Photophysical Investigation of the Thermally Activated Delayed Emission from Films of m-MTDATA:PBD Exciplex

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Understanding the delayed fluorescence mechanism behind the creation of emissive singlets from the non-emissive triplets in exciplexes is vital for the fabrication of highly efficient blue fluorescent emitters, and subsequent white light applications. In this article we report the spectroscopic investigation of the exciplex formed between 4,4′,4′′-tris[3-methylphenyl(phenyl)amino]triphenylamine (m-MTDATA) and 2-(biphenyl-4-yl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) in a 50:50 blended film. The mechanism behind extra singlet production in the blend is of E-type nature, that is, "thermally activated" delayed fluorescence. The exciplex singlet-triplet energy splitting is estimated to be around 5 meV, smaller than previously estimated at ≈50 meV. The absence of a well defined separation between prompt emission and emission components with very long lifetimes, >100 ns, is indicative of such a small exchange energy, and arises through multiple cycling between the resonant singlet and triplet manifolds before eventually being emitted from a singlet state. An observed redshift of the exciplex emission with time and increasing temperature is attributed to different exciplex species being formed between the m-MTDATA and PBD molecules.

1. Introduction

Organic light emitting diodes (OLEDs) are on a small scale already matching the efficiency of fluorescent tubes,[1] and with lighting accounting for 20% of home energy consumption and 50% of office energy consumption,[2] OLEDs could save a substantial amount of electricity usage. Furthermore, OLEDs provide excellent color rendering, making them ideal for white light applications. They are also mercury free and manufacturing can become relatively inexpensive and low in waste. For these reasons, the global market worth of OLED lighting and displays is projected to rise from $0.8bn in 2009 to $18.5bn in 2019, a compound annual growth rate of 37%.[2]

The main losses of efficiency in an OLED are dictated by light out-coupling and by the intrinsic quantum mechanical statistics that limits the production of the singlet excited states to 25% upon charge recombination.[3,4] Indeed, 75% of the excited states formed during the recombination are weakly emissive triplets and the ability to utilize all excited states is required in order to improve device efficiency four-fold.[3–5] This has been achieved through the use of phosphorescent heavy metal complexes.[6] In these complexes excited metal to ligand charge-transfer (MLCT) states are highly emissive due to strong spin-orbit coupling.[7] However, deep blue phosphors, mainly based on iridium atoms, are unstable and degrade quickly.[8] Furthermore, pushing the MLCT orbital to high energy makes highly efficient blue phosphor synthesis very difficult due to opening up of emission quenching via the metal d-orbital.[7] Finally, it is difficult to find suitable host for blue phosphor emitters especially in polymer based light emitting devices.[9]

The creation of deep blue emitting OLEDs is essential for achieving good color rendering and correlated color temperature for white light applications that are pleasing to the eye and match natural light.[10] It is therefore imperative to solve the deep-blue efficiency problem in order to create superior, commercially-viable devices. Interest on this matter has been directed towards enhancing fluorescence based OLEDs, and mechanisms have been found that can convert triplet states to emissive singlet states. Two such processes are singlet production through triplet-triplet annihilation (TTA),[11–13] and thermally activated delayed fluorescence (TADF),[14,15] where reverse intersystem crossing (RISC) from the triplet to the singlet state occurs via thermal excitation of the triplet excited state.

In TTA a maximum internal quantum efficiency of 62.5% is possible, whereas in TADF an internal quantum efficiency of 100% is theoretically possible.[16] TADF is therefore the preferable method of enhancing efficiency through delayed fluorescence.

The interconversion of triplet states into singlet states via TADF occurs by 'direct' reverse intersystem crossing. This involves firstly the thermal activated population of upper vibrational levels of T_1, which is described by Equation 1, with T_1* representing the fraction of triplets with total internal energy (electronic and vibrational) equal or larger than the electronic energy of S_1, ΔE_{ST} represents the singlet-triplet energy splitting, k is the Boltzmann constant and T the temperature, and in a second step, is followed by the adiabatic reverse intersystem crossing to the first excited singlet state, described by k^{-T}_{RISC}.

$$\left[T_1^*\right] = [T_1]\exp(-\Delta E_{\mathrm{ST}}/kT) \tag{1}$$

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If we assume that the rate of thermal equilibration between T_1 and T_1^* ($\approx 10^{12}$ s^{-1}) is much greater than $k^{-T}{}_{\mathrm{RISC}}$, then the frequency factor (A) in the reverse intersystem rate constant k_{RISC} (Equation 2, basically describes the average rate constant for the adiabatic $T_1^* \rightarrow S_1$ transition ($k^{-T}{}_{\mathrm{RISC}}$), and is therefore temperature independent.[17,18]

$$k_{\mathrm{RISC}} = A \exp(-\Delta E_{\mathrm{ST}}/kT) \tag{2}$$

It is clear that in order for the rate of reverse intersystem crossing to be significant the singlet-triplet splitting must be comparable to or smaller than kT, which is about 26 meV at 300 K.

Such small singlet-triplet splitting is not usually present in organic systems due to the strong localization of excitons and high electron exchange energy.[19] However, in exciplex emitters the singlet-triplet energy splitting should be particularly small,[20] due to the electron and hole being located on two different molecules, giving small exchange energy. Therefore, devices based on exciplex emitters have potential to maximize the TADF contribution, and have the further advantage of being simple in structure, meaning that they can operate on a lower drive voltage than their phosphorescent equivalent and could be easily scalable.[21]

This paper investigates the photophysics and excited state dynamics of an exciplex emitter between 4,4′,4″-tris[3-methylphenyl(phenyl)amino]triphenylamine (m-MTDATA) and 2-(biphenyl-4-yl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) in a 50:50 blended film. Although this system forms a green emitting exciplex, nevertheless, knowledge of its dynamics will allow to understand how highly efficient blue emitting exciplex systems can be realized.

The terms exciplex and charge transfer complex can be used interchangeably as has been suggested previously by Rothberg,[22] however, in this work we maintain the term exciplex when referring to the charge transfer complex formed between m-MTDATA and PBD for a better consistency with previous literature.[15]

The emission of PBD neat film peaks at 380 nm, and the emission of the m-MTDATA neat film at 430 nm, however, when m-MTDATA and PBD are mixed, the emission appears broader and peaking at ≈540 nm. This has been observed by us (**Figure 1**) and also by Goushi et al.,[15] Furthermore, Goushi et al. also asserted that the fluorescence from the exciplex in PBD:m-MTDATA blends is enhanced by 33–50%, due to the contribution of delayed fluorescence that appears as a result of thermally-activated reverse intersystem crossing from the exciplex triplet level to the exciplex singlet level, and assisted by the small singlet-triplet energy gap ΔE_{ST} of ≈50 meV.[15] However, the possibility that the observed delayed emission was due to TTA was not explored, and further investigation of this system is required. This is especially the case in light of recent findings by Jankus et al., showing that TTA can be the driving process for the observation of enhanced fluorescence in exciplex systems, where the low energy triplet state of the electron donor (or acceptor) acts as a sink for the triplet state of the exciplex.[21]

This system would allow us to study the complex photophysics of exciplex systems in general and in particular when both singlet and triplet charge transfer states are the lowest energy states of the system. In this situation the contribution of TADF and the mechanism supporting TADF can be studied without interference from TTA, therefore allowing for a simpler characterization of the electronic states involved in this process.[23] A diligent photophysical investigation of m-MTDATA:PBD in blended film was conducted here to answer these critical points.

2. Results and Discussion

2.1. Steady State Absorption and Emission

The energetics of the system, along with the molecular structure of both molecules, is shown in Figure 1. Excitation of

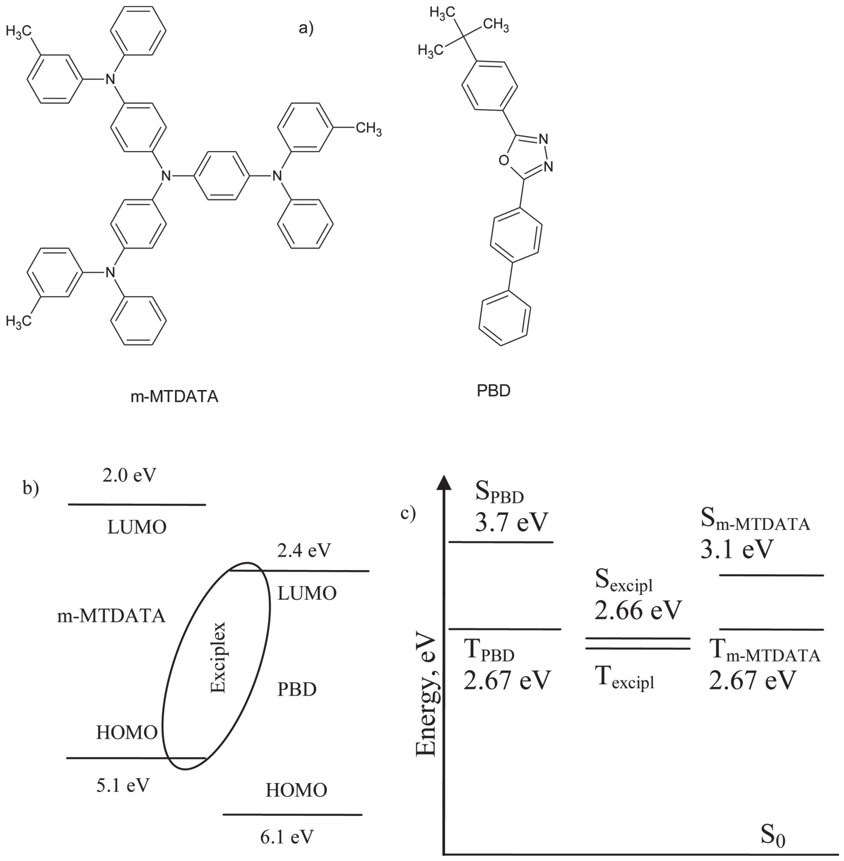


Figure 1. a) Molecular structure of m-MTDATA and PBD. b) Energetics of the m-MTDATA and t-Bu-PBD materials, and resultant location of exciplex taken from previous research by Goushi et al.[15] c) Singlet and triplet energy levels of m-MTDATA, PBD, and the resultant exciplex (taken as an onset of emission from our measurements and the literature).[15,25]

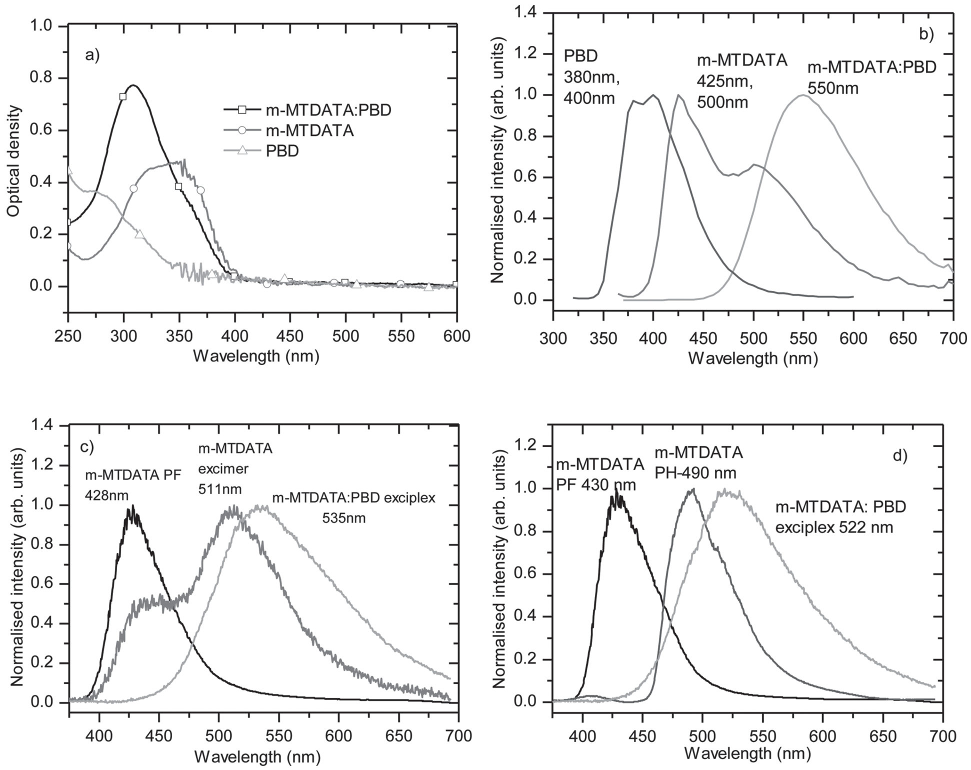


Figure 2. a) Absorption spectra of m-MTDATA, PBD and m-MTDATA:PBD (1:1) at room temperature. b) Photoluminescence spectra of PBD, m-MTDATA and m-MTDATA:PBD (1:1) films excited at 310 nm, 355 nm, and 355 nm respectively at room temperature. c) Peaks observed throughout time resolved emission spectroscopy of m-MTDATA and m-MTDATA:PBD (1:1) blends at room temperature and d) 20 K (16 K for m-MTDATA:PBD). Wavelengths represent peak position. c) Spectra are recorded at (from left to right) 1.2 ns, 4.2 µs, and 24 ns after excitation. d) Spectra are taken (from left to right) 1.2 ns, 75 ms, and 24 ns after excitation. Times given are the mean value of the time period of measurement.

the m-MTDATA donor (D), triggers the electron transfer to the PBD acceptor (**A**),[24] and leads to the rapid exciplex formation between m-MTDATA and PBD in the form $\mathbf{D^+A^-}$. Also shown in Figure 1 are the singlet and triplet energy levels of the constituent materials and the expected singlet and triplet energy levels of the exciplex. Note that the triplet levels of m-MTDATA and PBD are isoenergetic. The triplet level of the exciplex, however, is expected to lie below the D and A triplet levels.[15]

The absorption spectra of m-MTDATA, PBD and m-MTDATA:PBD (1:1) are shown in **Figure 2**a. The absorption onset for m-MTDATA neat film is at 400 nm and for PBD neat film at 345 nm.

The emission spectrum of m-MTDATA (Figure 2b) consists of two emission species at 425 nm and 500 nm respectively. The 425 nm peak shows a faster decay time than the 500 nm emission, and is assigned to m-MTDATA prompt fluorescence. It is likely that the emission peaking at 500 nm, characterized by the significant redshift with respect to the 425 nm peak and very long lifetime, is due to m-MTDATA excimer emission. As it is clear from Figure 2a, PBD does not absorb at 355 nm, but its emission spectra, when excited at 310 nm, is provided for reference. In the PBD film, emission occurs at around 380 nm with a resolved vibronic feature at 400 nm.

The emission of the m-MTDATA:PBD blend (1:1) appears broader and clearly redshifted relatively to the emission of both m-MTDATA and PBD, and peaks at 535 nm. The broadness and featurelessness of the emission in the blend, along with the considerable redshift with respect to both neat film emissions identify this as the emission from the exciplex of the $\mathbf{D^+A^-}$ complex.[15,20,24] Overlap of m-MTDATA excimer emission and blend exciplex emission is considerable, and this needs to be taken into account when measuring exciplex fluorescence lifetimes, for example. This is discussed in more detail below.

2.2. Time Resolved Excited State Measurements

2.2.1. Emission Spectra

Excimer emission can be very long lived[26] and thus it is necessary to avoid confusing it with the delayed fluorescence of the exciplex that we are attempting to characterize. Time resolved emission spectra were collected for both m-MTDATA and m-MTDATA:PBD (1:1) films at various delay times after laser excitation, in the range of 0–75 ms, and at both room and low temperatures (see Figure 2c,d). The predominant emissive species and time intervals at which they are observed are identified in **Table 1**.

The 511 nm emission peak in neat m-MTDATA film, first observed at 660 ns at room temperature, lives up to 0.84 ms.

Table 1. Characterization of each emissive species observed in time resolved emission spectroscopy. The first three peaks refer to experiments with m-MTDATA neat film excited by 355 nm pulsed laser, 100 µJ per pulse, and the last peak to experiments with m-MTDATA:PBD (1:1) film excited by 355 nm pulsed laser at 10 µJ per pulse.

Peak description	Observed between, 20 K neat or 16 K blend	Observed between, RT
m-MTDATA PF and DF ≈430 nm	Entire transient	0–12 µs
m-MTDATA excimer ≈511 nm	–	660 ns–0.84 ms
m-MTDATA phosphorescence ≈490 nm	3.4×10^4 ns - end of transient (also observed in blend)	-
m-MTDATA:PBD exciplex ≈530 nm	Entire transient	Entire transient

Previously it has been suggested that redshifted broad emission peaking ~530 nm appearing in neat m-MTDATA film is due to oxidation or chemical degradation.[27] This peak was reported to appear after annealing at 100 °C for 20 days in air or pure oxygen.[27] However, we did not anneal our samples and they were kept in nitrogen atmosphere at room temperature and lifetime measurements were performed in vacuum. In addition, we observed broad redshifted emission even in solution when exciting with very week xenon lamp (not laser). When dissolved in toluene at 10^{-6} M concentration no broad emission coming from m-MTDATA has been observed, whereas at increased 10^{-3} M concentration emission peaking at 550 nm was recorded (see supporting information). Furthermore, this emission is clearly absent at 20 K, showing that this emissive pathway is thermally dependant. Thus we attribute this emissive species from our thermally untreated films to m-MTDATA excimer emission, possibly having triplet character given its very long lifetime. At low temperature, due to insufficient thermal energy, molecular rearrangements are not possible and the excimer formation is not stabilized, thus this emission is absent. A well resolved emission feature with maximum at 490 nm is observed at low temperatures (Figure 2d and Table 1). This peak appears after a delay of $\approx 3 \times 10^4$ ns and is attributed to m-MTDATA phosphorescence (PH).[15]

Note that in the m-MTDATA:PBD blend no m-MTDATA and PBD emissions are observed (except m-MTDATA phosphorescence at very late times), instead the emission spectrum is entirely dominated by the exciplex emission at both RT and 20 K demonstrating almost 100% exciplex formation.

2.2.2. Photoluminescence Decay Transients and Intensity Dependence on Laser Fluence

The rate of exciplex formation in the m-MTDATA:PBD (1:1) film is below our time resolution, and as a result the exciplex emission is observed from the designated zero delay time up to 1–100 ms. This suggests a considerable contribution from delayed fluorescence.

Photoluminescence decay transients for the m-MTDATA:PBD blend (1:1) were obtained from integrating the emission between 473 nm to 694 nm in order to incorporate most of the spectrum and are displayed in **Figure 3**a. We have recorded decay transients at sixteen temperatures between 16 K and 300 K (see Supporting Information), but the physical picture can be drawn from investigation of just two transients at the edge temperatures of 16 K and 300 K. The dynamics revealed by the PL transients is complex and can only be described at both temperatures by multi-exponential fittings. Furthermore, the emission decay ends in a power law or mono-exponential decay at higher temperatures (discussed in detail later).

At room temperature from 0 ns to ≈1 µs the decay is tri-exponential, and from ≈1 µs to 50 µs a mono-exponential decay is observed. Finally, from 50 µs onwards a power law decay with slope –2.74 is recorded. At 16 K, the tri-exponential regime is observed from 0 ns to 10 µs, and from 10 µs onwards a power law with a slope of –0.83 is recorded. No mono-exponential decay is observed at 16 K.

We attribute the complex tri-exponential decay dynamics to the presence of a distribution of exciplexes in the blend film with slightly different molecular environments and different molecular geometric arrangements. These exciplexes have different charge transfer character, and therefore slightly different emitting energies and lifetimes (discussed in more detail in Section 2.2.3). This complicates the assignment of any of the exponents from tri-exponential regime to PF and/or DF. The complex interplay of the lifetimes of tri-exponential regime at different temperatures can be appreciated from Table S1 in Supporting Information.

To get a better understanding of the processes involved, PL intensity dependence on laser fluence was recorded between 5–105 ns, 4–34 µs, and 30 µs–10 ms at both temperatures. These times were chosen to coincide with the above mentioned transient regimes. In particular, the type of DF mechanism, TADF or TTA, can be determined from these intensity measurements. At all time periods, and at both temperatures, a strictly linear proportionality is observed (see Figure 3b, other graphs can be found in Supporting Information). This indicates a single photon process, where one input photon is required for each ‘delayed’ output photon to be created. Had the DF been caused by TTA the dependence would have been quadratic as previously shown for *N*,*N*′bis(lnaphthyl)*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine:1,3,5-Tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl exciplex; in TTA two triplet excitons are required for each DF photon created.[21] The evidence thus supports Goushi et al.‘s assertion that TADF is the photophysical mechanism responsible for the observation of DF.[15]

The power law regime occurring from 50 µs onwards at room temperature, with slope –2.74 ± 0.03, and at 16 K from 10 µs onwards, with slope –0.823 ± 0.009 might appear as a result of the exponential decay being violated at long decay times, and due to geminate pair recombination.[28,29] Nevertheless, both power law regimes can be explained by previous studies, and contribute very little to the overall PL intensity, for these reasons they are considered no further in this study.

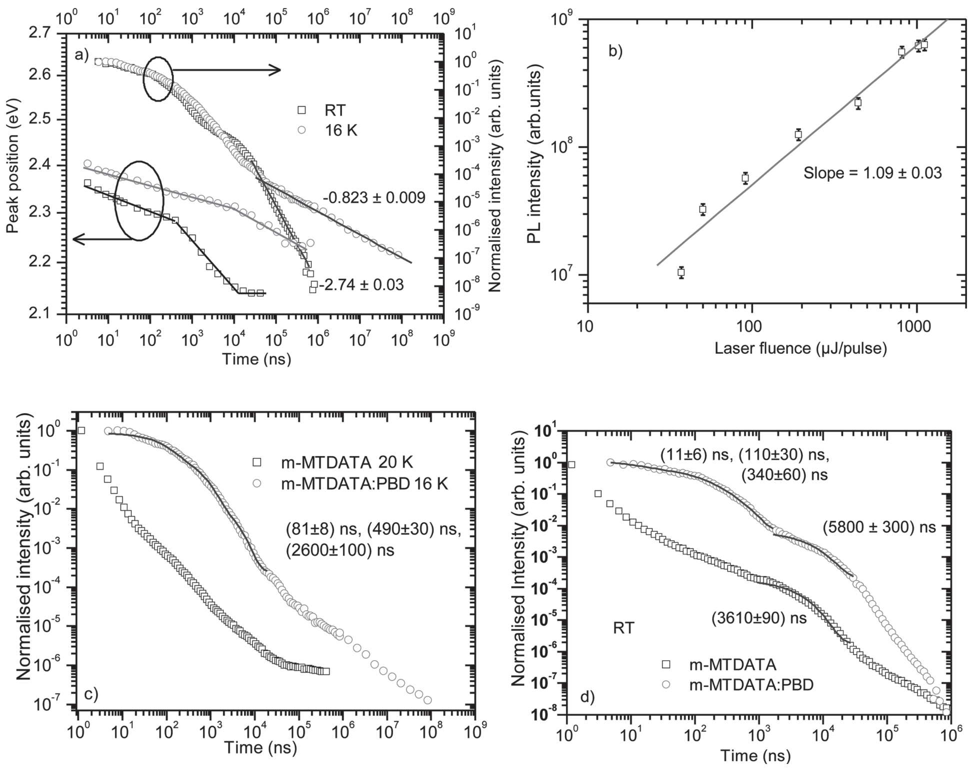


Figure 3. a) PL transients and position of peak maxima of MTDATA:PBD (1:1) films at room temperature (squares) and 16 K (circles), excited by 355 nm pulsed laser, 10 μJ per pulse. Straight line fits at the end of PL transients are power laws with slopes of –2.74 ± 0.03 (RT) and –0.823 ± 0.009 (16 K). For peak position data fit lines are drawn as a guide. b) PL intensity dependence on laser fluence, excited by 355 nm pulsed laser at RT and with delay and integration times of 5 ns and 100 ns respectively. c) Comparison between m-MTDATA and m-MTDATA:PBD (1:1) blend decay transients at low temperature (16 K blend, 20 K m-MTDATA) and d) room temperature. Direct comparison reveals that blend decay transient is influenced by m-MTDATA excimer emission. Both materials were excited with 355 nm pulsed laser at 10 μJ per pulse for blend and 100 μJ per pulse for m-MTDATA. Error bars to account for 10% laser intensity fluctuation are plotted, but are too small to be easily visible. Exponential and tri-exponential fits, along with their associated lifetimes, are also plotted.

Removing the power law regimes from consideration, the shape of the remaining transients are thus tri-exponential and mono-exponential at RT and tri-exponential at 16 K. Visual comparison between the two transients (see Figure 3a) shows an emission "bump" appearing between 1–30 μs. This emission bump is not present at 16 K, but is clearly visible at room temperature, and is well described by a single exponential with a lifetime of (5800 ± 300) ns, as shown in Figure 3d. The absence of this emission at 16 K, strongly suggests a thermally activated mechanism as the cause of this emission. Two candidates for such emission exist; it could be TADF appearing from the exciplex, or instead m-MTDATA excimer emission, formed between m-MTDATA molecules in the MTDATA:PBD (1:1) blend. Excimer formation is considered because thermal energy is required to re-orientate molecules to the appropriate configuration, and thus is also a thermally activated process.

To get better insight into the contribution of m-MTDATA excimer to the overall emission in m-MTDATA:PBD blend films, emission decay transients of m-MTDATA neat film were collected at room temperature and at 20 K, over the same spectral range, from 473 nm to 694 nm, with an excitation of 100 μJ per pulse. Direct comparison of both decay transients can be observed in Figure 3c,d.

The thermally activated mono-exponential decay observed between 1 μs and 30 μs in the blend film coincides exactly with the decay observed at similar times in the neat m-MTDATA films. The latter is caused by m-MTDATA excimer emission, and therefore we ascribe the mono-exponential feature between 1 μs and 30 μs in the blend as being due to the contribution of m-MTDATA excimer emission that is hidden under the exciplex spectrum, as both the exciplex spectrum and m-MTDATA excimer spectrum emit at similar wavelengths (see Figure 2c). No mono-exponential decay features in m-MTDATA neat film and m-MTDATA:PBD (1:1) blend are observed at 16 K.

The study into m-MTDATA:PBD (1:1) blend conducted by Goushi et al. recorded PL decay transients between 3 μs and 60 μs.[15] From this data the authors derive an activation energy of 50 meV for the observation of TADF, which would give a good estimative for the singlet-triplet energy splitting. However, the majority of their data is convoluted with m-MTDATA excimer emission, and is very likely that the estimated 50 meV activation energy is in fact dominated by the energy barrier of excimer formation. For example, Burkhart et al. found that triphenylamine related excimers have activation energy of very similar magnitude.[30]

We find that 78% and 82% of the total emission for room temperature and 16 K respectively can be ascribed to the tri-exponential regime. A tri-exponential fit, of the form given by Equation 3, was made and shown with associated lifetimes in Figure 3c,d.

$$I = I_0 + A_1 \exp(-t)\,\tau_1) + A_2 \exp(-t)\,\tau_2) + A_3 \exp(-t)\,\tau_3) \tag{3}$$

where I is the PL intensity, I_0 and A_n are constants, and τ_n are the associated lifetimes.

The fitted lifetimes of 81 ns, 490 ns, 2600 ns at 16 K and 11 ns, 110 ns, 340 ns at RT of the tri-exponentials varied only slightly depending on the initial parameters given and the exact data range selected. Average lifetimes τ (appropriately weighted by the pre-exponential factor) [7] were thus calculated from Equation 4, 240 ± 30 ns at room temperature and 830 ± 60 ns at 16 K.

$$\tau_{av} = \frac{\sum_{i=1}^{3} A_i \tau_i^2}{\sum_{i=1}^{3} A_i \tau_i} \tag{4}$$

Previous to our work,[24] slightly different decay lifetimes of m-MTDATA:PBD exciplex in polycarbonate matrix were recorded (40 ns and 180 ns at RT). This can be explained by the different molecular environment and thus slightly different excited state deactivation rate constants.

Interestingly, no clear separation between prompt and delayed fluorescence is possible in the exciplex emission. Even the shortest component at both temperatures is already in the order of tens of ns, and intermediate decay components on the order of hundreds of ns are clearly observed. This means that no region of the PL transient at either temperature could be easily ascribed to "classical" prompt fluorescence from the singlet exciplex state that is expected to last in the order of a couple of nanoseconds.[7] Consistent with this observation, the fluorescence decays of the m-MTDATA:PBD (1:1) blend, obtained with a single photon counting, with emission collected at 600 nm (not shown), were too long to be measured in the timescale of the first 10 ns of the decay and thus confirmed long emission lifetimes. It is very uncommon that a singlet excited state could live as long as 200 ns. For example, in a previous study on fluorene linked dyes, singlet exciplex lifetimes have been recorded to be 15 ns or shorter.[31]

We attribute such long decay lifetimes to the effect of singlet-triplet recycling, that is, to the rapid interchange between the singlet and triplet exciplex states that occurs due to the small singlet-triplet energy splitting in the exciplex. Singlet and triplet exciplex states can undergo rapid multiple forward and reverse intersystem crossing steps mediated by hyper fine interactions.[17,32] This is possible if the singlet-triplet splitting is less than kT, 26 meV, which is possible in exciplex systems given the efficient electron-hole separation over the exciplex. On examination of the data (Figure 3c,d) it appears that the energy gap between singlet and triplet energy levels must be almost negligible due to the clear display of thermally activated delayed fluorescence at 16 K (≈1.4 meV), as shown by the linear excitation power dependence of the emission at both temperatures. With such back and forth intersystem crossing steps, excited states are constantly 'recycled' between the singlet and triplet exciton states until they are eventually emitted from S_1. Such resonant excited state exchange processes prolongs the excited state lifetimes, by achieving a quasi equilibrium that is dominated by the longest lifetime species (the triplet exciplex in this case).[17,33,34]

Scheme 1 shows in a simplified way the recycling process between the singlet and triplet states of the exciplex.

Clear evidence for the presence of the thermally assisted reverse intersystem crossing in the m-MTDATA:PBD exciplex is given by the temperature dependence of the steady-state emission shown in **Figure 4**c, in the form of an Arrhenius type plot. Of particular interest is the linear region observed between 46 K and 175 K, with the emission intensity increasing with temperature increase, giving a slope of –61 K.

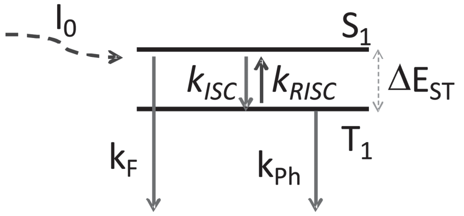
The determination of the energy barrier for the reverse intersystem crossing is very difficult in this system due to the absence of a clear separation between prompt and delayed emissions, and the absence of exciplex phosphorescence. However, using Scheme 1 and assuming a temperature independence of the rate constants in the temperature interval (except the rate of reverse intersystem crossing), from 46 K to 175 K, ΔE_{ST} can be estimated using Equation 5, which relates the steady-state exciplex emission intensity with the kinetic rate constants in Scheme 1, assuming that $k_{ISC} >> k_{RISC}$, k_F (see Supporting Information for more details):

$$I_{excp}^{SS} = k_{rad} \frac{I_0}{k_{Ph} k_{ISC}} k_{RISC} \tag{5}$$

Note that the assumption of having $k_{ISC} >> k_{RISC}$, k_F is reasonable. First, in the exciplex the ISC should be high, due to the strong charge transfer character of the exciplex, second k_F is slow ($<10^6$ s^{-1}) given small PLQY of exciplex,[15] and finally k_{RISC} represents a thermally assisted process, given by Equation 2, and thus determined by the ST energy splitting, therefore k_{RISC} can be easily much slower than the forward k_{ISC} step. Under these approximations, the ST energy splitting of 5 meV is estimated from Equations 2,5.

The increase in intensity with temperature clearly shows that heat is being drawn from the environment, and can be ascribed to the affects of overcoming the singlet to triplet gap, that is, $\Delta E = \Delta E_{ST}$. As this energy is of similar magnitude to the thermal energy even at 16 K (within 3–4 kT), such a small gap allows for the delayed fluorescence caused by TADF to be observed even at 16 K. Such a small singlet triplet gap (near resonant singlet and triplet energy levels) is very consistent with the long emission lifetime process we propose. Beyond 175 K the intensity drops off indicating the on-set of a competing excited state quenching process. This then explains the fact that at 16 K the lifetimes are longer than at RT when quenching mechanisms are present reducing lifetimes.

To check that the steady state intensity increase with increase in temperature is not controlled by excimer emission, also a thermally induced process, we integrate temperature dependent decays (see Supporting Information for decays) in two regions: triexponential region (ascribed to exciplex emission) and monoexponential/power law region (ascribed appropriately to excimer emission/geminate pair recombination). The result is in Figure 4d showing that emission is much greater in triexponential region and that its slope (according to Equations 2,5) is also approaching –60 K. The slope is –143



Scheme 1. Simplified kinetic scheme representing the recycling between singlet and triplet states in the m-MTDATA:PBD exciplex. S_1, and T_1 represent singlet and triplet states respectively, I_0 is the rate constant of S_1 population, k_{ISC} and k_{RISC} the rate constants of forward and reverse intersystem crossing respectively, k_F is the fluorescence rate constant from S_1, k_{Ph} the phosphorescence rate constant from T_1, and ΔE_{ST} the singlet-triplet energy splitting.

K for the monoexponential/power law emission and its overall intensity is smaller than that of triexponential regime, giving minimal influence to steady state intensity.

2.2.3. Peak Shift with Time and Effects of Temperature on Peak Shift

We turn our attention now to the emission shift observed in Figure 3a. The blend emission (predominantly exciplex) redshifts continuously with time, showing three distinct red shift regimes at room temperature, and two regimes at 16 K. At both temperatures the initial shift regime is coincident with the triexponential exciplex decay that we attributed to TADF emission. Time resolved spectra clearly show a simple monotonic red shift of the whole emission band, with no sign of two emission bands or isoemissive point,[35] which could be attributed to singlet and triplet exciplex emissions (see Supporting Information). Furthermore, no isoemissive point has been observed in steady state spectra with a change of temperature (see Supporting Information).[36] Given the 75 meV shift in the peak this would be readily resolvable if this were the case. Finally, the last peak shift regime at both temperature coincides with the power law components of the PL transients. The middle regime at room temperature occurs at roughly the same time where the excimer emission dominates. In intermediate temperatures, similar peak shift regime changes are observed (see Supporting Information).

Steady state emission spectra have also been found to redshift with increasing temperature, as shown in Figure 4a. Once again the shift in spectra is continuous and is a monotonic red shift of the whole band. For reasons currently unknown, the relationship is exponential in nature, as shown by the line of best fit provided.

The linear shape of the PBD molecules means that there can be potentially many orientations to which it is positioned with respect to the m-MTDATA molecules. This scenario is especially pertinent in our case of solid thin film, with a high degree of conformational disorder and where the molecules' freedom

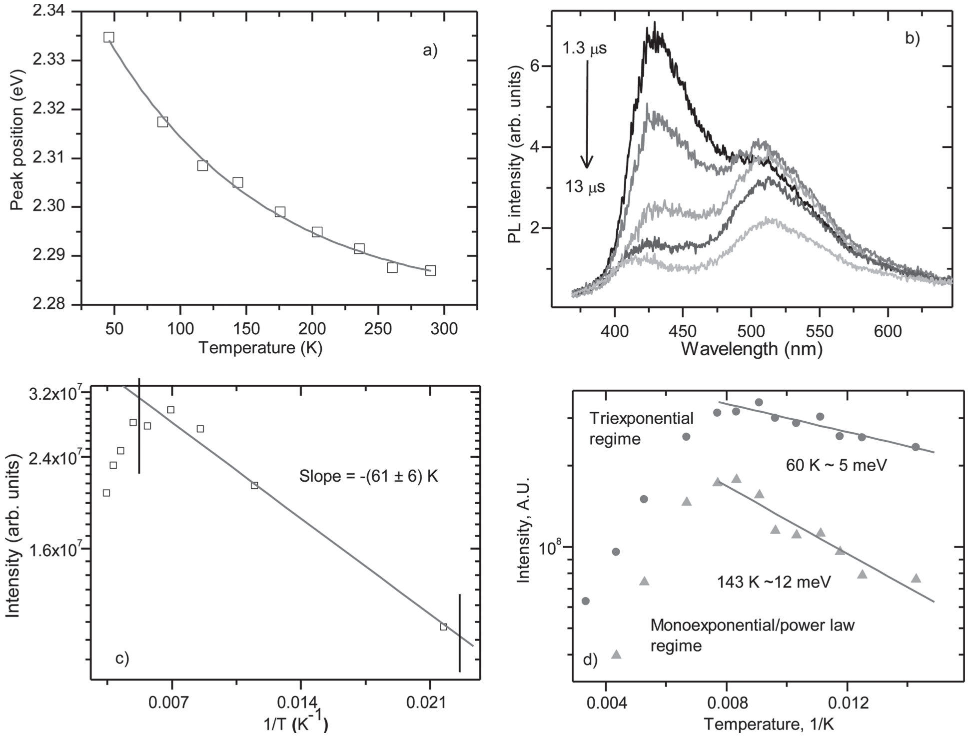


Figure 4. a) A plot of peak position against temperature, with an exponential line of best fit. b) m-MTDATA spectra recorded at different times indicated with an arrow increasingly from 1.3 µs (strongest intensity) to 13 µs (weakest intensity). Note that excimer emission, at about 510 nm does not noticeably redshift. c) Arrhenius plot of PL spectra intensity when excited at 380 nm. Line of best fit represents points within the two vertical bars. d) Intensity temperature dependence of two regimes: triexponential regime ascribed to mixed PF and DF from exciplex and monexpeonential/power law regime ascribed to excimer and geminate pair recombination, for more information please see text.

of movement is severely restricted. It is clear that different degrees of charge transfer within an exciplex will be likely. The more complete the charge transfer, the lower the coupling between the excited and ground state. This dispersion in charge transfer will give rise to red shift of emission as the CT character increases[37] and the concomitant reduced coupling to the ground state will increase the radiative lifetime of the exciplex.[38] Thus, at longer observation times we predominantly see the longer lived more red shifted exciplexes. Further, it is difficult to envisage exciplex migration given the nature of the excited state.

If respective degree of charge transfer is the main consideration then there should be less redshift in m-MTDATA excimer spectra with time, and this is indeed observed as shown in Figure 4b.

3. Conclusion

A 50:50 blend of m-MTDATA and PBD was fabricated, and exciplex emission at ≈525–550 nm was observed with little distinction between any prompt and delay components. The intensity dependence of the long lived (delayed) emission is found to be linear consistent with the photoluminescence being enhanced by the conversion of exciplex triplet to singlet states via thermally activated reverse intersystem crossing. From PL transient measurements complex lifetimes on the order of hundreds of nanoseconds are found, which we ascribe to be the effect of multiple back and forth intersystem crossings between nearly resonant singlet and triplet states. This is observed at both room temperature and 16 K, revealing that the singlet-triplet energy gap is almost zero, in the order of a few meV. Measurements of emission intensity change in steady state spectra with temperature have been used to estimate the $\Delta E_{\mathrm{ST}} = 5$ meV. This is in contrast to the 50 meV proposed in a previous study,[15] where the result may have been influenced by m-MTDATA excimer emission. Whilst m-MTDATA:PBD is not an efficient emitter system, other exciplexes with higher PLQY values and similar singlet-triplet splitting should give high efficiency blue emitters.

The exciplex spectrum‘s continuous redshift with time and with increasing temperature is ascribed to arise due to high degree of conformational disorder dictating the degree of charge transfer within an exciplex. More complete charge transfer gives lower coupling between the excited and ground state resulting in red shift of emission and the reduced coupling to the ground state will increase the radiative lifetime of the exciplex. Thus at longer times more redshifted exciplexes are observed.

4. Experimental Section

Thin film samples were made by co-evaporation deposition onto transparent sapphire substrates using a Kurt Lesker Spectros II deposition system under vacuum, 10^{-6} mbar, at a steady evaporation rate of ~1 Å s^{-1}. Deposition thickness was re-measured using a *J A Woolam VASE Ellipsometer*.

Both steady state absorption and emission are measured using commercially available machines, *UV-3600 Shimadzu* spectrophotometer and *Jobin Yvon Horiba Fluoromax 3* respectively. Time resolved spectra are obtained by exciting the sample with a 150 ps-pulsed, 10 Hz, 355 nm Nd:YAG laser (EKSPLA). Sample emission was directed onto a spectrograph and gated iCCD camera (Stanford Computer Optics). PL decay transients were obtained using exponentially increasing decay and integration times, as previously described.[36]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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