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# Identifying the Factors That Lead to PLQY Enhancement in Diluted TADF Exciplexes Based on Carbazole Donors

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## ABSTRACT

Here we compare the effects of solid-state dilution on the photophysical and electrical performance of three TADF exciplexes based on carbazole containing donors with a high-performance acceptor PO-T2T. We observe intrinsically different photophysical behaviour between the exciplexes, which is explained by the presence of a heterogeneous distribution of triplet energies in one of the donor molecules arising from a distribution of planar and highly twisted biphenyl bridges. This study of different donors demonstrates that the recently discovered efficiency enhancement of solid-state diluted exciplexes is independent of the separation associated spectral blueshift, with the latter being universal while the former is only found for donors with low structural rigidity. OLEDs produced from these carbazole based exciplexes show decreased electrical performance likely due to the relatively low conductivity of the donors and host, suggesting that functional conductive hosts may, in some cases, be required to translate optical efficiency enhancements into improved electrical performance.

## INTRODUCTION

The key remaining challenge in the commercialisation of organic light emitting diodes (OLEDs) is to obtain high efficiency and stable blue devices, which are critical for applications in the next generation of OLED based displays and lightning. High efficiency in the red and green has already been obtained using both phosphorescent heavy metal complexes, and more recently in single molecule thermal activated delayed fluorescence (TADF).[1–3] The latter materials exploit small energy differences between an emissive charge transfer singlet state ($^1$CT) and some isoenergetic localised excitonic triplet state ($^3$LE) to facilitate reverse intersystem crossing (rISC).[4,5] Nonetheless, both phosphorescent and conventional TADF materials still possess limitations as regards efficient blue emission and operational stability.

Recently it has been discovered that solid-state dilution of a TADF exciplex using an inert host leads to increasingly blue shifted emission and a considerable increase in the photoluminescence quantum yield (PLQY) that translates to improved external quantum efficiencies (EQEs) in electrical devices.[6,7] This approach provides a promising new strategy to achieve high efficiency blue OLEDs based on exciplexes, which do not have as stringent host requirements as intramolecular charge transfer TADF materials.[2] Although we rationalise the observed blue shift of the exciplex emission in terms of a decreasing coulombic interaction between the electrons on the donor (D) and the acceptor (A), the origin of the PLQY increment is not as well understood.

Here we compare the optical and electrical properties of three TADF exciplexes formed between carbazole based donors 1,3-bis(carbazol-9-yl)benzene (mCP), 4,4'-bis(carbazol-9-yl)biphenyl (CBP) and 4,4'-bis(carbazol-9-yl)-2,2'-dimethylbiphenyl (CDBP),with 2,4,6-tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine (PO-T2T) as acceptor (structures shown in Figure 1). 100 nm thick films of materials were prepared by thermal-vacuum double or triple co-evaporation, with the D and A being diluted in an optically transparent high triplet energy host[8], 1,3-bis(triphenylsilyl)benzene (UGH-3), using different host ratios, whilst keeping the ratio of D:A constant at 1:1 by volume. The co-evaporations were controlled by accurately monitoring and controlling the evaporation rate of each material.

Considering the molecular structures of CDBP and CBP, these differ only by the two central methyl groups that sterically induce a twist across the biphenyl bridge, locking its conformation. This twist reduces the conjugation across the molecule and leads to different triplet energies in CDBP[9] ($T_1 = 2.92$ eV) compared to CBP ($T_1 = 2.70$ eV). We also compare to mCP which also possess a twisted geometry, this time due to different nitrogen linkages and close packing of the carbazoles around the central benzene ring. These structural effects also lead to a high triplet level[10,11] ($T_1 = 2.97$ eV) similar to CDBP.

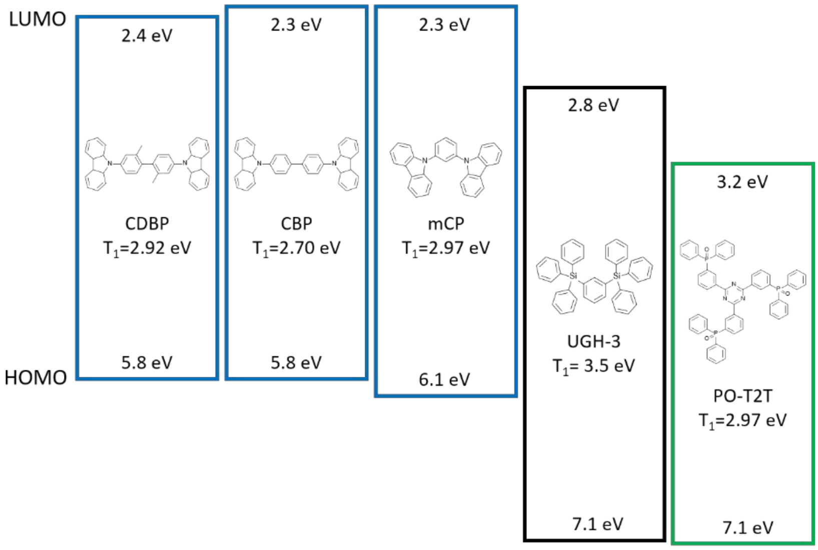

**Figure 1** Molecular structures and HOMO, LUMO and $T_1$ energy levels of the exciplex forming donors (CDBP, CBP and mCP), acceptor (PO-T2T[12]) and the host used to dilute the exciplexes (UGH-3[8]).

## RESULTS AND DISCUSSION

In Figure S1 the absorption spectra of the three dilution series are presented, showing that no ground state interaction is present, i.e. no direct charge transfer absorption band is observed,[13] and that the absorption intensity is directly proportional to the donor and acceptor content of the films. The films themselves are referred to by either their UGH-3 volume content, or as “neat” when no (diluting) host is included. The remaining volume of the films is made up of a 1:1 blend of D and A. Furthermore, to confirm that there is no interaction between the host and the three donors (exciplex formation or otherwise) the photoluminescence (PL) of the three donors in UGH-3 was also measured (Figure S2). Only the emission from the donor molecules is observed, confirming the inert nature of the host. The absorption spectra of the individual components were reported previously and confirm that only the donors have appreciable absorption at 330, 337, and 355nm used for excitation in subsequent optical experiments.[6,12,14,15]

All three exciplexes exhibit a blue shift of their PL with increasing dilution (Figure 2), consistent with our recent discovery of the dilution effect in the TSBPA:PO-T2T exciplex system.[6] This blue shift is rationalised in terms of a decreased coulombic energy term for the exciplex as the electron-hole separation of the charge transfer (CT) excited state increases. No donor emission is observed up to 25 vol% of UGH-3 in any film (Figure 2), while upon further dilution of the CDBP:PO-T2T and mCP:PO-T2T exciplexes only a small donor peak (365 nm) is observed at 50 vol% in the CDBP:PO-T2T and 75 vol% host in both CDBP:PO-T2T and mCP:PO-T2T. Stronger donor emission (360-380 nm) is observed in the CBP:PO-T2T films for the same dilutions, which suggests a stronger interaction of CDBP and mCP with PO-T2T compared to CBP, assuming that the electron transfer (ET) mediated through the host remains similar for all exciplexes and that the PLQYs of the donors are not greatly different. The former assumption is justified by the fact that the LUMO levels of the three donors CDBP (2.4 eV[16]), CBP (2.3 eV[17]) and mCP (2.3 eV[16]) all are above the LUMO of UGH-3 (2.8 eV[8]), thus allowing thermodynamically favourable electron hopping towards the deeper PO-T2T LUMO level (3.2 eV[6]).

The stronger interaction of CDBP and mCP with PO-T2T (compared to CBP, and leading to less donor emission in similarly diluted films) we believe is due to the molecular structure of the donors. The two methyl groups on the CDBP bridging benzene rings and the two closely connected carbazole units in the mCP both impart highly twisted structures. This twisted molecular structure leads to reduced conjugation across the molecules, resulting in similarly high triplet levels in both. Furthermore, CDBP and mCP have natural transition orbitals (NTOs) localised on the carbazole units,[10,14] in contrast to CBP where the NTOs are spread across the biphenyl bridge[14]. This localised donor electron density at the peripheries of the molecule may result in the increased capacity of CDBP and mCP to form exciplexes at large separation distances.

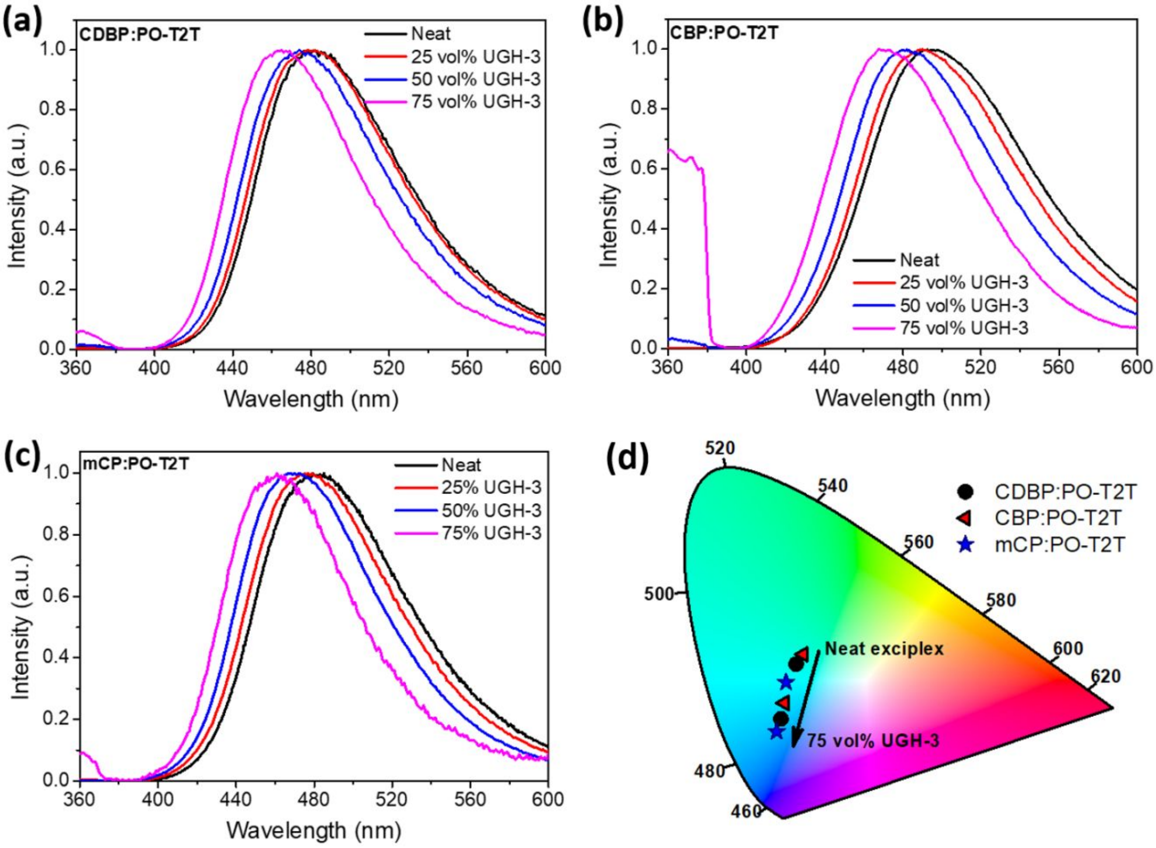

**Figure 2** Photoluminescence spectra of (a) CDBP:PO-T2T(b) CBP:PO-T2Tand (c) mCP:PO-T2T exciplex films (D:A ratio 1:1) in different vol% of UGH-3 (d) 1931 CIE chromaticity diagram schematically showing the blueshift of the electroluminescence emission coordinates with increasing % vol% UGH-3 in all materials.

Time-resolved PL decays at room temperature (RT) (Figure 3) reveal quite different behaviour with dilution for the CDBP:PO-T2T and mCP:PO-T2T exciplexes compared to CBP:PO-T2T. The CDBP:PO-T2T and mCP:PO-T2T exciplexes possess delayed fluorescence (DF) with single exponential decay kinetics at all dilutions, and in both cases the DF lifetime ($\tau_{DF}$) increases slightly with increasing dilution (Table 1). For the CDBP:PO-T2T exciplex an increase of $\tau_{DF}$ from 2.4 μs to 4.1 μs is observed from neat to 75% UGH-3 films, while for mCP:PO-T2T there is a much smaller change (2.1to 2.6 μs).

In contrast the CBP:PO-T2T DF decays are predominantly bi-exponential. We find that we are able to fit the first component using the same time constant as that obtained from the CDBP:PO-T2T DF decays at the corresponding dilution (as shown in Figure S3) with an additional longer lived component also required to fit the full DF region. An additional third exponential was also necessary to fully characterise the 75 vol% diluted film, with all fitting parameters reported in Table S1.

We interpret the behaviour of the CBP:PO-T2T films as arising from the presence of a distribution of CBP conformations with different dihedral angles across the biphenyl bridge. This distribution of CBP molecules (each with different levels of conjugation between the two carbazole moieties) implies the presence of a distribution of triplet levels and associated $\Delta E_{ST}$ gaps within the films, leading to the multiexponential DF observed. As we are able to fit the fast component of the CBP decays using the corresponding CDBP films results this indicates that a proportion of the CBP molecules are in the same conformation as CDBP, i.e. highly twisted bridging phenyls and so low conjugation across the biphenyl bridge. This twisting confers a similar high triplet level (2.92 eV) to some of the CBP molecules and therefore a small $\Delta E_{ST}$ gap and fast rISC rate according to Equation 1.[18] We note however that in phosphorescence (PH) measurements we can only observe the lowest energy CBP triplets (with onset energy 2.7 eV) because of downhill energy transfer to these during the very long triplet lifetime. The slow DF decay component is given by that population of CBP molecules that retain a higher degree of conjugation across the biphenyl bridge with less twisting, lower triplet (~2.70 eV), bigger $\Delta E_{ST}$ , and a much slower rISC rate.

$$k_{rISC} \propto e^{-\Delta E_{ST}/k_B T} \qquad \text{Equation 1}$$

For CDBP, the $^3$LE is always in close resonance with the exciplex $^1$CT level due to its sterically locked twisted conformation, which ensures the triplet level distribution is effectively homogeneous in the films. The resulting $\Delta E_{ST}$ gaps between the $^1$CT and the triplet of either the donor or the acceptor are always small, with values $0.03 < \Delta E_{ST} < 0.05$ eV (Table 2). CBP:PO-T2T forms an exciplex with very similar energy to CDBP:PO-T2T (Table 2) due to the very similar HOMO levels. Upon dilution in UGH-3 the distribution of CBP linkage angles is changed, leading to a different distribution of triplet energies, $\Delta E_{ST}$ gaps, and rISC rates. Any concentration quenching mechanisms common to both CBP and CDBP must also be similarly suppressed in both systems, leading to their PLQYs converging to values of roughly 50% (+- 5% error) at 50% dilution. Decreases in the PLQY at 75% dilution are likely due to the increased D-A distances hindering the electron transfer from D to A, leading to the observed increase in (low PLQY) donor emission.

The behaviour of the mCP dilution series further supports this interpretation since this material possesses CT and triplet energy levels very similar to CDBP, as schematically shown in Figure 3b and Figure 3f. The mCP triplet is always in close resonance with the exciplex energy, and this does not change upon dilution due its rigid molecular structure. For mCP:PO-T2T the PLQY barely increases upon dilution (within error) but drops quickly as exciplex formation is hindered at higher dilutions.

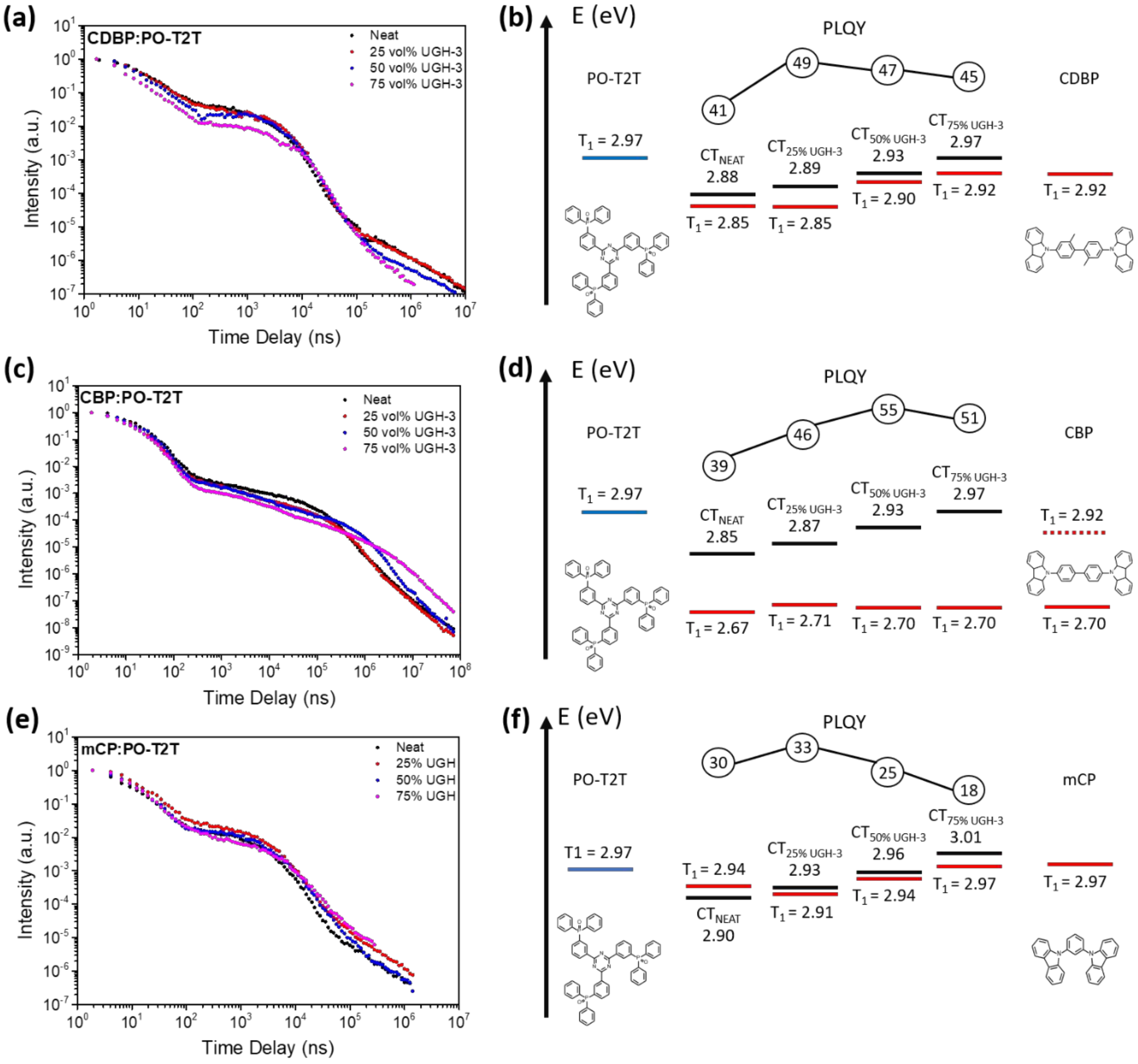

**Figure 3** Left: Time resolved photoluminescence decays collected at room temperature of (a) CDBP:PO-T2T (c) CBP:PO-T2T and (e) mCP:PO-T2T exciplexes in different vol% of UGH-3. Right: Energy diagrams showing the lowest lying measured local triplets (solid red lines) of the exciplex forming molecules and the blue shifted CT energy (black lines) with increasing dilution for (b) CDBP:PO-T2T (d) CBP:PO-T2T and (f) mCP:PO-T2T. The blue lines indicate the local triplet of PO-T2T,

while the dashed red line in d shows the level of the inferred triplet energy upon dilution, the same as in CDBP and discussed in the text below.

Figures S3-S5 show spectra obtained at different delay times for the CDBP, CBP and mCP exciplexes. Consistent with what was observed in our previous report,[6] increasing host vol% causes a reduction in the time-dependant spectral shift observed in the prompt (1.9 ns delay) and delayed emission (Table 1). In all cases the initial spectrum recorded at 1.9 ns is also found at higher energies at higher dilutions. The onset of this initial spectrum redshifts over time in each material, but by decreasing amounts at higher dilutions. This red shift is due to the presence of a heterogeneous distribution of $^1$CT lifetimes, where the highest energy CT states (with blue emission) decay fastest as they have more local LE character, stronger coupling to the ground state, and therefore the highest emission rate constants. The lower energy CT states decay more slowly as they are more weakly coupled to the ground state, leading to redder emission at longer times.[19]

The reduction of the onset shift at higher dilutions suggests that there are fewer low energy D-A "orientations" present in the film when the host vol% increases. This is intuitive, as these low energy (short D-A distance) exciplexes will be the first to be disrupted as the host is incorporated into the exciplex films.[19–21] The net result is this truncates the shorter end of the D-A distance distribution, and therefore limits the extend of the spectral redshift.

As shown in Table 1, both prompt and delayed emission onsets blueshift with increasing host vol%, similar to the steady state PL discussed above. The fact that the onset of the prompt fluorescence blueshifts indicates that new higher energy exciplexes are formed which are not present in the undiluted films. This indicates that the average D-A separation increases with increasing dilution, creating more isolated D and A that can only form pairs at distances otherwise prevented by a closer nearest neighbour in an undiluted film. This change in the D-A distance distribution -substantially blue shifting the "centre of mass" of the CT band in the diluted films- causes the CT energies to asymptote towards a value that correspond to separation distances at which the ET that forms the exciplex can no longer occur.

To exclude the contribution of other DF processes such as triplet-triplet annihilation (TTA) in our analysis, laser fluences (LF) were measured for different excitation doses in each exciplex at each dilution.[4] For the CDBP exciplex the LFs (Figure S7) were measured at a delay time and integration time of 0.25 µs and 1.5 µs respectively, to ensure that only the behaviour of the delayed part of the decay was assessed. The LFs measured were fitted with two linear regions. The high power region (laser power > 10µJ) showed a sublinear dependence of the measured emission intensity with excitation dose, indicating that singlet-singlet quenching is likely active at high excitation powers. In the low power region (laser power < 10µJ) a behaviour closer to the ideal slope of 1 is observed, indicating unimolecular rate laws and excluding bimolecular TTA as the DF mechanism. As phosphorescence is unlikely at room temperature in these systems, we therefore attribute the DF to a pure TADF mechanism in the CDBP:PO-T2T exciplexes across all dilutions.

Since the CBP exciplexes showed such a long DF, the LFs were measured both in the early and in a later time region of the DF to assess if different triplet harvesting processes were present (Figure S8). In both the early DF (0.5 µs delay time/1.5 µs integration time) and later DF (80 µs delay time/420 µs integration time) two regimes of laser power dependence were observed, similarly to the CDBP exciplex. In the high power region, a more severe sublinearity is observed, and for the neat film gradients are as low as 0.51 and 0.32 for the early and late high power LFs are observed. These results indicate stronger excitation quenching processes in the CBP exciplex, which is unsurprising based on the much slower triplet harvesting (and longer exciton lifetimes) in this exciplex series. Indeed, when comparing the early DF and later DF LFs in the high power regions we observe that the LF measured at longer delay time is always the more strongly quenched – indicating that the longest lived excitons (those least able to be rapidly harvested for emission) are the most likely to suffer quenching. We suggest that this triplet quenching is hindered by reduced triplet mobility at higher dilution leading to less significant sublinearity. The same trend is observed in the low power regions of the LFs, with the early time LFs always showing slightly higher gradients than the LFs measured at later time. Nonetheless these gradients are all close to 1, indicating that the CBP:PO-T2T exciplex is also dominated by the TADF mechanisms despite the measured CBP triplet energy being substantially lower than the exciplex $^1$CT energy at all dilutions.

The mCP:PO-T2T LFs were also measured in the DF region from 0.25 to 1.5 μs (Figure S9) showing trends similar to that discussed for the CDBP exciplex. In this exciplex again we observe excited state quenching in the high power region that disappears at 75vol% UGH-3. As was observed for the other two exciplexes, the low power region is characterised by a slope very close to 1 indicating the dominating TADF character of the DF at all dilutions.

Another trend also observed in the LFs of all three exciplexes is that the sublinearity of the high power region becomes less severe with increasing dilution. This can be explained by considering that with increasing dilution vol% in the films, the lower absolute film absorption means that the exciton density is lower at all times (fewer exciplexes per volume unit) making concentration dependant quenching less efficient[22]. The quenching mechanisms may include singlet-singlet annihilation during early time PF (depleting the exciton population available for DF emission later on), as well as non-emissive triplet-triplet annihilation or monomolecular triplet quenching in the DF region itself.

PL decays were also measured at low temperatures for both dilution series (Figures S10a, S12a and S13a). Even at 80K the CDBP and mCP exciplexes retain a strong DF component, but reduced compared to room temperature (in contrast to the CBP:PO-T2T films) as a result of the smaller $\Delta E_{ST}$ and faster rISC rate in the these exciplexes. Spectra were also measured at 80K with 80 ms delay (Figure S10b, S12b and S13b) in order to measure the phosphorescence (PH) of the exciplex films. For the CBP series, we always obtain structured emission (Figure S12b) even in the presence of PO-T2T with onset energy between 2.67 and 2.71 eV, consistent with literature reports of the CBP triplet energy.[9] Similarly the mCP series also showed consistent PH spectra (Figure S13b) with onset energy between 2.91 eV and 2.97 eV from the exciplex films.,

For the CDBP series (Figure S10b) these measurements failed to unambiguously resolve the PH of the films. The spectra collected are instead still from the exciplex state and are clearly blue shifted with dilution according to the steady state spectra (Figure 2a). This kind of concerted blue shift upon dilution is not expected for PH. In order to obtain a better estimation of the $\Delta E_{ST}$ of the CDBP:PO-T2T exciplex series, the PH of evaporated films of CDBP in UGH-3 were measured at concentrations of 10, 25 and 50 vol% without PO-T2T (Figure S11). The 10% CDBP films shows a PH onset of 2.92 eV, while the

25 and 50 vol% films possess a slightly lower PH onset of 2.90 eV and 2.85eV respectively. This redshift of the PH with the increasing concentration is likely due to excimer formation.[14]

**Table 1** Relevant metrics of the RT decays of the CDBP, CBP and mCP based exciplex series.

| | $\tau_{DF}$ (µs) | LF slope | CT prompt / delayed onset (eV) | CT prompt / delayed shift (eV) |
|---|---|---|---|---|
| **CDBP:PO-T2T** | | | | |
| *Neat* | 2.4 | 0.87 | 3.03 / 2.83 | 0.20 |
| *25 vol% UGH-3* | 3.1 | 0.95 | 3.07 / 2.85 | 0.22 |
| *50 vol% UGH-3* | 4.0 | 0.95 | 3.06 / 2.87 | 0.19 |
| *75 vol% UGH-3* | 4.1 | 1.01 | 3.11 / 2.96 | 0.15 |
| **CBP:PO-T2T** | | | | |
| *Neat* | - | 0.86 | 2.97 / 2.74 | 0.23 |
| *25 vol% UGH-3* | - | 0.86/1.32 | 2.96/ 2.76 | 0.20 |
| *50 vol% UGH-3* | - | 0.90 | 3.02 / 2.84 | 0.18 |
| *75 vol% UGH-3* | - | 0.95 | 3.13 / 2.92 | 0.21 |
| **mCP:PO-T2T** | | | | |
| *Neat* | 2.1 | 0.96 | 3.05 / 2.84 | 0.21 |
| *25 vol% UGH-3* | 2.1 | 0.96 | 3.07 / 2.89 | 0.18 |
| *50 vol% UGH-3* | 2.5 | 0.99 | 3.07 / 2.89 | 0.18 |
| *75 vol% UGH-3* | 2.6 | 0.96 | 2.11 / 2.96 | 0.15 |

PLQYs were measured for all exciplex films (Table 2) in anticipation of a significant efficiency enhancement with dilution as observed for TSBPA:PO-T2T in our previous report.[6] Instead, we find that the CDBP series shows only a small PLQY increment, from 41% for the neat exciplex to 49% at 25 % UGH-3 film. At 50 vol% UGH-3 the PLQY remains essentially unchanged while it deceases at 75% dilution to 45%. The mCP series shows only a decrease of the PLQY with dilution. For CBP:PO-T2T the PLQY instead increases from 39% in neat film to 55% at 50 vol% of UGH-3, then decreases slightly at 51% at 75% dilution. The general decrease of PLQY at 75 vol% dilution can be explained by the observed steady state PL spectra (Figure 2a), as at this level of dilution all three exciplexes show donor emission under optical excitation, inevitably lowering the PLQY.

The differences in PLQY behaviour for the different exciplex series is unexpected, and hints towards the mechanism of the efficiency enhancement. We conclude that this is correlated to the different rigidities of the donor molecules. Rigid CDBP and mCP possess NTOs localised on the peripheral carbazole moieties[9,10] and higher local triplet energies as a result of their reduced phenyl bridge conjugation, yielding a small $\Delta E_{ST}$ for the resulting exciplex. This rigidity may also reduce excited state quenching processes (eg, vibrationally driven internal conversion) that are otherwise active in more flexible CBP. As the inclusion of the UGH-3 host cannot change the rigid structure (and hence the triplet energy) nor further reduce any vibrationally activated quenching mechanisms. Dilution therefore cannot improve the PLQY from its starting value for these donors. Instead the PLQY can only decrease as exciplex formation becomes more and more hindered at large D-A distances resulting in reduced ET and increased donor emission. A blue shift in the emission is nonetheless observed, as the coulombic energy changes with increasing separation independent of any PLQY increase.

Conversely, dilution is able to enhance CBP exciplexes as packing effects of the rigid UGH-3 host likely increases the proportion of the twisted CBP molecules having higher triplet energy and thus more efficient rISC (similar to CDBP). Dilution will also spatially isolate any low triplet CBP molecules that could otherwise act as low efficiency triplet traps, populated by short range Dexter transfer. Therefore the PLQY is significantly enhanced on dilution of the flexible CBP exciplex, similar to what we observed previously for the flexible TSBPA based exciplexes.[6] The PLQY instead remains largely unchanged in the CDBP exciplex because there is no scope for the host to change the structure of the rigid donor. It is also therefore no coincidence that the CBP exciplex PLQY rises to meet that of the CDBP, while the radically different molecular structure of mCP means this exciplex shows uncorrelated behaviour on dilution.

**Table 2** Comparison between the PLQY values and the $\Delta E_{ST}$ of the CDBP, CBP and mCP based exciplex

| | **PLQY (%)** | **PL onset (eV)** | **PH onset (eV)** | **$\Delta E_{ST}$ (eV)** |
|---|---|---|---|---|
| **CDBP:PO-T2T** | | | | |
| *Neat* | 41 | 2.88 | 2.85[a] | 0.03 |
| *25 vol% UGH-3* | 49 | 2.89 | 2.85[a] | 0.04 |
| *50 vol% UGH-3* | 47 | 2.93 | 2.90[a] | 0.03 |
| *75 vol% UGH-3* | 45 | 2.97 | 2.92[a] | 0.05 |
| **CBP:PO-T2T** | | | | |
| *Neat* | 39 | 2.85 | 2.67 | 0.18 |
| *25 vol% UGH-3* | 46 | 2.87 | 2.71 | 0.16 |
| *50 vol% UGH-3* | 55 | 2.92 | 2.70 | 0.22 |
| *75 vol% UGH-3* | 51 | 2.97 | 2.71 | 0.26 |
| **mCP:PO-T2T** | | | | |
| *Neat* | 30 | 2.90 | 2.94 | -0.04 |
| *25 vol% UGH-3* | 33 | 2.93 | 2.91 | 0.02 |
| *50 vol% UGH-3* | 25 | 2.96 | 2.94 | 0.02 |

| | | | | |
|---|---|---|---|---|
| *75 vol% UGH-3* | 18 | 3.01 | 2.97 | 0.03 |

[a] *phosphorescence value measured for CDBP:UGH-3 evaporated films at 10-25 and 50 CDBP vol% (i.e. without PO-T2T)*

Finally, we prepared OLED devices using these diluted exciplexes to test these materials as emissive layers, Figures S14-S16. The OLED stack used for all the devices was NPB 40 nm|Donor 10 nm|Donor:PO-T2T in x vol% UGH-3 30 nm|PO-T2T 50 nm where Donor represents CBP, CDBP or mCP and x vol% values were 0 (neat exciplex), 25, 50 and 75. In all three dilution series we observe that the electroluminescence (EL) blueshifts in line with the PL. The maximum brightness monotonically decreases with increasing host vol% due to the decreased concentration and total loading of exciplex emitter in the emissive layer (EML). The only exception to this trend is the device with CBP diluted at 50 vol%, where the maximum brightness is higher than in the neat undiluted exciplex. This can be explained by considering that the CBP exciplex show a maximum PLQY value (55 %) at this dilution. The overall resistivity of the OLED devices increases, requiring higher driving voltage to reach similar currents due to the presence of the resistive UGH-3. In all exciplexes we also observe that the EQE decreases with increasing dilution, despite the increased PLQY values for the CBP exciplex.[6] We assign this unexpected result to the low conductivity of the chosen donors and host. We suggest that when exciplexes formed by donors with relatively low conductivity are diluted, the hole injection capability in the EML drops critically, making it impossible to achieve the full performance of the exciplex as an emitter as quantified by the PLQY. This was not observed on dilution of the more conductive TSBPA donor exciplex,[4] and may be remedied in future by using diluting hosts with ambipolar transport properties, although finding such a host that does not form a competing exciplex with PO-T2T will likely prove challenging.

## CONCLUSION

In conclusion we have compared the effect of dilution on the photophysical and electrical performances of three TADF exciplexes based on CBP, CDBP and mCP donors with PO-T2T. We have observed intrinsically different photophysical behaviour between CDBP and mCP exciplexes when compared to CBP. We assign this to a heterogeneous distribution of triplet energies in the CBP molecules arising from a distribution of molecular conformations –between fully planar and highly twisted across the biphenyl bridges. This distribution produces a range distribution of $\Delta E_{ST}$ gaps, as evidences by a highly multiexponential time resolved PL decay.

We furthermore show that the PLQY enhancement of the diluted exciplexes is independent of the separation associated spectral blue shift which is caused by reducing the coulomb interaction between the exciplex electrons, and suggest that only molecules with low structural rigidity are able to enhance exciplexes PLQY through dilution. Finally, OLEDs produced from these carbazole based exciplexes show decreased EQEs with increasing dilution which we have assigned to the relatively low conductivity of the carbazole based donors – more than outcompeting the modest increase in PLQY observed for CBP. This problem is linked to intrinsic donor conductivity, and might be addressed in future studies by employing functional hosts that can assist the charge injection and conduction across the EML, in contrast to resistive UGH-3.

**Supporting Information.**

Experimental methods; absorption spectra of exciplex films, emission spectra of donor molecules in UGH-3; time-resolved emission decays, spectra, and DF power dependences of neat and diluted exciplexes; time resolved decays at 80K and phosphorescence spectra; EQEs, J-V and EL spectra of OLEDs produced with the neat and diluted exciplexes as EML.

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## Notes

The authors declare no competing financial interests.

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# References

(1) Yook, K. S.; Lee, J. Y. Organic Materials for Deep Blue Phosphorescent Organic Light-Emitting Diodes. *Adv. Mater.* **2012**, *24*, 3169–3190.

(2) dos Santos, P. L.; Ward, J. S.; Bryce, M. R.; Monkman, A. P. Using Guest–Host Interactions To Optimize the Efficiency of TADF OLEDs. *J. Phys. Chem. Lett.* **2016**, *7*, 3341–3346.

(3) Lee, I.; Lee, J. Y. Molecular Design of Deep Blue Fluorescent Emitters with 20% External Quantum Efficiency and Narrow Emission Spectrum. *Org. Electron.* **2016**, *29*, 160–164.

(4) Jankus, V.; Chiang, C.-J.; Dias, F.; Monkman, A. P. Deep Blue Exciplex Organic Light-Emitting Diodes with Enhanced Efficiency; P-Type or E-Type Triplet Conversion to Singlet Excitons? *Adv. Mater.* **2013**, *25*, 1455–1459.

(5) dos Santos, P. L.; Dias, F. B.; Monkman, A. P. Investigation of the Mechanisms Giving Rise to TADF in Exciplex States. *J. Phys. Chem. C* **2016**, *120*, 18259–18267.

(6) Colella, M.; Danos, A.; Monkman, A. P. Less Is More: Dilution Enhances Optical and Electrical Performance of a TADF Exciplex. *J. Phys. Chem. Lett.* **2019**, *10*, 793–798.

(7) Yuan, P.; Guo, X.; Qiao, X.; Yan, D.; Ma, D. Improvement of the Electroluminescence Performance of Exciplex-Based OLEDs by Effective Utilization of Long-Range Coupled Electron–Hole Pairs. *Adv. Opt. Mater.* **2019**, *7*, 1801648.

(8) Ren, X.; Li, J.; Holmes, R. J.; Djurovich, P. I.; Forrest, S. R.; Thompson, M. E. Ultrahigh Energy Gap Hosts in Deep Blue Organic Electrophosphorescent Devices. *Chem. Mater.* **2004**, *16*, 4743–4747.

(9) Bagnich, S. A.; Rudnick, A.; Schroegel, P.; Strohriegl, P.; Köhler, A. Triplet Energies and Excimer Formation in Meta- and Para-Linked Carbazolebiphenyl Matrix Materials. *Philos. Trans. A. Math. Phys. Eng. Sci.* **2015**, *373*, 20140446.

(10) Dong, S. C.; Zhang, L.; Liang, J.; Cui, L. S.; Li, Q.; Jiang, Z. Q.; Liao, L. S. Rational Design of Dibenzothiophene-Based Host Materials for PHOLEDs. *J. Phys. Chem. C* **2014**, *118*, 2375–2384.

(11) Zhang, D.; Cai, M.; Bin, Z.; Zhang, Y.; Zhang, D.; Duan, L. Highly Efficient Blue Thermally Activated Delayed Fluorescent OLEDs with Record-Low Driving Voltages Utilizing High Triplet Energy Hosts with Small Singlet–triplet Splittings. *Chem. Sci.* **2016**, *7*, 3355–3363.

(12) Chapran, M.; Pander, P.; Vasylieva, M.; Wiosna-Salyga, G.; Ulanski, J.; Dias, F. B.; Data, P.

Realizing 20% External Quantum Efficiency in Electroluminescence with Efficient Thermally Activated Delayed Fluorescence from an Exciplex. *ACS Appl. Mater. Interfaces* **2019**, *11*, 13460–13471.

(13) Dias, F. B.; Penfold, T. J.; Monkman, A. P. Photophysics of Thermally Activated Delayed Fluorescence Molecules. *Methods Appl. Fluoresc.* **2017**, *5*, 012001.

(14) Bagnich, S. A.; Athanasopoulos, S.; Rudnick, A.; Schroegel, P.; Bauer, I.; Greenham, N. C.; Strohriegl, P.; Köhler, A. Excimer Formation by Steric Twisting in Carbazole and Triphenylamine-Based Host Materials. *J. Phys. Chem. C* **2015**, *119*, 2380–2387.

(15) Li, J.; Nomura, H.; Miyazaki, H.; Adachi, C. Highly Efficient Exciplex Organic Light-Emitting Diodes Incorporating a Heptazine Derivative as an Electron Acceptor. *Chem. Commun.* **2014**, *50*, 6174–6176.

(16) Wu, Z.; Yu, L.; Zhao, F.; Qiao, X.; Chen, J.; Ni, F.; Yang, C.; Ahamad, T.; Alshehri, S. M.; Ma, D. Precise Exciton Allocation for Highly Efficient White Organic Light-Emitting Diodes with Low Efficiency Roll-Off Based on Blue Thermally Activated Delayed Fluorescent Exciplex Emission. *Adv. Opt. Mater.* **2017**, *5*, 1700415.

(17) Zhang, T.; Liang, Y.; Cheng, J.; Li, J. A CBP Derivative as Bipolar Host for Performance Enhancement in Phosphorescent Organic Light-Emitting Diodes. *J. Mater. Chem. C* **2013**, *1*, 757–764.

(18) Dias, F. B.; Penfold, T. J.; Berberan-Santos, M. N.; Monkman, A. P. Photophysics of Thermally Activated Delayed Fluorescence in Organic Molecules. *Methods Appl. Fluoresc.* **2017**, *5*, 012001.

(19) Graves, D.; Jankus, V.; Dias, F. B.; Monkman, A. Photophysical Investigation of the Thermally Activated Delayed Emission from Films of M-MTDATA:PBD Exciplex. *Adv. Funct. Mater.* **2014**, *24*, 2343–2351.

(20) Moon, C.-K.; Huh, J.-S.; Kim, J.-M.; Kim, J.-J. Electronic Structure and Emission Process of Excited Charge Transfer States in Solids. *Chem. Mater.* **2018**, *30*, 5648–5654.

(21) Serevičius, T.; Skaisgiris, R.; Dodonova, J.; Jagintavičius, L.; Bucevičius, J.; Kazlauskas, K.; Juršėnas, S.; Tumkevičius, S. Emission Wavelength Dependence on the RISC Rate in TADF Compounds with Large Conformational Disorder. *Chem. Commun.* **2019**, *55*, 1975–1978.

(22) Fujitsuka, M.; Satyanarayana, K.; Luh, T.-Y.; Majima, T. Singlet–singlet and Singlet–triplet Annihilations in Structure-Regulated Porphyrin Polymers. *J. Photochem. Photobiol. A Chem.* **2016**, *331*, 56–59.

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