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The Role of Solid State Solvation on the Charge Transfer State of a Thermally Activated Delayed Fluorescence Emitter

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The influence of solid state solvation is crucial for understanding the device properties of 3rd generation organic light emitting diodes (OLEDs) based upon thermally activated delayed fluorescence (TADF), for which the native environment for the molecular emitter is an amorphous organic thin film. In this work we use quantum chemistry and molecular dynamics to demonstrate that the magnitude of static solid state solvation effects (SSSE) in a molecular excited state depends not only upon the dipole moment of the host, but also its rigidity and the dipole moment of the emitter in its electronic ground state. Subsequently, the molecular dynamics is used to study recently observed time-dependent aspects of solvation in TADF emitters. In contrast to the previously proposed guest-host interactions, the origin of these *dynamic* effects is proposed to be associated with the dispersion of charge transfer (CT) decay times, which are strongly sensitive to structural fluctuations of the emitter. Our findings extend the present understanding of SSSE in the context of 3rd generation OLEDs based upon TADF, which may be exploited to develop new strategies for high performing devices.

1 Introduction

Solvation plays a crucial role in driving, hindering, or modifying many fundamental non-equilibrium processes in chemistry¹. In general, the effects of a solvent may be separated into two distinct groups; passive or active. Active solvents are directly involved during the course of the chemical reactions by forming explicit interactions with the reacting species, which generally results in mechanistic changes and/or the formation of new reaction channels^{2–4}. In contrast, passive solvent effects do not change the quantum nature of the solute but, through the electrostatic field generated by the solvent, can alter the relative energies of the states involved. In such cases trends as a function of the solvent polarity are usually observed. While these can be expected to lead to changes in the branching ratio of the products, the solvent does not alter the underlying reaction mechanisms.

In electronically excited states, these passive solvation effects are most prominently observed in the case of charge transfer (CT) states. The large dipole moment associated with a CT state induces strong interactions with local solvent molecules, which reorient to form favourable dipolar interactions with the solute. These interactions lead to the usual bathochromic spectral shift observed in CT molecules with increasing solvent polarity. Simi-

lar effects, consistent with the theory of solvatochromism, are also observed in the solid state when a molecule exhibiting a low lying CT state is doped into host of relatively high polarity. In a process analogous to solute-solvent interaction, these materials can also stabilise the CT excited state and thus shift the emission to longer wavelengths, while in nonpolar host molecules the emission peak is not strongly affected⁵.

The role of such solid state solvation effects (SSSE) are especially important in the context of organic optoelectronic devices, such as organic light emitting diodes (OLED), in which the active emitting molecules are incorporated into an amorphous organic thin film. Importantly, while the general mechanism for SSSE can be seen as analogous to liquid state solvation, there are some important differences. Most pertinently is that in a solid the molecules are more sterically constrained than in the solution phase. This can give rise to strong, permanent local electric fields and restrict the reorientation of the solute around the emitter. These local dipolar interactions will also lead to the expected spectral shifts on the level of individual molecules as in the solution phase, but if the fields are random, as one would expect in a completely amorphous solid, then, after averaging over all the molecules in the film, there should be no net shift in either the absorption or emission spectra. Consequently, one might instead expect to observe a spectral broadening, due to the increased dispersion in the absorption and emission energies produced. However, if the molecular orientations are correlated, a

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net spectral shift could occur^{6–8}. This description is based purely upon dipole-dipole guest host interactions and other interactions, such as interactions between local charges and induced dipoles, can lead to spectral shifts⁹ distorting this picture.

SSSE have been shown to be especially important in 3rd generation OLEDs seeking to exploit thermally activated delayed fluorescence (TADF) to harvest both the singlet and triplet excitons generated under electrical excitation^{10–16}. The origin of this derives from recent work demonstrating that TADF is not simply a cyclic process between the singlet and triplet CT manifolds, but involves coupling to other states^{14,17–22}, such as local triplet $\pi\pi^*$ (³LE)¹⁷ or $n\pi^*$ states¹⁸. The effectiveness of the mixing between the states and therefore of the overall TADF process crucially depends on the energy gap between them. However, while CT states are strongly stabilised in hosts with higher polarity, other states, such as ³LE, will be less so (Figure 1a). Crucially this will alter the gap between these states and is likely to significantly change the efficiency of TADF¹⁴.

Fig. 1 (a) Schematic of the static solid state solvation effect where the polarity of the host stabilises the CT states more than the $^3\pi\pi^*$ (³LE) state¹⁴. (b) Schematic of the proposed origin of the dynamical solid state solvation effects whereby the dipole moments of the host molecules (green), which are randomly arranged when the TADF emitter (blue) is in its electronic ground state, reorientate when the emitter is excited so that their dipole moments are aligned to those of the CT state of the emitter.¹⁵ This illustrates parallel alignment, i.e. like charges interacting. Consequently, the anti-parallel configuration which is of course also possible is most favourable.

Besides this static polarity effect, largely analogous to solution phase solvation, a number of interesting subtle effects for TADF emitters in the solid state have also been observed^{15,16}. These display a temporal component to their behaviour and consequently we henceforth refer to them as *dynamic* effects. After photoexcitation an initial red-shift of the emission is observed. This is associated with the structural rearrangement of the emitter and local embedding environment in the excited state. This red shift continues, albeit at a slower rate into the nanosecond timescale^{15,16}. However, from ~100 nanoseconds until the microsecond time frame a pronounced blue-shift is observed. It is noted that the magnitude and the exact timescales of the processes involved are dependent on the particular guest-host combination used.

This phenomenon was interpreted by Mehes *et al.*¹⁵ as local interactions between the dipole moment of the host molecules and the excited state dipole moment of the emitter leading to alignment of the dipole moments of the host along the direction of the emitter (Figure 1b). An alternative explanation, proposed by Dias *et al.*¹⁶ is the presence of conformational heterogeneity among the ensemble of TADF molecules¹⁶, i.e. the presence of a distribution of CT states emitting at lower energies for later times.

Despite this evidence that the local embedding environment of a molecule can have a strong effect on the photophysics and therefore the performance of OLEDs, especially when charge transfer states are involved, the number of theoretical studies taking this into account have so far been limited. Recently, Sun *et al.*²³ used time-dependent density functional theory (TDDFT) based upon optimally tuned^{24,25} range separated functionals and a continuum model for the environment. They reported that the polarization effect can lead to a significant reduction in the energy gap between the lowest singlet and triplet states, making TADF more favourable. This decrease was due to the hybrid characters of the lowest singlet and triplet excited states, whose dominant contribution switches to charge-transfer-like with increasing polarity. However, while useful, this work does not provide an explicit insight into the dynamics and an atomistic description of the environment effect.

Fig. 2 The structures of the molecules used: (a) PTZ-DBTO2. (b) bis(2-(diphenylphosphino)phenyl)ether oxide (DPEPO) (c) 2,6-dicarbazolo-1,5-pyridine (PYD2) (d) 4,4'-N,N-dicarbazole-biphenyl (CBP).

In this paper we study the effect of three hosts, shown in Figure 2, on the lowest singlet CT state of a prototypical TADF molecule, a donor-acceptor (D-A) molecule composed of a phenothiazine donor and a dibenzothiophene-S,S-dioxide acceptor (PTZ-DBTO2)^{17,26,27}. We show that the magnitude of the SSSE depends not only upon the dipole moment of the host, but also on its rigidity and the dipole moment of the emitter in the electronic ground state. Our molecular dynamics simulations also reveal no longer (>ps) dynamics of the energy of the lowest singlet CT state. Consequently, we use these simulations to propose that the origin of the *dynamic* effects is associated with the conformational heterogeneity (dispersion) of charge transfer (CT) decay times, which are strongly sensitive to structural fluctuations of

the emitter.

2 Methods and Computational Details

2.1 Quantum Chemistry

The ground state geometries and properties of all molecules were obtained by optimisation using DFT within the approximation of the M062X exchange and correlation functional^{28,29}. A def2-SVP basis set was used. These simulations were performed using the Gaussian quantum chemistry package³¹. All excited state properties were calculated using TDDFT(M062X)³⁰ and the same basis set. Throughout the Tamm-Dancoff Approximation was used. The M06-2X functional is used because, as with most TADF molecules, the strong CT character means that functional with a large portion of exact exchange is required. Throughout our extensive characterisation of PTZ-DBTO2¹⁷ and related compounds, we have found that the M06-2X functional consistently and accurately reproduces the excited state properties for this class of TADF compounds. In the interest of convergence, optimisations were performed in the absence of any environment. However the subsequent energy calculations used a polarisable continuum model³². Emission energies were calculated using the S_1 optimised geometries, and a state-specific polarizable continuum model (SS-PCM)³³. For the SS-PCM, the energy of both the S_1 and ground state were calculated within an S_1 optimised solvation structure, yielding the vertical emission energy.

2.1.1 Classical Molecular Dynamics

The classical Molecular Dynamics (CMD) were performed using the Amber MD package³⁴ with the emitter, PTZ-DBTO2, fully solvated in one of the hosts, 4,4-N,N-dicarbazole-biphenyl (CBP)³⁵, 2,6-dicarbazolo-1,5-pyridine (PYD2)³⁶ or bis(2-(diphenylphosphino)phenyl)ether oxide (DPEPO)³⁷ (Figure 2). For comparison to the continuum model simulations, simulations were also performed in toluene. An NPT ensemble was used throughout. The force fields for the molecular dynamics were generated using with the General Amber Force-Field (GAFF)³⁸. DFT(PBE0)/def2-SVP determined Mulliken charges were used throughout for the force-fields. Other approaches, such as CHELPG, were tested, and while they do shift (<0.2 eV) the energies reported below, the trends reported remain unchanged. The Mulliken charges were adopted as they provided a good description of the dipole moment of the CT state of PTZ-DBTO2 from cDFT, as described below.

The emitter was initially solvated in a box with initial solvent radii of 49 Å. The system was then equilibrated by classical MD using a constant pressure of 1 atm and a temperature of 300 K until all properties (energy, temperature and pressure) were converged. After initial equilibration, the box was heated to 1000 K for a random number time steps between 10-30 ps. As this is above the melting point for each of the guest-host systems it enabled free movement of the molecules and therefore faster conformational sampling. The box was then cooled to 300 K until equilibrated. The dynamics were propagated for a further 200 ps. All of the properties of the ground state were simulated from the final 200 ps dynamics, using the sampling approach described below.

The dynamics in the excited charge transfer state were simulated by changing the atomic charges within the force field to those associated with the CT state, generated using constrained DFT (cDFT)³⁹ as implemented within Qchem⁴⁰ within the approximation of the PBE0 functional and a def2-SVP basis set. The constraint adopted was that the donor unit had a charge of +1 and the acceptor unit had a charge of -1, i.e. we are assuming a full charge transfer of the excited state. While this is an approximation, the non-overlapping HOMO and LUMO orbitals centred on the donor and acceptor groups, respectively and which constitutes the main transition of the S_1 state, means that this assumption is a good approximation. An additional approximation is that only the electronic structure changes in the excited state. While clearly an approximation, the geometric structural rearrangement of PTZ-DBTO2 in the excited state is relatively small. This approach was adopted to make it possible to identify spectral shifts arising purely from the interaction between the guest and host molecules, without convolution with structural changes. This is discussed in more detail below. Each excited state simulation was started from a configuration extracted from the ground state simulations. The charges were then changed and the simulation continued. The results presented are averaged over 20 different starting configurations.

Fig. 3 The HOMO and LUMO orbitals of PTZ-DBTO2.

Sampling of both the ground and excited state energies was achieved using Time-Dependent Density Functional Theory (TDDFT) calculations within the Tamm-Dancoff approximation (TDA) and the M06-2X exchange and correlation functional, using the Gaussian Quantum Chemistry package³¹. As above a def2-SVP basis set was used throughout. The emitter was treated quantum mechanically, while the environment was treated using classical point charges whose positions were obtained from the classical molecular dynamics. In total a radius of 8 Å of host molecules was used, as this was found achieved convergence of the S_1 state. The point charge model was adopted, in contrast to a quantum treatment of the whole cluster as it represents a significant computational saving. However, because the T_1 energy levels of the host molecules are higher than PTZ-DBTO2, the excited state on the emitter is well confined to that molecule only and therefore the influence from the environment is predominately electrostatic as captured by the point charges. It is noted however that while such a model will describe dipolar interactions, it cannot capture dipole (guest) - induced dipole (host) interac-

tions. For the hosts studied herein, the polarisability was found to be smallest for PYD2 and therefore its absence from the present simulations will not alter the conclusions.

3 Results

3.1 Energetics of PTZ-DBTO2: Continuum Solvation

Table 1 shows the vertical excitation energy for the lowest singlet excited state, S_1 , of PTZ-DBTO2 which is an almost pure HOMO-LUMO transition and therefore as shown by the HOMO-LUMO orbitals in Figure 3 is of CT character¹⁷. The energies are shown at both the ground state and S_1 geometries capturing the absorption and emission energies, respectively. These are calculated in *Vacuo* and for a range of solvents, described using the polarisable continuum model⁴¹. At the ground state geometry, the S_1 state exhibits almost no effect of the environment with the lowest CT state absorbing around 3.70 eV (335 nm) consistent with the onset of the absorption band of PTZ-DBTO2 reported in ref.²⁷.

For emission the picture is unsurprisingly somewhat different, due to the large dipole moment of PTZ-DBTO2 in the S_1 and the state specific solvation optimised for this dipole moment to capture the emission energy³³. In *Vacuo*, the emission occurs at 2.65 eV (467 nm) and corresponds to a theoretically derived Stokes shift arising entirely from the structural changes of PTZ-DBTO2 in its excited state of ~ 1.0 eV. Despite the large shift observed in Table 1, the structural change between the ground and excited state minima is relatively small. The principle change is an elongation of the C-N bond between the donor and acceptor units, which increases from ~ 1.43 Å to ~ 1.48 Å. Importantly, because of the $1/R$ dependence, where R is the distance between donor and acceptor groups, for the excitation energies of charge-transfer states this small structural change is sufficient to account for the significant Stokes shift. The other change is a nitrogen pyramidalisation between the donor and acceptor groups which goes from 130° to 100° , although this has a much smaller effect on the energy of the ^1CT state.

Upon inclusion of a state-specific PCM model a distinct solvation effect is observed in the excited states with emission energy decreasing significantly with increasing ϵ as expected due to the large excited state dipole moment of the strongly CT singlet state. The emission in toluene, ~ 1.99 eV, is in reasonable agreement with the peak of the emission of PTZ-DBTO2 which is approximately ~ 2.05 eV²⁷. In zeonex, a low polarity polymer, the emission is ~ 2.38 eV again broadly consistent with the methylcyclohexane and in *Vacuo* values. As expected, upon increasing the polarity of the solvent (dicloromethane and ethanol) a significant decrease in the emission energies is observed, indicating the large excited state dipole. However no experimental emission spectra have been reported for these higher polarity solvents.

Consistent with the conclusion of Sun *et al.*²³, increasing the polarity of the solvent decreases slightly the already weak oscillator strength. This is because the CT state, which initially has some hybrid character becomes further removed from the $\pi\pi^*$ excited states and mixes less, switching to a purer CT character with increasing polarity and therefore small oscillator strength.

In summary, after photoexcitation of PTZ-DBTO2 into the ^1CT

	ϵ	S_1^{abs} (eV)	S_1^{em} (eV)	f
in <i>Vacuo</i>	-	3.61	2.65	0.0007
in methylcyclohexane	2.06	3.65	2.08	0.0004
in Toluene	2.37	3.65	1.99	0.0003
in dicloromethane	8.93	3.69	1.45	0.0002
in Ethanol	24.85	3.71	1.30	0.0001

Table 1 The energy of the S_1 CT state at the ground (absorption) and S_1 (emission) state geometries of PTZ-DBTO2 as a function of solvent polarity (ϵ). The oscillator strength (f) is calculated at the S_1 (emission) excited state geometry.

state, the initial absorption band of ~ 3.6 eV undergoes a Stokes shift of ~ 1.7 eV in toluene as observed experimentally²⁷. Of this, ~ 1.0 eV is associated purely with the structural change, primarily the distance between the donor and acceptor groups. The remaining ~ 0.7 eV is an interaction with the environment caused by the large excited state dipole moment of PTZ-DBTO2. This present understanding, which exploits a continuum model is founded upon the assumption that SSSE is analogous to solution phase solvation effects and depends only on polarity. In the following section we consider this in more detail by studying the effect of the environment in solid state hosts and explicit solvation through the point charge model.

3.2 PTZ-DBTO2 with Explicit Environment

Table 2 shows the vertical excitation energy for the ^1CT state of PTZ-DBTO2 for both the ground and excited state electronic configurations as described in the method section. It is reiterated, that in order to isolate the effect of solvation on the energetics, only the charges in the force-field of PTZ-DBTO2 have been changed. Consequently, the 1.0 eV shift in the excited state energy associated with structural changes, identified in the previous section, will be absent from the present simulations. Any changes are solely a result of the interaction of the host molecules in response to the new electronic configuration of PTZ-DBTO2. It is again noted that the point charge model adopted will not capture dipole-induced dipole effects.

These simulation have been performed with three organic host materials, CBP, DPEPO and PYD2 all of which exhibit different dipole moments (Table 2). To enable a direct comparison between the point charge model and PCM models, we have also performed these simulations with toluene. The S_1^{abs} and S_1^{em} for toluene using the PCM model was 3.65 eV and 1.99 eV, respectively. As identified using the in *Vacuo* simulations, ~ 0.7 eV of this corresponds to the effect of the solvent. In Table 2 S_1^{abs} and S_1^{em} for toluene using the point charge model are 3.43 ± 0.18 eV and 2.77 ± 0.11 eV, respectively. This yields a relative shift of 0.66 eV, consistent with the PCM model in the absence of any structural change of PTZ-DBTO2. The only difference is therefore an ~ 0.2 eV shift of both states. However, because it is the relative shifts of the two states which are important, this does not represent any issue for the following discussion and confirms the validity of our present model.

As observed in the implicit solvent models, the S_1^{abs} exhibits

	S_1^{abs} (eV)	S_1^{em} (eV)	Oscillator Strength	μ (D)
in CBP	3.49 ± 0.26	2.84 ± 0.18	0.011 ± 0.015	0.01
in Toluene	3.43 ± 0.18	2.77 ± 0.11	0.012 ± 0.012	0.43
in PYD2	3.33 ± 0.42	3.36 ± 0.28	0.011 ± 0.014	2.67
in DPEPO	3.37 ± 0.21	2.26 ± 0.20	0.009 ± 0.011	8.06

Table 2 Excited state energies and their standard deviation for ^1CT at the ground (S_1^{abs}) and CT S_1^{em} state electronic configuration. The oscillator strength (f) is calculated at the S_1 (emission) excited state geometry. The dipole moment (μ) in Debye (D) corresponds to a single host molecule calculated in *Vacuo*.

Fig. 4 Time dependence of $\cos(\theta)$, where θ is the angle between the dipole moment of the guest and the surrounding (8 Å) host molecules in DPEPO (a) and PYD2 (b). Before time zero the molecular dynamics used the charges for PTZ-DBTO2 corresponding to the molecular ground state, after time zero the charge transfer charges were used.

a relatively small shift. However a moderate shift is observed for the hosts with a larger dipole moment (PYD2 and DPEPO). In contrast S_1^{em} , corresponding to the emission energy, exhibits a large shift as a function of the hosts polarity with the exception of PYD2, which shows no change from S_1^{abs} . The shifts for CBP and DPEPO are consistent with a dipolar interaction with the guest and host molecules analogous to solvation effects in the solution phase. For PTZ-DBTO2 in PYD2, the absence of shift is because of the rigidity of PYD2¹⁵ which provides a tightly-packed molecular environment for PTZ-DBTO2, reducing the ability of the host to exhibit any reorientation after excitation of the guest. This is supported in Figure 4 showing the time dependence of $\cos(\theta)$, where θ is the angle between the dipole moment of the guest and the

surrounding (8 Å) host molecules in DPEPO (a) and PYD2 (b). Before time zero the molecular dynamics used the charges for PTZ-DBTO2 corresponding to the molecular ground state and in both cases $\cos(\theta)$ is close to zero showing little alignment associated with the CT state. After time zero the charge transfer charges were used, and a distinct shift to negative values of $\cos(\theta)$ is observed, consistent with a slight anti-parallel (favourable) alignment of the guest-host dipole moments. In contrast for PYD2 no overall change is observed, except for a narrowing of the standard deviation which is also observed in the case of DPEPO. In addition, it is noted that the Stokes shift in the peak position of the prompt emission (<60 ns) and width of delayed emission of ACRF in PYD2¹⁵ is smaller than DPEPO, illustrating the more restrictive environment. PYD2 has also been widely used to enhance the quantum yield of Cu based TADF emitters as the restrictive environment decreases the rate of non radiative decay⁴².

Figure 5a show the dynamics of the S_1 (^1CT) state (a) and ΔE_{CT-^3CT} energy gap (b) for 200 ns after excitation into the ^1CT state, averaged from 20 different initial configurations, as described in the methods section. The red trace shows the energetics of PTZ-DBTO2 without including the effect of the environment in the quantum chemistry calculations of the sampled configurations. As expected this shows no shift and the dispersion (error bars) results from thermal fluctuations of PTZ-DBTO2 at 300 K. The black trace shows the dynamics observed upon inclusion of the environment in a point charge fashion. These dynamics are incredibly simple and exhibit only a strong initial shift associated with the increased dipolar interaction between the guest and the host, attributed to small local dipole reorientations. Subsequently, there are no further shifts in the emission energy during the 200 ns. This is in contrast to the dynamics observed in refs^{15,16} and suggests that the spectral shifts on this timescale do not reflect guest-host interactions. This is discussed in detail in the following section. The errors bars represent a standard deviation of the 20 sampled configurations at each time step, these correspond to the expected width of the ^1CT emission band, important in the context of colour purity of TADF emitters. These are smaller when the environment is not included, indicating that ~70% of this width derives from thermal fluctuations of the emitter. In Figure 5b, the energy gap becomes slightly smaller after excitation, as the stabilisation reduces the mixing of the ^3CT state with other low lying triplet states, such as ^3LE , it is therefore a purer CT state.

Fig. 5 Time dependence of the S_1 (1CT) state (a) and $\Delta E_{1CT-3CT}$ energy gap (b) during the first 200 ns after population of the 1CT of PTZ-DBTO2 in DPEPO with (black) and without (red) the effect of the local environment. The error bars correspond to the standard deviation of the 20 sampled configurations at each time step.

4 Discussions

In the previous sections we have performed ground and excited state simulations of PTZ-DBTO2 with both explicit and implicit solvation to understand the role of SSSE in TADF emitters. In the following subsections these results are discussed.

4.1 Solid State Solvation

In solution, excitation of a solute produces an excited state with a larger, or even simply different, dipole moment from the ground state. The surrounding solvent molecules experience a new electric field and respond to this, i) through electron cloud reorganisation (i.e., polarisability), and ii) through reorientation of the nuclear positions. These two processes can be considered fast (picoseconds), in comparison to the timescales of TADF and will modify the energy levels of the solute. The same general concepts also applies in the context of solid state solvation, however in a solid the molecules are sterically constrained, which can restrict the reorientation of the solute around the emitter.

In our present simulations, both S_1^{abs} and S_1^{em} exhibit spectral shifts correlated with to the dipole moment of the host, except for PYD2. This suggests some alignment of the host molecules with

the dipole moment of PTZ-DBTO2, which is larger for S_1^{em} due to the larger dipole moment of PTZ-DBTO2 in the CT state. Interestingly no net change in the emission energy as a function of the dipole moment of the host was observed for the spiro-acridine compound 10-phenyl-10H-spiro[acridine-9,90-fluorene]-20,70-dicarbonitrile (ACRF), during the first μs in ref. ¹⁵. In this case, it suggests a completely randomly orientated amorphous thin film, even in the CT state. This is because the dipole moment of ACRF in the ground state is only 1.4 D¹⁵. This will not give rise to any significant dipolar coupling between guest and host in the ground state leading to a randomly orientated film. In contrast the ground state dipole moment of PTZ-DBTO2 is 5.5 D, this creates a propensity for the host molecules to align, to some degree, with the dipole moment of the emitter already in the electronic ground state, as proposed in ref. ⁸. Because the ground and excited state dipole moments of PTZ-DBTO2 are in the same direction, this alignment in the ground state enhances the dipolar coupling in the excited state creating the ability to stabilise both S_1^{abs} and S_1^{em} . In the solid state, because reorientation of the dipoles is more restricted, the random orientation of guest-host blends of ACRF which exists in the ground state cannot be changed in the excited state. However for PTZ-DBTO2, some alignment already exists, this alignment can be enhanced in the excited state by smaller fluctuations of the host when the guest is excited into the CT state. This highlights if one wishes to control the spectral shifts of TADF emission, it is crucial to consider the ground state molecular dipole moment of the emitter.

4.2 Time-dependent emission energies

Our present results fail to observe any spectral shifts of the emission energy between 20 and 200 ns after excitation of the emitter into the 1CT state (Figure 5). As described in the introduction, refs ^{15,16} have recently reported such temporal changes with time dependent red and then blue shift occurring on the nano- and micro- second timescales. The lack of dynamics observed herein, suggests that this is not a guest-host effect and would appear to rule out the proposal made in ref. ¹⁵, in which this time dependent shift is caused by a slow reorientation of the host to align with the dipole moment of the emitter. At this point, it is emphasised the timescales (200 ns) studied herein do not correspond to those reported in ref. ¹⁵ for ACRF, which extend into the micro- and millisecond time domain, which are not considered here due to the length of the simulations. However similar shifts are observed on this timescale experimentally in ref. ¹⁶ for the D-A-D analogue of PTZ-DBTO2. Despite, the fact that we therefore cannot conclusively rule out the proposals made in ref. ¹⁵, the following discussion remains relevant.

Importantly, the proposal by Mehes *et al.* ¹⁵ relies upon population of a 3CT state on the microsecond timescale. This creates a strong dipole moment of the emitter forcing local alignment of the host molecules, stabilising the 3CT state and causing the typical bathochromic shift for guest-host systems exhibiting stronger dipolar interactions. This state then decays into a $\pi\pi^*$ state on the millisecond timescale. As this state does not exhibit a large molecular dipole moment, the host molecules become ran-

domised again leading to the blue spectral shift.

For this mechanism, the two triplet states must be coupled, most likely by nonadiabatic coupling, as expected for high performing TADF materials¹⁷. This coupling means that the molecular wavefunction will be mixed between the two states. Because nonadiabatic coupling is usually a lot stronger than spin orbit coupling between the singlet and triplet states, these two states will rapidly form an equilibrium on a timescale much faster than the reverse intersystem crossing (rISC). Consequently, because of this mixing, it is not possible to assign the molecule to being purely ³CT or ³LE. The molecular dipole moment of this mixed configuration will therefore be expected to be smaller and is unlikely to explain the rather significant dynamics observed in ref.¹⁵

To address an alternative mechanism, Figure 6 shows a plot of the energy gap between the ¹CT and ³CT states (ΔE_{S-T}) and the oscillator strength of the ¹CT state. The linear correlation expected is observed. Therefore conformations with a large ΔE_{S-T} , which derives from larger exchange energy, will exhibit a higher E_S . But larger ΔE_{S-T} configurations also have a larger oscillators strength. Consequently, the states with higher ¹CT energy will emit first. This will lead to the red shift in the initial prompt emission with time before the system decays into the triplet manifold.

Fig. 6 The oscillator strength of the ¹CT state as a function of ΔE_{S1-T1} (eV) over all of the configurations of PTZ-DBTO2 sampled.

The blue shift at longer times is observed in both refs^{15,16}. Here we explain this with a mechanism which we refer to as *reverse dispersion*. Once in the triplet state, the rate of TADF can be expressed:

$$k_{TADF} = k_f \exp\{-\Delta E_{ST}/k_b T\} \quad (1)$$

This equation is strictly only valid for cases in which the rate constants of these nonradiative transitions are much larger than the rate of fluorescence. This is not the case here, but nevertheless provides a guiding illustration of the effect of *reverse dispersion*. Equation 1 shows that molecules with a larger radiative rate might be expected to emit first, but because of the large exchange energy, ΔE_{ST} will be larger, slowing TADF. Therefore the

molecules with the largest ΔE_{ST} , and therefore highest S_1 energy will emit later, and consequently a blue shift will be observed. Taking as an example Figure 6, in the case the radiative rate doubles, the energy gap roughly triples. This means that ratio of the k_{TADF} can be expressed:

$$k_{TADF1}/k_{TADF2} = \frac{k_f \exp\{-0.05/k_b T\}}{2k_f \exp\{-0.15/k_b T\}} \quad (2)$$

$$= \frac{1 \exp\{-0.05/k_b T\}}{2 \exp\{-0.15/k_b T\}} \sim 24.5 \quad (3)$$

This is to say that although molecular configurations with smaller ΔE_{ST} also have a smaller radiative rate, the triplets state harvested from these configurations ~ 25 times quicker than those with a larger energy gap due to the exponential dependence of the energy gap on the TADF process. This proposes that the *dynamic* SSSE observed for TADF emitters is purely a result of the dispersion of CT states. Importantly the aforementioned proposed mechanism is consistent with the spectral shifts seen in ref.¹⁶ for both non-polar (zeonex) and polar (CBP) molecules. However, the mechanism proposed in ref.¹⁵, would result in no spectral shift being observed when a TADF emitter is embedded within the non-polar polymer zeonex.

Finally, it is important to note that in the case of PTZ-DBTO2, the presence of the ³LE makes a full description of *reverse dispersion* more complicated. However, this state should be little affected by the environment and as shown in ref.¹⁹, even in the spin-vibronic mechanism involving the ³LE state, it is still the gap between the CT states which is most important.

5 Conclusions

In the present work we have used quantum chemistry and molecular dynamics to shed insight into static and dynamical solid state solvation effects of a TADF emitter embedded within an amorphous organic thin film. We find that the so called static SSSE are analogous to solvation effects observed in the solution phase. However, we demonstrate that the magnitude of shifts in the excited state depends not only upon the dipole moment of the host, but also its rigidity and the dipole moment of the emitter in its electronic ground state.

Studying time-dependent aspects of solvation in TADF emitters, we observe no dynamics of the spectral shift. This enables us to rule out guest-host interactions as dominant in the time-dependent solvation dynamics observed for TADF emitter. Instead we proposed the mechanism summarised in Figure 7. After photoexcitation, the charge redistribution of the emitter leads to a stabilisation of the excited state. This occurs on the picosecond to early nanosecond timescale and originates from the structural changes of the guest, but also reorientational dynamics of the host consistent with solvation in the solution phase. This latter component will of course depend on the rigidity of the host. Subsequently, the continued red shift on the nanosecond timescale derives from the dispersion effect of the CT state. Indeed, as shown in the lower inset in Figure 7, the exchange interaction lifts the energy of singlet excited states. As the magnitude of the exchange is linked to the orbital overlap, increased exchange is generally

Fig. 7 Schematic of ^1CT energetics and the mechanisms responsible, during the excited state lifetime of a TADF emitters in the solid state. The exact timescales do depend on the nature of the guest and host systems involved.

associated with increased overlap and therefore a stronger oscillators strength. Consequently, the high energy states, with more orbital overlap will emit first, due to a fast radiative rate. This applies only to prompt fluorescence and the timescale of this process is therefore also in competition with the rate of ISC. Once in the triplet state, the longer time blue shift in the emission is associated with, what we now term, reverse dispersion. Here, although the molecular configurations with more orbital overlap will have a larger radiative rate, there will also be a larger energy gap between the singlet and triplets states, making the rISC slower. As this has an exponential dependence it will dominate. Consequently, the initial delayed fluorescence will be dominated by configurations with small exchange and therefore lower singlet energy.

In terms of designing new materials for OLEDs, it is important to minimise the effect of the host on the guest and remove the time-dependence to achieve consistent device performance. This can be achieved adopting: i) A rigid host with a small dipole moment to reduce guest-host dipole-dipole interactions. ii) An emitter with a small ground state dipole moment to avoid strong local interaction. iii) An emitter with a narrow distribution of donor-acceptor distances to limited the dispersion effect. This latter requirement is the most challenging. In principle, for the present case this could be achieved by making the C-N bond more rigid. This would also result in a narrower emission band and therefore improve colour purity. However, one must be careful, as rigidification of this bond would slow the D-A torsion implicated in the spin-vibronic mechanism¹⁷ and quench TADF as observed in ref.²⁶. Consequently, a careful balance between the two requirements has to be achieved.

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Data availability

Data supporting this publication is openly available under an "Open Data Commons Open Database License". Additional meta-data are available at: 10.17634/153015-4. Please contact Newcastle Research Data Service at rdm@ncl.ac.uk for access instructions.

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