Regio- and conformational isomerization critical to design of efficient thermally-activated delayed fluorescence emitters

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Regio- and conformational isomerization are fundamental in chemistry, with profound effects upon physical properties, however their role in excited state properties is less developed. Here two regioisomers of bis(10H-phenothiazin-10-yl)dibenzo[b,d]thiophene-S,S-dioxide, a donor–acceptor–donor (D–A–D) thermally-activated delayed fluorescence (TADF) emitter, are studied. 2,8-bis(10H-phenothiazin-10-yl)dibenzo[b,d]thiophene-S,S-dioxide exhibits only one quasi-equatorial conformer on both donor sites, with charge-transfer (CT) emission close to the local triplet state leading to efficient TADF via spin-vibronic coupling. However, 3,7-bis(10H-phenothiazin-10-yl)dibenzo[b,d]thiophene-S,S-dioxide displays both a quasi-equatorial CT state and a higher-energy quasi-axial CT state. No TADF is observed in the quasi-axial CT emission. These two CT states link directly to the two folded conformers of phenothiazine. The presence of the low-lying local triplet state of the axial conformer also means that this quasi-axial CT is an effective loss pathway both photophysically and in devices. Importantly, donors or acceptors with more than one conformer have negative repercussions for TADF in organic light-emitting diodes.

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hernally activated delayed fluorescence (TADF)\(^1\) has emerged as one of the most attractive methods for achieving luminescence from triplet states via reverse intersystem crossing (rISC)\(^2\) in organic molecules\(^3\),\(^4\). However, designing efficient TADF molecules is not a trivial task due to the restrictions on achieving the correct energy level ordering, splittings and coupling\(^2\). Until recently, the design focus was based upon an equilibrium picture, where efficient devices were believed to require solely a small singlet-triplet gap. While this energy gap is a critical component, this approach neglects the complexities of the rISC mechanism where subtle effects of molecular properties, such as vibrational degrees of freedom, have recently been shown to be vital\(^7\),\(^8\). Moreover, the roles of molecular geometry and isomeric structures have only recently started to be considered\(^9\),\(^10\).

One way of achieving efficient TADF is to use donor–acceptor–donor (D–A–D) molecules possessing strong intramolecular charge-transfer (CT)\(^10\),\(^11\). However, contrary to initial thoughts\(^4\), rISC is not driven by direct spin–orbit coupling (SOC), which within the one electron limit is forbidden between the 1CT and 3CT states. In fact, it is a more complex second-order spin-vibronic SOC mechanism that facilitates efficient rISC. In this process an energetically close local triplet (3LE) state acts as a mediator to couple the 2CT to the 1CT states and induce a second-order SOC (ref. 6). It is thus the small energy gap between the 3LE and CT states (both 1CT and 3CT) that gives rise to the thermally-activated nature of the rISC\(^7\),\(^13\) and efficient OLED performance\(^14\). The second-order vibronic coupling model of rISC (refs 6,7) enables us to understand the effects of energy ordering, and in this context we show how conformational and regio-isomerism can greatly effect rISC, TADF and ultimately device efficiency. These structural factors must also be considered in designing the highest efficiency TADF emitters along with energy level ordering\(^11\),\(^12\) and host environment within the device\(^6\),\(^14\).

While it is one key factor for TADF that these D–A–D structures exhibit a small \(\Delta E_{S_T}\) gap, choice of substituents based purely on their donating or accepting properties may still lead to avoidable losses. Phenothiazine (PTZ) is a well-known donor and has been studied in many TADF systems, with great success. However, less well known is the fact that it has two heterogenous conformers that exhibit very different electronic and optical properties\(^8\),\(^15\),\(^16\). Ignoring the potential for conformational changes when using PTZ as a donor molecule may lead to unexpected and unavoidable losses in the system. Lessons learnt from this archetypical donor will apply to all future designs of donor units. Understanding the fundamental limitations imposed by molecular structure and conformation in TADF molecules, which can initially be gauged on their crystal structure, will help avoid those that have such intrinsic loss pathways that inhibit TADF and greatly reduce device efficiency.

There is a great deal of previous work on the observation of dual fluorescence in organic molecules\(^8\),\(^18\),\(^19\). However these have overwhelmingly displayed emission from a locally excited (LE) singlet state and a singlet CT state\(^18\),\(^19\). The observation of dual emission arising from two equally stable CT states of a molecule is a more recently discovered phenomenon\(^22\),\(^23\), and in the following systems is as a result of the folding of the PTZ donor unit. It is the intrinsic nature of PTZ, and its ability to form H-intra and H-extra folded conformers that allows formation of parallel quasi-axial (ax) and perpendicular quasi-equiatorial (eq) CT states in the bis(10H-phenothiazin-10-yl)dibenzo[b,d] thiophene-SS-dioxide (DPTZ-DBTO\(_2\)) molecule. These conformers are taken with respect to the N–S axis and plane of the phenyl rings (nomenclature first suggested by Stockmann et al.\(^17\)). Dual emission from these states has been observed in this work and in the literature\(^19\),\(^20\),\(^22\).

Here we use two regioisomers of an efficient TADF emitter, bis(10H-phenothiazin-10-yl)dibenzo[b,d]thiophene-SS-dioxide (DPTZ-DBTO\(_2\)), to demonstrate that the configuration of the D–A–D molecule has a profound effect on the conformation of the PTZ donor. These conformers are equally stable but based on calculations and optical measurements contribute very differently to triplet harvesting, device efficiency and to the fluorescent properties of these molecules. The two possible conformers of the PTZ result in dual (CT excited state) fluorescence from the molecule, of which only one contributes to TADF and increased device efficiency. The quasi-equatorial conformer is observed in both isomers and yields efficient rISC and TADF. However, the quasi-axial conformer forms a CT state of much higher energy and thus in line with the spin–vibronic coupling mechanism of rISC, this prevents the state from undergoing TADF and contributing to high internal quantum efficiency. Most importantly, the presence of the lower-lying 3LE state results in the quasi-axial CT state being an effective triplet quencher, which adversely affects device efficiency.

### Results

**Molecular structures.** The two regioisomers have two electron donor units (PTZ) linked to the 2,8- and 3,7-positions on the acceptor unit dibenzothiophene-SS-dioxide (DBTO\(_2\)). Figure 1 shows the X-ray crystal structures of 2,8-DPTZ-DBTO\(_2\) (2,8-Bis(10H-phenothiazin-10-yl)dibenzo[b,d]thiophene-SS-dioxide)\(^11\) and 3,7-DPTZ-DBTO\(_2\) (3,7-Bis(10H-phenothiazin-10-yl)dibenzo[b,d]thiophene-SS-dioxide). 2,8-DPTZ-DBTO\(_2\) is seen to have both D–A arranged in a quasi-equatorial conformation, whereas 3,7-DPTZ-DBTO\(_2\) has a mixed eq–ax conformation. On closer inspection both PTZ units in the 2,8-DPTZ-DBTO\(_2\) are in the H-intra conformation, whereas the 3,7-DPTZ-DBTO\(_2\) isomer has one H-intra PTZ and one H-extra, of which the H-extra forms the higher-energy quasi-axial CT state. In the case of the H-intra conformation, the nitrogen lone pairs delocalize into the phenyl rings of the PTZ.

**Excited states of each isomer.** Figure 1 shows a schematic of experimental energy levels of the two regioisomers and the effect of polarity. The TDDFT(M062X) calculated dipole moment of the charge-transfer state in 2,8-DPTZ-DBTO\(_2\) (15.0 D) is larger than that of 3,7-DPTZ-DBTO\(_2\) (14.1 D) consistent for the different shifts of the CT bands as a function of solvent polarity. The HOMO and LUMO levels of the isomers were measured by cyclic voltammetry (Supplementary Fig. 1 and Supplementary Table 1). The LUMO levels of both 2,8-DPTZ-DBTO\(_2\) and 3,7-DPTZ-DBTO\(_2\) are at the same energy, \(-3.05\) eV, whereas the HOMO levels are slightly different at \(-5.40\) eV for 3,7-DPTZ-DBTO\(_2\) and \(-5.45\) eV for 2,8-DPTZ-DBTO\(_2\). This narrowing of the HOMO–LUMO gap in 3,7-DPTZ-DBTO\(_2\) is also observed in the absorption and emission spectra of the isomers in non-polar methycyclohexane (MCH) solution, shown in Fig. 2. Careful inspection of the oxidation waves of 3,7-DPTZ-DBTO\(_2\) shows a double peak indicative of two species with slightly different oxidation potentials, consistent with the mixed axial-equatorial conformation (Supplementary Fig. 1b). Spectroelectrochemical measurements, along with EPR spectroscopy, reveal the strong decoupling of the D and A in these molecules consistent with their near orthogonality (Supplementary Figs 2–4 and Supplementary Tables 2 and 3).

The absorption spectrum of 2,8-DPTZ-DBTO\(_2\) is formed from the sum of the donor and acceptor absorptions, with a weak \(n–\pi^*\) absorption band on the red edge that directly creates the 1CT state\(^3\). This is consistent with the H-intra conformation where the nitrogen lone-pair electrons are localized on the donor.
In 3,7-DPTZ-DBTO₂ the donor absorption contribution is enhanced and red-shifted, and the lowest energy transitions gain considerable oscillator strength redistributed from the acceptor, suggesting strong mixing of the $n^*$ and $p^*$ transition moments in 3,7-DPTZ-DBTO₂ (ref. 23). This may indicate that the quasi-axial conformer, with its associated H-extra PTZ conformation enhances conjugation between the donor and acceptor via the bridging nitrogen $n$ electrons and hence pronounced mixing of the $n^*$ and $p^*$ transition moments.

These lowest energy absorption bands in 3,7-DPTZ-DBTO₂ show no blue-shift with increasing solvent polarity (see Fig. 3b and Supplementary Fig. 5) in contrast to 2,8-DPTZ-DBTO₂ (Fig. 3a) where the $n^*$ states do blue-shift (Supplementary Fig. 6a is not at sufficiently high concentration to observe the blue-shift but is included for completion)¹³. This agrees with TDDFT(M062X) calculations, which yield an oscillator strength of the lowest donor transitions of 0.23 for 2,8-DPTZ-DBTO₂ and 0.71 in 3,7-DPTZ-DBTO₂, a factor of ca. 3 greater.

Even in a non-polar solvent¹⁴, red-shifted and featureless emission bands are observed in both molecules (see Fig. 2a,b and Supplementary Fig. 6b), indicating the strong CT character of the lowest donor transitions of 0.23 for 2,8-DPTZ-DBTO₂ and 0.71 in 3,7-DPTZ-DBTO₂, a factor of ca. 3 greater.

Orbital calculations also show that the mixed ax–eq donor conformation in 3,7-DPTZ-DBTO₂ (Figs 1b and 4) results in localization of the HOMO on one of the donor groups, giving rise to two distinct and energetically well-separated CT states ($D_{ax}^- > A$ and $D_{eq}^- > A$) as shown in Fig. 2b. The lower energy
The two distinct energies of the CT states relate to the electronic properties of the two PTZ conformers, H-intra and H-extra. In the H-extra orientation, which is the origin of CTax, there is less localization of the nitrogen lone-pair into the phenyl rings and a lowering of the HOMO energy. This will lead to a higher-energy CT state as observed, and a weaker CT via the weaker decoupling of donor and acceptor. This arises from the increased conjugation between the donor and acceptor mediated by the lone pairs in the axial conformer. Each regioisomer can, in principle, exhibit three different conformational isomers (ax–ax, eq–eq and ax–eq). The origin for the specific structures of 2,8-DPTZ-DBTO2 and 3,7-DPTZ-DBTO2 is energetic, as shown in Supplementary Table 4, using density functional computations (diagrams of all potential conformers are shown in Supplementary Figs 2–6 of our recent work). An example of how this method was used for Fig. 2a is shown in Supplementary Fig. 21, with extracted values in Supplementary Table 15. (c) The PLQY of the two isomers with and without oxygen in a zeonex host. The PLQY is shown as a function of excitation energy and the absorption is included to show the wavelength dependency. The error bars are the s.e. based on 10 repetitions for each excitation energy.

Figure 3 | High concentration band edge absorption as a function of solvent. (a) The band edge absorption of 2,8-DPTZ-DBTO2 in a variety of solvents at 1 mM concentration. The hypsochromic shift unveils the n–π* nature of the low-energy absorption in this molecule. (b) Conversely for 3,7-DPTZ-DBTO2 at 1 mM concentration there is no significant shift in the absorption thus emphasising the mixed nature of the absorption in this system.
degassing reveals that a significant fraction of increased intensity in the emission comes from 3LE phosphorescence (see Supplementary Fig. 11) in 3,7-DPTZ-DBTO2. To understand these differences and the effect of \( n^-\pi^* \) and \( \pi^-\pi^* \) character of its low-lying transitions preventing direct 1CT formation. The radiative decay of 4LED competes with electron transfer and ISC, which will reduce the overall yield of delayed emission.

Both regioisomers show higher PLQY in inert atmosphere as expected. 2,8-DPTZ-DBTO2 exhibits an increase in the PLQY (>40%) around the absorption band edge (~3 eV) due to the direct excitation of the 1CT states via the \( n^-\pi^* \) transition\(^{15}\). In 2,8-DPTZ-DBTO2 this PLQY increase is also seen in the absence of oxygen, indicating competition between 3LED and 1CT formation, a result of slow electron transfer\(^{13}\); however, the 3LED states formed from the 1LED are still harvested by rISC. The effect on PLQY clearly shows that the 1LED ISC is a very efficient quenching channel for the excited donor. The general increase in PLQY is also observed in 3,7-DPTZ-DBTO2 (when compared to the decreasing absorption cross section) but there is no sharp increase at the band edge. This is due to the strongly mixed \( n^-\pi^* \) and \( \pi^-\pi^* \) character of its low-lying transitions preventing direct 1CT formation.

The phosphorescence spectra of 2,8-DPTZ-DBTO2 and 3,7-DPTZ-DBTO2 in a zeonex matrix are shown in Fig. 6a. 2,8-DPTZ-DBTO2 shows contributions from both 3LE\(_A\) (2.70 eV) and 3LE\(_D\) (2.58 eV) phosphorescence as previously observed\(^{13}\), whereas the band shape in 3,7-DPTZ-DBTO2 exhibits less well-resolved vibronic components. From the phosphorescence onset, the energy of the lowest triplet state is 2.54 eV. This is below that of the 3LED in 2,8-DPTZ-DBTO2, and corresponds to the local donor triplet state of the H-extra PTZ, 3LED,\(_{ax}\). Critically, we note that the CT state onsets of this conformer are at ca. 3.1 eV (Fig. 2b), consequently the CT-3CT gap is much larger than that of the equatorial conformer, by ca. 0.5 eV and this gap is sufficiently large to make rISC unlikely, therefore only 3LED,\(_{ax}\) phosphorescence should be observed from this axial conformer. Energy transfer from 3LED,\(_{eq}\) to 3LED,\(_{ax}\) is improbable given the donors orthogonality and large spatial separation. This observation now helps to explain why in certain sterically hindered D–A–D systems where both PTZ donors are stabilized in the H-extra conformer, no delayed 1CT fluorescence (DF) at all is observed, only very strong room temperature phosphorescence, because the S-T gap is too large and the energetically low-lying axial triplet acts as a sink for all excitations\(^{27}\).

**Photoinduced absorption.** To confirm the presence of a 3CT,\(_{eq}\) population, which is the lowest energy triplet state of 3,7-DPTZ-DBTO2, photoinduced absorption (PIA)\(^{28}\) of the isomers in zeonex was measured (Fig. 6b). Both isomers show a characteristic, slightly structured induced absorption in the region of the 3LE,\(_D\),\(_{eq}\) \( \Gamma_1 \rightarrow \Gamma_N \) absorption\(^{29-31}\). This absorption is more
Figure 6 | Phosphorescence emission and the out of phase and differential PIA of the DPTZ-DBTO2 isomers. (a) The phosphorescence spectra are measured at 80 K in a zeonex matrix at 0.5 ms delay time. (b) The peak that is located below 2.4 eV in both spectra is attributed to the T1-TN absorption of phenothiazine. The broad absorption up to 1.4 eV found in 3,7-DPTZ-DBTO2 is attributed to the CT states emphasizing the energy diagram shown in Fig. 1c. The normalized differential is shown to emphasize the CT state PIA and the shift in the 3LE PIA.

defined in 2,8-DPTZ-DBTO2, and is consistent with population of this state by both directly photocreated 3LE states (ISC from 1CT) and those created via efficient ISC from 1CT. In contrast, 3,7-DPTZ-DBTO2 has an additional broad induced absorption between 2.2 and 1.4 eV, which is attributed to the 3CTeq state, and has characteristics similar to the donor cation (Supplementary Fig. 2), consistent with the 3CTeq state being the lowest energy state, and the observed DF lifetime of ca. 13.7 μs. The signal in 3,7-DPTZ-DBTO2 is also 5 times smaller than in 2,8-DPTZ-DBTO2, consistent again with the larger pool of triplet excitations initially formed in 2,8-DPTZ-DBTO2 but there is also a contribution in the 3,7-DPTZ-DBTO2 spectrum from this direct 3LE production channel.

Subtracting the normalized PIA signals of 2,8-DPTZ-DBTO2 from 3,7-DPTZ-DBTO2 the 3CTeq induced absorption in the 3,7-DPTZ-DBTO2 signal is elucidated and also a low-energy triplet PIA component, ~200 meV below that of the 3LEeq T1→TN transition, assigned to the 3LEeq,ax T1→TN transition. This supports that 3LEeq,ax is lower in energy than 3LEeq in 3,7-DPTZ-DBTO2.

Time-resolved spectroscopy. Figure 7 shows the emission decay profiles of the two isomers in degassed solutions (MCH and toluene; see Supplementary Table 5 for parameters). In all decay profiles, there are two characteristic time regimes; the first (early times) is related to prompt 1CT fluorescence (PF); the second (longer times) relates to the DF. This DF arises from excitations harvested from the triplet states (3LE) via rISC, as it is quenched by oxygen. The spectra of the prompt and delayed CT emission correspond exactly in both 2,8-DPTZ-DBTO2 and 3,7-DPTZ-DBTO2 and the DF has linear power dependency in both cases as expected for TADF (ref. 32; Supplementary Figs 13 and 14).

In 3,7-DPTZ-DBTO2, we observe fast emission from CTax appearing in the first couple of nanoseconds, however, the measurement system has insufficient time resolution to resolve it. In MCH the PF lifetime of 2,8-DPTZ-DBTO2 is twice that measured in 3,7-DPTZ-DBTO2, 15.4±0.9 ns compared to 7.7±0.3 ns, in line with the calculated oscillator strengths of the 1CT states of both isomers, 2.3×10−4 for 2,8-DPTZ-DBTO2 and 5.1×10−4 for 3,7-DPTZ-DBTO2. This reflects the π−π and π∗−π coupling of each to the ground state. The DF in 2,8-DPTZ-DBTO2 is 15 times stronger than 3,7-DPTZ-DBTO2, and has characteristics similar to the donor cation 19,20, which is attributed to the 3CTeq state. This supports that 3LED,ax is lower in energy than 3LED,eq in 2,8-DPTZ-DBTO2 (Fig. 7). This disparity is because of the enhanced population of 3LE states formed by direct ISC from the long-lived 4LE state in 2,8-DPTZ-DBTO2, compounded by excited states lost via the axial conformer channel in 3,7-DPTZ-DBTO2. This is a peculiarity of optical excitation and is different to the mechanisms that will occur in a device. The DF lifetime in 3,7-DPTZ-DBTO2 is found to be 3.8±0.2 μs and for 2,8-DPTZ-DBTO2 5.2±0.3 μs. The DF rate is a combination of the rISC rate and the 1CT radiative rate and the difference between 2,8-DPTZ-DBTO2 and 3,7-DPTZ-DBTO2 is a manifestation of the small oscillator strength of the former and the rISC rate of the Deq-A unit of 3,7-DPTZ-DBTO2 being half that of 2,8-DPTZ-DBTO2 (ref. 9; Fig. 8, with parameters shown in Supplementary Tables 6–8).

A factor of two increase in the prompt 1CT emission lifetime occurs when the molecules are in a more polar solvent (toluene). This increase is related to higher CT stabilization through the polar medium (Fig. 1c), which reduces the energy of the 1CT state and hence increases the energy gap between the CT and LE states, reducing the rate of ISC (ref. 7). The solvent also has an influence on the DF behaviour, decreasing the lifetimes from 5.2 to 1.0 μs in 2,8-DPTZ-DBTO2 and 3.0 to 2.6 μs in 3,7-DPTZ-DBTO2. The significant decrease in 2,8-DPTZ-DBTO2 is due to the larger energetic shift. Concomitantly the DF/PF ratio for 2,8-DPTZ-DBTO2 in toluene is reduced to 5 (ref. 13).

Photophysics in solid state. The decay profiles, along with the time-resolved emission for each isomer (dispersed in zeonex) are shown in Fig. 9a,b (see Supplementary Table 9 for parameters). For 2,8-DPTZ-DBTO2 the PF has two components, 3.3 and 24 ns, the former is 1LED emission contribution and the longer dominant contribution is from prompt 1CT emission (with very similar lifetime to that measured in MCH). The time-resolved spectra for 3,7-DPTZ-DBTO2, Fig. 9d, shows a clear early time contribution from the axial conformer in contrast to those for 2,8-DPTZ-DBTO2 (Fig. 9c). A 1CTax lifetime of 3.3 ns is accompanied by a prompt 1CTeq emission with a lifetime of 9.4 ns, similar to that measured in MCH, this is consistent with 1CTax having much more 1LE character than 1CTeq. Given the similar intensities of both contributions, the observation of the 1CTax emission in the MCH steady-state spectra and the small red-shift of the emission compared to the donor, we ascribe the fast component to the 1CTeq state. The viscosity of the surrounding media seems to have little effect on the initial decay. This is in accord with the observation of 1CTax and 1CTeq emission in solution, showing that both conformers are stable and do not interconvert in non-polar environments. The delayed fluorescence has a lifetime of 7.4 and 14 μs, for 2,8-DPTZ-DBTO2 and 3,7-DPTZ-DBTO2, respectively. 2,8-DPTZ-DBTO2 again shows more intense DF due to the far larger initial 3LE population with a very similar lifetime to that measured in MCH. In
3,7-DPTZ-DBTO₂, the DF lifetime is double that of 2,8-DPTZ-DBTO₂ indicating very inefficient rISC in keeping with the larger gap. Further, as can be seen in Fig. 9b the DF turns from an exponential into a power law decay. Such a power law decay component is observed in all solid-state samples to varying degrees and we ascribe this to inhomogeneity, that is, molecules with different torsion angles and environments giving rise to an energy dispersion in the CT-3LE gaps which causes a dispersion in rISC rates and thus lifetimes. Finally, phosphorescence is observed with lifetimes in the hundreds of microseconds for both molecules. In this time range the 2,8-DPTZ-DBTO₂ spectrum blue-shifts further than 3,7-DPTZ-DBTO₂, consistent with the stronger 3LEₐ contribution. This arises from 3LEₐ to 3LEₐ coupling in 2,8-DPTZ-DBTO₂, as confirmed by calculations shown in Fig. 8 and the phosphorescence in Fig. 6a. Although the energy gap between the 3LEₐ-3LEₐ states means that their coupling is only a minor perturbation to the ISC and rISC rates, it shows that there is a small population of 3LEₐ arising from the coupling. It is also responsible for the 3LE states in 2,8-DPTZ-DBTO₂ exhibiting a single lifetime, despite the 3LEₐ and 3LEₐ states having different phosphorescence lifetimes (130 and 64 μs, respectively)[10]. This is not present in 3,7-DPTZ-DBTO₂ due to the weaker coupling between the states; a result of their energetic ordering, that is, the low-lying CTₑq in zeonex. This type III arrangement and the larger gap between the 3LEₐ,ₐx and 3LEₐ states means that vibronic coupling is weakened.

We have measured the behaviour of 3,7-DPTZ-DBTO₂ in zeonex as a function of temperature (Supplementary Figs 15d and 16d and Supplementary Table 10). Given the rather weak emission, there is no prompt 1LE contribution, but emission from both 1CTₐx and 1CTₑq. The lifetimes of 1CTₐx is rather insensitive to temperature remaining at ca. 4 ns at 80 K. The 1CTₑq emission lifetime has a weak temperature dependence, however, the DF lifetime stays approximately constant at ca. 1.5 μs (within the fitting error) until ~150 K, when it then lengthens to ca. 4 μs at 80 K. This demonstrates weak thermal activation, consistent with a small CT-3LE gap in non-polar zeonex.

**Figure 7** | Plots of the integrated intensity of the emission of the molecules as a function of time. (a) 2,8-DPTZ-DBTO₂ and (b) 3,7-DPTZ-DBTO₂ in MCH solution and (c) 2,8-DPTZ-DBTO₂ and (d) 3,7-DPTZ-DBTO₂ in toluene solution.

**Figure 8** | Theoretical calculations of the rISC rate as a function of conformer and 3 versus 4 state coupling. (a) The rISC rate in D-A versions of the two isomers, showing that the D-A unit of 2,8-DPTZ-DBTO₂ is twice as efficient at rISC compared to the Dₑq-A unit of 3,7-DPTZ-DBTO₂. (b) Comparing the 3 and 4 state model showing that there is minimal change with the consideration of a fourth state (3LEₐ). Computational details for these simulations are shown in Supplementary Table 14.
Figure 9 | Emission decays and time-resolved spectra of the two isomers in zeonex. (a) Emission decay of 2,8-DPTZ-DBTO₂ in zeonex. (b) Emission decay of 3,7-DPTZ-DBTO₂ in zeonex. (c) Time-resolved spectra of 2,8-DPTZ-DBTO₂ in zeonex. (d) Time-resolved spectra of 3,7-DPTZ-DBTO₂ in zeonex.

In a dense matrix, CBP (Supplementary Figs 15a and 16a, and Supplementary Table 11), the decay of 2,8-DPTZ-DBTO₂ is very simple. A fast decay component with average lifetime ca. 5 ns from ¹LE₀ is observed, which is invariant for temperatures above 160 K. This is accompanied by a longer lifetime prompt ¹CTeq component, ca. 43 ns, which is constant with decreasing temperature (Supplementary Fig. 15a and Supplementary Table 11). We assume CBP prevents most non-radiative decay apart from ISC, so this behaviour reflects the very small CT - 3LE gap in CBP and the down-hill nature of the ISC. The DF component shows a clear monotonic increase in lifetime with decreasing temperature, from 6µs at 300 K (the same as in zeonex) to 16 µs at 80 K. This is simply due to the decreasing thermal activation and rISC rate, and reflects the up-hill nature of rISC in 2,8-DPTZ-DBTO₂. Turning to 3,7-DPTZ-DBTO₂ in CBP (Supplementary Figs 15c and 16c and Supplementary Table 12), the prompt decay contains three well-defined exponentially decaying components; we observe a 1 ns signal corresponding to the ultrafast decay of the ¹LE₀ state, the ¹CTax component with a temperature invariant lifetime ca. 6.5 ns, and ¹CTeq decay with lifetime ca. 23 ns. The DF component in 3,7-DPTZ-DBTO₂ decays faster than in 2,8-DPTZ-DBTO₂, a result of the slower rISC and larger radiative rate of ¹CTeq decay in 3,7-DPTZ-DBTO₂; which is temperature dependent. The lifetime increases from 2.5 µs at 300 K to 14 µs at 80 k reflecting the decreasing thermal energy available to drive the vibronic coupling mechanism. 3,7-DPTZ-DBTO₂ in CBP also has a very large power law decay component, which competes with the ‘exponentially decaying DF’. This behaviour is strong in CBP because the samples are made by vacuum co-deposition, so 3,7-DPTZ-DBTO₂ molecules have significant thermal energy and are rapidly ‘frozen’ in a particular geometry during deposition. In zeonex, films are deposited from solution so have more time and free volume to attain equilibrium geometry. 3,7-DPTZ-DBTO₂ has greater inhomogeneity than 2,8-DPTZ-DBTO₂ because of its non-symmetric eq-ax mixed conformer structure. Thus, a large proportion of the DF will have a longer lifetime and in a device, using a CBP host, we would expect this to manifest itself as increased efficiency roll-off at high drive currents. The time-resolved spectra of 2,8-DPTZ-DBTO₂ and 3,7-DPTZ-DBTO₂ in CBP at room temperature can be found in Supplementary Fig. 17.

To observe the effect of a changing CT-3LE gap and temperature on the decay trends, we measured 2,8-DPTZ-DBTO₂ decays in a polyethylene oxide host, the polarity of which changes with temperature (Supplementary Figs 15b and 16b and Supplementary Table 13). We have shown that DF reaches a resonant maximum at the point when the CT-3LE gap approaches zero, verifying the second-order spin-vibronic mechanism in this system². The fits of the emission decay curves at different temperatures show that the prompt ¹CTeq lifetime also follows the resonant behaviour, reaching the longest lifetime of 47 ns at the CT-3LE zero gap point. This can be rationalized because with increasing coupling of ¹CT-3LE as the gap diminishes, a mixed state evolves where the ¹CT lifetime lengths (towards that of 3LE) and that of the 3LE shortens. At low temperatures, where the gap grows again, the temperature dependence of ISC dominates and the lifetime remains high because of low ISC. The DF follows a similar trend as expected from the theory⁹,¹¹ but the lengthening of the DF lifetime is even greater. From these results, we see that the CT-3LE gap dominates ISC and rISC rates whilst temperature has a far smaller effect, especially when the gap is small. For 2,8-DPTZ-DBTO₂ in MCH, where there is a small gap, this resonant lifetime increase may also play a part.

OLED device characterization. The electroluminescence spectra of the devices made from both isomers are similar to the prompt and delayed fluorescence of the pure emitters (Supplementary Fig. 18b). The maximum external quantum efficiency (EQE) of 2,8-DPTZ-DBTO₂ devices was higher (18.2%) compared to 13.3% for 3,7-DPTZ-DBTO₂ (Fig. 10). This difference is ascribed
to charge-recombination populating both axial and equatorial conformers in 3,7-DPTZ-DBTO2. Even though the rISC rate is faster and the radiative decay rate of the 3,7-DPTZ-DBTO2 1CT state is twice that of 2,8-DPTZ-DBTO2 this loss channel has a marked effect on device efficiency. Given that 3LE\textsubscript{ax} effectively quenches the CT\textsubscript{ax} states, the long residence time in 3LE\textsubscript{ax} makes them highly susceptible to polaron excitation quenching in the device\textsuperscript{33}. Note, charge-recombination directly creates CT states, not initial 1LE\textsubscript{0} states\textsuperscript{13}. This emphasizes that donor or acceptors that have multiple conformers are problematic for efficient TADF OLEDs.

To further understand the differences that the isomeric structures introduce to device performance, devices of 2,8-DPTZ-DBTO2 and 3,7-DPTZ-DBTO2 were also made in a polar DPEPO host\textsuperscript{14}. From optical measurements the CT-3LE gap is larger and both systems have slow rISC rates. Again, we find that 2,8-DPTZ-DBTO2 yields devices, at 7% EQE, that are 1.75 times more efficient than 3,7-DPTZ-DBTO2 at 4% EQE (Supplementary Fig. 19) concomitant with the reduced rISC efficiency and axial loss channel in 3,7-DPTZ-DBTO2. Further, we see a stronger efficiency roll-off in the 3,7-DPTZ-DBTO2 devices through increased polaron excited state quenching.

**Discussion**

This study of D–A–D regioisomers has established that the different arrangement of the D and A units between 2,8 (2,8-DPTZ-DBTO2) and 3,7 (3,7-DPTZ-DBTO2) stabilizes different conformations of the PTZ units and increases conjugation between donor and acceptor in the 3,7 isomer. In the 3,7 isomer the quasi-equatorial CT, arising from the H-intra PTZ conformer has a lower CT energy that is in resonance with its local triplet state, 3LE\textsubscript{eq} and yields efficient TADF. Whereas, the H-extra PTZ conformer is also stabilized in the case of 3,7-DPTZ-DBTO2. The presence of this mixed conformer structure allows dual CT emission in the system, with the quasi-axial CT state arising from the H-extra PTZ conformer. This state is higher in energy and does not undergo rISC or TADF as a result because of its low-energy 3LE\textsubscript{ax} triplet (of this axial CT). This then acts as an effective loss pathway due to this lower-lying ‘local axial triplet’. This additional loss channel in 3,7-DPTZ-DBTO2 is responsible for the reduced device performance compared to 2,8-DPTZ-DBTO2 because CT excitations are created directly via charge-recombination and so either the quasi-equatorial CT or quasi-axial CT state is populated statistically during charge recombination in a device. This explains why in other D–A–D systems with both PTZ donors in the H-extra conformer no DF at all is observed because of this large S-T gap and low-lying axial triplet ‘trap’\textsuperscript{27}. In general, a further result of the required vibronic coupling of the 1CT and 3LE states for efficient rISC and ISC means that when the S–T gap is very small, near zero, the CT and 3LE states mix very effectively and the lifetime of the CT state increases through this strong state mixing. In the two isomers studied here, we show how the different conformers are stabilized differently on each isomer yielding different TADF efficiency. Accordingly, we can say that flexible donors and acceptors that exhibit multiple conformers should be avoided in TADF material design\textsuperscript{34,35}. Planar donor and acceptor structures are better suited for TADF as they will avoid such conformationally different structures and losses. Further, isomer effects can be used to control the stabilization of different D–A conformers. These new observations and theoretical predictions show how even subtle changes in D–A–D structure radically effect the excited state behaviour and resultant photophysical properties of charge transfer molecules giving a further set of design criteria to be considered.

**Methods**

**Optical characterization.** Optical measurements in solution used concentrations in the 10\textsuperscript{−3}–10\textsuperscript{−2} M range, and samples were deoxygenated using 5 freeze/thaw cycles. (2,8-DPTZ-DBTO2/3,7-DPTZ-DBTO2):zeonex films were prepared by spin coating at a ratio of 1:20 w/w. (2,8-DPTZ-DBTO2/3,7-DPTZ-DBTO2):CBP films were prepared by co-evaporation (10% weight of dopant). Absorption and emission spectra were collected using a UV-3,600 double beam spectrophotometer (Shimadzu), and a Fluorolog fluorescence spectrometer (Jobin Yvon).

**Time-resolved emission decay.** Phosphorescence, prompt fluorescence (PF), and delayed emission (DF) spectra and decays were recorded using nanosecond gated luminescence and lifetime measurements (from 400 ps to 1 s) using either a high-energy pulsed Nd\textsubscript{2}Y\textsubscript{3}MG laser emitting at 355 nm (EKSPLA) or a N\textsubscript{2} laser emitting at 337 nm. Emission was focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics) having sub-nanosecond resolution\textsuperscript{24}.

**Photoinduced absorption.** The quasi-CW PIA measurements of the excited state absorption (and emission) spectra\textsuperscript{25}, were performed using a 375 nm pump beam (Vortran Stradus 375-60) modulated at 73 Hz, with a continuous laser driven white light source (Energietec EQ-99X) as the probe. The probe beam was then passed through a Bentham TM300 monochromator and incident on a Si detector connected to the Signal Recovery dual channel 7,225 digital lock-in amplifier that also provides the reference frequency modulation for the pump laser.

**Photoluminescence quantum yield.** The PLQY measurements were performed using a Quantaurus-QY Absolute PL quantum yield spectrometer. Initially a background was taken using a clear substrate and then the (2,8-DPTZ-DBTO2/3,7-DPTZ-DBTO2):zeonex films were measured both under N\textsubscript{2} and in air.

**Device fabrication.** All organic evaporated compounds were purified by vacuum sublimation using a Creaphys organic sublimation system. The suppliers and the full chemical names of the materials used are as follows: CBP–4,4′-bis...
Quantum chemistry. Quantum dynamics simulations probing the mechanism for efficient rISC were performed using the density operator formalism of the multi-dimensional time-dependent Hartree method. Here we adopt a closed quantum system, using the Hamiltonian described in ref. 6. The energy gap between the \( ^1\text{CT} - ^3\text{CT} \) states was as calculated in ref. 20, however the gap between the \( ^3\text{LE} - ^3\text{CT} \) states was extracted experimentally. The full details of the simulations and the model Hamiltonians used is provided in the Supplementary Information.

Data availability. Data supporting this publication are openly available under an ‘Open Data Commons Open Database License’. Additional meta-data are available at: 10.17634/153015-2. (theoretical) and 10.15128/r27d6v7h84t (experimental). Please contact Newcastle Research Data Service at rdms@ncl.ac.uk for access instructions.

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