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STUDY OF TADF EMITTERS IN OLEDS

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Abstract

Delayed fluorescence through thermally activated delayed fluorescence (TADF) has great potential for the creation of inexpensive and highly efficient white lighting applications, with superior colour rendering. Currently the highest external quantum efficiencies are achieved with small donor-acceptor-donor molecules utilising intramolecular charge transfer (ICT) states, and these molecules require a suitable host matrix to reside in. This thesis studies the effect of host material on the model molecule 2d, a proven efficient TADF emitter through diligent photophysical investigation. A combination of steady state and nanosecond time resolved spectroscopic studies confirm the importance of a high host triplet level to ensure that the ICT state is the lowest energy excited state to avoid high levels of quenching. More interestingly it is shown that the functional group combination of emitter and host is crucial in achieving efficient TADF in OLED devices. In particular combinations where both the host and dopant are carbazole-based should be avoided due to the formation of carbazole dimer. The effect of such dimerisation is to lower the host triplet level significantly, and further to deactivate the ability of the 2d dopant to produce the ICT state required for TADF by locking the 2d dopant in the 'planar' configuration. It is therefore clear that the chemical composition of the host is of critical importance for the design of future OLED devices. Experiment also suggests that there is a complex interplay between exciplex and ICT emission in 2d systems in the solid state, insofar as CT emission of any description has so far only been observed in conditions where exciplex can and does occur.

Acknowledgements

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Introduction

OLEDs have surpassed fluorescent tubes in efficiency, and have superior colour rendering[1]. They therefore have the potential to meet both society's artificial white lighting needs and the urgent need to cut CO_2 emissions being released into the environment[2]. Phosphorescent OLED emitters have been developed with an internal quantum efficiency approaching 100%[3]. These heavy metal based compounds provide the spin-orbit coupling required to produce triplet metal-to-ligand states with enough state mixing of singlet character to be highly emissive[4]. However rare earth metals are expensive and an efficient blue phosphorescent emitter, so greatly desired for white light applications, has yet to be developed. The reason for this is twofold. Firstly a 'blue' excited singlet is often quenched by a non-emissive lower lying metal d-orbital[4]. Metal-centred transitions in these compounds involve a transition from a non-bonding to an anti-bonding orbital, resulting in an increasing metal-ligand bond length. This greatly enhances non-radiative deactivation as it facilitates overlap in wave functions between low and high vibrational energy levels of the excited and ground state respectively.[5] And secondly, the blue phosphors designed have so far proven to be inherently unstable. In a paper on the light blue FIrpic, heat generated by device operation is shown to separate the weak anionic picolinate ligand from the rest of the compound.[6] It therefore suggests that for blue phosphors the energy of the singlet level is also similar to the energy required for molecular dissociation.

A new generation of highly efficient fluorescent emitters have been developed in recent years. The prompt fluorescence of these emitters is enhanced by thermally activated delayed fluorescence, herein known as TADF. In TADF first an upper vibrational level of the triplet excited state is populated by thermal activation, followed by an adiabatic spin-flip

and subsequent conversion to the singlet manifold in a process known as reverse intersystem crossing (RISC) [7]. In TADF theoretically 100% of excited states can be utilised provided that the energy gap between the singlet and triplet is sufficiently small in the order of 10^{-3} to 10^{-2} eV, given that kT at room temperature is around 26meV[7].

The benchmark of OLED TADF-emitting device performance is currently at around 20% external quantum efficiency (EQE), using small donor-acceptor-donor (D-A-D) molecules that create an intramolecular charge transfer (ICT) state between the electron donating and accepting moieties.[8-16] The HOMO of the molecule is thus localised on the donor, and the LUMO on the acceptor. This minimises the exchange energy, a quantum mechanical effect responsible for the singlet-triplet energy splitting, making the energy gap small enough to enable TADF.[14] [17]. Yet much is still unknown about charge transfer states and the TADF mechanism, and further knowledge in order to obtain good (and better) TADF devices more reliably is highly desirable. While the design of the TADF molecules is undoubtedly of great importance, the dopant-host interaction is just as crucial. Indeed, as shown recently by Jankus et al., the choice of host can be the difference between devices having no CT emission, and CT emission with efficiencies exceeding 14%![15]

The conditions for a suitable host are widely identified as thus: high triplet level, suitable energetics for hole and electron injection to the dopant, balanced charge injection and morphological stability[18]. This paper builds on this work, using photophysical techniques to investigate the efficiency of triplet harvesting in model molecule 2d doped at around 10% within various hosts in thin film. We demonstrate that in addition to the aforementioned criteria, the host must also facilitate the formation of the dopant in the ICT (twisted) state. Clear guidlines for achieving this are outlined in this thesis.

The twisted state is important as it is a way to break the conjugation of the molecule[15]. This, along with the donor-acceptor nature of the molecule means that the HOMO becomes localised on the donor and the LUMO on the acceptor moiety with only a small overlap between the two as shown in Figure 1, allowing the formation of ICT[19].
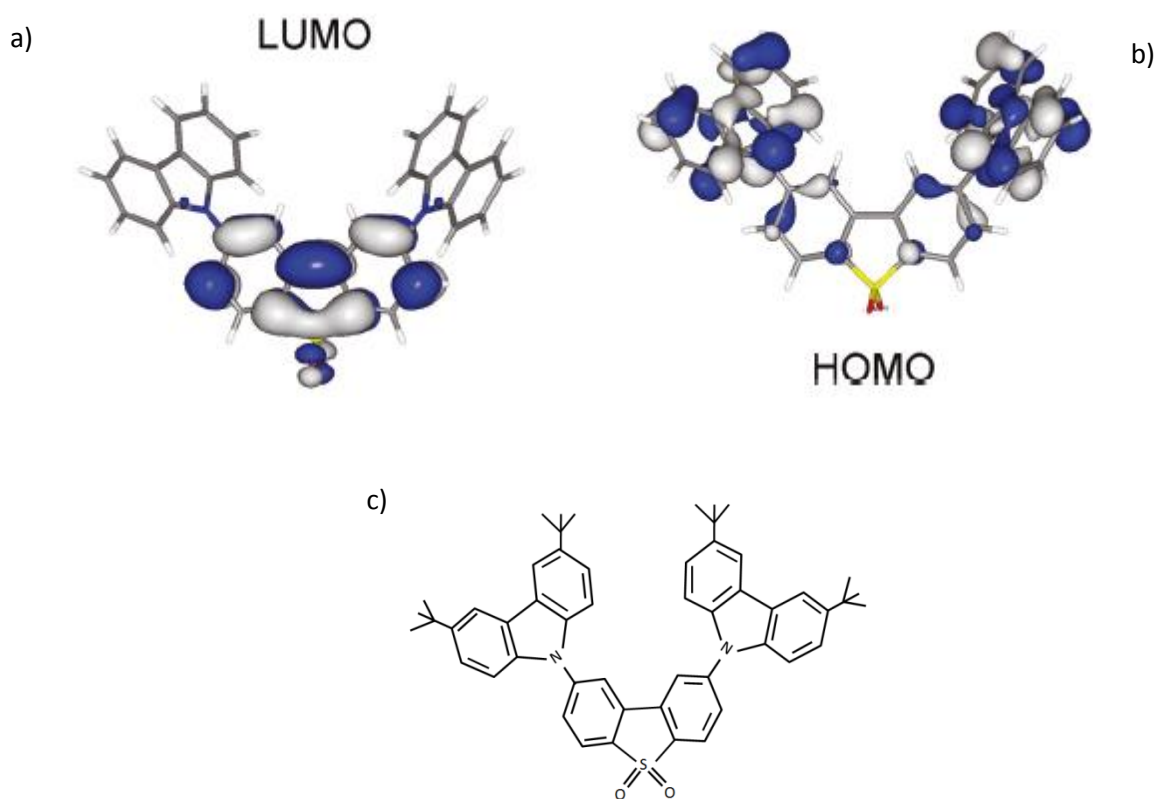
Figure 1: a) LUMO and b) HOMO orbitals for a molecule called 21a, as calculated by density functional theory (DFT) [19]. Note that 21a is identical to 2d in every way except it lacks butyl attachments on the donor fragments that were added to increase solubility. It is not thought that the butyl groups will affect the donating ability of the donor carbazole group, and thus orbital calculations are expected to be almost the same. c) The structure of the 2d molecule[15].

Chapter 1: Background Theory

Sources of delayed fluorescence

The degradation problem of blue phosphors has prevented widespread industrial adoption[6]. In devices, electronically excited states are constrained by quantum mechanical spin statistics, producing 25% highly emissive singlets and 75% 'dark' triplets. Excited triplets are weakly emissive because the ground state of organic molecules is typically singlet, and due to the spin flip required the triplet-singlet transition is thus forbidden to zero order approximation. With singlet-singlet transitions no such spin flip is required and as such is 'allowed'. Delayed fluorescence is therefore an area of intense research as a method to exceed the 25% IQE limit imposed by spin statistics[20]. There are two different sources of delayed fluorescence, outlined below.

Triplet – triplet annihilation

Triplet- triplet annihilation is a bimolecular process, where two T_1 triplets fuse together to form either of the following[21]:

$$T_1 + T_1 \rightarrow T_n + S_0 \qquad (1)$$

$$T_1 + T_1 \rightarrow S_1 + S_0 \qquad (2)$$
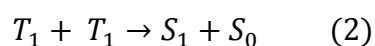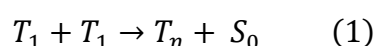
"S" and "T" denote "singlet" and "triplet" respectively and the subscript specifies what singlet or triplet state is being referred to, with "1" being the lowest excited state and "n" being an unspecified higher energy state with $n>1$. Theoretically quintuplet states are also possible, but in almost all organic materials tested the quintuplet state exceeds twice the triplet energy and so quintuplet states are never formed[22]. Furthermore, the T_n states created quickly relax to the T_1 state, and this T_1 can be utilised in further TTA reactions[22]. If

T_n is also energetically unviable, i.e. $2T_1 < T_n$, the theoretical limit of TADF is 50% (one triplet is always converted to the ground state) which means a maximum internal quantum efficiency of 100 x (0.25 + 0.5 x 0.75) = 62.5%[22]. This is distinctly less than the IQE of near 100% achieved by heavy metal phosphorescence and so TTA is ultimately an unsatisfactory solution.

Yet TTA is often found in TADF systems[15] [23] [24] (see later), provided that excitation fluence and therefore excitation density is sufficiently high, and if there is a low lying triplet level that can act as a sink for CT triplet states. TTA can be identified in time resolved spectroscopy as spectra that are very similar to the prompt emission spectra as both prompt and TTA emission ultimately emit from the same state[15]. Yet the lifetime of the TTA emission will be much longer than the prompt emission due to the circuitous route that the excited state must undergo before arriving at the emissive singlet[24].

Singlet-triplet splitting, the exchange energy and achieving efficient TADF through careful design

The gap between the excited singlet and triplet states in localised Frenkel excitons can be of the order of eV[17], which is too big to be surpassed by thermal activation at room temperature (kT ~ 26 meV). In charge transfer states, singlet-triplet splitting is greatly reduced to around 5meV – 0.2eV[7, 17], which is small enough for TADF to occur. The singlet-triplet splitting is determined by twice the exchange energy between two electrons, a purely quantum mechanical effect[5]. Electrons are indistinguishable, and so upon exchange must have a definite symmetry in their wave functions – either symmetric or antisymmetric. As electrons are fermions the wave function must indeed be antisymmetric[25]. Due to the weakness of the spin-spin interaction, we can split the wave function into a spatial and a

spin component, $\Psi=\Phi\cdot S$[25]. Thus in the triplet state the spin function is symmetric meaning that the spatial function must be antisymmetric, and visa versa for the singlet state[25]. By antisymmetric it is meant that the two electrons must occupy different orbitals, whereas symmetric means that the same orbital can be occupied by both electrons – the Pauli exclusion principle. The electrons in the singlet state are therefore on average in closer proximity to one another than when in the triplet state, therefore the coulomb repulsion between electrons in the singlet state will be higher. Because of this extra coulomb potential energy the singlet state is higher in energy than the triplet state[5]. The exchange energy K can be represented quantitatively in Equation 3, below[5].

$$K = const \times \langle\pi(r_1)\pi^*(r_2)\left|\frac{1}{r_{12}}\right|\pi(r_2)\pi^*(r_1)\rangle \qquad (3)$$

The symbols π and π^* are the HOMO and LUMO functions respectively, r_1 and r_2 are the spatial coordinates of the electrons and r_{12} is the electron-electron separation distance[5]. The singlet-triplet energy splitting is given by 2K because ±K is the perturbation in energy from the classical Coulomb energy calculated before the indistinguishability of the electrons are taken into account (+K for the symmetric space coordinate and –K for the antisymmetric coordinate) [25].

Looking at equation 3 we can see that the exchange energy is proportional to the HOMO-LUMO wave function overlap, and inversely proportional to its spatial separation. Therefore to minimise singlet-triplet splitting we aim to minimise HOMO-LUMO wave function overlap, and maximise their spatial separation over the whole molecule or even between molecules. This is achieved by ICT states and exciplexes, respectively.

Because of the exchange energy, the singlet state is always above the triplet state energetically. Through design, as K tends to zero the singlet and triplet states become isoenergetic as shown above. A theoretical study by Difley et. al. claims that the triplet charge-transfer state could be even higher in energy than the singlet charge-transfer state, invoking the principle of 'kinetic exchange' [26]. However this paper appears to be isolated in such a claim (and on the idea of kinetic exchange occurring), and to this author's knowledge has not been observed experimentally.

Yet the donor and acceptor wave functions cannot be completely decoupled, as quantum theory clearly states. Fermi's golden rule directly relates wave function overlap to the transition rate *T* (transition probability per unit time) between energy eigenstates |i> and |f> that has been caused by a perturbation, as shown in Equation 4 below[27].

$$T_{i-f} = 4\pi^2\, h\, |\langle f|H'|i\rangle|^2 \rho \qquad (4)$$

Planck's constant is *h, H'* is the perturbation Hamiltonian, and ρ is the density of states. Note that the matrix element $\langle f|H'|i\rangle$ would be zero without any wave function overlap between initial and final states, thus meaning that the transition rate will be zero also. Complete decoupling from the ground state would thus prevent CT emission. Thus a CT state would not be stabilised. Small wave function overlap reduces the rate of radiative decay, and so the CT state becomes vulnerable to non-radiative deactivation pathways. Transition rate and singlet-triplet energy splitting are therefore two competing processes that have to be optimised for efficient TADF.

Similarly linked, an important design consideration is to make the CT state the lowest excited state in the system in order to prevent a lower lying weakly emissive level from

acting as a sink for excited states[24]. Achieving an efficient TADF system therefore is not just about minimising the singlet-triplet splitting – it is also about carefully orchestrating the relevant rate constants to make sure that the radiative decay constant is the dominant deactivation pathway compared to all the others.

As previously mentioned, the CT state is achieved in a donor-acceptor system. This can either be an intermolecular system between two molecules (an exciplex CT) or an intramolecular CT state formed by a single molecule with both donor and acceptor moieties.

Thermally activated delayed fluorescence

If the singlet-triplet splitting between the excited singlet and triplet state is sufficiently small then triplet excitations can be thermally excited from the triplet to the singlet. Coined thermally activated delayed fluorescence (TADF), it is in fact two processes. First, there is a thermal excitation of the triplet to a vibronic level at least as energetic as the lowest energy level of the excited singlet state[7]. Second, once the triplet is at this energy an adiabatic spin flip can occur and thus a transition from the triplet to the singlet manifold[7]. As the singlet triplet splitting in CT states is of the order of meV it is presumed that the required spin flip is caused by spin-orbit coupling. This is because hyperfine splitting is of the order of μeV, which is three orders of magnitude smaller than the CT exchange energy [27]. A schematic of the TADF mechanism is outlined in Scheme 1 below.
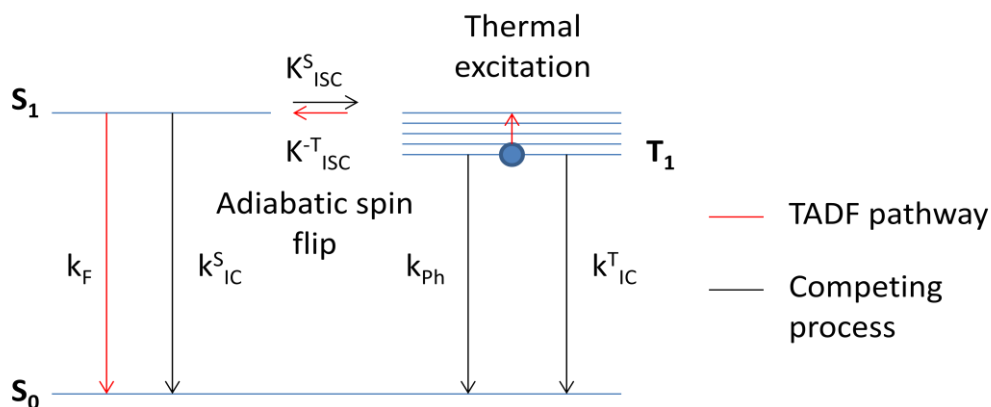
Scheme 1 – *A simplified Jablonski diagram showing the mechanism of TADF* [28].

The triplet excited state in the TADF molecule (the system) and its surroundings (the reservoir) is an example of a canonical ensemble[29]. By assuming that there is no more than one excited electron per TADF molecule we fix the number of microstates per vibronic level to be one. As the energy of the system is much smaller than the surrounding reservoir, and using the definition $1/k_B T = d \ln \Omega / dE$ it is therefore trivial to show that the probability $P(\varepsilon)$ that the system has energy ε is proportional to the Boltzmann factor, $exp(-\varepsilon/k_B T)$[29]. Thus it is clear that the greater the energy gap ε is in proportion to the thermal energy kT from the surroundings, the less likely the triplet excited state is going to have the energy to surpass it.

The Boltzmann proportionality obtained can of course be scaled to consider all TADF molecules, with $P(\varepsilon)$ proportional to the number of triplets found in state ε. If [T*] represents the fraction of triplets with total internal energy greater than the excited singlet electronic energy then we get the Equation 5[7]. Note that activation energy ε is the now considered to be the singlet-triplet energy gap, ΔE_{ST}.

$$[T^*] = [T]\exp\left(-\frac{\Delta E_{ST}}{kT}\right) \qquad (5)$$

The second process in the TADF mechanism, the adiabatic spin flip, is a quantum mechanical process called (reverse) intersystem crossing[7]. By zero order approximation this process would be forbidden due to violation of the principle of the conservation of momentum[30]. Yet the electron is not in isolation and so the momentum can be injected via external forces from the surroundings[30]. As discussed, spin-orbit coupling is most likely the dominant intersystem crossing process in these organic materials.

Thermal equilibrium typically occurs at a rate of $10^{12}s^{-1}$[7], yet rates of intersystem crossing are experimentally found to be of the order of 10^7s^{-1} [30]. This shows that out of the two processes constituting TADF it is the adiabatic spin flip stage which is the rate determining step. The rate of reverse intersystem crossing (RISC) can thus be expressed in Equation 6 as follows[7]:

$$k_{RISC} = A exp\left(-\frac{\Delta E_{ST}}{kT}\right) \qquad (6)$$

The pre-exponential factor A is akin to the average rate of the adiabatic spin flip step, and as it is temperature independent for the temperature ranges considered in experiments with organic materials we are left with a simple Arrhenius relationship[7].

In order for TADF to be a competitive process $k_{isc}^S \gg k_f + k_{IC}^S$ and $k_{RISC} \gg k_{PH} + k_{IC}^T$ as is clear when considering Scheme 1[28]. Furthermore to minimise quenching processes to other energy levels it is highly desirable that there are no lower energy levels than the singlet and triplet levels involved in the TADF[24].

Exciplexes

An exciplex is an excited state between two different molecules, caused by the interaction between an excited electron donor and an electron acceptor in the ground state (or vice versa) [17]. According to perturbation theory, the respective HOMO and LUMO energy levels mix forming a new exciplex HOMO and LUMO. Thus despite involving a pair of molecules, an exciplex is a single neutral emissive species[30].
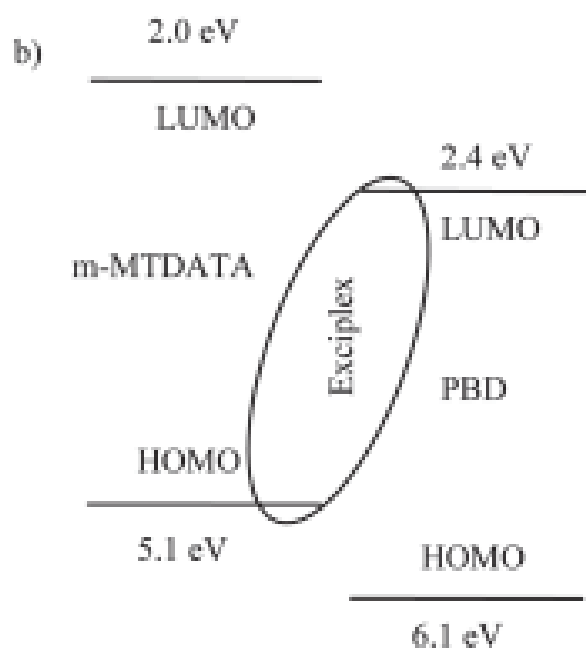
Figure 2 – Resultant exciplex formation between the donor and acceptor molecules m-MTDATA and PBD. Figure taken directly from Graves et. al.[7]

A simplified representation of an exciplex is presented in Figure 2 for the example of m-MTDATA:PBD. It appears that exciplexes are predominantly stabilised by a charge transfer interaction, unlike excimers[17]. This is because exciplexes are only observed in a 'donor-acceptor' pair, where the LUMO of the acceptor is at least ~0.5eV lower than the LUMO of the acceptor. Such an offset in photophysical studies provides sufficient driving force for a degree of electron transfer to occur from the donor to the acceptor[15]. This offset is also the reason why exciplex emission is

always red shifted from the initial donor molecule excited singlet spectra. It also seems to be the case that donor and acceptor HOMOs need to be offset by a similar amount[15]. In electroluminescence the exciplex formation occurs directly from an electron on the acceptor and a hole on the donor. Upon photo excitation the route to exciplex formation is via the singlet exciton state of the donor molecule[7]. Yet despite this difference in formation route the same degree of charge transfer is experimentally observed in photo and electro-induced exciplexes , as their spectra are identical[15].

Exciplex (and excimer) emission is also characteristically featureless and Gaussian[4]. This is because the ground state complex, DA, are in the repulsive electrostatic regime to one another, as the ground state is not stabilised as described above[30]. The ground state therefore separates into its individual components almost immediately within a couple of vibrational quanta. Thus there can be no distinct vibrational states, and often neither is the ground state DA in sufficient concentrations to be observed in absorption spectra[30].

Exciplex emitters have been found to produce very small singlet-triplet splitting. In a recent photophysical study of an m-MTDATA:PBD exciplex by Graves et. al. an activation energy of only 5meV was found[7]. Thus remarkably TADF was clearly observed at temperatures as low as 16K and was found to decay as a triexponential with an average lifetime lasting hundreds of nanoseconds. Due to the near isoenergetic nature of the CT singlet and triplet states, there is strong resonance between the singlet and triplet states with eventual emission from the singlet state. With such resonance the exciton takes on both singlet and triplet characteristics: emissive (i.e. singlet) and long lifetime (i.e. triplet)[7].

ICT materials

In ICT materials, choosing the right donor and acceptor combination is important. Too little CT nature and there is insufficient spatial separation to minimise ΔE_{ST}, too much and decoupling from the ground state leads to poor PLQY as discussed. The ideal seems to be a result of the mixing of LE and CT states to create an energy level with both high PLQY and small ΔE_{ST} respectively.

Furthermore, putting the donor and acceptor moieties together is often not enough to separate the LUMO (on the donor) and HOMO (on the donor) sufficiently[23]. Localisation can be increased through the introduction of a steric twist that breaks the conjugation between the donor and acceptor[15]. Spatial overlap in wave functions is minimised if the steric twist creates orthogonality between the donor and acceptor moieties[28]. Other research attempts have used spacers, such as benzene rings, to increase the physical distance between donor and acceptor, thus reducing wave function overlap[31]. Yet to get an efficient TADF emitter relies on much more than careful molecular design. TADF dopant and host interaction is very important too, as we shall soon see.

Chapter 2: Experimental Methods

This thesis is primarily a photophysical study. Creating excited states optically rather than through electroluminescence allows greater insight into the excited state species and dynamics of the organic emissive layer, crucial to fully understanding and utilising TADF. This is because electrical excitation pulse widths confines study to delayed fluorescence, and the effects of moving free charges complicates the physical interpretation of results. In contrast photo-excitation pulse widths can be mere picoseconds wide, allowing the study of excited states in the first few nanoseconds post-excitation. Free charges are also not present, as photo-excitation creates an electron-hole pair locally on the same molecule (so we do not need concern ourselves with electron and hole mobility), and the lack of an external E-field prevents charge separation. Furthermore electroluminescence requires analysis of *devices*, complete with additional transport layers and electrodes, all of which obscures the physics of the emissive layer that we are trying to analyse. In photophysics we can experiment upon the emissive layer in isolation.

All samples analysed in this thesis are thin organic films, of the order of a few hundred nanometres thick. Physics of the same organic systems is often different in the solid state compared to in solution. This is because, unlike in solution, in the solid state thermally-induced kinetics is restricted and dominated by intermolecular forces and morphological considerations. Photophysical analysis of thin films is thus much more relevant to understanding the physics happening in OLED devices.

In this thesis we are looking at the TADF dopant molecule 2d incorporated into various solid state host matrices. Doping concentration of 2d with respect to host is around 10%. This has previously been found to be a good compromise between electronic isolation of the TADF

dopant, required to keep excited states on the dopant, and having enough TADF dopant emitter so that emission is bright enough for good photophysical analysis.

Sample preparation – Evaporation Deposition

One method of fabricating the dopant-host blended films was evaporation deposition using a *Kurt Lesker Spectros II* machine. Powdered constituents are placed in crucibles surrounded by an ohmic heater, connected to temperature controllers managed by Sigma software. The ohmic heaters evaporate the organic materials in a vacuum of 10^{-7} mbar, with the heating elements controlled directly by input voltage in the range of 1-2V. The material is evaporated onto sapphire substrates directly above the material crucibles, rotating the substrates to ensure even evaporation coverage. Exposure to the evaporated materials is controlled by a shutter between crucible and substrate, allowing control over the thickness of film produced. Quartz crystal thickness monitors measure the film thickness. The sensor is in a different spatial location to the sapphire substrates, and furthermore evaporation deposition thickness rate as function of heating temperature is material dependant. Each sensor for the exact crucible in use must therefore be calibrated for each material. All materials used in this report have been used previously within the OEM group here in Durham and so this calibration had already been performed. The way you would go about this would be to measure the real film thickness (e.g. by using an ellipsometer and Cauchy function modelling) and compare it to the thickness measured by the sensor – and then correct the sensor's "tooling factor" appropriately.

Evaporation rate was controlled to be between 0.1 – 5 Angstroms s^{-1}, with the lower bound for the dopant and the higher bound for the host to achieve the required blend percentage. Thus it should be stressed that sample percentage is based on evaporation rate rather than

molecular mass. As all molecules used were relatively similar in size the discrepancy in values is expected to be small. Furthermore, as I am interested in the photophysics of the system in general rather than optimising device performance the degree of accuracy using evaporation rate is more than adequate.

The controlling Sigma software allows for the evaporation of two materials at the same time, as long as the materials come from separate crucibles that are controlled by separate heaters and measured by a different thickness monitor. Co-evaporation is vital for blending the 2d molecule evenly within the host material and thus avoids 2d aggregation.

Sample preparation – Drop casting

Drop-casting is an extremely efficient way of creating blended film samples, much quicker than evaporation deposition. Stock solutions of each constituent material are prepared by dissolving the solid into 40 degrees centigrade toluene at a ratio of 1:1 solid (mg) to toluene (ml). From the stock pots a third solution of the required blend – usually 10% dopant 90% host – is created. The blended solution is then pipetted directly onto a clean sapphire substrate on a 70 degrees centigrade hotplate. Due to the low dopant concentration, it is imperative to create a thick film so that the sample is suitably emissive for photophysical analysis. The pipetting stage is therefore repeated three to four times (waiting each time for the toluene to evaporate before repeating) to ensure that a thick film has accumulated. Toluene was chosen as a solvent on an experimental basis as it seems to produce fairly even film coverage. Another solvent tested, chlorobenzene, tended to cause the solid to aggregate in clumps rather than form a film as it is too volatile at the 70˚C deposition temperature.

The disadvantage of dropcasting is of course that the film quality is poorer, and it is likely that the dopant is not as well mixed as in the case of evaporation deposition. Furthermore, organic film morphology can vary drastically with production procedure and so it was important to test that the physics obtained would be the same regardless of whether dropcasting or evaporation deposition was used. Thus a few experiments were repeated with both production methods, and the results (not shown), show that at least qualitatively this was the case.

Steady state absorption and emission spectroscopy

Steady state absorption measurements were used to confirm photo-absorption of the 2d dopant at 355nm, as well as ascertain to what extent the surrounding host matrix absorbs at this wavelength. Measurements were conducted with a commercial *UV-3600 Shimadzu* spectrophotometer. Excited via either a halogen or deuterium lamp, sample absorbance is compared to a reference sapphire substrate by a detecting photomultiplier tube.

Steady state emission measurements were utilised to quickly ascertain whether an ICT state was dominant using the commercially available *Jobin Yvon Horiba Fluoromax 3*. Excited with a 450W xenon light source, two monochromators select both the excitation wavelength range and wavelength range incident on the photomultiplier tube detector. Excitation light and photomultipler tube are perpendicular, with the sample excited at 45° to its normal plane.

Time resolved emission spectroscopy

The photoluminescence of organic materials has been attributed to a wide variety of processes, each of which occurs over a large dynamic range. The problem with steady state

measurements are that often only the brightest emission will be observed, with weaker emissions not seen at the same sensitivity. Furthermore knowing when a certain type of emission occurs, and at what intensity, allows us greater insight into the excited state dynamics of the system.

Time resolved emission spectroscopy, (TRES), measures the spectra and intensity at various sequential time "windows", with no gaps in the timeline. This is achieved by setting a delay time after triggering at which the camera records for an integration time, the time the camera measures for. The capability of our system is such that emission can be measured from zero time up to 100ms, with a resolution of 300ps.

Excitation is achieved with a 150ps-pulsed, 10Hz 355nm Nd:YAG laser (EKSPLA), as most samples considered absorb in the UV. Light emitted from the sample under 10^{-4} mbar vacuum passes through a filter that blocks out most of the reflected 355nm light to avoid saturating the camera, and then passes through a spectrograph before arriving for detection at the gated iCCD camera. In this way a spectra of the sample is measured as shown in Figure 3 below.
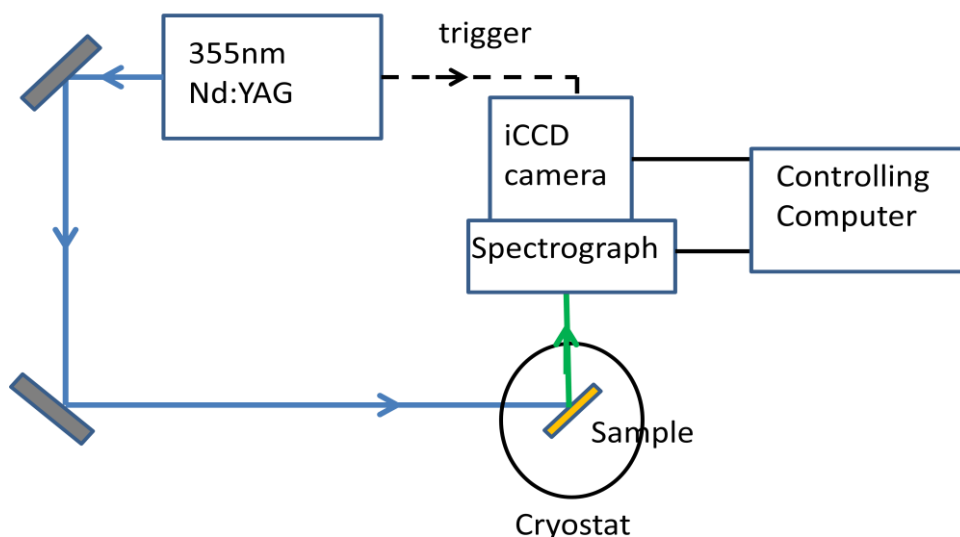
Figure 3: A block diagram of the nanosecond TRES set-up. The 355nm Nd:YAG laser excites the sample and the resultant emission is passed through a spectrograph and measured by a gated iCCD camera that are controlled by computer.

Emission in the spectral range of 365nm and 685nm is measured with a gated iCCD camera (Stanford Computer Optics) of resolution 1ns[21]. This camera is crucial to being able to measure nanosecond time resolved emission spectroscopy. Light incident on the camera first strikes a photocathode, causing the release of a photoelectron which is then guided towards a phosphor by an applied electric field. At long delay times (and short integration times) the input photon signal will be very weak, thus a gain medium is required. This is provided by the photoelectron passing through a charged microchannel plate (MCP plate), where the number of additional electrons released per photoelectron is dependent on the voltage applied across the plate. The electrons are then incident on a phosphor screen, which is coupled to the CCD via optical fibres.

Gating is controlled by the voltage between the photocathode and phosphor screen. Apply a negative voltage and the camera is 'on', reverse it and the electrons never reach the CCD detector. The gating itself is controlled by an electronic trigger sent from the laser directly to the camera. The trigger signal arrives approximately 975ns before zero time, with zero time being the time at which the peak of the pulse arrives at the CCD detector.

The delay and integration times are fed to the camera via a controlling computer. There is a maximum delay plus integration time of 100ms, as this is the time between laser pulses. The input delay and integration times increase logarithmically, to correspond with the PL decay of the sample which is usually of an exponential nature. The spectra collected then have to be corrected to account for the non-linear response of the iCCD camera with time and wavelength (both previously calibrated using a reference light source). Camera response to wavelength will depend on what wavelength from the spectrograph is centred upon it; it is important to use the correct calibration file for both camera position and slit width.

The intensity of measured signal can be adjusted in the following ways in order to avoid saturation/to get a measurable signal: adjusting the MCP voltage (750V-950V with greater intensities attributed to higher voltages), adjusting the slit width of the spectrograph in front of the camera or by adjusting/filtering the input laser intensity. However the trade off for increasing the slit width is a reduction in spectral resolution, and the emission spectra obtained in some organic samples can be dependent upon the incident laser fluence. For certain materials the emission in the microseconds timeframe can be too weak to be detected with the normal collection protocol; the integration and corresponding delay times can be made longer in the region in which the camera correction factor for time is continuous and equal to one. You can also take multiple measurements of the same setup –

this is the number of frames that you choose. The more frames the better the signal to noise ratio, and thus the better the spectral resolution due to improved signal to noise ratio. Due to time constraints, 50 frames per measurement is considered sufficient for PL decay transients, but with more demanding measurements it is prudent to use between 100-500 frames per measurement.

Finding triplet levels, and Intensity dependence on laser fluence

Decay and integration times can of course be adjusted manually. This can be used to find the triplet level for example, by cooling the sample down in a cryostat and measuring at long decay and integration times. The cryostat is a He displex cryostat, connected to a vacuum pump that takes the air pressure down to 4.02×10^{-4} mbar. The cryostat is helium cooled enabling temperatures of down to around 15K to be achieved, with temperatures higher than this up to around 300K achieved through the use of an electric heater. The sample is cooled directly from a copper gold finger, with an indium contact. This ensures that heat equilibrium, in agreement with the temperature sensor, is rapidly achieved – of the order of twenty to thirty minutes.

A similar setup can be used for other experiments. Measuring the intensity dependence on laser fluence is an important method for determining whether the emission you are measuring is a single (e.g. TADF) or two (e.g.TTA) photon/molecule process. Plotted in log-log scale, the former would yield a slope of +1 and the latter a slope of +2. The utility of the TRES setup is that emission from any of the decay transient in the wavelength range of 365 nm -865 nm can be probed in this manner. At lower laser fluencies, variation in laser fluence can be quite high. Therefore to get an accurate measure of laser fluence, intensity measurements with a power meter are made over a long period of time (about a minute),

and sum the total emission over a high number of frames such as 200. In this way the

fluctuations become statistically insignificant and a good average is achieved.

3. Results and Discussion - The behaviour of 2d in various host matrices
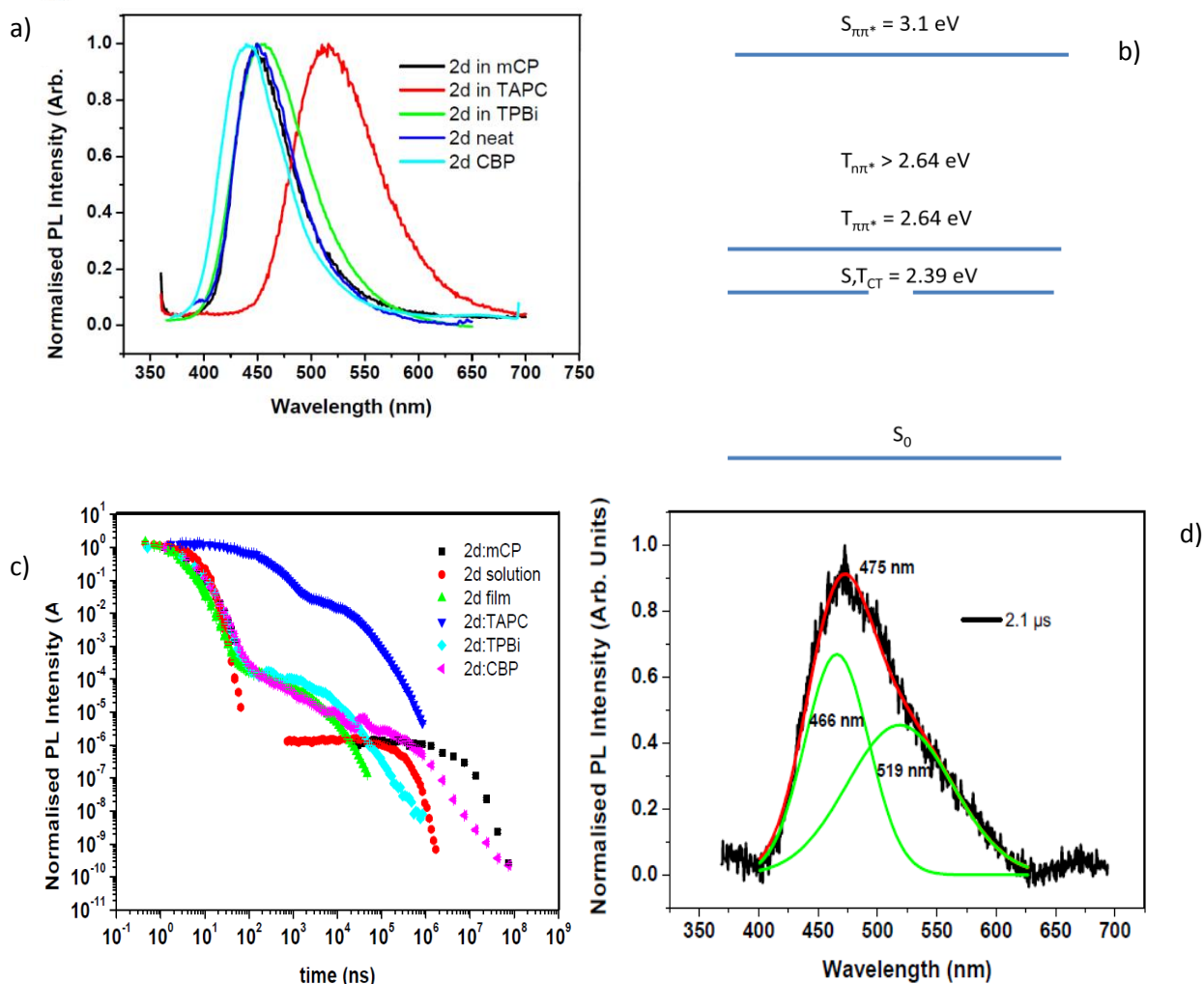

Figure 4: *a) PL spectra of 2d neat film, 2d:TPBi, 2d:CBP, 2d:mCP and 2d:TAPC in the steady state. b) The energy levels of the 2d molecule[15] c) Normalised PL decay transients at room temperature for various 10% 2d:host systems d) Delayed fluorescence spectra of 10% 2d:TPBi at 2.4us after excitation, complete with two Gaussian fit.*

The hosts chosen for this investigation are TPBi, CBP and mCP, and the results will be compared with previous studies into 2d neat film and 2d:TAPC. The emission of 2d neat film peaks at around 450nm, as shown in Figure 4a along with 2d:TPBi, 2d:CBP and 2d:mCP emissions for comparison. The doping of 2d into CBP, TPBi and mCP seems to have little effect on the position of the normalised steady state spectra, despite a range of host dipole moments from (theoretically) 0.0D in CBP to 3.4D in TPBi[32]. Compare this to 2d in hexane and ethanol solution, with dipole moments of 0D to 1.69D respectively[33]. In hexane 2d emission is centred at ~400nm and has clearly resolved vibronic structure. This emission is identified as the "localised exciton" singlet LE state of the 2d molecule (donor). Whereas in ethanol an ICT state is stabilised, with broad Gaussian emission centred at ~525nm. With 2d, 2d:CBP, 2d:TPBi and 2d:mCP in the solid state, the lack of vibronic structure and narrow Gaussian shape at 450nm points to a mixed localised exciton (LE) + CT state indicative of a heterogeneous ensemble of D-A molecule systems[15]. In the case of 2d:CBP the spectra is slightly blueshifted with respect to 2d neat film, and this is due to the absence of a permanent dipole moment in CBP. With TPBi, peak position is identical to that of 2d neat film but the extended red edge is caused by a small TADF contribution as time resolved measurements later in this paper will reveal. Considerable Stokes shift occurs only in the 2d:TAPC system, showing strong charge transfer characteristics. Yet with a dipole moment of just 1 Debye[34], it is clear that this shift cannot be explained merely in terms of dipole moment.

3.1 The importance of a high host triplet level

Host Material	(LE) Triplet energy in eV	DF/PF	Dipole moment (D)
2d	2.64	0.082	
CBP	2.61	0.44	0.03*[32]
TPBi	2.73	0.12	3.38[32]
mCP	2.90	1	1.34
TAPC	2.95	1.8 (approx.)	1[34]

* Asterix denotes calculation from DFT

Table 1 – The triplet level, DF/PF ratio and ground state dipole moment for the 2d molecule and hosts involved.

Table 1 displays the triplet level of the host material, the delayed to prompt fluorescence ratio for the 2d:host system and the ground state dipole moment of the host material. The importance of a high host triplet level can be adequately explained by a comparison of two cases: 2d:TPBi and 2d:TAPC. Figure 4b shows the energy levels of the 2d molecule. To avoid the quenching of the emitting state the host triplet must be above the CT state. Figure 4d is the delayed emission spectrum of 2d in TPBi 2.1 µs after excitation. CT emission of 2d in TPBi is very weak, and only contributes to the red shoulder of steady state emission with respect to 2d neat film. It is clear therefore that CT stabilisation does not occur, and as such is not the lowest excited state energy level in the system.
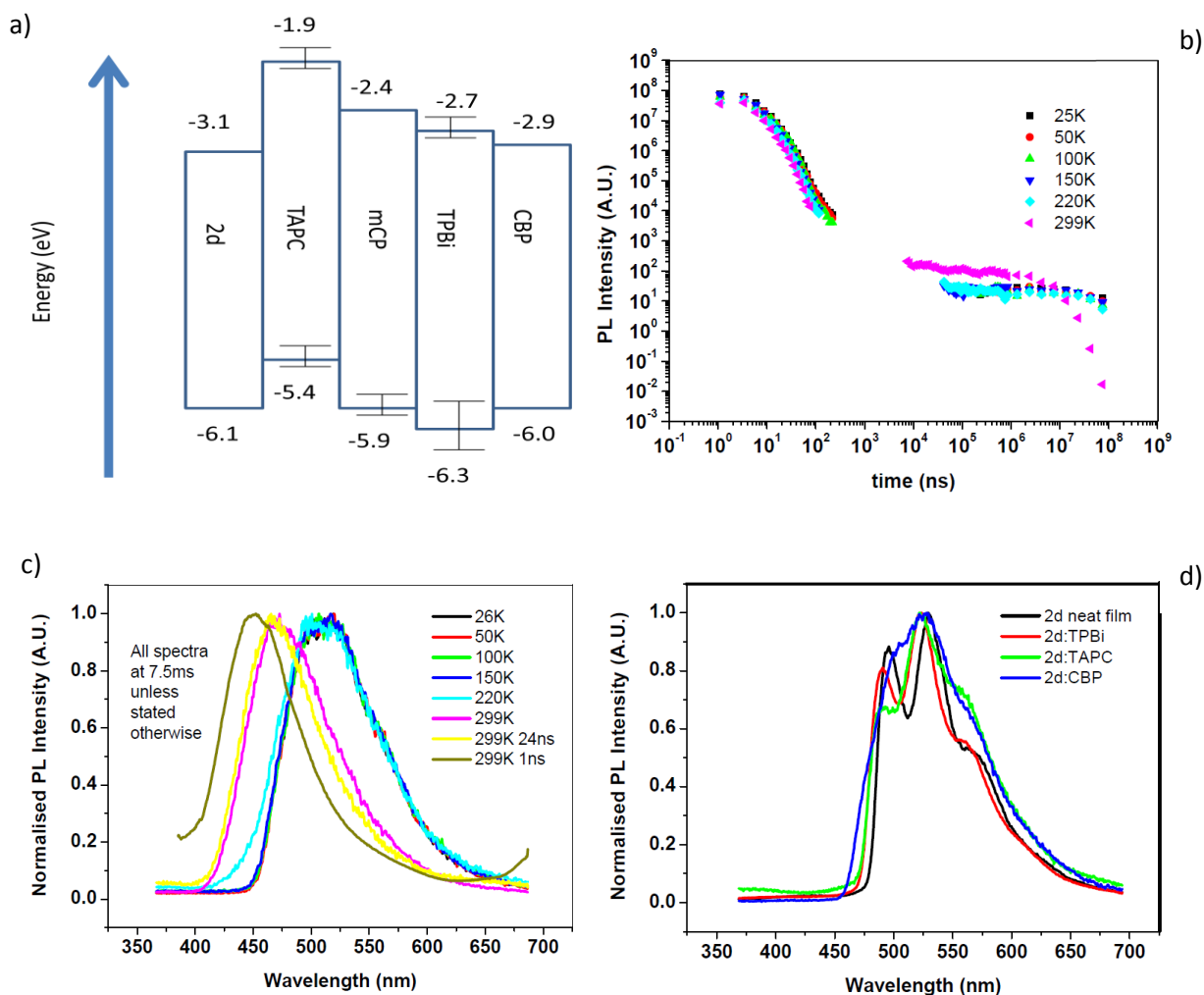
Figure 5 – a) HOMO and LUMO levels of the 2d molecule and investigated hosts[35] [36] b) PL decay transients of 10% 2d doped in mCP at various temperatures between 25K and 299K. c) Time-resolved spectra for 10% 2d doped into mCP. Times given are the delay time + ½ integration time. d) The triplet levels found in the 2d and 2d:host systems. Delay and integration times were 70ms and 20ms respectively for 2d, 2d:TPBi and 2d:TAPC. Delay and integration times were 1ms and 80ms for 2d:CBP.

Figure 4c displays the normalised photoluminescence decay transients of all the 2d systems under investigation at room temperature. The decay transient of 2d in TPBi corresponds closely to the

decay transient of 2d neat film, as Figure 4c shows. The delayed emission spectrum of 2d in TPBi is displayed in Figure 4d. The delayed emission is fitted well by two Gaussians, peaking at 468nm and 518nm, suggesting a combination of two emissive species. This behaviour has already been observed in 2d neat film [15]. The bluest emission, peaking in the same place as the prompt fluorescence but with a much longer decay time, has been identified as TTA emission. The redder emission is attributed to weak ICT emission (see Figure S1 for intensity dependence on laser fluence of 2d, taken from Jankus et. al.[15]. The presence of both species is because of a wide spread of 2d molecular orientations created during the evaporation deposition process, with a planar configuration favouring TTA and a twisted configuration favouring ICT emission [15].

In both 2d neat film and 2d in TPBi it is the low-lying triplets of the 2d and TPBi at 2.64 eV and 2.73 eV respectively that act as a triplet sink. Migrating between these low-lying triplets, it is the time taken for two triplets to find each other and annihilate that dominates the delayed fluorescence lifetime. The visible product of the annihilation process is in 2d singlet emission, which is of the same emissive species as the prompt emission. The observance of the same blue emission peak in both prompt and delayed emissions, with the delayed emission having a considerably longer lifetime, is thus explained.

The slight difference in the TTA mechanisms of 2d and 2d in TPBi is of course down to the presence of the TPBi in the latter. Due to the greater numerical prevalence of TPBi over 2d it is likely that the triplet-triplet annihilation will occur on the TPBi. Emissive singlets will thus be predominantly formed upon the TPBi. Yet the lack of TPBi emission, or to be more precise, the observance of only 2d emission, shows that there is efficient Förster energy transfer from the TPBi to the 2d. Förster energy transfer occurs when the emission of the first molecule (TPBi) overlaps with the absorption of the second molecule (2d). Efficient Förster energy transfer is unsurprising given the broad nature of 2d absorption as shown in Figure 7b. Furthermore, similar behaviour has been observed by *Jankus*

et. al. in the exciplex system of NPB and TPBi, where the NPB acts as the sink for the triplet excited states[24].

In 2d:TAPC, the triplet level is at a very high 2.95 eV (420 nm) which is above the onset of the 2d ICT emission. This means that ICT quenching does not occur and so we see the strong ICT emission of 2d in 2d:TAPC unlike in 2d:TPBi. Yet *Jankus et. al.* shows that ICT emission is not the only charge transfer state in the 2d:TAPC system – whilst the prompt fluorescence originated from ICT emission the delayed fluorescence was exciplex in origin between the 2d and TAPC molecules[15]. For exciplex emission to occur, the LUMO of the acceptor must be ~0.5eV lower in energy than the LUMO of the donor to provide sufficient driving force for charge transfer, and the HOMO of the donor must be lower than the HOMO of the acceptor by a similar amount [15]. Figure 5a shows the HOMO and LUMO levels of all the materials under investigation. From inspection of Figure 5a it is apparent that these conditions are satisfied if TAPC is the electron donor, and the 2d molecule is the electron acceptor. It is also apparent that from the same figure that out of all the host materials tested in this study only TAPC is capable of forming exciplex with 2d. It is also the *only* system to have a stabilised CT emission of any description as clearly shown by the steady state emission of Figure 4a.

Figure 5d shows the triplet levels found in the 2d and 2d:host thin films, measured at low temperature and millisecond delay times. The presence of a populated 2d triplet is observed in the 2d:TAPC system (Figure 5d), although of such negligible intensity that it is only observed milliseconds after initial excitation. The rates of CT formation and emission are thus considerably higher than the (intersystem crossing) mechanisms involved in localised triplet formation. However it is indeed fortunate that 2d LE triplet is observed as it reveals important information about the 2d molecule's molecular conformation. With respect to 2d in neat film the first "0-0" vibronic greatly decreases in proportion to the "0-1" maximum,

with the "0-2" vibronic transition increasing by a similar amount. The 2d molecule is therefore more distorted in the 2d:TAPC medium than in the 2d neat film. This in turn helps to localise the HOMO and LUMO on different parts of the 2d molecule, thus facilitating the formation of the ICT state.

The motivation of putting 2d in a high triplet host matrix is to get highly efficient ICT emission, and as such the exciplex between 2d and TAPC (despite in this case not detracting from overall device performance) was an unwelcome addition. Thus mCP as a suitable host material was considered, due to its high triplet level of 2.90eV and its inability to form exciplex (to convince yourself, refer back to Figure 5a). Yet no stabilised CT emission of any description is observed in 2d:mCP, and so it is clear that there are other considerations to be taken into account when choosing a suitable host than just a high LE triplet level.

3.2 The problem with carbazole-based hosts

We know that the 2d molecule can only form a stabilised ICT state in the twisted configuration, and so we conclude that TAPC facilitates the twist. Similarly we conclude that in mCP the 'linear' 2d configuration is prevalent in the solid state, and so the CT state cannot be stabilised.

Figure 5b shows the temperature dependence of the PL decay transient of 2d:mCP between 25K and 299K. The PL decay transient of 2d:mCP at 298K has clear prompt and delayed components with a DF/PF ratio of around 1. Analysis of all time resolved spectra confirm the absence of any ICT state. Instead the PF regime is ascribed entirely to prompt singlet LE emission, originating from the carbazole donor. In the DF regime the same spectra as prompt times is observed, but as it is now in the microseconds timescale it cannot be

attributed to prompt fluorescence. It is instead delayed fluorescence generated through triplet-triplet annihilation from a low lying triplet sink as previously described. Figure 5c shows some select time-resolved 2d:mCP spectra between temperatures of 26K and 299K. From Figure 5c it is clear that as the temperature drops TTA gives way to phosphorescence due to the reduction of triplet mobility. The presence of a triplet sink suggests the presence of additional triplet levels in the mCP when in solid film. The most likely cause of this is through the formation of dimer in the mCP molecule.

Figure 6 shows the structures of the host molecules investigated. mCP is a small molecule, and is carbazole based – the same as the donor unit of 2d. Furthermore, the carbazoles are bonded in the meta position just like the carbazoles in the 2d are (Figure 6). The bonding in the meta position of the benzene ring means that the conjugation between the carbazole moieties is broken. The molecule 2d is also meta-bonded and carbazole based and so the donor and acceptor moieties are not conjugated.

Previous research by Jankus and Monkman on the polymer PVK clearly demonstrates a strong tendancy in carbazole to rotate and align with one another to form carbazole dimer [37]. This dimerisation was identified through phosphorescence studies and the dimer triplet was found to be at 2.5eV – lower than the molecular LE triplet of mCP at 2.9eV, and at a similar energy to the 2d LE triplet. Spectral shape comparison (Figures 5c and 5d) suggests that phosphorescence spectra of 2d neat film and 2d:mCP systems are indeed different triplet species and are 2d LE triplet and carbazole dimer triplet respectively. The small size, and similarity in molecular structure of mCP compared to 2d, means that the mCP molecule can align in close proximity allowing the carbazole units to pi-stack in sandwich formation and thus form carbazole dimers. Pi-stacking is likely to create a more ordered structure, and

thus narrow the triplet DOS. This increases the probability of triplet hopping and thus the probability of triplet-triplet annihilation[21]. This explains the much higher DF/PF ratio and decay transient of 2d:mCP to 2d:TPBi, despite the similarities of having TTA through a low lying triplet sink.

2d molecules do not have this dimer forming capability despite being meta-bonded and carbazole based. We hypothesise that this is due to the butyl attachments to the carbazoles in 2d which make the 2d molecule much more bulky. The butyl groups prevent 2d molecules from getting close enough to one another to stack and form dimer, whereas the mCP molecule is small enough to pass through this spatial barrier. It is important to note that the prompt emission of the 2d:mCP system is that of the 2d molecule and not the dimer singlet. First of all, it is evident from Figure 4c that prompt emission lifetime behaviour (and spectrally) is essentially invariant across all systems with the exception of 2d:TAPC including 2d in the host TPBi which is not carbazole based. We therefore conclude that the exciton pathway must therefore be 1LE$\rightarrow$ 3LE$\rightarrow$ 3Dimer.

The formation of carbazole dimer between the 2d molecule and the mCP also effects the distribution of molecular geometries for the 2d molecule. The prevalence of pi-pi stacking between carbazole units is likely to encourage the planar configuration of 2d and thus prevent the formation of a stabilised CT state.

The system of 2d in CBP fits nicely mid way in our analysis between 2d:mCP and 2d:TPBi. Whilst PF components are near-identical, by eye the emission after 10us seems to be a mixture of 2d:TPBi and 2d:mCP behaviour (Figure 4c). Analysis of the time resolved spectra shows that this is indeed the case (Figure 5c, 5d, S2, S3). This suggests that in 2d:CBP *some* carbazole dimerization occurs, but not to the same extent as 2d in mCP. Further evidence

for this is that the DF/PF ratio of CBP is 0.44, almost halfway between the DF/PF ratio of
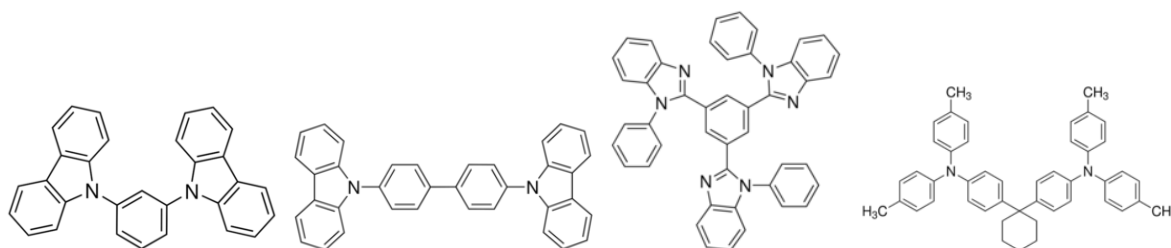
2d:TPBi (0.12) and 2d:mCP (1).

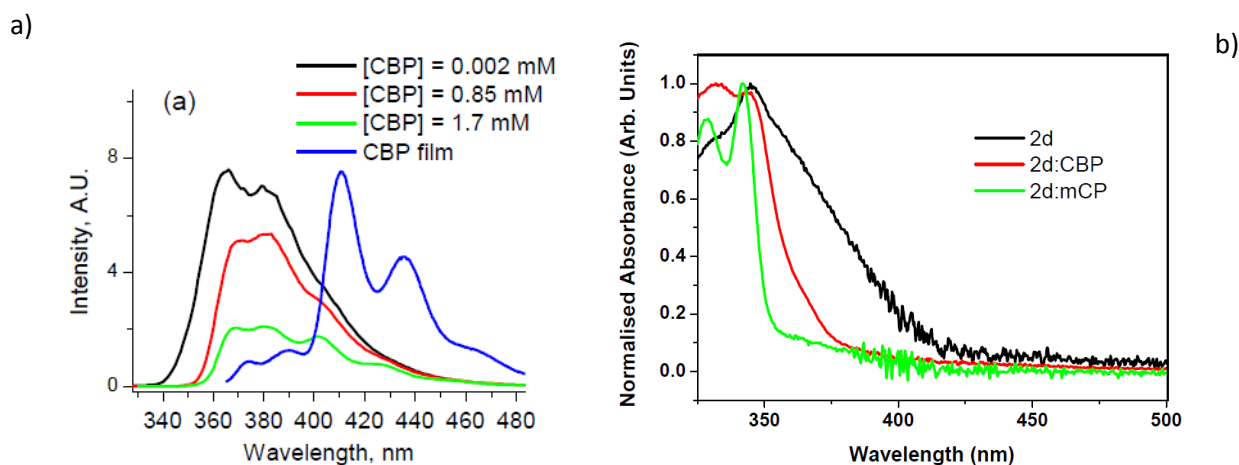FIGURE 6 – From right to left – mCP, CBP, TPBi and TAPC

Figure 7 – By comparing a) CBP emission (figure from the thesis of Vygintas Jankus)[21] with

b) 2d absorption sufficient spectral overlap is apparent, thus efficient energy transfer from

CBP host to dopant 2d is facilitated.

This could be down to the shape of the molecule CBP which does not resemble that of 2d –

it may be harder for the CBP molecule to pass the spatial barrier of the 2d's butyl groups.

Furthermore the two carbazole groups are joined to the di-benzene molecular centre by the

para-position, meaning that conjugation is not broken unlike in mCP. As a result DFT has

shown that the HOMO and LUMO of the CBP molecule is located much more on the di-

benzene centre and not the carbazole units[38]. It could therefore be that the reduction of electronic prevalence on the carbazole units reduces the CBP's ability to pi-stack and form a carbazole dimer.

Unlike mCP, CBP absorbs strongly at 355nm and as it is at a far higher concentration than the 2d dopant it will absorb the majority of the incident light. Yet there is a complete absence of CBP fluorescence at early times. Figure 7 shows the emission and absorption of CBP and 2d respectively. We can therefore conclude with confidence that there is efficient energy transfer between the CBP host and 2d dopant as expected when comparing HOMO/LUMO levels (Figure 4b), and CBP emission/2d absorption (Figure 7).

3.3 The interplay between exciplex and ICT emission

And now we return to the success of 2d:TAPC. It has a high triplet level, and is made of triphenylamine rather than carbazole so carbazole dimerisation is prevented. The triplet level of TAPC is thus genuinely high at 2.95eV and furthermore the lack of dimer means it is allowed to contort into the twisted configuration, leading to efficient TADF. Of great interest also is that a CT state of 2d in solid state has only ever been observed when the conditions for exciplex (LUMO and HOMO offsets of ~0.5eV or greater) are satisfied. In *Jankus et. al.*, 2d CT emission was also found in 2d:m-MTDATA and 2d:NPB[15]. In 2d:TAPC the prompt emission is ICT and exciplex emission only appears as delayed fluorescence, thus showing a complex interplay with the ICT state feeding the slightly redder in energy exciplex state. The intriguing possibility therefore is that 2d ICT state can **only** occur if the conditions for exciplex are present, despite ICT emission coming first in time. On the other hand it is indeed possible that ICT emission in 2d in the solid state is possible on its own, if a suitably high triplet, non-carbazole based host is found. Further investigation into this area is

therefore likely to be of great interest to understanding the excited states of these kind of

D-A-D donor:host systems, which in turn would be of great benefit for maximising OLED

device performance.

Conclusions

The importance of dopant-host interaction has been conclusively proven for efficient TADF. This is especially the case when using strongly interacting component units such as carbazole for the dopant, where its tendency to form dimer lowers the host triplet level significantly from 2.90eV to 2.50eV in the case of mCP. The molecular shape of mCP exacerbates this problem by being small enough and symmetrically similar to the 2d emitter to pass through the spatial barrier provided by the butyl groups on the 2d. In this way the mCP molecule was able to drastically alter the behaviour of the 2d molecule and prevent the stabilisation of a CT state. Furthermore, the prevalence of carbazole dimer is likely to lock the 2d molecule in the 'planar' confirmation, which prevents the formation of ICT. It is therefore prudent to avoid a host made of the same component unit as the dopant in order to prevent dimerisation. It should be especially at the forefront of researchers' minds that due to the low dimer triplet carbazole based hosts, especially mCP, may not be the high triplet host solution to efficient OLED devices. As well as having a high triplet level >2.9eV, the ideal host will, like TAPC, facilitate the formation of the 'twisted' 2d molecular configuration which is required for molecules like 2d to form stabilised ICT states and thus efficient TADF. The alternative is to develop TADF emitters where the required steric twist, or other method of conjugation break, is 'built in' and thus more robust to the packing effects of the surrounding host molecules. Intriguingly stabilised CT emission has only been observed in systems where exciplexes can and do form. The possibility that the exciplex orbitals are required to create the ICT state in 2d is an intriguing one, and pursuing this avenue of inquiry is likely to yield much knowledge of excited state charge transfer systems.
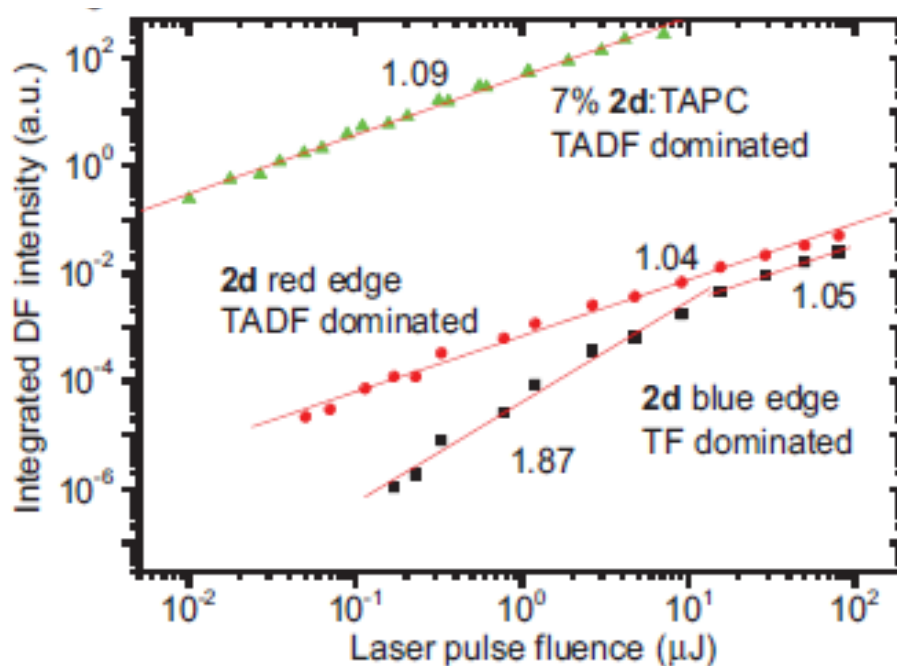
Supplementary Information

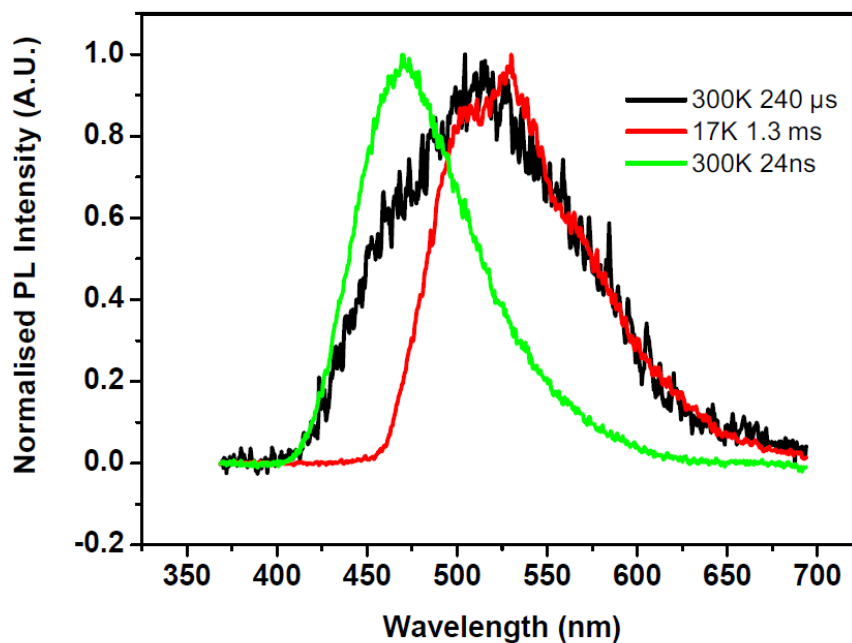*Figure S1 - DF laser fluence measurements from 2d:TAPC paper[15].*

Figure S2 – At late times 2d:CBP emission at 300K is a combination of TTA and 2d phosphorescence. Spectra uncorrected by calibration file.
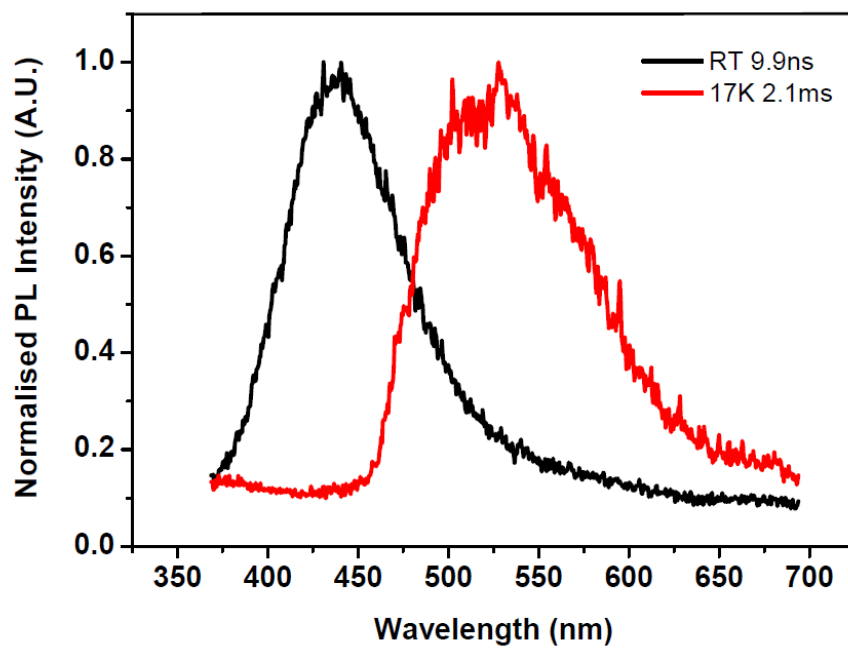
Figure S3 – CBP fluorescence (above) is not observed in 2d:CBP, showing efficient energy transfer.

Publications

The following publications have come about as a result of work within this thesis:

Vygintas Jankus, Przemyslaw Data, David Graves, Callum McGuinness, Jose Santos, Martin R. Bryce, Fernando B. Dias, Andrew P. Monkman, **Highly Efficient TADF OLEDs: How the Emitter–Host Interaction Controls Both the Excited State Species and Electrical Properties of the Devices to Achieve Near 100% Triplet Harvesting and High Efficiency**, *Advanced Functional Materials*, 2014, **24**, 39

David R. Graves, A. P. Monkman, **How the emitter-host conformational and electronic interaction can determine TADF performance,** to be submitted.

Fernando B Dias, David Graves, Jose Santos, Przemyslaw Data, Mark Fox, Tiago Palmeira, Mário N. Berberan-Santos, Martin R. Bryce, Andrew P. Monkman, **High Performance TADF OLEDs avoid critical loss mechanisms to give extremely high device efficiency**, *submitted.*

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15. Vygintas Jankus, P.D., David Graves, Callum McGuinness, Jose Santos, Martin R. Bryce, Fernando B. Dias, Andrew P. Monkman, *Highly Efficient TADF OLEDs: How the Emitter–Host Interaction Controls Both the Excited State Species and Electrical Properties of the Devices to Achieve Near 100% Triplet Harvesting and High Efficiency.* Advanced Functional Materials, 2014.
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