functional Theory (DFT) calculations, can be seen in one previous publication [13].

A blend solution was produced by adding 0.085 mg/mL of probe molecules to 0.675 mg/mL of (N-carbazolyl) benzene (mCP) molecules, both dissolved in chloroform (CHCl_3), corresponding to an initial mass ratio $m_{\text{Probe}}/m_{\text{mCP}} = 0.126$. Solutions of relatively lower concentrations were obtained by consecutive dilutions, always mixing 50 μL of the last blend solution with a 1 mL of the based solution of mCP at 0.675 mg/mL. The consecutive $m_{\text{Probe}}/m_{\text{mCP}}$ mass ratios of these diluted solutions are described in Table 1. Dropcast films S3, S4, S5, S6 and S7 with decreasing $m_{\text{Probe}}/m_{\text{mCP}}$ mass ratio were then fabricated by spreading 100 μL of the respective diluted solutions on glass substrates in atmospheric conditions. The (N-carbazolyl) benzene (mCP), an organic molecule, as yet said, was used in this work as an optically inert and conductive host in order to disperse and give a higher rigidity to the probe molecules in the blended films.

The steady-state fluorescence (FL) and phosphorescence (PH) of the dropcast films were measured at room temperature as shown in the experimental scheme of Fig. 2. For the excitation of the films it was used a CW 371 nm laser line. The scattered FL and PH steady-state emissions, appearing simultaneously or not in the spectra, were acquired into an ANDOR-Shamrock-303i spectrometer.

Absorption measurements of the blended probe:mCP dropcast films S3, S4, S5, S6 and S7, and for the dropcast film made from the mCP based solution at 0.675 mg/mL were performed at room temperature in a spectrophotometer Rayleigh, model VIS-723G.

As also shown in Fig. 2 time-resolved FL decays of monomer and dimer singlet states, obtained via time correlated single photon counting (TCSPC) technique, were collected deviating the emission beam (by the removable mirror) to a spectrograph Oriel-MS125TM, connected to a PMA-M photomultiplier detector assembly (instrument response function about 120 ps) from PicoQuant. The excitation of the films was made by a pulsed 375 nm laser line (repetition rate of 80MHz) and all TCSPC measurements were controlled by the PicoHarp 300, a picoseconds histogram accumulating processor, both from PicoQuant. Time-resolved PH measurements were not performed in this work, however, references to them, when necessary to complement further discussions, are indicated in the text.

III – Results And Discussions

The steady-state FL and PH spectra for the dropcast films S3, S4, S5, S6 and S7 can be seen from Figs. 3a up to 3e, respectively, with the indication of the main emission peaks. The CW laser beam was addressed to several positions P_n (n from 1 to 6) on the films, in order to obtain the emission of different domains of the Probe molecules. The spectra are shown normalized and displaced in the Y-axis intensity, in order to be comparable. These spectra form the basis for the main discussion of all FL and PH steady-state results presented in this article.

For different positions of the laser on the surface of the films, different spectra are observed with peaks of intensity covering the entire visible region of the electromagnetic spectrum. In all the samples, predominant emissions are observed from the blue color (400 nm to 470 nm), going through the green color (500 nm to 550 nm) and going to the orange-red color (570 nm to 700 nm). Whitish emissions were also observed in which comparable contributions of the blue, green and red color occur simultaneously. The great aspect diversity of spectra indicates a clear heterogeneity of the dispersion of the probe molecules in the mCP matrix, showing the presence of several probe molecular conformations due to the manufacturing method of the films [14], forming monomers, dimers and/or more complex molecular conformational structures.

In a previous work [13], using delayed fluorescence technique together with results obtained via Density Functional Theory, in dropcast films of probe molecules inserted in a Zeonex matrix, emission bands in the 400 nm to 470 nm wavelength region were identified as being from monomeric species of the probe molecule, while emissions in the 500 nm to 550 nm wavelength region were identified from aggregated dimer states, formed by stacking two monomeric units of the probe molecule. Both emission regions come from recombination of singlet states. Tridimensional forms of these monomers and dimers can be seen in the same previous work [13]. Emissions from the 570 nm to 700 nm wavelength region were associated to the phosphorescent recombination from triplet states [11, 12]. This paragraph and the references contained therein are intended to indicate to the reader our first results, with references to delayed fluorescence measurements of the monomer and dimer states of 1,2,3-triazole phenazine molecules, and particularly to the determination of their emissions of phosphorescence and its temporal characteristics.

It is important to highlight the presence of a phosphorescent emission relatively intense at room temperature in the spectra shown in Fig. 3. It was only possible to observe such PH intensity due to the mCP matrix, which stiffens the probe molecule and limits non-radioactive losses due to inhibition of molecular vibrations, favoring the phosphorescent emission. The mCP matrix also has the function of isolating the conformational probe molecular structures, separating them from the others. However, even in the lowest concentration solutions we still find evidence of the formation of dimers and possibly more complex conformations. The mCP matrix improves the conductive properties of the active layer, but in fact its emission properties, observed at steady-state, are very similar of those when using the Zeonex [14]. This favors the use of the mCP as an effective and optically inert matrix.

The experimental results here, also allowed access to the diverse molecular conformations and their emission spectra (Fig. 3). In addition, the presence of the mCP matrix, separating the conformational probe molecular structures, minimized the occurrence of triplet-triplet annihilation, that would compete with the phosphorescent emission [13]. Certainly, studies on the electro-optical properties of mCP:probe blends would bring new information like how electroluminescence would depend on probe concentration, also on the choice of a different common solvent, or if the emission of the mCP:Probe active layers would present color selectivity on voltage. However, these subjects are not within the scope of this manuscript, which aims mainly for the applicability of the mCP matrix to favor the PH emission and configuring a conductive medium.

As observed in early works [13, 14] the spectral range from 350 nm up to 470 nm would correspond to the main region of absorption of the probe molecular structures. The comparison of the absorption spectra of the S3, S4, S5, S6 and S7 mCP:probe films with the absorption spectrum of the neat mCP film in Fig. 4, definitely confirms the absence of the absorption characteristics of the probe molecular structures in all films. This would be mainly explained due to their respective and relatively low concentration of the probe molecular structures. Just a common weak and noisy bump characteristic, occurring around 381 nm at the end of the mCP absorption band, is observed in all spectra. It is worth saying that the dropcast method of making the films does not allow us to control the distribution of the probe molecules inside the matrix. The solvent drying process can also lead to the formation of very heterogeneous layers as to the width and distribution of the mCP matrix molecules on the substrates. This is assumed as the main cause of the observed optical density variation of the background absorption occurring at different spectra in Fig. 4. Thus, although the absorption measurements seem to indicate low sensibility to detect the very diluted probe molecular structures, the presence of clear and relatively intense emission bands seen in Fig. 3, strongly indicate that direct excitations of the probe molecular domains have occurred by the incident laser beam .

Characterization by time resolved spectroscopy using TCSPC technique was very useful to study the singlet emissions of monomer and dimer states in our dropcast films. We will focus on the emission spectra of monomer (Fig. 5) and dimer (Fig. 6) states that appear in a more isolated form, with relatively less contribution of triplet states, allowing a more clear analysis of these singlet states. As stated in the Abstract, the analysis of the temporal decays will be done using a different approach based on the Exponentially Modified Gaussian (EMG) function. The reason for using the EMG approach is because we can introduce new parameters for a better understanding of the observed decays.

The applicability of EMG function can be found in different areas: it was originally used to fit strongly overlapped chromatographic peaks [15, 16]. It was also applied in Biomedical Sciences and related discipline [17]. In Physics, the EMG function has been used for the analysis of short excited-state lifetime measurements of photosensitive species in crystals [18]. In Astrophysics the EMG has been used to the direct measurement of the abundance of flux ratio between neutral oxygen and neon in solar heliosphere [19].

The EMG function $[F(t)]$, used in this work [15] to fit decays of monomer and dimer singlet states of the probe molecules, is defined by the ensemble of Eqs. 1 to 3.

$$F(t) = \sum_{k=1}^2 \left[\frac{A_k}{2T_k} e^{\left(\frac{t_m}{T_k} + \frac{t_\sigma^2}{2T_k^2} - \frac{t}{T_k} \right)} \operatorname{erfc} \left(t_k^* \right) \right],$$

1

where $A_k = h_k t_\sigma \sqrt{2\pi}$. The argument t_k^* of the *erfc* function is given by

$$t_k^* = \left[\frac{1}{\sqrt{2}} \left(\frac{t_m}{t_\sigma} + \frac{t_\sigma}{T_k} - \frac{t}{t_\sigma} \right) \right],$$

2

and *erfc* is the complementary error function defined as

$$\operatorname{erfc} \left(t_k^* \right) = \frac{2}{\sqrt{\pi}} \int_{t_k^*}^{\infty} \exp \left(-x^2 \right) dx$$

3

The EMG function is the result of the convolution process of the Gaussian and exponential probability density functions. The parameters, corresponding to the Gaussian distribution are: its amplitude h , its mean value t_m , and its standard deviation t_σ . The EMG function is interpreted as the probability distribution in which the mean value (t_m) of the Gaussian distribution varies randomly as a shifted exponential distribution.

The t_m value can be understood as an estimation of the raising-time [20] before starting the exponential decay behavior. It depends on the time scale of the TCSPC measurements. In order to make t_m values comparable it is necessary to take the initial increasing ramp of all decay curves at the same time position. This was considered and can be visualized comparing Figs. 7 and 8. The time position of the maximum intensity of the fluorescence decay curves, occurring after the increasing ramp, is directly dependent on t_m value. So, this term is important to first regulate the EMG peak position function. On the other hand, t_σ represents the time dispersion of the Gaussian function. It will feature how large will be the range between the increasing ramp and the start region of the exponential decay. The t_σ term acts as the spreading time involved in the random absorption of available states and their intra- or inter-molecular interactions up to the system reaches its final multi-molecular conformation.

Finally, the exponential tails of the decay curves are represented by the lifetime terms T_k , which values are the recombination lifetimes of the corresponding exponential part of the decay curves and are very

dependent on the monomer or dimer conformational states. Note the sum in Eq. 1 is considered to account the contribution of more than one exponential term for the better fitting of the decays. Two exponential terms (see TABLE 1) were applied for a corresponding example of a dimer case shown in Fig. 8. It is worth mentioning that the index k was only used for the lifetime term T_k , its use for the t_g and t_m components would mean a generalization of the EMG functions that was not necessary for the temporal analysis of the monomer and dimer singlet states of this work.

The introduction of the EMG analysis represents an improvement in respect to our precedent work [14] where probe molecular domains were inserted in an insulating Zeonex matrix. The new EMG method enabled us to obtain a complete and incisive analysis of the temporal dynamics of the monomer and dimer singlet states, differentiating in terms of the t_g , t_m and T_k temporal parameters their morphological characteristics that would not be possible just using standard terms of exponential decays.

In Fig. 5, although the shape of the spectra of the monomer states varies considerably in intensity and peak position from sample to sample, we note that the lifetimes T_1 of these states are very close, see TABLE 1. Another common factor is that for all these monomer states, a single exponential component was enough to adjust the decay curves in the different films. An example of this good fitting process is given in Fig. 7. The pulse curve (dashed line) in the Fig. 7 shows the laser reference curve, confirming that the experimental system has the experimental time resolution needed.

It is assumed that in the molecular structures [13] of dimers the wave function spreads over a larger volume, giving an agile and faster access to the absorption of dimer states by excited carriers. This would explain the decrease of t_g for dimers in comparison to those of monomers (see TABLE 1). However, shorter t_g values are not exclusive to dimer states only. In the TABLE 1, for the monomer state of S5 film, a shorter t_g of 0.06 ns, was observed. It is worth noticing that for the same film a decrease of the t_m had also occurred. The emission spectrum of this film, differently from others in the Fig. 5 presents contributions from the dimer and triplet states around 510 and 687 nm, respectively. Thus, the relative decreases of t_g and t_m for the S5 film seem to be induced by possible interactions with dimer and triplet states, presumably occurring based on its spectroscopic characteristics.

For the emissions of dimer states shown in the Fig. 6a, the analysis of their temporal decays reveals the need for two lifetimes for a perfect fit of the decay curves (see the Fig. 8 for the decay curve of the film S4 as an example). Note also in Fig. 6a the dimer spectra are more centralized in the green emission region, with the presence of a shoulder around 457 nm due to the contribution of monomeric states. The longer T_1 values and the T_2 shorter ones in the TABLE 1 are related, respectively, to the contributions of dimer and to the monomer states, that coexist in the same molecular domains, in agreement with this last paragraph and also with our earlier studies [13, 14]. The h_1 amplitudes of the Gaussian parts of the decay curves (in TABLE 1) reveal the preponderance of the contribution of states of dimers while the smaller h_2 amplitudes correspond to a smaller contribution from the monomer states. Again, it was only possible the

discussion about these temporal characteristics between states of monomers and of dimers with considering the treatment of the decay curves with the EMG function.

In general, the phosphorescent bands of greater wavelength (around 700 nm), appear concomitantly with the bands of emission of dimers, never appearing completely isolated, as can be seen in the ensemble of spectra Fig. 3. In particular, the spectrum of the S4 film in Fig. 6a is enlarged, masking the monomeric emission. Higher lifetimes T_1 and T_2 (see TABLE 1), were obtained for the S4 film. The origin of these greater lifetimes could come from interactions between the triplet (with relatively longer lifetimes) and the dimer states, since the spectrum of emission of this film presents a phosphorescent band around 682 nm more enhanced than that of the others.

As yet said the t_o values, observed for the dimer states of the S3, S4 and S6 films, present between them very similar values and are shorter than the ones corresponding to the monomer states. It is also worth mentioning that their corresponding raising times t_m (as shown in TABLE 1 for monomer and for dimer states) does not vary considerably. The index "k" in the Eq. 1 was not taken into account for t_o and t_m temporal terms. Although not indexing them in the sum, their fitting values, mainly that for t_o , bring the information of what is the more relevant molecular conformation of the emission spectrum. A lower t_o value would indicate a greater contribution from dimer states, while a higher t_o value would indicate a greater contribution from monomer states.

The spectra with phosphorescent bands of shorter wavelengths (around 620 nm), corresponding to the films and their respective positions S4-P5, S5-P1, S5-P6, and S6-P5 of Fig. 3, only appear when the intensity of emission of monomer states, compared to the intensities of dimer states, is predominant. It is also interesting to note that phosphorescent bands close to 600 nm always have a shoulder at longer wavelengths, even if small and not defined as the S5-P1 spectrum (Fig. 3), making it evident that the origins of the emissions at 620 nm and 700 nm are not completely disconnected.

For the spectra of films S5, S6 and S7 shown in Fig. 6b, although all of them came from preponderant emissions of dimer states, it was not possible to measure their decay curves using the TCSPC technique. The decays proved to be very long, above the temporal resolution of the technique, making it impossible to acquire a really correlated photon count. Note that two spectra from film S6 are shown in Fig. 6a and Fig. 6b, respectively. They were obtained from excitation of different regions on the film. At first glance, they are not so different, however in Fig. 6a there is a sharp shoulder around 457 nm and no remarkable spectral features appear at higher wavelengths, indicating none or a very weak emission of triplet states. This shoulder around 457 nm, indicating the contribution of the monomer states, seems to dictate the main conformational character of the emission spectrum, enabling us to measure the corresponding decay curve. In the spectrum of the film S6 in the Fig. 6b, no shoulder indicating the contribution of monomer states was observed. However, an enhanced phosphorescent band has appeared at greater wavelengths, making the TCSPC technique unable to be used due to the corresponding longer lifetimes. The decay curves for the films S7 and mainly for the S5 were not acquired due to the same reason.

Thus, the related results discussed above in the text, show that the temporal terms have a strong dependence on the specific molecular conformation of the probe molecular domains and, therefore, that the fit model using EMG functions it is malleable enough for a reasonable physical interpretation of the monomer and dimer experimental decays.

Iv - Conclusions

Dropcast films containing random domains of few phenazine 1,2,3-triazole molecules (probe molecules) embedded in an inert and conductive 1,3-Bis (N-carbazolyl) benzene (mCP) matrix were produced at relatively low concentrations and investigated by steady-state and time resolved fluorescence at room temperature. The emission properties of these probe molecules have been observed due to their direct excitation by the incident laser beam. The strong morphological heterogeneity of the films was demonstrated by the diversity of distinct emission spectra coming from monomer and dimer species, as well as distinct phosphorescence emissions from different molecular conformations.

An experimental result worthy of attention is the distinction of phosphorescent emissions when induced by the formation of states of monomers or dimers. Due to the formation of predominantly singlet dimer states in the domains of the probe molecules, the corresponding phosphorescent band appears shifted more towards the red than that which it is more predominantly correlated with the singlet monomer states. In both phosphorescent emissions, whether of one type or another, there is a complete absence of vibrational modes of spin-orbit interaction. This was attributed to the character of the domains, containing few probe molecules and, therefore, with relatively less vibrational modes available, allowing the dropcast films to be classified as systems with few interactive probe molecules.

The analysis of the time decay curves was done via an alternative approach using an exponentially modified Gaussian function (EMG). This implied an interpretation of the decays in a more complete way, allowing to quantify not only the lifetimes of the states but also to obtain information on how the dispersion of absorption of available singlet states occurs, associating with it more or less significant contributions to the formation of dimers and or monomers.

As a general conclusion, probe:mCP blend films have been shown to be compatible for use as an active layer in completely organic light-emitting devices. The mCP matrix allows electrical conduction and does not influence the optical properties of probe molecules, in addition to providing mechanical rigidity, creating conditions for an effective phosphorescent emission. We have the advantage of working with a single material that emits in a balanced way in blue, green and red, avoiding the formation of interfaces that could be restrictive to a better electrical conduction. However, we still need to investigate new synthesis methods to control the formation of monomer and dimer structures, in order to better balance the phosphorescent emission.

Declarations

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Author Declarations

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There are no conflicts of interest to declare

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Consent to participate:

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Code availability:

Not applicable

Authors' Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by PBP, KCTC, ENSJ and LAC. The first draft of the manuscript was written by LAC and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript

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Tables

TABLE I: Table of the $m_{\text{Probe}}/m_{\text{mCP}}$ mass ratio for the dropcast films S3, S4, S5, S6 and S7 and the corresponding parameters, obtained from the fit processes of the experimental decays using the Gaussian function Exponentially Modified (EMG), for specific monomers (Fig. 5) and dimers (Fig. 6) states, whose emissions were observed in a more isolated form. The λ_{Collect} were chosen to acquire the respective decay curves taken at wavelength positions around the corresponding regions of the emission peaks. In all decay measurements a pulsed laser (80 MHz) emitting at $\lambda_{\text{Exc}} = 375$ nm was used. h_k ($k = 1$ or 2) is the amplitude of the Gaussian part of the EMG fitting function; T_k ($k = 1$ or 2) is the lifetime of the exponential decay part; t_σ is the time dispersion of the Gaussian part, representing the spreading time involved in the event of absorption due to the occupation of different conformational molecular states; t_m can be understood as an estimation of the raising-time period before starting the exponential decay behavior. The error estimated from the fitting processes for the correlated amplitudes of the Gaussian part and for all correlated times, T_k ($k = 1$ or 2), t_σ and t_m is of the order of 2.0 %.

	Dropcast Films	S3	S4	S5	S6	S7
	$m_{\text{Probe}}/m_{\text{mCP}}$	$5.74 \cdot 10^{-5}$	$2.87 \cdot 10^{-6}$	$1.43 \cdot 10^{-7}$	$7.18 \cdot 10^{-9}$	$3.60 \cdot 10^{-12}$
Monomer States	λ_{Collect} (nm)	413	413	464	415	466
	h_1	33366	31084	28667	22800	39270
	T_1 (ns)	0.66	0.67	0.68	0.68	0.67
	t_{σ} (ns)	0.11	0.12	0.06	0.10	0.11
	t_m (ns)	0.82	0.85	0.78	0.82	0.88
Dimer States	λ_{Collect} (nm)	497	505	-	520	-
	h_1	42347	44578	-	53688	-
	T_1 (ns)	1.94	2.55	-	2.22	-
	h_2	16486	25149	-	16287	-
		0.42	0.90	-	0.48	-
	T_2 (ns)	0.04	0.05	-	0.04	-
	t_{σ} (ns)	0.75	0.80	-	0.78	-
	t_m (ns)					

Figures

Figure 1

Molecular structures of the phenazine 1,2,3-triazole (a) and the (N-carbazolyl) benzene (mCP) (b).

Figure 2

Scheme of the fluorescence and time resolved setups used in the experimental measurements.

Figure 3

(Color Online) Steady-state normalized fluorescence spectra at different positions P_n (n from 1 to 6) of the laser beam on dropcast films S3 (a), S4 (b), S5 (c), S6 (d), and S7 (e). The sequence of spectra at each corresponding figure were displaced in the Y-axis intensity for sake of clarity. All the fluorescence measurements were made in the air at room temperature.

Figure 4

(Color Online) Absorption spectra of the neat mCP film and the S3, S4, S5, S6 and S7 mCP:probe blend films. As described in the Samples and Experimental Details section all dropcast films were fabricated by spreading 100 μL of the respective diluted solutions on glass substrates. After drying the solvent, the amount of material on the respective substrates was very low, resulting in a relatively thin layer with a non-homogeneous distribution of guest molecules on the surfaces. This resulted in a not very large and non-uniform optical density of the films, as observed in the figure.

Figure 5

(Color Online) Normalized fluorescence spectra showing isolated monomer emissions of dropcast films S3, S4, S5, S6, and S7 in air at room temperature, which were obtained by excitation with a pulsed laser line at 375 nm (80 MHz). The sequence of spectra was displaced in the Y-axis intensity for sake of clarity.

Figure 6

(Color Online) Normalized fluorescence spectra showing isolated dimer emissions of dropcast films S3, S4, and S6 (a); and of dropcast films S5, S6, and S7 (b) in air at room temperature. The spectra in (a) are those from which it was possible to acquire the TCSPC decays as stated in TABLE 1, while the spectra in (b) showed enough contributions from triplet states, making their lifetimes very long, out of the resolution of our TCSPC equipment. All the spectra were obtained by excitation with a pulsed laser line at 375 nm (80 MHz). The sequence of spectra in (a) and (b) was displaced in the Y-axis intensity for sake of clarity.

Figure 7

(Color Online) Fluorescence decay curve as an example for an isolated monomer state spectrum of the film S3 shown in Fig. 5. The full black line represents the fitting curve using only one exponential component as the corresponding fitting parameters stated in TABLE 1. The dashed line represents the laser reference curve (Pulse).

Figure 8

(Color Online) Fluorescence decay curve as an example for an isolated dimer state spectrum of the film S4 shown in Fig. 6a. The full black line represents the fitting curve using two exponential components as the corresponding fitting parameters stated in TABLE 1.