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Controlling through-space and through-bond intramolecular charge transfer in bridged D–D'–A TADF emitters†

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Donor–donor'–acceptor molecules where the donor' bridges the donor and acceptor have different possible interaction pathways for charge transfer. Here we study a series of donor–donor'–acceptor molecules, having the same acceptor and donor' but different donors, and donor'–phenyl spacer–acceptor to change the spatial separation and overlap between potential through-space donor–acceptor charge transfer (CT) in competition with donor'–acceptor through-bond CT. We determine that the charge transfer driving force plays a large role in dictating which charge transfer channel is favoured. Strong donors and acceptors with large driving force favour through-space CT. We also find that solid state host packing plays an important role, with small molecule hosts that pack tightly, distorting the guest molecules, reducing D–A separation to stabilise the through-space CT state over the through-bond state. Only the through-space CT states give fast reverse intersystem crossing and efficient TADF. These results give the first insight into the photophysics of through-space CT compared to through-bond states on the same molecule.

Introduction

Organic molecules showing thermally-activated delayed fluorescence (TADF) are considered as the third generation of materials for organic light-emitting diodes (OLEDs).¹ Unlike phosphorescent emitters, TADF molecules harvest triplet excitons by a reverse intersystem crossing (rISC) mechanism

between the triplet (³CT) and the singlet (¹CT) charge-transfer states, mediated by vibronic coupling between ³CT and a local excited triplet state (³LE) that enables spin orbit coupling (SOC), when the energy gap between all three states becomes small, <100 meV. Mediation by the third state is required when ³CT and ¹CT are so close in energy because direct spin orbit coupling (SOC) between them is forbidden because they have effectively the same orbital and no change in orbital angular momentum occurs during the direct transition ³CT → ¹CT.^{2,3} One of the simplest ways to achieve extremely small electron correlation energy, *i.e.* singlet–triplet splitting energy (ΔE_{ST}), is the use of conformational twisting between directly bridged donor (D) and acceptor (A) units in order to minimize the overlap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).^{4,5} Beyond the subtle manipulations of the degree of intramolecular through-bond charge transfer to control TADF properties, recent interest in through-space charge transfer between D and A, mediated by strong D A intramolecular π – π dipolar interactions has been motivated by the potential of increasing photoluminescence quantum yield.^{6,7} Such intramolecular through-space charge transfer is much like an exciplex state except that it offers far more control over the spatial separation and orientation of D and A compared to the random orientation of D and A in the intermolecular exciplex state. In a conjugated system, the D and A can be arranged co-facially, in close spatial proximity, using a non-coplanar molecular scaffold (bridge).⁸ This approach has also been used in the design of non-conjugated polymers with spatially separated pendant D and A.^{9,10} Despite the growing interest of intramolecular through-space charge transfer states as a means to TADF, very little photophysical study of the excited state dynamics and molecular conformations of such systems has been made.¹¹ Here we investigate the excited state dynamics of new molecules configured with asymmetrical donor–donor'–acceptor (D–D'–A) architectures, where the co-facial overlap between D and A is controlled by the introduction of a common

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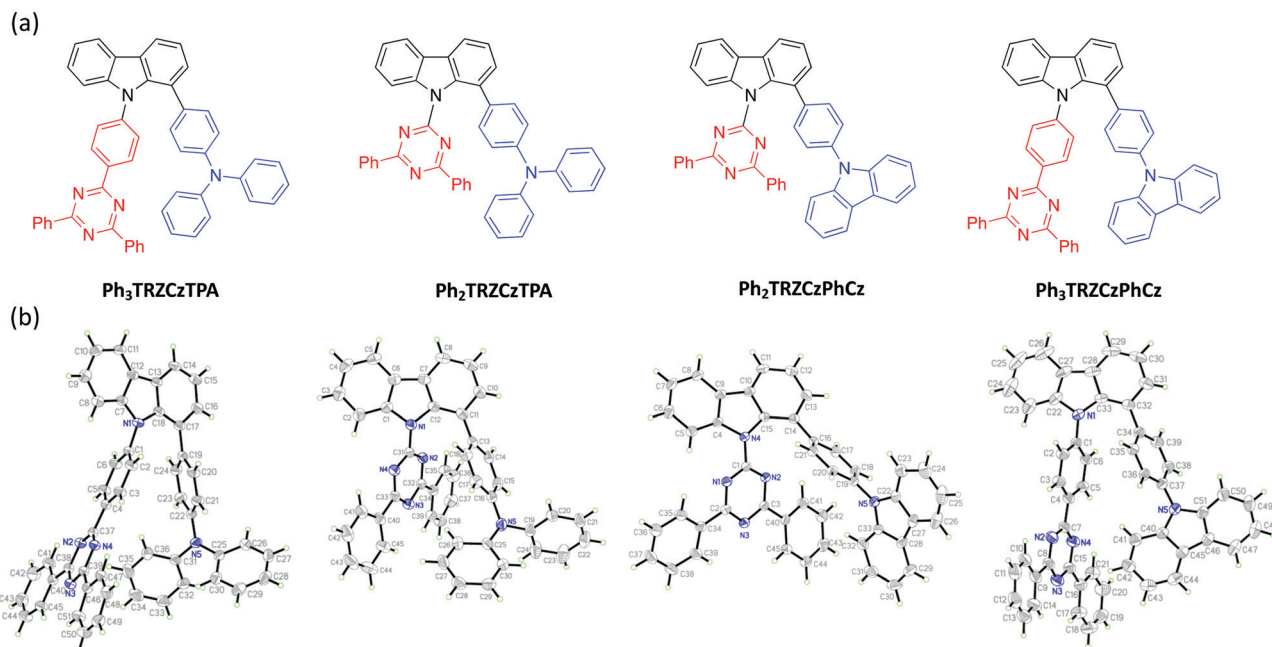
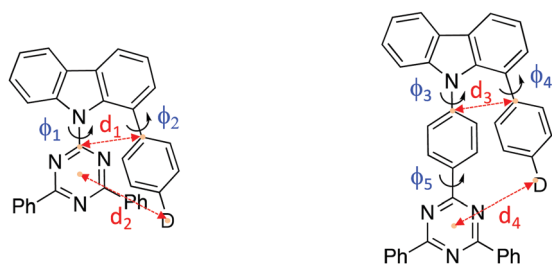


Fig. 1 The chemical structures (a) and X-ray structures (b) of **Ph₃TRZCzTPA**, **Ph₂TRZCzTPA**, **Ph₂TRZCzPhCz** and **Ph₃TRZCzPhCz**, thermal ellipsoids were drawn at a 50% probability level.

Table 1 The dihedral angles and distances of **Ph₂TRZCzTPA**, **Ph₃TRZCzTPA**, **Ph₂TRZCzPhCz**, and **Ph₃TRZCzPhCz**

	φ_1 (°)	φ_2 (°)	φ_3 (°)	φ_4 (°)	φ_5 (°)	d_1 (Å)	d_2 (Å)	d_3 (Å)	d_4 (Å)
Ph₂TRZCzTPA	49.3	55.2				3.093	4.985		
Ph₂TRZCzPhCz	36.5	47.1				3.373	4.926		
Ph₃TRZCzTPA			75.1	70.9	0.6			3.150	5.295
Ph₃TRZCzPhCz			65.4	57.8	2.5			3.201	4.924



weak (rigid) carbazole donor bridge (D') and by the introduction of phenyl spacer units between the acceptor and bridge, shown in Fig. 1. A common diphenyltriazine (dTRZ) acceptor is used and either a weak phenyl carbazole (PhCBZ) or strong triphenylamine (TPA) donor.

Results

Synthetic methods and characterization of these new D–D'–A molecules and model compounds used in this study are reported in ESI† (Scheme S1–S3). Fig. 1b shows their single crystal structures and crystallographic data is summarized in Table S1 (ESI†). As shown, the pendant (spacer) aryl rings are

highly twisted from the carbazole bridge (D') due to congested steric interactions. All dihedral angles between the D, A and bridging D', selected closest atom-to-atom distances between the donor and the acceptor branches (3.09–3.37 Å), and distances between the donor N-atom and the centre of triazine acceptor ring (4.93–5.30 Å) are summarized in Table 1.

In general, **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** (triphenylamine donor) show larger donor-bridge dihedral angles as compared to those of the counterpart **Ph₂TRZCzPhCz** and **Ph₃TRZCzPhCz** (PhCBZ donor). In addition, **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** show shorter closest atom-to-atom distances, but slightly longer distances between the donor N-atom and the centre of triazine ring. These distorted conformations and short distances imply that a through-space interaction between the donor and acceptor branches due to the stronger electron-donating ability of TPA may stabilize the twisted molecular structures. All of the molecules show excellent thermal stability required for stable film and device formation, and calculated HOMO/LUMO energy levels obtained from cyclic voltammetry (Fig. S1, ESI†) are given in Table 2. **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** show higher HOMO energy levels (–5.28/–5.27 V) as compared to **Ph₂TRZCzPhCz** and **Ph₃TRZCzPhCz** (–5.85/–5.57 V) in accord with donor strength. Since the acceptor of all compounds is the same, the LUMO energy levels are similar (*ca.* –2.75 V) in all cases.

DFT calculations

The ground state structures were first optimized at a B3LYP/6-311G(d) level. The calculated HOMO and LUMO distributions as well as energy levels are shown in Fig. S2 (ESI†). The HOMOs of **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** are mainly located at the



Table 2 The electrochemical properties and thermal properties of **Ph₂TRZCzTPA**, **Ph₃TRZCzTPA**, **Ph₂TRZCzPhCz**, and **Ph₃TRZCzPhCz**

	$E_{\text{onset}}^{\text{oxi}}$ ^a (V)	$E_{1/2}^{\text{red}}$ ^b (V)	HOMO ^c (eV)	LUMO ^c (eV)	E_g^d (eV)	T_d^e (°C)	T_g^f (°C)	T_m^f (°C)
Ph₂TRZCzTPA	0.98 ^b	−1.45	−5.28	−2.73	2.55	324	111	212
Ph₃TRZCzTPA	0.97 ^b	−1.53	−5.27	−2.74	2.53	389	111	279
Ph₂TRZCzPhCz	1.21	−1.47	−5.85	−2.79	3.06	340	127	n.d. ^g
Ph₃TRZCzPhCz	1.23	−1.50	−5.57	−2.77	2.80	419	129	338

^a Calculated from the onset potential. ^b $E = (E_{\text{p,a}} + E_{\text{p,c}})/2$, where $E_{\text{p,a}}$ and $E_{\text{p,c}}$ stand for the peak potential at which anodic- and cathodic-direction scan, respectively. ^c HOMO and LUMO were determined from the electrochemical results in CH₂Cl₂ and DMF solution, respectively. ^d $E_g = \text{LUMO} - \text{HOMO}$ using electrochemical results. ^e T_d was analyzed using TGA (5% weight loss). ^f T_g and T_m were determined by DSC.

^g Not detected.

TPA moiety and slightly extend to the carbazole bridge. The HOMOs of **Ph₂TRZCzPhCz** and **Ph₃TRZCzPhCz** are mostly positioned at the pendant PhCBZ donor with limited contribution from the carbazole bridge. Not surprisingly, the LUMOs of **Ph₂TRZCzTPA** and **Ph₂TRZCzPhCz** are located at the dTRZ, which are well separated from their HOMOs. Whereas, the LUMOs of **Ph₃TRZCzTPA** and **Ph₃TRZCzPhCz** are located at the TRZ together with a small contribution on the carbazole bridge, giving weak but non zero HOMO–LUMO overlap. Obviously, the stronger donor, TPA, leads **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** to have higher HOMO levels as compared to those of **Ph₂TRZCzPhCz** and **Ph₃TRZCzPhCz**. Whereas **Ph₂TRZCzTPA** and **Ph₂TRZCzPhCz** without the aryl spacer between acceptor and bridge show slightly lower LUMOs. The calculated results are consistent with the observed CV data.

TD-DFT calculations were then made using a hybrid meta-generalized gradient-approximation functional, m06-2x/6-311(d), to optimize the S_1 and T_1 structure of these four molecules and calculate the natural transition orbitals (NTOs). The HONTO and LUNTO distributions are shown in Fig. S3 (ESI[†]). For the S_1 state of **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA**, the HONTOs distribute on the TPA moiety, while the LUNTOs delocalises at the dTRZ and TRZ, respectively. Since there is nearly no overlap between the HONTO and LUNTO, a through-space charge transfer character for the S_1 state is suggested. For the T_1 state configuration, the HONTO of the **Ph₃TRZCzTPA** is delocalised on the TPA and TRZ, exhibiting both CT and LE transition character. On the other hand, the HONTO of the **Ph₂TRZCzTPA** only distributes on the dTRZ, indicating the

^3LE state is the lowest triplet state. Notably, a distinguishable change between the S_1 and T_1 orbitals could be observed for **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA**, which is a prerequisite for an allowed SOC spin-flip transition. Very interestingly, the different orbital distributions of S_1 and T_1 states could also be observed in the case of **Ph₂TRZCzPhCz**. The HONTO of the S_1 state distributes on the PhCBZ donor and the carbazole bridge, while the LUNTO locates on the dTRZ. On the other hand, the HONTO of the T_1 state of **Ph₂TRZCzPhCz** delocalises mainly on the dTRZ group and slightly on the phenylene of the pendant PhCBZ donor, whereas the LUNTO only locates on the dTRZ group. Thus, **Ph₂TRZCzPhCz** is anticipated to possess both through-bond and through-space CT character due to the slight overlap of HONTO and LUNTO. For **Ph₃TRZCzPhCz**, the HONTO of the S_1 state distributes on the pendant PhCBZ, whereas the LUNTO distributes on the TRZ group, leading to a through-space CT transition character. The HONTO and LUNTO distributions of the T_1 state are similarly delocalised on the PhCBZ and slightly coupled with the carbazole bridge, resulting in an apparent LE transition character. Although **Ph₃TRZCzPhCz** shows considerable orbital deformation between S_1 and T_1 states, the larger ΔE_{ST} undermines the probability of reverse intersystem crossing process.

Steady state photophysics

Steady state absorption and emission of each compound was measured in methycyclohexane (MCH) are shown in Fig. 2a and b, and in a range of different polarity solvents and solid state hosts in Fig. 3, for direct comparison.

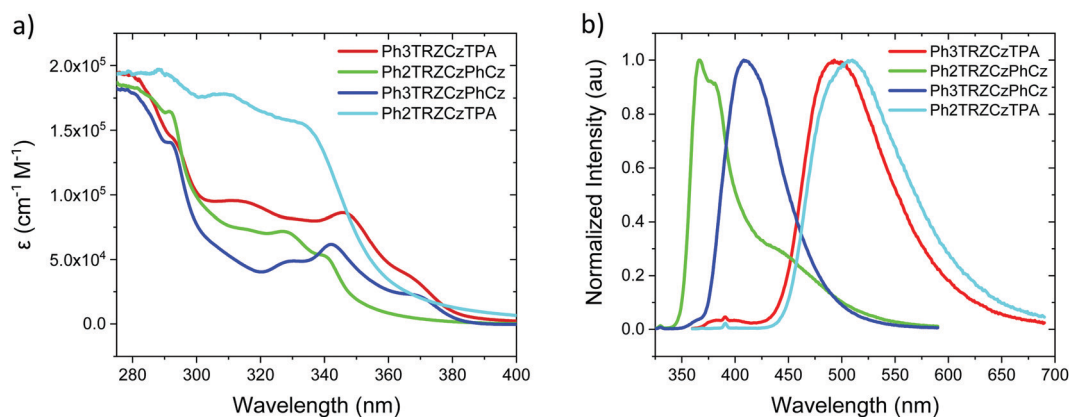


Fig. 2 Extinction coefficients (a) and emission spectra (b) of the molecules in MCH solution (20 $\mu\text{M L}^{-1}$).



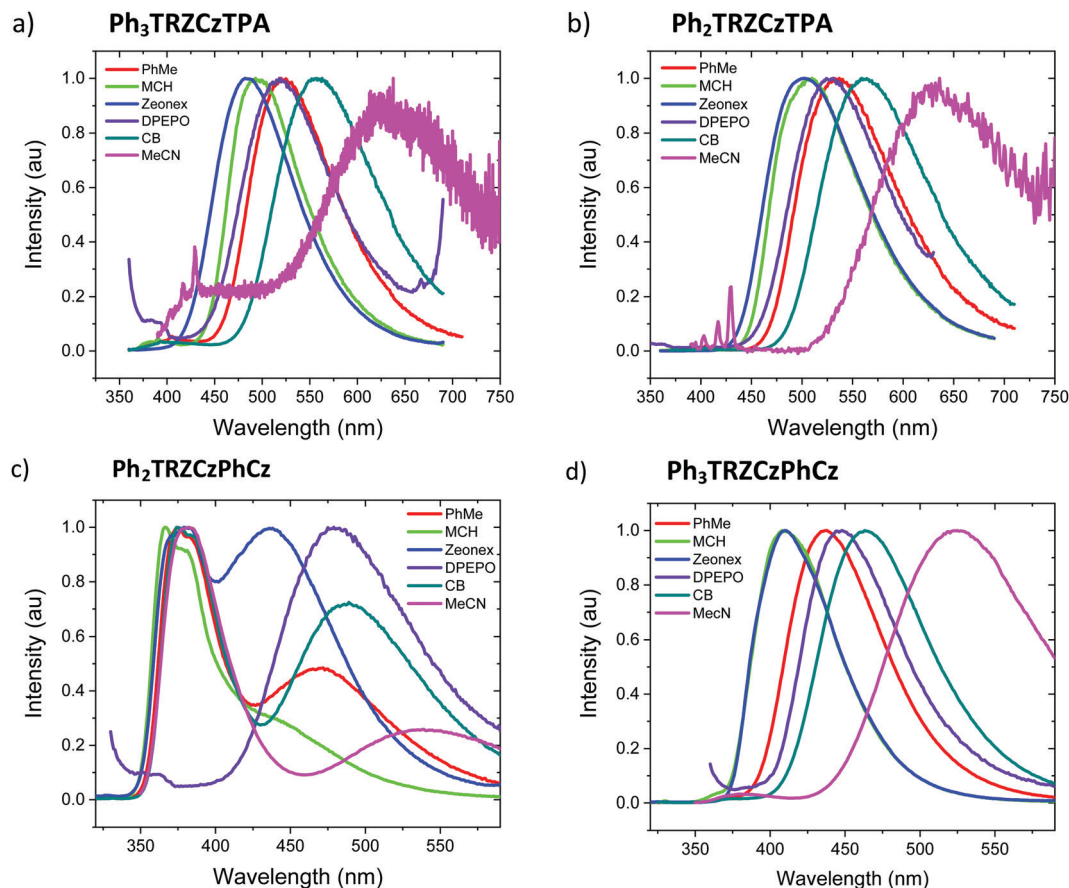


Fig. 3 Emission spectra of the compounds (a) **Ph₃TRZCzTPA**, (b) **Ph₂TRZCzTPA**, (c) **Ph₂TRZCzPhCz** and (d) **Ph₃TRZCzPhCz** in film and different solvents, methylcyclohexane (MCH), chlorobenzene (CB) and acetonitrile (MeCN).

The lowest energy absorption band, peaking at *ca.* 375 nm in **Ph₃TRZCzPhCz** and **Ph₃TRZCzTPA** is absent in **Ph₂TRZCzTPA** and **Ph₂TRZCzPhCz**. In **Ph₃TRZCzPhCz** this band correlates very well to the lowest energy absorption band in the model compound, 9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9*N*-carbazole, **CzPhTrz**, as observed by Sharma *et al.*,¹² having strong $\pi\pi^*$ character, and indicates a more delocalised acceptor unit, *i.e.* the phenyl spacer between A and bridge forms part of the acceptor unit itself in both cases, as suggested by our TD-DFT calculations. The magnitude of the extinction coefficients of these lowest energy bands is also $> 2 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ indicating that they are not direct CT absorption bands as observed in typical D–A–D through bond TADF molecules.⁴

Emission spectra measured for each compound in MCH, Fig. 2b, show energy on-sets at; 2.89 eV, 2.79 eV, 3.59 eV and 3.32 eV for **Ph₃TRZCzTPA**, **Ph₂TRZCzTPA**, **Ph₂TRZCzPhCz** and **Ph₃TRZCzPhCz**, respectively. **Ph₂TRZCzPhCz** gives dual emission in MCH from a local donor at 3.59 eV and a charge transfer (CT) state at lower energy, in excellent agreement with the TD-DFT calculations. **Ph₂TRZCzTPA** emission shows some mixed local/CT character, indicated by the weak structure on the emission band. The stronger donor strength of **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** is clearly manifest by the large Stokes shift observed in their CT emission spectra. With increased solvent polarity, Fig. 3. **Ph₃TRZCzTPA**,

Ph₂TRZCzTPA, and **Ph₃TRZCzPhCz** all show strong solvatochromism, giving a positive Stokes shift indicative of CT emission. Emission of **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** in MeCN is highly red shifted and extremely weak indicating very low emission yields.

In general, the molecules with a Cz donor emit at higher energy than those having a TPA donor, in line with donor strength. This also dictates the driving force for charge transfer in each pair. The CT driving force may be estimated from the following equation;

$$\Delta G_0 = EA_A - EA_D - \Delta E_b$$

Where EA_x are the electron affinity of A and D fragment respectively, and ΔE_b is the difference in binding energy between the initially created exciton and the relaxed charge separated state, see Scheme S3 (ESI†). In the case of these rigid orthogonal intramolecular D A molecules we assume that this difference in binding energy to be very small in non-polar media. Taking the measured (electrochemical) ionization potentials for the two families as that of the D units, the EA of the D units were estimated by adding the D optical excitation energy, yielding $EA_{Cz} = -2.21 \text{ eV}$ and $EA_{TPA} = -1.76 \text{ eV}$. The measured EA of the A unit in all cases being -2.75 eV from the CVs. For **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** we then estimate a CT driving force of *ca.* 1 eV, and for **Ph₂TRZCzPhCz** and



Ph₃TRZCzPhCz, *ca.* 0.5 eV. We thus find a near double CT driving force for **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** compared to **Ph₂TRZCzPhCz** and **Ph₃TRZCzPhCz**. It is interesting to note that for these rigid D–A intramolecular systems, in non-polar environment (minimising the Coulomb attraction energy) we also find that the difference between the (optical) D exciton energy and CT energy also gives very similar values, 0.8 eV for **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** and 0.5 eV for **Ph₂TRZCzPhCz** and **Ph₃TRZCzPhCz**, yielding a potential very simple way to estimate the driving energy for photoexcited charge transfer in highly decoupled intramolecular D–A molecules.

The solution measurements for **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** are similar as can be seen in Fig. 3a and b, the bands shift by the same amount in different polarity solvents. Comparing the film spectra, we see that the zeonex films behave just like the MCH solutions for these materials with **Ph₃TRZCzTPA** even showing a small blue shift compare to MCH. **Ph₂TRZCzPhCz** also shows the same ¹LE and ¹CT dual emission bands, but the CT state has increased relative intensity in zeonex. However, in DPEPO films, no ¹LE component is observed from **Ph₂TRZCzPhCz**, only the ¹CT emission is observed, at about the same peak wavelength as the corresponding **Ph₂TRZCzPhCz** CT emission in toluene solution.

Ph₃TRZCzPhCz, Fig. 3d, is seen to have a very similar spectrum with weakly structured emission in MCH compared to the model systems CzPhTrz¹² and *meta*-CzTRZ reported by Liu *et al.*¹³ Thus, we ascribe its excited state as a through-bond CT state between the bridge Cz and TRZ D'–A pair. The CT state shows both weak solvatochromism and in solid state the emission has very similar band shape and width as in solution, mostly unaffected by host packing effects. Only in highly polar MeCN does the band become highly red shifted and very broad, which may point to a different excited state origin such as a through-space CT state.

Ph₂TRZCzPhCz on the other hand is obviously different, being the only compound showing dual CT emission and very strong local emission, consistent with the X-ray data that shows a shallow 36.5° dihedral angle between D'–A. Cz donor units tend to have shallow ground state D–A dihedral angles giving strong LE character.¹⁴ This is further emphasised by the localisation of the HOMO on the pendant Cz unit found in our DFT calculations. We therefore synthesised the model compound, 2-(carbazol-9-yl)-4,6-diphenyl-1,3,5-triazine (**CzTrz**), Fig. S4 (ESI†). The absorption spectrum of **CzTrz** indicates electronically decoupled D and A units, absorbing above 350 nm. Excitation into the A (TRZ) band yields both TRZ¹⁵ and weak CT emission, whereas excitation into the D (Cz) band yields strong CT emission, onset at 3.26 eV. The CT emission on-set shifts to 3.1 eV in toluene and dominates the emission spectra. This shift is 35 nm more to the red than for the model **CzPhTrz** in toluene, which we ascribe to a smaller electron hole separation in **CzTrz** therefore larger Coulomb attraction energy, which is relaxed more strongly by the increasing solvent polarity red shifting the energy of the CT state to a greater extent.¹⁶ This clearly corresponds with the CT state seen in **Ph₂TRZCzPhCz** which can then be identified as a through-bond

CT state between the bridge Cz (D') and dTRZ unit. The higher intensity, narrow linewidth blue emission band with vibronic structure, also observed in **Ph₂TRZCzPhCz**, onset *ca.* 3.54 eV, showing little or no solvatochromic shift, must be emission from a local excited state. Considering the individual D and A units in the molecule, PhTRZ is only very weakly emissive through excitation at 280 nm, emission onset at 3.44 eV, with slight vibronic structure.¹⁵ Emission in our model **CzTrz** peaking at *ca.* 290 nm seems highly plausible to be from the dTRZ unit. This is not what we observe in **Ph₂TRZCzPhCz**, however, carbazole shows strong emission, onset at 3.54 eV¹⁷ and so we conclude that this local emission band in **Ph₂TRZCzPhCz** comes from the pendent Cz D unit, consistent with the DFT calculations. This Cz must be strongly decoupled from the rest of the molecule as the emission is always present even in high polarity solvent, ruling out a through-space CT state. In highly polar MeCN, there is a small population of CT states in giving rise to the highly red shifted band which we believe to be through-space CT states, Fig. 3c.

With this in mind, we turn to **Ph₂TRZCzPhCz** in zeonex (a branched polyolefin) and DPEPO (bis[2-(diphenylphosphino)phenyl]ether oxide) host films. In both cases the CT band is much stronger than in solution. In zeonex dual emission is still observed but the CT emission has equal intensity to the local emission, whereas in tightly packed DPEPO host, only a strong, red shifted and very broad CT emission is observed. As there can be no 'solid state solvatochromic effect' in a rigid solid host,^{18,19} this must be due to a packing effect of the host. If the host forces the D and A units closer together, improving co-facial overlap, a through-space CT state can be stabilized and the increased charge transfer rate would effectively quench donor emission from the pendent Cz unit. Thus, in DPEPO we conclude that a through-space CT state is stabilized on **Ph₂TRZCzPhCz**, in-line with TD-DFT calculations that strongly suggest both through-space and through-bond CT states are possible. We also note that this CT emission band in DPEPO is much broader and more red shifted than the CT emission observed from **Ph₃TRZCzPhCz** in DPEPO. This we believe indicates a very inhomogeneous process stabilising the through-space CT state, clearly in-line with random host packing effects. The stable through-bond CT state in **Ph₃TRZCzPhCz** remains narrow in DPEPO, which potentially indicates that the extra flexibility introduced by the spacer phenyl ring enables closer co-facial separation of D and A stabilising the through-space CT state so that host packing has little extra effect on this conformation. To confirm this hypothesis we measured **Ph₂TRZCzPhCz** in both mCP (1,3-bis(*N*-carbazolyl)benzene) and CBP (4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl) hosts, both having very low dielectric and polarizability values compared in DPEPO. In both cases clear CT emission is observed from **Ph₂TRZCzPhCz**, Fig. S5 (ESI†), confirming that host packing plays a major role in stabilising through-space CT in these materials.

To understand **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** we recall an important observation from our previous work. A CT complex can form between TRZ and TPA in solution.¹¹ The



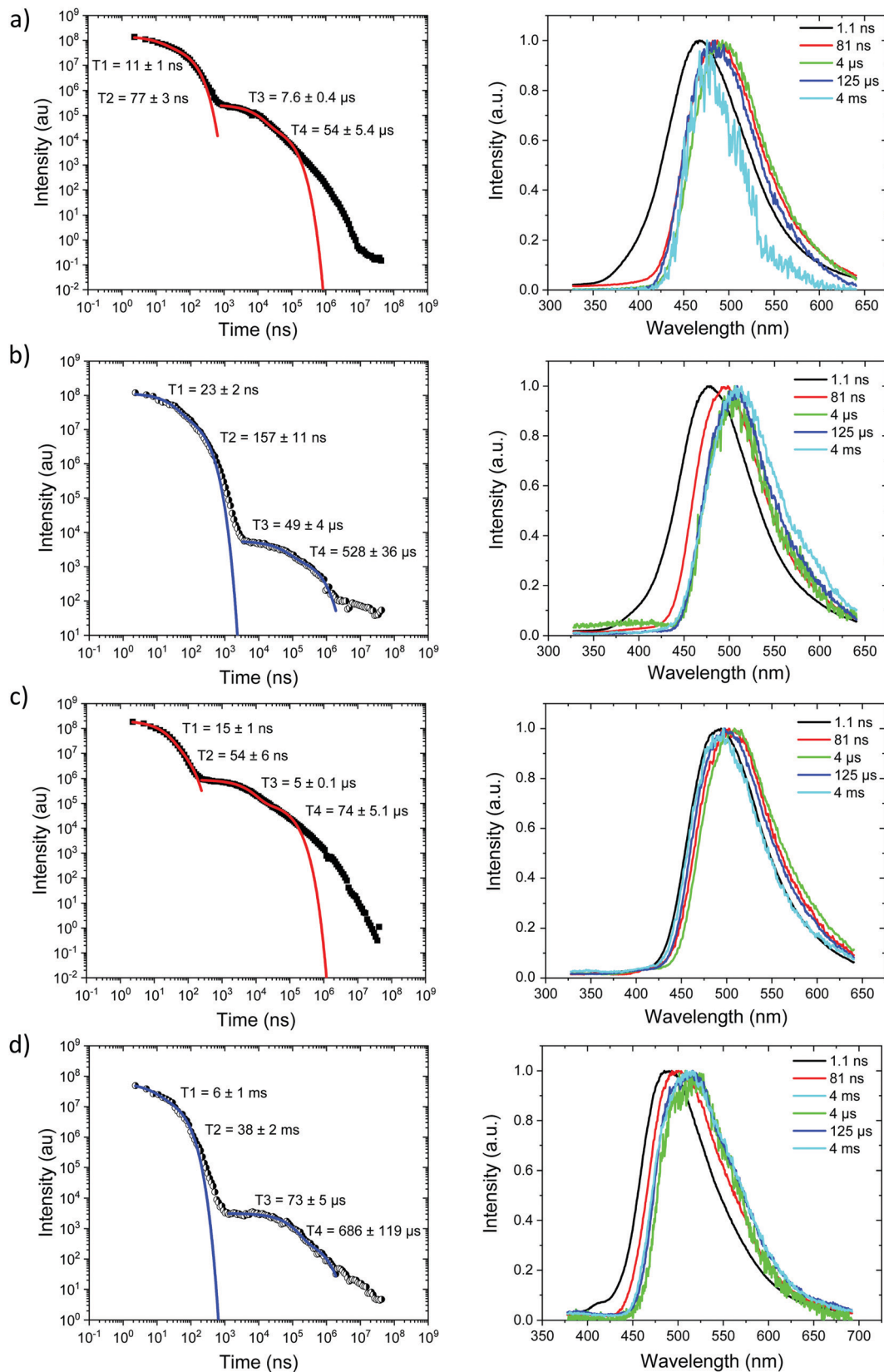


Fig. 4 Time-resolved spectrally integrated intensity decay (left) and representative time resolved spectra (right) of **Ph₃TRZCzTPA** (a) 300 K and (b) 80 K; **Ph₂TRZCzTPA** (c) 300 K and, (d) 80 K in zeonex matrix. Spectral times given in ns, and decay fitting data included in the decay plots.



Ph₂TRZCzPhCz at RT in zeonex, Fig. 5a, has a PF energy of 3.54 eV that decays within a few nanoseconds as expected for D emission. A simultaneous CT emission band (on our 1 ns timescale), onset at 3.10 eV, is also observed that decays very rapidly, within 100 ns, shown in detail in Fig. S18 (ESI[†]). At 100 ns we also see a weak transient CT emission band, onset at 2.95 eV, which also decays rapidly. This is similar to what we observe in DPEPO (see later) and may indicate a small population of weakly stabilised through-space CT states in **Ph₂TRZCzPhCz**, as predicted by our calculations, and that are stabilised in high polarity MeCN solution, Fig. 3c. This band is better resolved at 80 K, Fig. 5b, with all prompt emission decayed by 200 ns. From 200 ns to 10 μ s we observe no emission (above the noise floor of the iCCD), Fig. S7 (ESI[†]). At

At 80 K, Fig. 4b and Fig. S8 (ESI[†]), we see similar behaviour but the ns region prompt emission energy relaxation is slower. However, the emission band has a constant additional 60 meV red shift and exactly matches the band shape and energy position (in time) of the emission observed in **Ph₂TRZCzTPA** (both at RT and 80 K, Fig. 4c and d). The large decrease in DF

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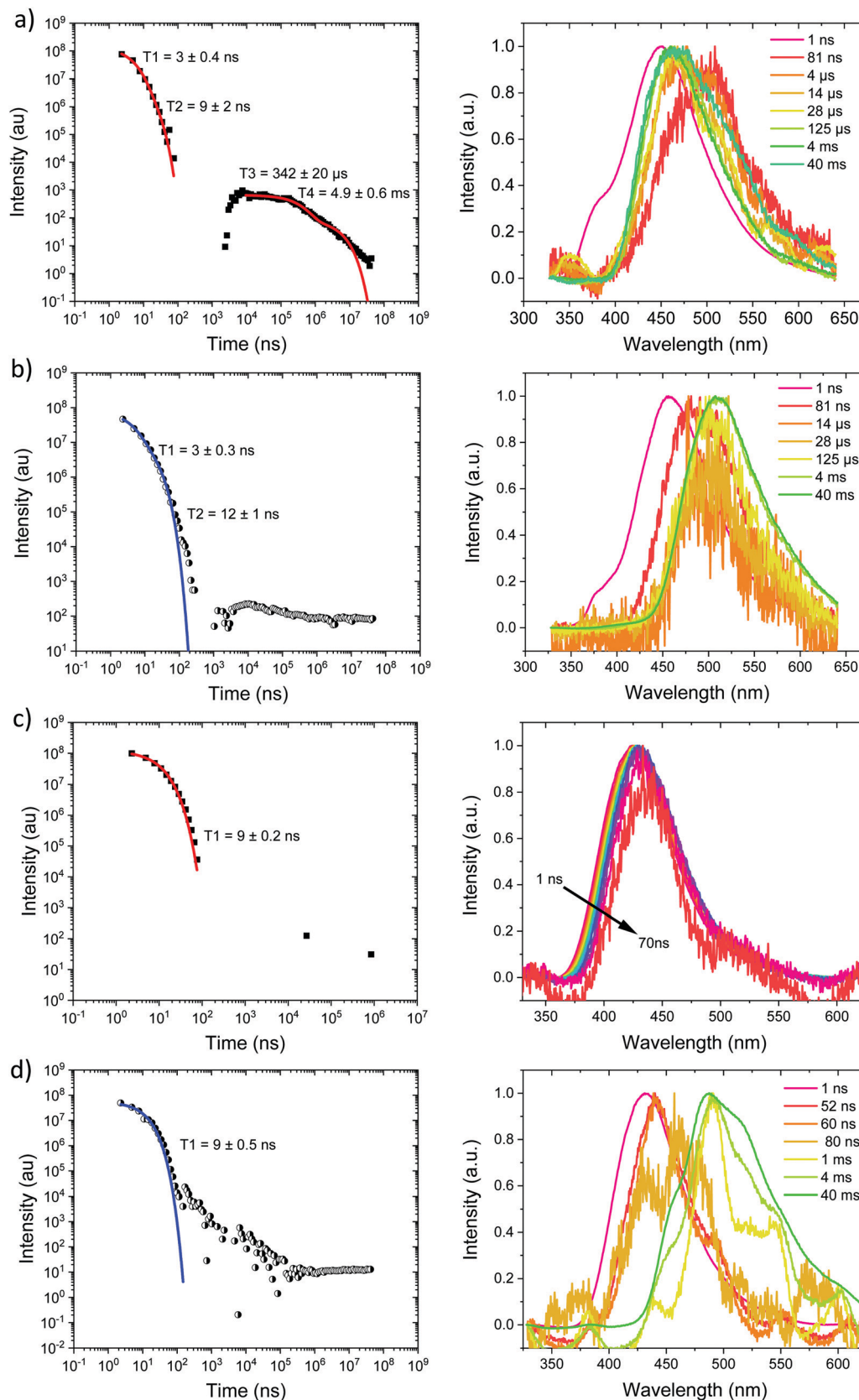


Fig. 5 Time-resolved spectrally integrated intensity decay (left) and representative time resolved spectra (right) of (a) **Ph₂TRZCzPhCz**, (a) 300 K and (b) 80 K; **Ph₃TRZCzPhCz**, (c) 300 K and, (d) 80 K in zeonex matrix. Spectral times given in ns, and decay fitting data included in the decay plots.



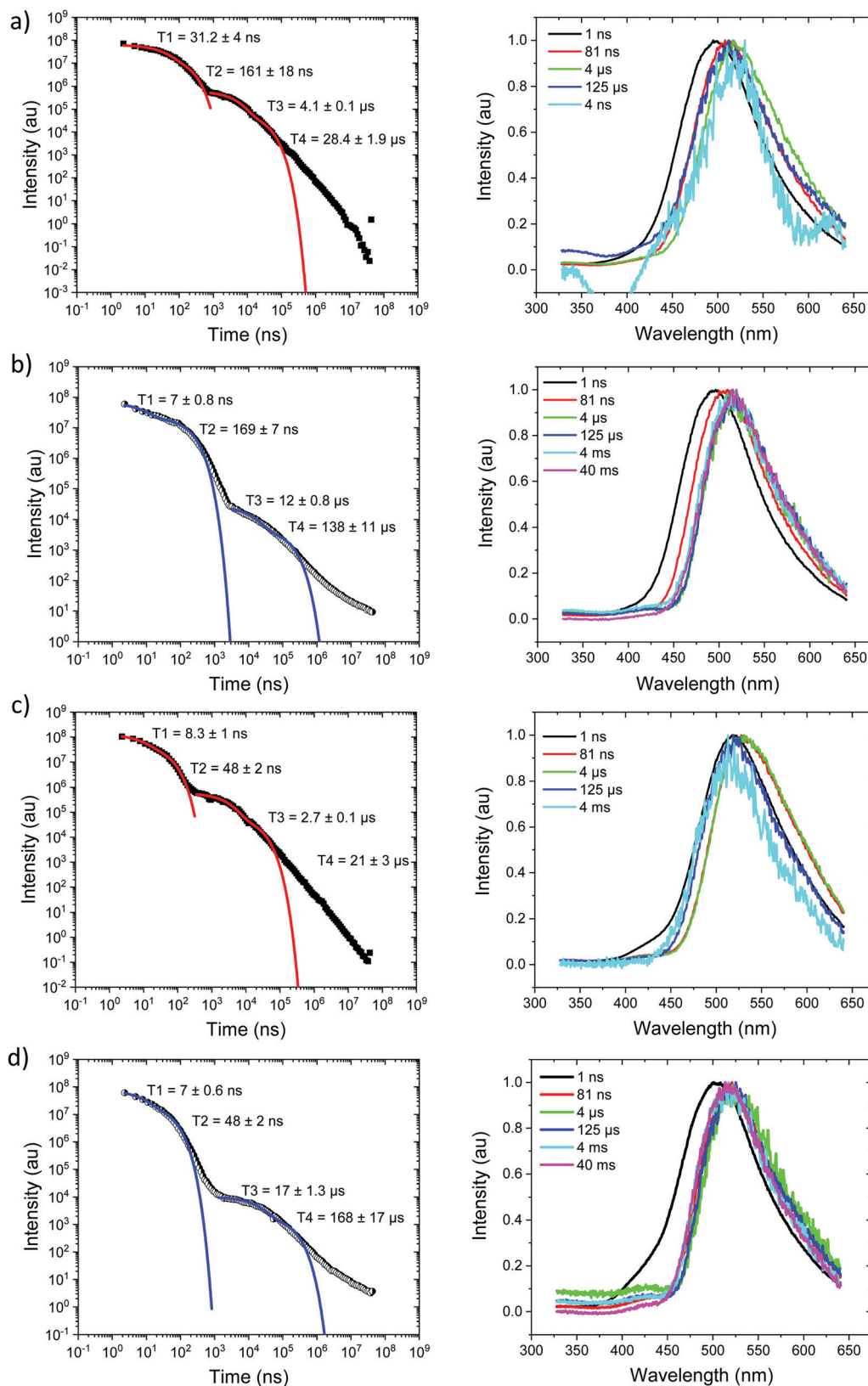


Fig. 6 Time-resolved spectrally integrated intensity decay (left) and representative time resolved spectra (right) of **Ph₃TRZCzTPA** (a) 300 K and (b) 80 K; **Ph₂TRZCzTPA** (c) 300 K and (d) 80 K in DPEPO host. Spectral times given in ns, and decay fitting data included in the decay plots.



Ph₃TRZCzPhCz at RT and 80 K, Fig. 5c and d, behaves like a simple fluorescence emitter, having only a single emission band, onset 3.35 eV with mono exponential lifetime of 9 ns. Over its lifetime, the blue edge of this band decays faster than the red edge, a typical red edge effect. No DF is observed from this band at either temperature. At 80 K phosphorescence is observed in the 1–10 ms range, having an extremely well resolved spectrum, onset at 2.88 eV which is a clear match to a carbazole phosphorescence spectrum.²³ Further, by 40 ms the band shape has evolved, losing much of its structure, onset at 2.91 eV. The spectral band shape can be deconvolved into a linear combination of the carbazole phosphorescence and the phosphorescence band we observe in **Ph₂TRZCzPhCz**, Fig. S9 (ESI[†]), indicating dual phosphorescence in **Ph₃TRZCzPhCz** as well. This yields a ΔE_{ST} of *ca.* 470 meV.

Measurements were also made at 10% by weight loading in DPEPO host, which has higher dielectric coefficient and polarizability than zeonex, also the DPEPO matrix greatly restricts the movement of the molecules because of tighter packing than the zeonex polymer matrix. Concomitantly, all CT emission is seen to be red shifted. In the case of **Ph₃TRZCzTPA** the prompt emission at RT has onset at 3.0 eV, Fig. 6a. By 80 ns the emission has relaxed to 2.85 eV and from 500 ns until 4 μ s we see DF at 2.89 eV, Fig. S10 (ESI[†]). After 12 μ s until 4 ms weak emission is observed with onset at 2.85 eV. At 80 K, Fig. 6b, bi-exponential prompt emission, with lifetimes of 7 ns and 169 ns is observed, onset at 3.0 eV with a very weak blue knee ascribed to rapid D emission along with the longer lived prompt CT emission. The prompt and delayed CT emission behave similarly to room temperature but the DF intensity is lower, again showing thermal activation, Fig. S11 (ESI[†]). From 120 μ s to 40 ms emission is seen with slight structure and onset at 2.75 eV consistent with phosphorescence from the lowest triplet state. **Ph₂TRZCzTPA** at RT shows dual PF, onset at 3.26 eV with lifetimes of 8.3 ns and 48 ns, Fig. 6c. From 80 ns until 4 μ s DF is observed at 2.64 eV, Fig. S10 (ESI[†]). From 12 μ s until 4 ms very weak emission onset *ca.* 2.79 eV is seen, ascribed to phosphorescence. At 80 K, Fig. 6d, the PF is again bi-exponential and the same delayed emission behaviour is

observed, Fig. S11 (ESI[†]). At 40 ms we again see phosphorescence at about 2.73 eV but the signal is very weak here. In both **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** the ³LE energy from low temperature zeonex measurements at 2.76 and 2.80 eV respectively, is very consistent with the phosphorescence seen in DPEPO. This would then set ΔE_{ST} at around 150–200 meV in DPEPO, consistent with the observed thermally activated delayed emission.²⁴ The calculated rISC rates of **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** in DPEPO films were calculated using a kinetic model. At RT, we estimated rates of $6.3 \times 10^4 \text{ s}^{-1}$ and $1 \times 10^5 \text{ s}^{-1}$ respectively, and at 80 K, $1.4 \times 10^4 \text{ s}^{-1}$ and $1 \times 10^4 \text{ s}^{-1}$ respectively, Fig. S12–S15 (ESI[†]).

For **Ph₂TRZCzPhCz** in DPEPO at RT, Fig. 7a, emission is observed at 3.1 eV (onset) having a bi-exponential decay of 5.8 ns and 32 ns. From 500 ns to 35 μ s very weak emission is seen with an onset of 2.88 eV, Fig. S10 (ESI[†]), and at 4 ms there may be phosphorescence with onset at 2.92 eV but the signal is very weak. At 80 K, Fig. 7b, again we observe prompt emission at 3.1 eV and then very weak emission from 500 ns to 35 μ s at 2.88 eV, Fig. S11 (ESI[†]). At 40 ms emission is still seen at 2.83 eV which we ascribe to phosphorescence. The 3.1 eV CT band is red shifted by over 300 meV compared with that in zeonex and so we believe this shows that in DPEPO the through-space CT state is stabilised by the packing effect of the DPEPO forcing the D and A units closer together. In order to confirm this hypothesis, we measured **Ph₂TRZCzPhCz** decays in both mCP and CBP hosts as well. In both cases, clear 3.1 eV CT emission is observed from **Ph₂TRZCzPhCz** with long lifetime confirming DF, Fig. S5 (ESI[†]). These observations confirm that host packing plays a major role in the underlying physics of the CT states in **Ph₂TRZCzPhCz**. All delayed emission in **Ph₂TRZCzPhCz** is rather weak, and if we assume the same triplet energy as found in zeonex then ΔE_{ST} will be of order 250 meV implying inefficient rISC in line with the very long lived weak DF. The CT band is also broaden which we assume implies a high degree of disorder within the host DPEPO, again consistent with an inhomogeneous, packing induced through-space CT state. **Ph₃TRZCzPhCz** also shows similar behaviour to **Ph₂TRZCzPhCz**, Fig. 7c and d. At RT we observe bi-exponential decay with lifetimes of 6 ns and 20 ns, emission onset at 3.1 eV. From 100 ns to 4 μ s this emission shifts to 2.91 eV, Fig. S10 (ESI[†]). Again the CT band is red shifted compared to zeonex pointing to DPEPO stabilising the through-space CT excited state and giving weak DF. At 80 K, prompt emission starts at 3.26 eV and shifts to 3.1 eV by 80 ns. The decay is bi-exponential, 6.3 ns and 31 ns, in line with a D emission as well as prompt through-space CT emission. There is little DF at 80 K, Fig. S11 (ESI[†]), in line with inefficient TADF, but at 40 ms clear phosphorescence emission with some structure is seen, onset at 2.95 eV in line with that observed in zeonex. All lifetimes are summarised in Table 4.

Ph₃TRZCzTPA and **Ph₂TRZCzTPA** were selected as the emitters to investigate electroluminescent (EL) characteristics. Four commonly used high-triplet energy hosts including;

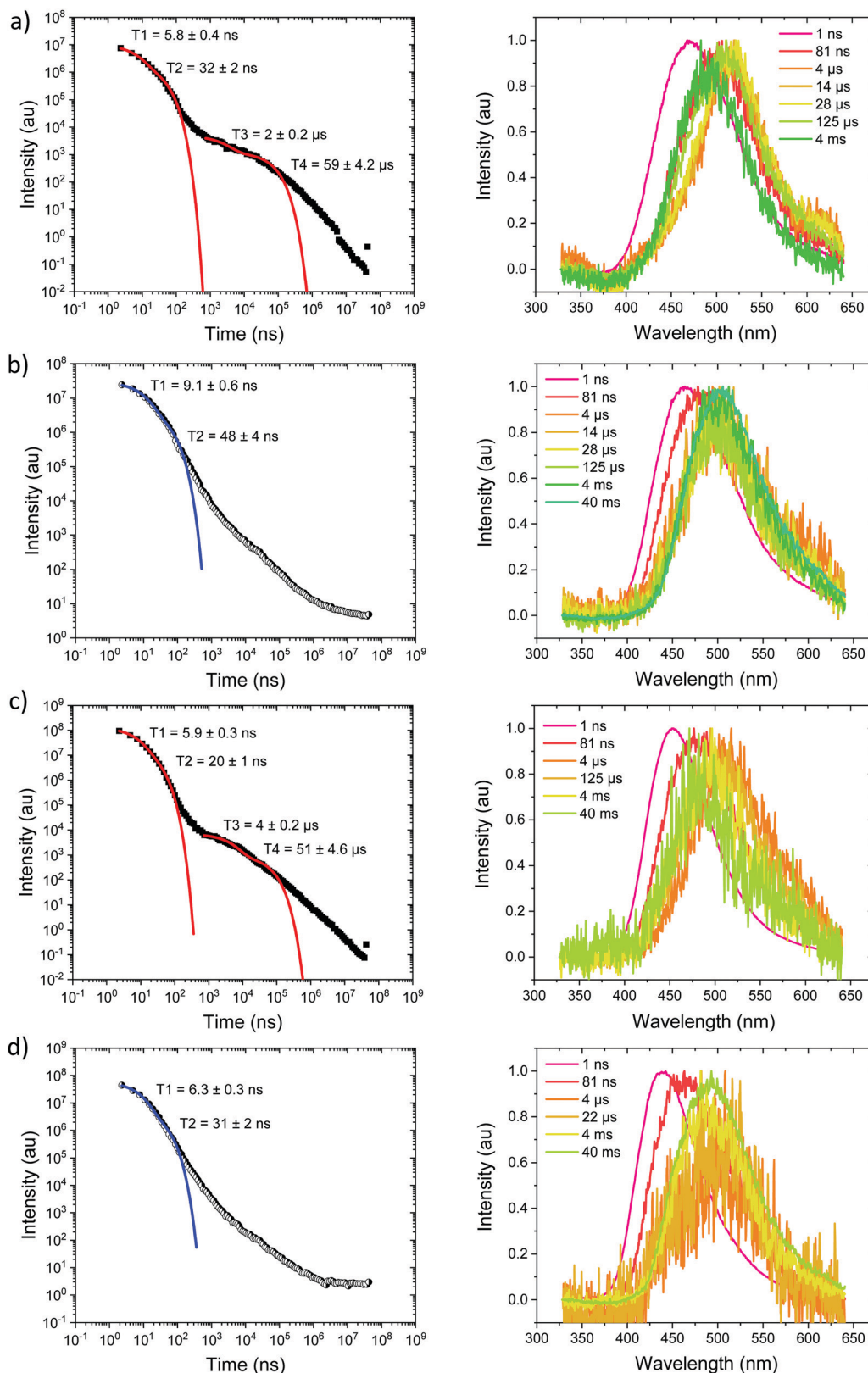


Fig. 7 Time-resolved spectrally integrated intensity decay (left) and representative time resolved spectra (right) of $\text{Ph}_2\text{TRZCzPhCz}$, (a) 300 K and (b) 80 K; $\text{Ph}_3\text{TRZCzPhCz}$, (c) 300 K and (d) 80 K in DPEPO host. Spectral times given in ns, and decay fitting data included in the decay plots.

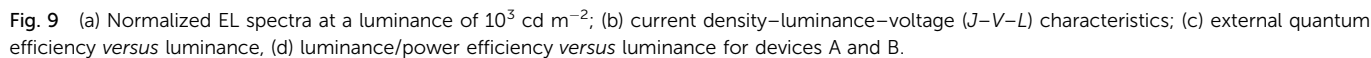


^a Local (LE) and charge transfer (CT) emission energies calculated from the on-set of the emission band. ^b Prompt (τ_{PF}) and delayed fluorescence (τ_{DF}) component lifetimes calculated from fits to the measured intensity decay curves. ^c Local triplet energy taken from the on-set of the phosphorescence measured at 80 K. ^d ΔE_{ST} is the energy difference between the ¹CT and ³LE energies.

Figure 8 (a) shows the chemical structures of six materials used in OLEDs: TAPC (tris(4-methylphenyl)amine), CBP (2,2',2'',2'''-terphenyl), mCP (1,3-bis(methylphenyl)benzene), 26DCzPPy (2,6-dimethyl-2',6'-diphenylpyridine), CzSi (1,3-bis(4-methylphenyl)-5,5'-bis(trimethylsilyl)-2,2'-bipyridine), and TmPyPB (2,2',6,6'-tetramethyl-3,3'-bipyridine). Part (b) shows the schematic structures of two OLED devices. Device A consists of Glass, ITO, TAPC (40 nm), mCP/Ph₂TRCzTPA (20 nm), TmPyPB (50 nm), and LiF/Al. Device B consists of Glass, ITO, TAPC: MoO₃ 20 wt% (20 nm), TmPyPB (50 nm), 26DCzPPy/Ph₃TRCzTPA (25 nm), and LiF/Al.

peak EQE of 16.3%, 49.7 cd A⁻¹, and 59.3 lm W⁻¹ found at 12 wt% **Ph₂TRZCzTPA**.

26DCzPPy was found to be the best host for **Ph₃TRZCzTPA**. In addition, MoO₃-doped TAPC was adopted as a hole injection layer to decrease the energy barrier between the ITO anode and the organic layer, Fig. 8. Fig. S17 (ESI[†]) depicts the EL characteristics while the corresponding parameters are summarized in Table S5 (ESI[†]). A weak emission from 26DCzPPy was observed in the EL spectra at doping concentrations of **Ph₃TRZCzTPA** below 2 wt%, indicating the incomplete host-guest energy transfer. As the doping concentration increased from 2 wt% to 24 wt%, the devices showed the EL spectra red-shifted from 518 nm to 530 nm. The current density of the devices increases with the doping concentration, indicating the favourable carrier transport capability of **Ph₃TRZCzTPA**. Given the inferior carrier mobility of 26DCzPPy; 2 wt% **Ph₃TRZCzTPA** the turn-on voltage was 5.0 V but continuously decreased to 4.4 V with a higher doping concentration, to 24 wt%. The optimized concentration was found at 20 wt% **Ph₃TRZCzTPA**, giving maximum EQE of 13.3%, 40.3 cd A⁻¹, and 28.6 lm W⁻¹. The corresponding EL characteristics of the optimized devices with **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** (*i.e.* devices A and B) are shown in Fig. 9 and the data are summarized in Table 5. Overall, the results demonstrate that both **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** give efficient TADF devices from through-space CT excited states.



Device	Host	Emitter	V_{on}^a [V]	L_{max} [cd m ⁻²]	EQE [%]	CE [cd A ⁻¹]	PE [lm W ⁻¹]	λ_{Peak} [nm]	CIE ^d [x, y]
A	CBP	Ph₂TRZCzTPA (12 wt%)	2.9	27 158 (12.4 V)	16.3, ^b 14.7, ^c 10.9 ^d	49.7, ^b 44.9, ^c 33.4 ^d	59.3, ^b 28.2, ^c 15.0 ^d	522	0.32, 0.55
B	26DCzPPv	Ph₃TRZCzTPA (20 wt%)	4.4	26 434 (11.0 V)	13.3, ^b 12.4, ^c 9.7 ^d	40.3, ^b 37.5, ^c 29.4 ^d	28.6, ^b 23.3, ^c 15.8 ^d	529	0.34, 0.54

Discussion

In all cases where we observe a measurable DF signal, we observe a strongly non-exponential decay at long times. We believe this comes from the inhomogeneous environment of the doped films, with the hosts imposing various degrees of restriction and packing effects on the TADF molecules.

The through-space CT state systems seem to be particularly prevalent to this which is not surprising, showing a potentially high sensitivity to exact spatial separation and orientation of the D and A in a host environment. Recently, Suresh *et al.*²⁵ have discussed such a long time non-exponential DF tail in terms of combined TADF and TTA emission, however here we have only used 1% loading of the TADF molecules in zeonex and 10% in DPEPO which probably rules out TTA. However in devices where much higher loadings are used a TTA contribution along with TADF cannot be ruled out.

Ph₃TRZCzTPA and **Ph₂TRZCzTPA**, by comparison to the model TRZ-TPA excited state CT complex (exciplex), are seen to have stable through-space CT excited states. The stabilising of the through space CT state over a A-D' through bond CT state is ascribed to the larger CT driving force arising from their strong D, strong A, structure. From the time resolved decays and spectra, we do though see that in **Ph₃TRZCzTPA**, an initial higher energy transient CT state which we tentatively ascribe to a short lived through-bond CT state (by comparison to model systems), potentially stabilised by the effect of the extra phenyl ring between acceptor and bridge. Relaxation of this phenyl ring configuration could then stabilise the through space CT state. Alternatively the through bond state may occur on a small population of **Ph₃TRZCzTPA** molecules trapped in a non relaxed geometry in the film. This behaviour is observed in both zeonex and DPEPO which we believe favours the former explanation. Certainly we see no such behaviour in **Ph₂TRZCzTPA** which lacks the spacing phenyl unit. **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA** show intense temperature dependent delayed emission, clearly TADF. The measurable differences between rISC rates of the two molecules we believe arises from differences in relative co-facial separation and orientation of D and A due to the phenyl spacer between A and D' (bridge) in **Ph₃TRZCzTPA**, as seen in the X-ray data. This controls their magnetic coupling, *i.e.* spin orbit coupling matrix elements, that dictate rISC rate, given they have very similar, small singlet triplet energy gaps. By comparing the photophysics of these two systems, we see that strong acceptor, strong donor pairs favour through-space charge transfer whereas strong acceptor weak donor favours through-bond charge transfer, in line with both the driving force for charge transfer and the spatial separation and orientation of the non-conjugated D A pair. This clearly sets some basic design criteria for TADF intramolecular through-space charge transfer systems. The differences between the two molecules are also reflected in the device performance. We find that **Ph₂TRZCzTPA** gives better device performance than **Ph₃TRZCzTPA**, very much in line with the difference in rISC rates and the lack of possible residual through-bond CT states in **Ph₃TRZCzTPA**. From these device results we again see sensitivity to D A orientation, flexibility of linkage to the bridge and also host packing effects. Much like exciplex emitters, these effects need to be carefully managed and controlled.²⁶

In **Ph₂TRZCzPhCz** and **Ph₃TRZCzPhCz**, the lowest local triplet state of the molecular resides on the pendant Cz unit which quenches higher energy D' (bridge) triplets leading to

negligible mediation of rISC for the through-bond CT state. All of our observations clearly align very well with ideas recently put forward by Wada *et al.* from their through-space charge transfer TADF molecule.²⁰ We also see that the effect of host packing has profound effects on the through-space CT states and these effects cannot be ignored, especially in devices.

Conclusions

From this new series of D-D'-A materials we have gained a great deal of new understanding about through-space CT states, competition with through-bond CT formation and the role a host plays in controlling this equilibrium. In the two materials having strong D and strong A, **Ph₃TRZCzTPA** and **Ph₂TRZCzTPA**, we unambiguously identify stable through-space CT states *via* comparison to model compounds and solution state D A complexes. This stabilisation we ascribe to the large driving force for charge transfer (*ca.* 1 eV) and subsequent larger charge separation distance. For the weak D strong A pair, **Ph₂TRZCzPhCz** and **Ph₃TRZCzPhCz**, a through-bond CT state between the A and the bridge D' is stabilised as the CT driving force is much less, *ca.* 0.5 eV. Little DF is observed unless an external perturbation further stabilises the CT state, *i.e.* solvent polarity or host packing forces. Indeed, in DPEPO, CBP and mCP with large packing forces we observe highly red shifted CT formation and subsequent TADF, which we ascribe to stabilization of a through-space CT state in **Ph₂TRZCzPhCz** and **Ph₃TRZCzPhCz**. This shows that such external forces can distort the molecule, forcing the D and A branches closer together to fully stabilise the through-space CT state over the through-bond state. Very satisfyingly, our TDDFT calculations identified the possibility of **Ph₃TRZCzPhCz** having both through-space and through-bond CT excited states. In **Ph₃TRZCzTPA** having an additional 'spacer' phenyl group between the bridge D' and A we observe a large temperature dependent red shift in the energies of both the ¹CT and ³LE excited states. We ascribe this to thermal motion of this phenyl ring which reduces planarity between the A and the bridge, decoupling the phenyl ring from the dTRZ A moiety, making the **Ph₃TRZCzTPA** act in a very similar fashion to **Ph₂TRZCzTPA**. This decrease in conjugation also localises the ³LE state on the dTRZ unit, increasing the phosphorescence energy as we observe. In view of these observations, having such a spacing phenyl unit that can rotate between the D and A units, might not be the optimum design strategy for TADF materials, as we find that **Ph₂TRZCzTPA** gives better performing devices than **Ph₃TRZCzTPA**. We also find that **Ph₂TRZCzTPA** has faster rISC rates than **Ph₃TRZCzTPA** which we believe indicates more optimal co-facial orientation (not separation) of D and A forming the through-space CT state, which is critical in controlling SOC properties and thus rISC, as proposed by Wada *et al.*²⁷ These differences in photophysics are also reflected in device performance with **Ph₂TRZCzTPA** giving better performance in optimised devices. This first in-depth study of the physical properties and correlated device performance of through-space compared to



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