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The key role of geminate electron-hole pair recombination on delayed fluorescence in Rhodamine 6G and ATTO-532

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In this paper we investigate the delayed fluorescence (DF) phenomena in the widely used laser dyes, Rhodamine 6G and its derivative ATTO-532 as a function of excitation energy using highly sensitive time-resolved gated nanosecond spectroscopy. Excitation with UV laser radiation results in delayed emission which arises from singlet states created from geminate pair recombination not triplet annihilation. For the first time the origins and photo-physical properties of delayed fluorescence in these highly fluorescent molecules are elucidated.

Introduction

Rhodamine 6G, a well-known laser dye [1] and its derivative ATTO-532 are purely organic materials that show very high fluorescence yields (≥~95%), [2] which makes them attractive for biological applications, in bioassays as fluorescence labels, for example of DNA/RNA molecules, [3] and also in high resolution microscopy, such as Direct Stochastic Optical Reconstruction Microscopy [4] (dSTORM) and Stimulated Emission Depletion Microscopy (STED). [5] In addition of common applications, the photo-physical and the photo-chemical properties of these fluorophores have been extensively investigated in the past. Ringemann et al.[6] reported one of the most promising features of Rhodamine 6G and ATTO-532, showing fluorescence enhancement via reverse intersystem crossing (rISC). We have been studying rISC in order to improve external quantum efficiency (EQE) in OLED devices, and Rhodamine 6G and ATTO-532 appear as excellent reference materials to study this interesting mechanism. However, the rISC experiments made way for discovering an unnoticed phenomenon on the photophysics of delayed fluorescence (DF) in these materials, which nobody mentioned previously in literature, and this is the subject of this letter. In our observations, the DF emission appears to be dependent on the excitation energy, it's only when excited with high energy lasers (355 nm and 337 nm), but not with 532 nm, that DF is observed. Somehow when excitation is at higher energies, the triplet states are able to cross back to the singlet manifold more efficiently, from where the delayed fluorescence emission occurs.

Several works have been addressed the formation of complexes of these dye molecules in solution. It's well-known that Rhodamine 6G for example forms dimers [7] and even trimmers [8] which has been confirmed by mass spectroscopy and detailed balance analysis by Toptygin et al. [9] and S Dare-Doyen et al., [10] additionally Bryukhanov et.al [11, 12] used binary mixtures of polar and non-polar solvents to determine the formation of complexes and the dependence of delayed fluorescence on solvent polarity. Furthermore, the triplet state of aggregated molecules of Rhodamine 6G has also been studied using the flash photolysis technique. [11] From all these studies, it results evident that dimer and even complexes of higher order have significant role on the observation of the delayed fluorescence from Rhodamine 6G and ATTO-532.

Delayed fluorescence can arise as a result of two main processes: from triplet-triplet annihilation (TTA) when two triplet state molecules collide and give rise to an emissive excited singlet state molecule, [13, 14, 15] and from thermally assisted delay fluorescence (TADF) occurring when the triplet state molecules undergo reverse intersystem crossing back to the higher energy singlet state, using the thermal energy bath. [16, 17, 18]

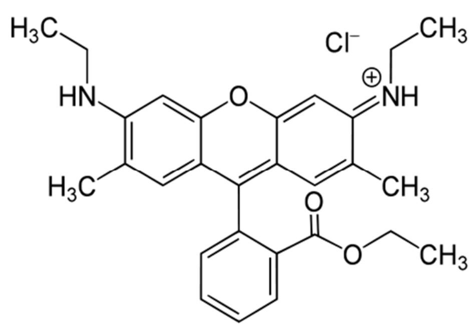
A third, but less studied mechanism in solution involves the recombination of geminate electron-hole pairs (GP) also gives rise to the delayed formation of singlet state excitons and thus results in the observation of delayed fluorescence. [19] In the liquid phase, photo excitation generates electron-hole pairs on a molecule, which is enclosed in a solvent "cage", the molecule can then geometrically relax and in polar environments stabilise the excitation in a charge separated state, often referred as an intramolecular charge transfer state (ICT). This ICT state can itself radiatively decay to yield red shifted CT emission, due to the loss of the relaxation energy. In the solid state, optical charge carriers can be produced as direct result of the photo excitation process in which electron-hole pairs are generated by dissociation of a neutral optical excitation, [20] usually between two molecules, or by dissociation if the photoexcitation step gives enough excess energy, which is required to drive charge separation from the molecular excited states. [21] In the latter case, the coulombic capture distance between the separated electrons and holes play crucially important role and dictates whether fully dissociation or rapid geminate recombination occurs.

Several previous investigations have reported on the dynamics of geminate pair generation and recombination process within their mutual Coulombic potentials. The various excited state dynamics involve the kinetics of transitions and Monte-Carlo simulation techniques are commonly used for modelling. [22, 23] As a result of these studies, the key role of energetically disordered localised sites was highlighted along with the electron-hole separation of the GP. It was also shown that strong disorder is observed to dominate geminate pair kinetics at low temperatures, where the carriers stay far from their equilibrium separations. However, modelling the dynamics is not the case of our investigations in here.

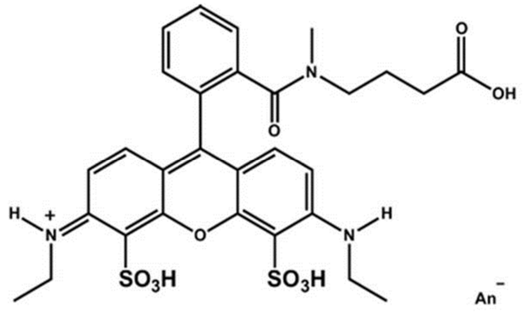
In this letter we examined the source of the delayed fluorescence from these dyes, both in dilute degassed solution and in a molecularly isolated solid environment. [24] The main objective of this work is to identify the origin of the DF for these molecules. We proposed that the DF in Rhodamine 6G and ATTO-532 arises due to the recombination of optically generated electron hole pairs rather than the TTA or TADF mechanisms. To get a better understanding of the GP dynamics, we used time-resolved spectroscopic techniques. [25]

Experiment

ATTO-532 (ATTO-TEC) and Rhodamine 6G (Exciton) (see Figure 1 for chemical structures) were dissolved in polar solvents such as ethanol, dimethyl sulfoxide and dichloromethane and left them to stir overnight to get well-solved solutions. The concentration of the solvents were closely prepared such as from 4.4 E-5 M to 5.5 E-6 M for Rhodamine 6G and from 4.0 E-5 M to 5.0 E-6 M for ATTO-532. Absorption and emission measurements were taken in quartz cuvettes (6Q) with a path length of 1 cm, using a Shimadzu UV-3600 UV/VIS spectrometer. And for the steady state photoluminescence measurements Jobin-Yvon Horiba Spex Fluoromax 3 spectrometer was used. Time-resolved decay measurements were taken in degassed solutions using at least three freezing-thaw cycles in a long necked quartz degassing cuvette. For the solid phase measurements, we used polymeric surfactant, poly-vinyl-alcohol (PVA) (M_w 89000-98000 and 99+% hydrolysed), to isolate and confine the molecules in rigid matrix. Essentially, high temperature was required (around 90 ^oC) to completely solve the PVA in the polar-solvent of dimethy sulfoxide (DMSO), then the solved PVA was mixtured with ATTO-532 and Rhodamine 6G at the ratio of 9%wt/wt and drop casted on sapphire discs.



a)



b)

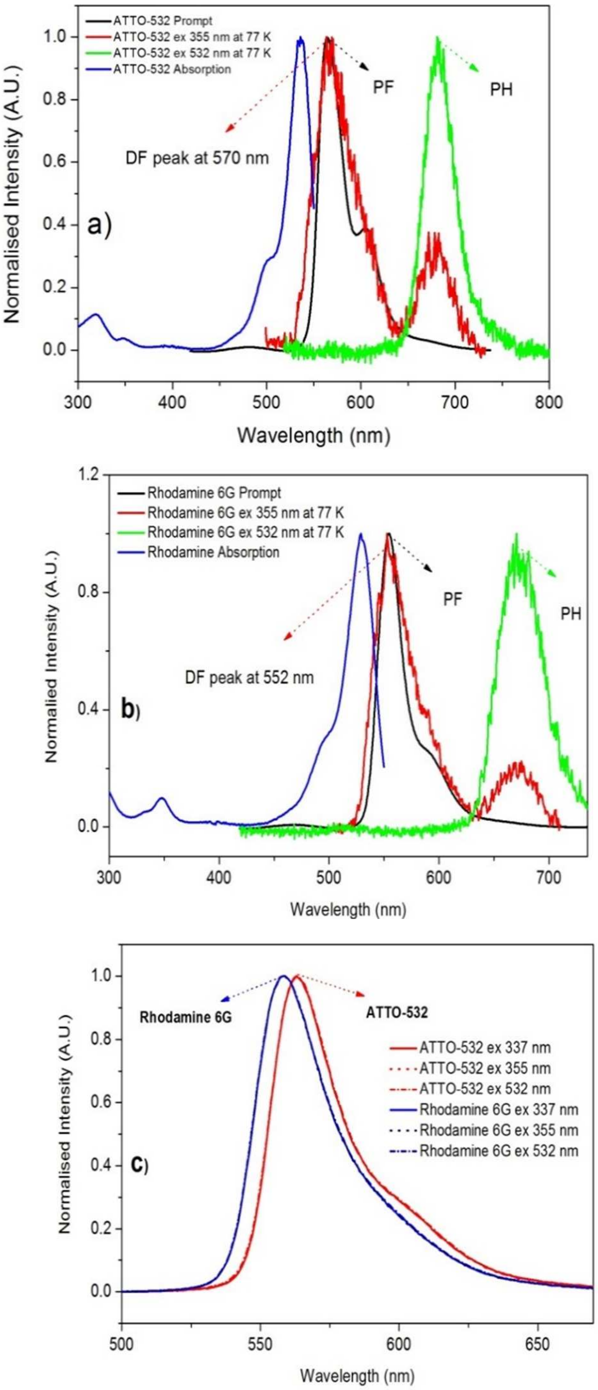
Figure 1 Chemical structures of Rhodamine 6G (a) and ATTO-532 (b)

Nanosecond gated luminescence and lifetime measurements (from 400 ps to 1 s) were performed using a high energy pulsed Nd:YAG laser excitation (SL312, EKSPLA) emitting at 2.33 eV (532 nm) and 3.49 eV (355 nm) pulse duration is approximately 150 ps. During the measurements, the energy per pulse was arranged below 100 µJ to avoid the saturation effects. All solid state time-resolved measurements were performed under a dynamical vacuum of $<10^{-4}$ Torr using displex helium cryostat. Also, a high energy Nitrogen laser (LTB Lasertechnik Berlin) pulse width 3 ns, energy 60-100 µJ per pulse emitting at 3.68 eV (337 nm) was used as an excitation source. The samples in solution phase were placed in liquid nitrogen cryostat (Janis) and the emission was focused onto a monochromator (Triax 180, Jobin Yvon-Spex) and finally, detected on a sensitive gated iCCD camera (4 Picos, Stanford Computer Optics.), actually, more details on decay measurements by exponentially increasing gate and delay times can be found elsewhere. [25] The decay measurements were taken with the laser systems operating at a repetition rate of 10 Hz until the camera gate reaches an upper limit of 100 ms, after this time frame, 1 Hz repetition rate was used. A variable delay time was chosen up to 10 µs to detect the weak delayed fluorescence after the decay of the intense prompt fluorescence, thus, each spectrum has been recorded over 100 laser pulses in order to increase the signal to noise ratio.

Results and Discussion

Figure 2a and 2b shows the absorption, prompt fluorescence (PF), phosphorescence (PH) and delayed fluorescence (DF) spectra of ATTO-532 and Rhodamine 6G in diluted ethanol solution (2.0 E-5 M for Rhodamine 6G and 9.0 E-6 M for ATTO-532), upon excitation at two different wavelengths (532 nm and 355 nm). The absorption spectrum in both materials is characterized by a main absorption band (π to π^*) at ca.530 nm, a (relatively) weaker, secondary band at 350 nm. The shoulder on the blue edge of the main absorption band (ca.489 nm) has been previously shown to mark the presence of the molecular monomers, dimers [7] and higher complexes. [21] In particular, in high concentration (Up to 10^{-2} M) polar solvent conditions, Bojarski et al. has shown the energetically well separated 'aggregate ' monomeric (~505 nm) and dimeric (~540 nm) states. In our case, we used ethanol and dichloromethane solutions and confirmed this energy splitting, at a variety of concentrations in these solvents as well (see supplementary; Figure 1 a, b and Figure 2 a, b for ATTO-532), however, using very dilute solutions (~E-5 M and E-6 M) we do not observe such obvious energy separation. Indeed, we only observed much pronounced spectral changes around 540 nm absorption band for ATTO-532, which was due to dimers, [7] and also, weaker band changes were observed for Rhodamine 6G comparing within two solutions. We further investigated whether the triplet states have any involvement on formation of the absorption bands or not. Addressing this point, the absorption measurements were taken in air-saturated and degassed ethanol solutions (see supplementary Figure 1c and 2c), results showed that triplet states play no role on formation of any additional absorption band structure and this proposal was confirmed with steady-state photoluminescence measurements, in which the samples were excited at 355 nm and the photoluminescence intensities were identical both within air-saturated and degassed ethanol solutions (see supplementary Figure 1d and 2d).

Time-resolved emission spectra were collected using 355 nm excitation wavelengths which resulted the delayed fluorescence peaks at the same position as the prompt fluorescence (PF) at 570 nm and 552 nm for ATTO-532 and Rhodamine 6G, respectively. Interestingly, excitation at 532 nm resulted in only phosphorescence emission, but, no delayed fluorescence was observed, even though, the measurements were taken in the same delayed (50ms) and integration time (1ms). Additionally, the steady-state emission peaks of both materials were identical at different excitations (Figure 2c). So, the question was why the delayed fluorescence was disappeared at low energy excitations? And what could be the reason for generation of delayed fluorescence at high energy excitations? Bojarski et al. [7] suggested that the total fluorescence appeared as a result of both monomers and dimers contributions, and the dimer bands were energetically separated into two bands E_J and E_H. In that scenario, the E_J band was energetically below, and the E_H band energetically above the monomer band. So, in this case, our observation of the delayed fluorescence with 355 nm excitation wavelength can be linked with this scenario, if these two energetically separate dimer bands exist, excitation of the higher energy E_H band only can make a contribution to the total fluorescence upon recombination. In the other case, the E_J band of dimer cannot contribute to the delayed fluorescence, because there is not enough energy to create an excited monomer to yield delayed fluorescence, hence, the excess energy is so that the E_H band can be excited. Additionally, we measured the photoluminescence of samples in different polarity solvents, showing moderate solvatochromic shifts (Figure 2d). In particular, in more polar solvents (higher refracting index) the emission slightly broadens and red shifts, and assigned as π -π* transition which indicates (relatively) stronger dye-solvent interactions as a result of the charge transfer character of the excited state, hence, these interactions reduces the energy differences between the excited state and the ground state.



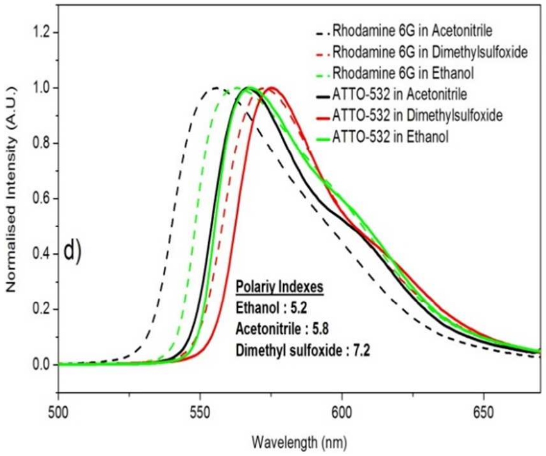


Figure 2 a) Fluorescence, delayed fluorescence and phosphorescence spectra of ATTO-532 in degassed ethanol solution at 77 K, the absorption spectrum was taken in air-saturated ethanol solution at RT. The red line shows the DF and PH of ATTO-532 simultaneously, the measurement was taken at 50ms delay time and 1ms integration time using 355 nm excitation wavelength. The green line shows only the PH of ATTO-532, the measurement was taken at 50ms delay time and 1ms integration time using 532 nm excitation wavelength **b)** Fluorescence, delayed fluorescence and phosphorescence spectra of Rhodamine 6G in degassed ethanol solution at 77 K, the absorption spectrum was taken in air-saturated ethanol solution at RT**.** The red line shows the DF and PH of Rhodamine 6G simultaneously, the measurement was taken at 50ms delay time and 1ms integration time using 355 nm excitation wavelength. The green line shows only the PH of Rhodamine 6G, measurement was taken at 50ms delay time and 1ms integration time using 532 nm excitation wavelength. **c)** ATTO-532 and Rhodamine 6G steady-state emission in air-saturated ethanol solution with excitation 337 nm, 355 nm and 532 nm at RT, showing the same peak overlap **d)** Steady-state emission spectra of ATTO-532 and Rhodamine 6G in air-saturated (different polarity) solvents. Dashed and solid lines were chosen for Rhodamine 6G and ATTO-532, respectively.

Figure 3a depicts the time-resolved decays of prompt and delayed fluorescence of materials in PVA drop casted films at RT and 15 K. In solid state measurements (Figure 3a), the PF lifetime is only weakly temperature dependent. In contrast, delayed fluorescence, which decays exponentially, is highly temperature and concentration dependent (see supplementary Figure 3), and the intensity of DF is dramatically changing from RT to 15K (see Table 2 for more details). In Figure 3b, we showed the solid states (15K) and the frozen solution (77K) lifetime decays in one graph to give better insight into photo-physical behaviours in different environments. In solution, the DF decayed with obeying the power law regime, instead, the DF decayed exponentially comparing in the solid phase. That points to the role of polarity stabilisation of the dimerization species in solution. This stabilisation gives rise to reduce the coupling between the excited and ground state, and concomitantly causes long-lived power law lifetime decays of the DF.

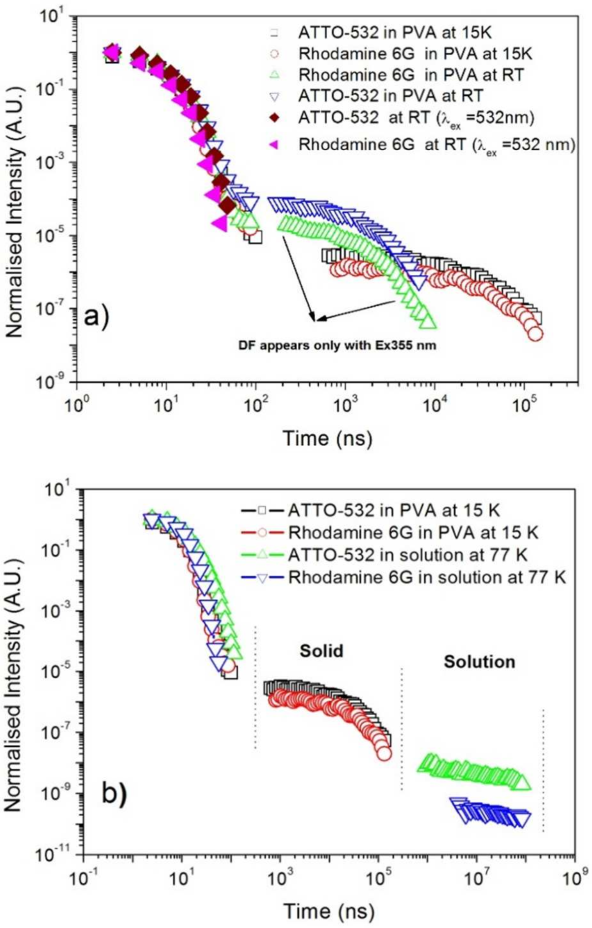


Figure 3 a) Prompt and delayed fluorescence of materials recorded exciting at 355 nm and at 15 K and RT **b)** also solid and solution phase of materials are plotted which compares the decay of the delayed fluorescence shifts

In order to clarify the origin of DF, we need to distinguish between the known mechanisms for generating DF; triplet-triplet annihilation (TTA); thermally assisted delayed fluorescence (TADF); and geminate pair recombination. The laser fluence dependence of the DF is most useful here. At this point, it is appropriate to outline briefly the kinetic aspects of DF generated by TTA. Theoretically, if DF arises via TTA, it should depend on the triplet concentration time evolution given following related equations [26]

$$\frac{d[T]}{dt} = -(k_m)[T] - k_{tt}[T]^2 \qquad (1)$$

Where k_m is monomolecular decay rate, k_{tt} - bimolecular decay rate, [T] - triplet concentration. This results in two radiative channels which deplete the population of triplet states with time, phosphorescence, with a decay rate k_m, which is linearly dependent on triplet concentration and thus linear with laser power.

$$PH \sim [T] = [T_0]\exp(-[k_m]t)$$

(2)

The triplet concentration at time 0 when the triplet state initially formed by intersystem crossing (ISC). And the delayed fluorescence, arising from triplet-triplet annihilation, which is proportional to the square of the triplet concentration

$$DF \sim [T]^2 = [T_0]^2 \exp(-2[k_m]t) \qquad (3)$$

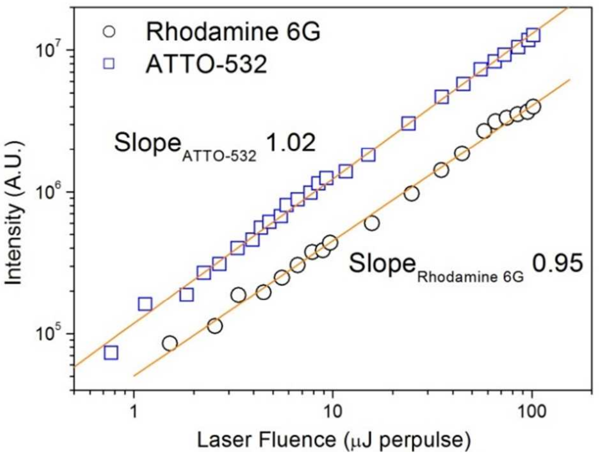
Thus, within the TTA framework the delayed fluorescence should decay with a rate twice as fast as phosphorescence decay. To confirm this, the Rhodamine 6G and ATTO-532 DF lifetimes in degassed ethanol solution and in PVA were recorded and compared with their PH lifetimes at 77 K and at 15 K (table 1 and 2), however, no PH emission was observed in the PVA drop casted films. Further, the DF/PF ratios were also calculated, which are related to the yield of singlet states harvested from triplet states.

Table 1 Rhodamine 6G and ATTO-532 lifetimes of PF, DF and PH in ethanol solution at RT and at 77 K. DF/PF ratio is also provided and compared with respect to the temperature.

Materials	τ_{PF} at RT / 77 K (ns)	τ_{DF} at RT/15K (μs)	DF/ PF ratio at RT/77 K	PLQY Ex 355 nm (%)	PLQY Ex 500 nm (%)
Rhodamine 6G	4±1	0.99 ± 0.05 23.5± 0.02	0.0028 0.0057	14.3	29.4
ATTO-532	4±1	1.2±0.03 30.3±0.04	0.0102 0.0132	12.7	26.8

Table 2 Rhodamine 6G and ATTO-532 lifetimes of PF and DF in solid state films. The DF/PF ratio is provided and compared with respect to the temperature. PLQY of the materials is provided with at two excitation wavelengths (355 nm and 500 nm).

From table 1, we conclude that the lifetime of DF is equal to the (within the error) or longer than the lifetime of PH which is not convenient with the suggested equations above. Clearly, the DF does not arise via TTA in these materials. To get a better understanding of the process involved, the DF intensity dependence on laser fluence, $I_{exc,}$ was recorded between 50ns delay time and and 2µs integration time at both temperatures for the dyes in Figure 4. The DF intensity is linearly dependent (slope 1.02 for ATTO-532 and slope 0.95 for Rhodamine 6G) on excitation power over 2 orders of magnitude laser power, at ≤ 100 µJ per pulse per cm^2. In particular, the type of DF mechanism can be determined from these intensity measurements. If the DF arose from TTA, the power dependency should have a quadratic dependence at low to medium laser intensities, this evidence also supports that TTA cannot be the responsible mechanism behind the DF of ATTO-532 and Rhodamine 6G.



Materials	τ_{PF} at RT / 77 K (ns)	τ_{DF} at RT (ns)	τ_{DF} at 77 K (ms)	τ_{PH} at 77 K (ms)	DF/ PF ratio at RT/77 K
Rhodamine 6G	4±1	370 ± 10	780 ± 25	760 ± 25	0.0018-0.0023
ATTO-532	4±1	375 ± 10	785 ± 25	765 ± 25	0.0288-0.0304

Figure 4 The DF intensity dependence of ATTO-532 and Rhodamine 6G in solution, laser fluence (I_{exc}) exciting 337 nm in log-log scales at RT. The DF intensity grows linearly with excitation density. 50 ns delay time and 2 µs integration time has been chosen

The observation of a linear dependence of the D intensity with excitation energy in both materials would be consistent with E-type delayed fluorescence (or TADF), which forms the singlet manifold via direct reverse intersytem crossing from thermally activated upper lying vibronic states of T_1 to S_1, in this case, the energy gap between the singlet and triplet states, ΔE_{ST} (electron exchange energy) is required to be as small as possible. We calculated the energy splitting gap (ΔE_{ST}) as 0.38 ±0.02 eV for Rhodamine 6G and 0.36 ± 0.02 eV for ATTO-532 which is a reasonable energy gap for weak TADF, [16] such a small gap allows for the DF caused by TADF. However, clear evidence for the absence of the thermally activated delayed fluorescence in these dyes was given by the temperature dependence of DF in Figure 5. The decrease in intensity with temperature clearly was not consistent with the TADF mechanism.

According to the Kasha's rule, [27,28] the molecules, which are excited to the upper singlet states, relax non-radiatively to emissive singlet state and emit at the same emission wavelength, which means the emission wavelength is independent of excitation wavelength. Strictly speaking, that gives us strong evidence that TADF is independent of excitation wavelength, hence, the DF must appear at all excitations wavelengths (both 355 nm and 532 nm). In our case, the DF is completely excitation wavelength dependent which is also inconsistent with TADF phenomena.

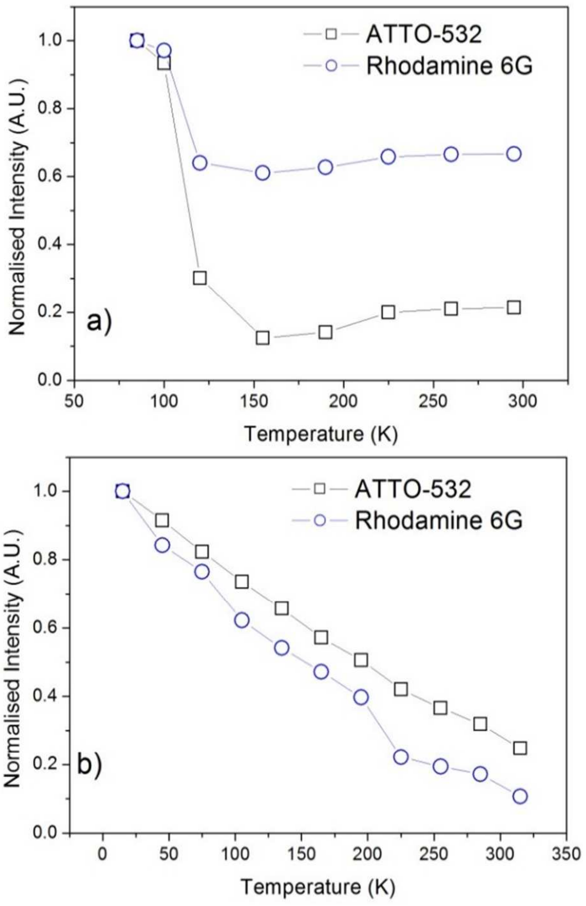


Figure 5 a) Temperature dependence of delayed fluorescence of ATTO and Rhodamine 6G in Ethanol solution **b)** and in solid phase using PVA matrix. Measurements were taken in 200 ns delay time and 3 μs integration time.

Hence the only possible origin of the DF is from the coulombically bound geminate pair recombination. Given that the linear absorption of both materials show the characteristic blue shoulder ascribed to dimer species absorption, it is thus very reasonable to assume that the photoexcited charge transfer occurs between the two molecules forming dimer species. The recombination process of GP can be explained simply by the coulombic attraction and Onsager's theorem. [29]According to the Onsager theorem, the carriers are found in a distance at which the electrostatic binding energy of two oppositely charged carriers is thermal energetically equal. Energy must be provided which is considerably larger than the thermal energy, *kT,* to separate such pairs. The energy of an individual GP is given by the mean charge separation distance, the Coulomb attraction radius, $r_{c.}$(Equation 4), and the probability of recombination rate is also directly proportional to r_c and will reduce at longer times scales. Given charge separation across a dimer state, rapid geminate recombination can be avoided. In the solution phase, there are more energetically disordered localised sites compared to the solid phase, because of this the recombination time (t) takes longer time and the DF lifetimes range up to milliseconds at low temperatures.

$$r_c = \frac{e^2}{4\pi\varepsilon\varepsilon_0 kT} \tag{4}$$

Where ε is the dielectric constant, k is the Boltzmann's constant and T represents the temperature.

From the Coulombic attraction distance, the dielectric constant of environment also plays a crucial role on this recombination process, generally in organic materials the dielectric constant of environment is low, hence, the coulombic binding energies are relatively large, typically the energy of the dimer state exceeds the energy of the singlet excited state around ~0.2-0.5 eV. The binding energy in polar solvents will also be relatively lower because of the higher dielectric constants and those results in added stabilisation of the charge separation over longer distances as well as giving more disordered states. This gives rise to a distribution of tunnelling distances for the recombination process which in term has been shown leads to a power law decay of the emission [30] which we observe here also. Further, the general solvatochromism of both materials in different concentrations, indicate the presence of ICT character of the π-π* states (Figure 2d), especially the highest dielectric constant belongs to dimethyl sulfoxide solution and results in more broadened and more red-shifted emission where can be seen that the more red shifted emission for the dimer species shifts relatively further than the π* states.

From the difference we observe between excitation at 532 nm (purely into the ππ* states) where no delayed emission is seen, compared to the 355 nm excitation which leads to excitation of the higher dimer species (assumed E_H band of dimers), yielding the delayed emission, as a result of long lived geminate recombination process. It is clear from our observations on Rhodamine 6G and ATTO-532 that the DF is only observed when there is sufficient excess energy to excite the dimer states. The geminate recombination of well-separated charge pairs on dimer (and higher) species, which eventually recombine monomolecularly have enough energy to populate the ππ* singlet state and emit DF at the same peak position as π-π* prompt emission. In addition to this the key observation of the cause of the DF, the long lasting lifetime in frozen solution at 77 K (see table 1), compared with shorter life time in PVA, is consistent with more aggregate species in frozen solution, the molecules are stabilised by the polar environment giving longer time to recombine monomolecularly. However in PVA, dimerisation has less chance to form on the PVA matrix which acts to help molecular solubilisation yielding well isolated molecules, [24] and recombination occurs at relatively shorter times (see table 2). The lifetime remains long at low temperatures, as a result of slower recombination process. Consistently, the DF/PF ratios increase at low temperatures that are also reasonable comparing with the temperature dependence of DF (see Fig.4). Given that the dimer species absorption must overlap with the singlet absorption under the main "absorption" band, the observation of DF will be highly dependent on where within the main absorption band excitation occurs. Thus, at 532 nm no DF is observed, but it must be assumed that excitation at higher energies will give rise to dimer excitation and concomitant DF.

Conclusions

In this paper we interpret the origins of DF of Rhodamine 6G and ATTO-532. It is clearly shown how the origins of DF can be distinguished from the previously suggested DF mechanisms and triplet state involvements. [31] We propose that DF results from the geminate pair recombination of optically generated electron-hole pairs on dimer species rather than from triplet-triplet annihilation or TADF. If the DF was to arise from triplet-triplet annihilation (TTA), the DF will have a decay rate twice as fast as PH; its laser fluence dependency would follow a quadratic law initially and later turn to a linear regime at very high triplet densities. Whereas the laser fluence dependency is found to be linear from low intensities up to high intensities. Furthermore, the temperature dependence of DF in frozen solution and in PVA demonstrates high intensity increment approaching the lower temperatures that also confirmed the source of DF cannot be explained with TADF. Therefore, we can only conclude that the origin of DF is from the geminate recombination of dimer (and higher species) electron-hole pairs. They may recombine monomolecularly and populate the molecular π* states as they are higher energy states so that there is enough excess energy in the separated pairs. Power law decay of the DF indicates a distribution of charge separation distances in the disordered manifold of dimer and higher species. For the first time the origin of DF has been clarified and the photophysical properties shown for Rhodamine 6G comparing with its derivative, ATTO-532, along with the role played by excess energy necessity for the formation of DF via geminate electron-hole pairs has been confirmed.

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Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Table of Contents

List of Figures

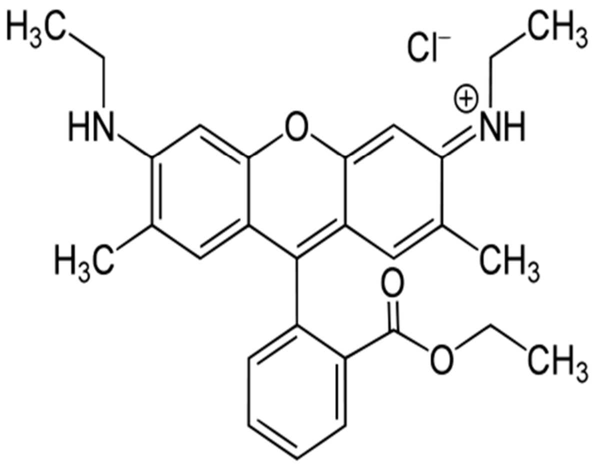

Figure 1a Chemical structure of Rhodamine 6G

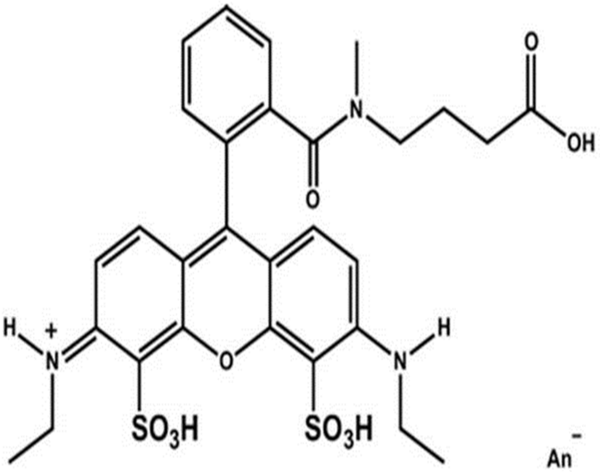

Figure 1b Chemical structure of ATTO-532

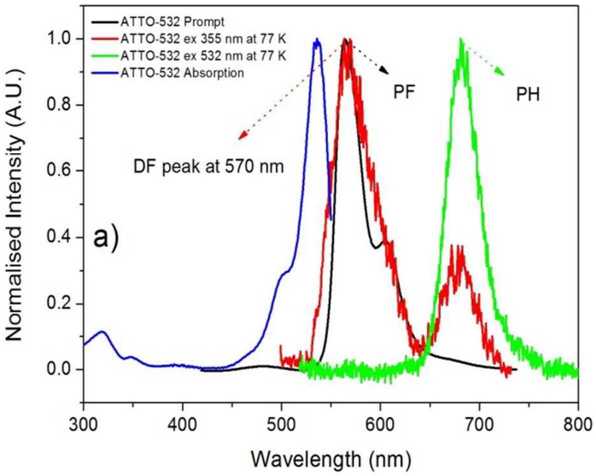

Figure 2a Fluorescence, ABS, DF and PH spectra of ATTO-532 at 77 K

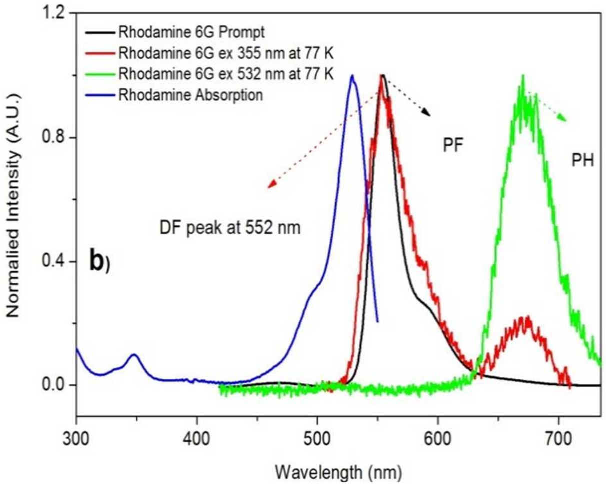

Figure 2b Fluorescence, ABS, DF and PH spectra of Rhodamine 6G at 77 K

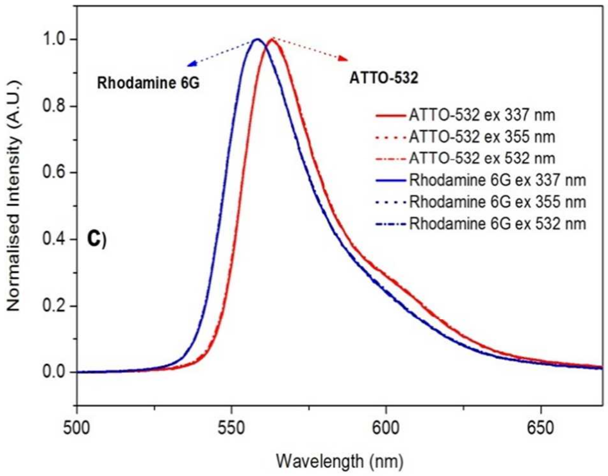

Figure 2c Steady-state spectra of ATTO-532 and Rhodamine 6G under different excitations

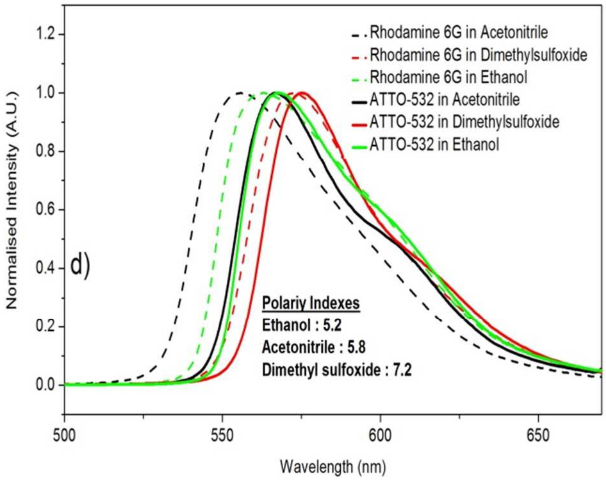

Figure 2d Steady-state spectra of ATTO-532 and Rhodamine 6G in different polarity solvents

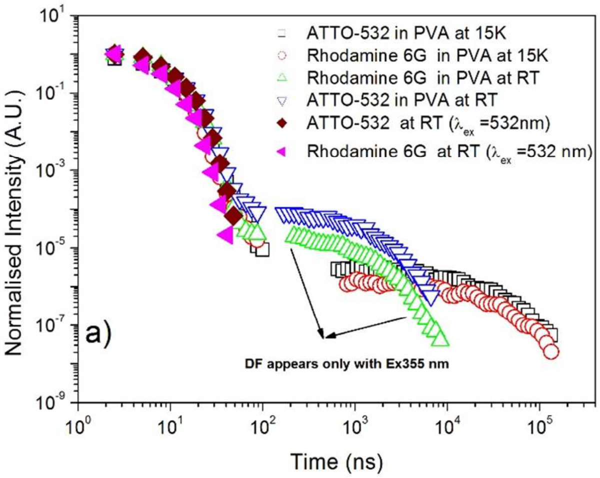

Figure 3 a) PF and DF decay of materials recorded exciting with 355 nm and at 15 K and RT

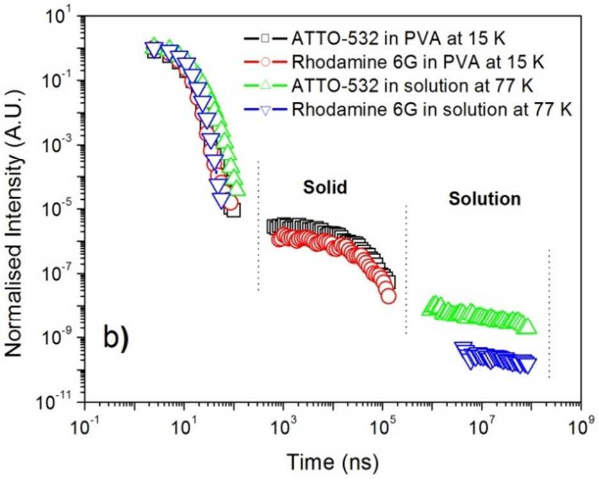

Figure 3b) Solid and solution decays of materials are plotted in the same graph

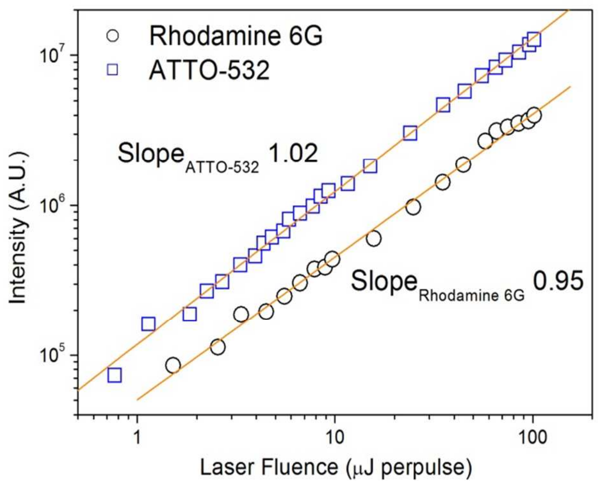

Figure 4 The DF intensity dependence of ATTO-532 and Rhodamine 6G in solution

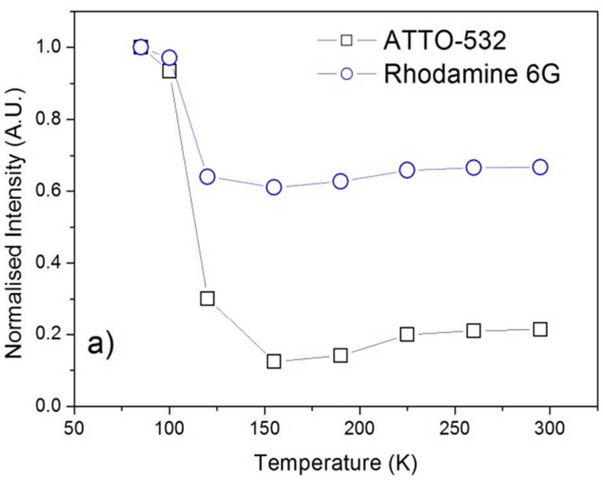

Figure 5 a) Temperature dependence of the DF of ATTO and Rhodamine 6G in solution

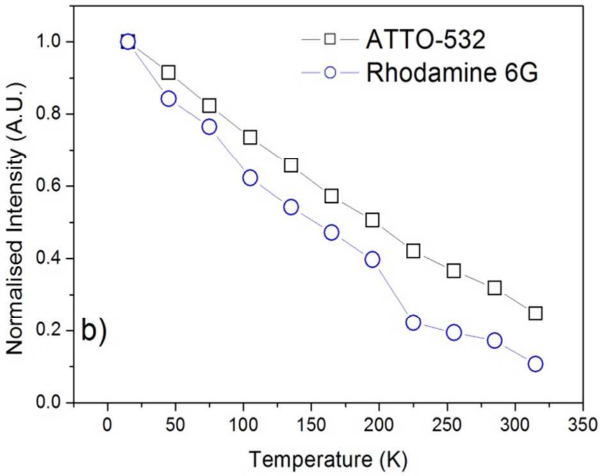

Figure 5 b) Temperature dependence of the DF of ATTO and Rhodamine 6G in PVA matrix

List of Tables

Materials	**τ_{PF} at RT / 77 K (ns)**	**τ_{DF} at RT (ns)**	**τ_{DF} at 77 K (ms)**	**τ_{PH} at 77 K (ms)**	**DF/ PF ratio at RT/77 K**
Rhodamine 6G	4±1	370 ± 10	780 ± 25	760 ± 25	0.0018-0.0023
ATTO-532	4±1	375 ± 10	785 ± 25	765 ± 25	0.0288-0.0304

Table 1 Lifetimes of PF, DF and PH in solution

Materials	**τ_{PF} at RT / 15 K (ns)**	**τ_{DF} at RT/15K (µs)**	**DF/ PF ratio at RT/15 K**	**PLQY Ex 355 nm/Ex 500 nm (%)**
Rhodamine 6G	4±1	0.99±0.05 23.5 ± 0.02	0.0028 0.0057	14.3 29.4
ATTO-532	4±1	1.2±0.03 30.3±0.04	0.0102 0.0132	12.7 26.8

Table 2 Lifetimes of PF, DF and PH in solid state