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Persistent Dimer Emission in Thermally Activated Delayed Fluorescence Materials


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Supporting Information

ABSTRACT: We expose significant changes in the emission color of carbazole-based thermally activated delayed fluorescence (TADF) emitters that arise from the presence of persistent dimer states in thin films and organic light-emitting diodes (OLEDs). Direct photoexcitation of this dimer state in 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) reveals the significant influence of dimer species on the color purity of its photoluminescence and electroluminescence. The dimer species is sensitive to the sample preparation method, and its enduring presence contributes to the widely reported concentration-mediated red shift in the photoluminescence and electroluminescence of evaporated thin films. This discovery has implications on the usability of these, and similar, molecules for OLEDs and explains disparate electroluminescence spectra presented in the literature for these compounds. The dimerization-controlled changes observed in the TADF process and photoluminescence efficiency mean that careful consideration of dimer states is imperative in the design of future TADF emitters and the interpretation of previously reported studies of carbazole-based TADF materials.

INTRODUCTION

Thermally activated delayed fluorescence (TADF) has become a topic of intense interest to improve the performance of organic light-emitting diodes (OLEDs) through the utilization of the nonemissive triplet manifold.1 The triplet states formed in the emitter molecules during device operation are converted back into emissive singlet states through the reverse intersystem crossing (rISC) mechanism. Recent experimental and theoretical evidence has shown that rISC in these organic emitters is not simply reliant on a small singlet-triplet gap between two states, but that spin-vibronic coupling plays a significant role.4,5

A typical molecular scheme to achieve TADF is a donor–acceptor (D–A) system that can form intramolecular charge-transfer (CT) states with a very small singlet–triplet energy gap. However, there is significant evidence to suggest that a close-in-energy locally excited triplet state (3LE) is required to mediate rISC between the charge-transfer triplet (3CT) and charge-transfer singlet (1CT) states.4,5 This mediation of rISC by 3LE is the basis of the spin-vibronic coupling mechanism. Due to the sensitivity of these CT states to their local environment (i.e., solvent or solid-state host), the spin-vibronic model explains the ability to tune the rISC and TADF by changing the polarity of the host, and thus minimizing the energy gap between the CT manifold and 3LE.11 As a result, the choice of emitter host has become a crucial factor during OLED fabrication.

Going beyond the polarity of the host, concentration-induced shifts of the photoluminescence9–11 and electroluminescence3–7 maxima in samples that employ 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) as an emitter are commonly reported in the literature. A study by Kim et al.9 showed that increasing the concentration of 4CzIPN in a nonpolar host caused a significant shift in the CT state emission of 4CzIPN. They attributed this shift to the polarity of the dopant 4CzIPN molecules (ground-state dipole moment, 3.95 D)11 influencing other 4CzIPN molecules indirectly, just as solvent molecules would do in solution. Due to its similarity to the polarity effect of solvents on CT state emission, the shift of CT emission in films is known as the solid-state solvation effect (SSSE). It implies that consideration

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of the concentration of the emitter is also an important variable for fabrication of TADF OLEDs.

However, recent work by Northey et al.\(^{19}\) has shown that SSSE is not as effective as the analogous phenomenon in liquid solvents in changing the emission of CT states when comparing solvents and hosts of similar polarity. The difference arises due to the inability of the solid-state host to reorganize around the emitter molecule, which is the manifold that gives rise to the solvatochromism in solution. In this work, we use 4CzIPN (Figure 1a) to demonstrate that, rather than SSSE, the formation of aggregated/dimer states is instead the predominant reason for the significant emission shifts observed with concentration for multi-carbazole TADF emitters. This explanation is based on the wealth of literature relating to carbazole-based compounds, e.g., poly(N-vinylcarbazole) (PVK) and 4,4′-bis(N-carbazolyl)-1,1′-biphenyl (CBP) as well as carbazole’s known propensity for intermolecular interactions through either fully overlapped (FO) or partially overlapped (PO) co-facial dimers (Figure 1b).\(^{20–24}\) This aggregate/dimer interpretation is built on recent work performed on several multifunctional materials that exhibit aggregation-induced emission, TADF, and mechanochromic luminescence (MCL)\(^{25–30}\) while enabling further discussion on how to tackle the problem of color purity for TADF molecules. On this basis, we expect that future studies of TADF-active emitters will benefit from the use of a broader range of analytical techniques to fully interpret novel molecules’ properties.

\section*{RESULTS AND DISCUSSION}

In this study, 4CzIPN is used as the model system. However, to provide supporting evidence for the conclusions and to expand the generality of our findings, four other similar molecules were also investigated (Figure 1a). Synthetic procedures and NMR spectroscopic characterization can be found in Schemes S1–S3 and Figures S1–S8 in the Supporting Information.

\subsection*{Photoluminescence of Dilute Solutions and Crystals.}

Differences in the emission energy between dilute solutions and crystals are not conclusive evidence for aggregation/dimerization and could be explained by SSSE. However, the significant emission shifts we observed for all molecules (Figures 2a,b and S9) would be difficult to explain by SSSE alone. The energies of the peaks and onsets of the emission spectra of the molecules in solution and crystal states are shown in Table 1.

The crystals of both 4CzIPN and 4CzTPN have an emission onset lower in energy than equivalent solutions in acetonitrile. If the shifts in emission energies were solely a result of SSSE, considering the findings reported by Northey et al., it would imply that these small molecules have the same solvation effect as acetonitrile (dielectric constant (\(\varepsilon\)) = 37.5), even though they lack the ability to reorganize. Furthermore, while the full-width at half-maximum (FWHM) of a molecule’s CT emission profile typically increases with increasing solvent polarity,\(^{31–33}\) the emission spectra of the crystals feature relatively sharp peaks. Therefore, their narrower FWHM contradicts the hypothesis that the solid-state emission energies are influenced significantly by SSSE. We suggest that the red shift in emission is instead a result of direct intermolecular interactions.

The need to go beyond SSSE as an explanation for these emission shifts is further emphasized in Figure S10 which shows the difference between polycrystalline 4CzTPP and 4CzTPN in dimethylsulfoxide (DMSO). Upon allowing the crystals to take up DMSO solvent, we observe that the fluorescence of the polycrystalline sample changes from orange to yellow (emission blue shift). This would suggest that 4CzTPN in the crystal has a polarity effect greater than DMSO (\(\varepsilon = 47.2\)). Based on the findings by Northey et al.,\(^{19}\) we consider it implausible that such a solid-state shift arises from SSSE, thus we must consider that the breakup of the

\begin{figure*}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) Structural formulas of TADF-active compounds. (b) Fully overlapped (FO) and partially overlapped (PO) dimers formed by two carbazole units.}
\end{figure*}

\begin{figure*}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{(a) Steady-state photoluminescence of 4CzIPN in a series of solvents (20 \(\mu\)m) and in crystal form (Fraction 1 from sublimation). (b) Solvent series for 4CzTPN (10 \(\mu\)m, due to low solubility) and as a crystal (Fraction 1 from sublimation). (c) Photograph of 4CzIPN after sublimation. The sublimation tube is illuminated by an ultraviolet torch and the observed colors are indicative of crystal polymorphs with different emission properties. The regions referred to as Fractions 1, 2, and 3 are labelled. (d) The steady-state fluorescence spectra of Fractions 1, 2, and 3 of 4CzIPN.}
\end{figure*}
intermolecular interactions (dimerization/aggregation) is the cause for such a large perturbation of the emission. Figure S9 also reveals that the bulky tert-butyl groups of 4CzIPN-\textsubscript{Bu\textsubscript{8}} and 4CzTPN-\textsubscript{Bu\textsubscript{8}} do very little to stop dimer formation in these molecules, as they behave like their non-tert-butylated analogues.

The spectra attributed to the crystal form for these compounds relate to the first fraction obtained by sublimation, “Fraction 1”, which is identified in the photograph (Figure 2c) using 4CzIPN as an example. It is also apparent from this photograph and Figure 2d that the emission color of 4CzIPN changes as a function of recrystallization temperature along the sublimation tube. These differences in the emission spectra of the sublimation “Fractions” of 4CzIPN will be explained in more detail later.

**Photoluminescence of Doped Zeonex Thin Films.**

These intermolecular interactions not only dominate in the crystalline form but are also present in doped thin films. Figure 3 shows that the emission spectra of 4CzIPN-doped zeonex films red-shift as a function of increasing concentration of the emitter. At 10 weight percent (wt %), with the shift saturating between 6 and 10 wt %.

![Figure 3](image)

**Figure 3.** (a) Normalized absorption of 4CzIPN in a zeonex host at different doping concentrations. The band edge begins to red-shift at 1 wt %, with the shift saturating between 6 and 10 wt %. (b) The photoluminescence of the same films showing the same red shift in emission with increasing concentration. The shift occurs at the same concentrations as for the absorption and again saturates between 6 and 10 wt %. The high-energy tail in the high concentration films (3 wt % and above) is attributed to inhomogeneous dimer/aggregate formation, leaving regions of relatively isolated 4CzIPN.

Table 1. Onset and Peak Emission Energies of the Compounds in Solution and Crystal States

<table>
<thead>
<tr>
<th>compound</th>
<th>MCH</th>
<th>PhMe</th>
<th>2-MeTHF</th>
<th>MeCN</th>
<th>crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>4CzIPN</td>
<td>2.80 (2.58)</td>
<td>2.71 (2.41)</td>
<td>2.68 (2.34)</td>
<td>2.57 (2.16)</td>
<td>2.47 (2.33)</td>
</tr>
<tr>
<td>4CzTPN</td>
<td>2.58 (2.42)</td>
<td>2.49 (2.28)</td>
<td>2.52 (2.22)</td>
<td>2.44 (2.04)</td>
<td>2.23 (2.06)</td>
</tr>
<tr>
<td>4CzIPN-\textsubscript{Bu\textsubscript{8}}</td>
<td>2.68 (2.47)</td>
<td>2.60 (2.33)</td>
<td>2.58 (2.25)</td>
<td>2.44 (2.05)</td>
<td>2.52 (2.35)</td>
</tr>
<tr>
<td>4CzTPN-\textsubscript{Bu\textsubscript{8}}</td>
<td>2.48 (2.34)</td>
<td>2.41 (2.21)</td>
<td>2.41 (2.16)</td>
<td>2.21 (2.04)</td>
<td></td>
</tr>
<tr>
<td>4CzIPN-Br\textsubscript{1}</td>
<td>2.80 (2.60)</td>
<td>2.72 (2.43)</td>
<td>2.71 (2.35)</td>
<td>2.57 (2.16)</td>
<td>2.50 (2.27)</td>
</tr>
</tbody>
</table>

\(^*\)Peak energies are in parentheses. All values are in eV.

The time-resolved photoluminescence of \(^1\text{CTD}\) in 4CzIPN (Figure 4) was measured by exciting the 10 wt % film at 2.33 eV [532 nm], which is significantly below the 4CzIPN monomer charge-transfer (\(^1\text{CT}\)\textsubscript{M}) absorption (2.5 eV). The emission spectrum of \(^1\text{CTD}\) remains constant as a function of time and is identical to that observed in both the high concentration films in Figure 3 and the emission spectra of the neat films reported in the literature. \(^1\text{CTD}\) is also found to be TADF active, meaning that it is not just the monomer species of 4CzIPN that undergoes rISC in this material. The delayed fluorescence (DF) lifetime of \(^1\text{CTD}\) is 2.7 μs at room temperature (RT), which increases to 4.8 μs at 80 K. The presence of delayed emission at 80 K suggests an efficient rISC process and a small singlet–triplet energy gap for \(^1\text{CTD}\). The

![Figure 4](image)

**Figure 4.** Time-resolved emission spectra and decays of 10 wt % doped 4CzIPN:zeonex film excited at 532 nm. (a, b) The room temperature spectra of the film, showing the consistent line shape maintained throughout the prompt and delayed time regions. (c, d) The spectra also remain unchanged at 80 K, and TADF is still observed, suggesting a very small singlet–triplet gap. (e) Time-resolved emission decay at RT and (f) at 80 K.
full kinetic fittings for the room temperature and 80 K data are shown in Table S1. All of the data include a short lifetime (4–6 ns) contribution, arising from the tail of the high-energy laser pulse (>200 μf) required to achieve reasonable signal-to-noise using direct 1CTD excitation.

Overlaying the prompt emission spectra of 1CTD with the time-resolved photoluminescence spectra of the 0.3, 1, and 10 wt % films (excited at 355 nm i.e., into the monomer absorption band) allows the significant influence of this dimer state to be fully uncovered (Figure 5).

![Figure 5](image-url)

**Figure 5.** Time-resolved emission spectra of the doped 4CzIPN-zeonex films at room temperature. (a, b) The prompt and delayed emission of the 0.3 wt % doped film, which is dominated by monomer emission in a nonpolar environment (onset 2.78 eV [446 nm]). (c, d) The 1 wt % film has a small red shift at intermediate times of 50–100 ns because of the dimeric species and returns to full monomer TADF at longer times. (e, f) The 10 wt % film is dominated by the dimer emission but has contributions from the monomer species at prompt and long times, a result of the slower rISC rate for the CTD in a nonpolar environment. The filled yellow peak overlaid in each panel is the dimer emission observed after a 11 ns delay time from a 10 wt % zeonex film of 4CzIPN at RT using 532 nm excitation (as shown in Figure 4a).

While the 10 wt % film emission is predominantly from 1CTD (shaded area), even in the 1 wt % film there is also a small red shift at intermediate times as a result of the dimer. The observation of dimer contribution in such a dilute film is very surprising and conflicts with the assumption (often tacit) in previous studies of 4CzIPN that emission from “low” concentration films (<10%) comes exclusively from the monomer. In the 10 wt % films, a small contribution from 1CTM is present, which accounts for the high-energy onset of 2.78 eV [446 nm] in the prompt spectra. This high-energy component is absent with 532 nm excitation, giving further support to the assertion that the 532 nm laser excites 1CTD directly, rather than through donor 1LE excitation. The formation of 1CTM by 355 nm excitation accounts for the emergence of monomer TADF line shape in the 10 wt % film at longer times. The full shifts of the emission peaks of these doped films as a function of concentration and temperature are shown in Figure S12.

The prompt lifetimes of 1CTM in these films is approximately 5–7 ns, which is shorter than the 8 ns lifetime observed for 1CTM in methlycyclohexane (MCH) solution (Figure S13 and Table S2). This small reduction in lifetime is attributed to quenching of 1CTM to form 1CTD states (lifetime 20–30 ns) in the solid state. The 10 wt % film at room temperature has a shorter DF lifetime (2.05 μs) than the MCH solution and 0.3 and 1 wt % films, which is attributed to the faster rISC in 1CTD. The full decay profiles and fittings are shown in Figure S14 and Tables S3–S5.

The photoluminescence quantum yields (PLQYs) of the 10 and 1 wt % films were measured to identify if quenching processes shorten the measured DF lifetimes. The natural lifetimes for the DF are shown in Table S6. Even considering the significant reduction in PLQY with increasing concentration, the natural lifetime of 1CTD is still shorter than 1CTM, consistent with the smaller 1CTD=3LEDM energy gap (∆EST for the dimer).

Spectra and decays obtained at 80 K (Figure S15) show that the 1CTM TADF in the 0.3 and 1 wt % films is significantly reduced, although delayed emission from 1CTD remains. This smaller temperature dependence in the 1CTD delayed emission intensity is further evidence that 1CTD has a much smaller singlet–triplet energy gap—with its associated dimeric locally excited triplet (3LED)—than the monomer. This phenomenon is also seen in the 10 wt % film, where the 1CTD exhibits significant TADF even at 80 K. For all films at long times, the phosphorescence of the monomer species (3LEDM) is observed (onset 2.69 eV [460 nm]), which is a direct result of the excitation wavelength (355 nm) exciting the 3LEDM state of the molecule.

Excitation fluence dependence measurements of the delayed emission (Figures S16 and S17) confirm that emission arises from TADF and not any bimolecular process occurring in the aggregate regions, even at low temperature where rISC is inhibited.

**Evaporated Films and Device Physics.** The photophysical analysis of the doped zeonex films demonstrates that dimer formation for 4CzIPN and related molecules is critically dependent on the conditions of sample preparation. In Figure 6, the photoluminescence spectra of evaporated films of 4CzIPN in 3,3′-bis(N-carbazolyl)-1,1′-biphenyl (mCBP) show the same trend as that observed in zeonex films. This surprising presence of dimer species even in evaporated films also explains the observed behavior of 4CzIPN and related materials in OLED devices.

This red shift in emission is also replicated in the electroluminescence spectra from model devices with an emissive layer of 4CzIPN co-doped in mCBP at different concentrations. A full series of concentration measurements is shown in Figure S18, and the device structure is detailed in the caption of Figure 6. The changes in the electroluminescence spectra are consistent with the photoluminescence emission observed in different regions and are thus independent of the device structure and transport layers. The phenomena are related to the emission layer only and are consistent with the emission red shifts reported in solution-processed and evaporated films by
lower in energy than that of the dilute (0.3 and 1 wt %) even though it is most likely the monomer state of solvent. Also completely reversible by dissolving the annealed films before and after heating to 250 °C. Upon analyzing the powder X-ray diffraction (PXRD) data obtained from these samples (Figure S26a), it appears that the contribution from 1CTD in Fractions 2 and 3 is due to a blue shift in the TADF. The prompt and DF emission lifetimes of 1CTM and 1CTD are consistent with those observed in the neat films (Figure S25 and Tables S9–S11).

The structure observed in the time-resolved spectra of the sublimed crystals is attributed to the nature of the dimer state. We consider the dimers to be intermolecular species, and there will be a fixed distance between the carbazoles in a single crystal. Consequently, certain modes and geometries will be prevalent. This phenomenon is the origin of the vibronic structure in the spectra of the sublimed crystals.

Upon analyzing the powder X-ray diffraction (PXRD) data obtained from these samples (Figure S26a), it appears that the contribution from 1CTM in Fractions 2 and 3 is due to a reduction in the long-range intermolecular order. The diffraction patterns from the powdered samples are in good agreement with the simulated PXRD pattern based on the single crystal X-ray structure of material obtained from Fraction 1 (Figure S26b).

**Sublimed Crystals.** To deconvolute the steady-state spectra of the 4CzIPN crystals obtained after sublimation, the time-resolved photoluminescence of these samples was analyzed (see Figures S23 and S24). While the spectra are dominated by 1CTM emission, all fractions have a small contribution from 1CTD, resulting in the high-energy onset above 2.6 eV [477 nm]. This monomer contribution is more prominent in Fractions 2 and 3, where there is also a blue shift in the TADF. The prompt and DF emission lifetimes of 1CTM and 1CTD are consistent with those observed in the neat films (Figure S25 and Tables S9–S11).

The structure observed in the time-resolved spectra of the sublimed crystals is attributed to the nature of the dimer state. We consider the dimers to be intermolecular species, and there will be a fixed distance between the carbazoles in a single crystal. Consequently, certain modes and geometries will be prevalent. This phenomenon is the origin of the vibronic structure in the spectra of the sublimed crystals.

**Solvent-Grown Crystals.** Crystals formed as solvates were grown from solvent mixtures of acetone/hexanes, tetrahydrofuran (THF)/hexanes, and chloroform/hexanes. The 532 nm-excited 1CTD spectrum matches perfectly with the time-resolved emission of these solvent-grown crystals (Figures S27 and S28). For the pristine, annealed, and 1 wt % films is shown in Table 2, alongside the singlet–triplet gap and empirical rISC rate. The difference between the annealed and 1 wt % emission is attributed to SSSE and the mechanism proposed by Kim et al.,9 however, the further shift between the annealed and pristine films arises from the intermolecular interactions.

Emission from 1CTD still dominates the time-resolved spectra of the pristine neat film at room temperature and 80 K, whereas the annealed film retains the higher energy contribution from 1CTM (Figures S20 and S21). At longer times in the 80 K spectra, both films tend toward the dimer phosphorescence (3LED), which is almost isoenergetic to the 1CTD emission. The lifetime fits are shown in Figure S22 and Tables S7, S8.

By comparing the natural lifetimes (see Table S6) of the films, 1CTM in a neat film is found to have a shorter DF lifetime than 1CTD, even though they have very similar energy gaps. The rISC rate of 1CTM is slow in zeonex and fast in the annealed film due to the change in the 1CTM−3LED energy gap from 0.09 eV to approximately 0.03 eV due to SSSE. The experimentally calculated rISC rate of 1CTD is quite low considering its small singlet–triplet energy gap. However, this is attributed to the low PLQY of the dimer state.

**Pristine and Annealed Neat Films.** The dimer state in 4CzIPN can be controlled through thermal annealing. This was demonstrated by measuring the emission of a neat dropcast film before and after heating to 250 °C. Upon heating, the emission onset of the film blue-shifted from 2.55 eV [486 nm] to 2.66 eV [466 nm] (Figure S19). This was attributed to the breakup of dimer species in the pristine film and is a property shared by 4CzIPN and 4CzIPN·Bu3 as shown in Videos S1 and S2. This further implies that the addition of tert-butyl groups to the compounds is insufficient to prevent these intermolecular interactions. The process is also completely reversible by dissolving the annealed film in solvent.

Interestingly, the emission onset of the annealed film is lower in energy than that of the dilute (0.3 and 1 wt %) films even though it is most likely the monomer state of 4CzIPN. The comparison of the onset and peak energies of the emission

Table 2. Measured Energies of 1CT and 1LE, Respective ΔE_{S,T}, and Reverse Intersystem Crossing Rates of 4CzIPN Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔE_{S,T} (eV)</th>
<th>k_{rISC} (10^9 s^{−1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine</td>
<td>0.09</td>
<td>3.8</td>
</tr>
<tr>
<td>annealed</td>
<td>0.02</td>
<td>1.2</td>
</tr>
<tr>
<td>1 wt % zeonex</td>
<td>0.03, 0.16</td>
<td>28</td>
</tr>
</tbody>
</table>

Peak energies are in parentheses. a Monomer 1LE. b Dimer 1LE.
and S28), as do the decay lifetimes (Figure S29 and Tables S12–S14).

Crystal Structures and Polymorphism. Single crystal X-ray diffraction data of the Fraction 1 sublimed crystals of 4CzIPN and 4CzTPN (Figure 7) reveal face-to-face contacts between the aromatic groups of the molecules, particularly in the structure of 4CzTPN. 4CzIPN also has some neighboring-molecule interactions reminiscent of PO carbazole dimers (Figure 1b), which account for the red shift compared to MCH solution in Figure 2a. The same is true for the remaining compounds in the series (Figures S30 and S31). The dimer emission in the solvent-grown crystals is also explained by these interactions (Figures S32 and S33).

Although 4CzIPN was isolated as a crystalline solid after synthesis, the sublimation of the sample gave several visually different fractions (Figure 2c). Nonetheless, all fractions gave NMR spectra identical to the original material showing that these changes in appearance, like the color change of the annealed neat film, are not a result of decomposition. Fractions 1 and 2 were characterized by differential scanning calorimetry (DSC) (Figure S34) and thermogravimetric analysis (TGA) (Figure S35). For both fractions, the DSC data show two possible melting peaks ranging from 650.1 to 651.0 K (Figure S34), whose prevalence depends on the preparation conditions. Upon grinding the crystals obtained from chloroform/hexanes, only one sharp melting peak at 650.1 K appears in the DSC. This observation provides evidence that mechanical force can modulate the dimer formation in solid-state samples of this compound (to be discussed in detail later).

On the other hand, 4CzTPN and 4CzTPN-Bu do not show polymorphism. After sublimation, both 4CzTPN and 4CzTPN-Bu retain their orange color both in reflectance and fluorescence, characteristics that are attributed to the dimer species of these molecules. The emission profiles also do not change during the excited-state lifetime of 4CzTPN at room temperature and 80 K (Figure S36), which is attributed to the intermolecular interactions/dimers that are seen in its crystal structure (Figure 7). The DF lifetime of the dimer state in 4CzTPN at room temperature is 1.89 μs as shown in Figure S36 and Table S15. The lifetime fit at 80 K is shown in Figure S37.

Mechanochromic Luminescence (MCL). The MCL of 4CzIPN (Figure S38) is also related to these dimeric interactions. When crystals of sublimed 4CzIPN were ground by hand in a pestle and mortar, a significant red shift and broadening of the emission occurred. This red shift was attributed to an increase of the dimer states and the resultant emission is consistent with that of 1CTD. However, when a host molecule was included in the grinding, weaker MCL and a reduced red shift in emission were observed. Even the introduction of a polar host bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO), which has a ground-state dipole moment of 8.06 D, did not lead to the significant shifts in emission observed upon grinding of the neat crystals. The reduction in the red shift of the emission by introducing a more polar molecule than 4CzIPN once again confirms that SSSE cannot explain the reported emission shifts in 4CzIPN and related molecules.

CONCLUSIONS

We have discovered that 4CzIPN and related molecules form intermolecular ground-state dimers, which impact on their emission energy and TADF performance, even in evaporated films previously assumed to emit only from 4CzIPN monomers. The influence of these aggregate/dimer states on the TADF mechanism has been characterized through analysis of their fluorescence (in crystal, film, and solution), crystal structures, and MCL behavior. The crystal analysis shows that the molecules pack closely leading to this aggregate/dimer formation, which explains previously reported phenomena, including a significant emission red shift observed by Kim et al. Interestingly, the dimer state (1CTD) undergoes TADF with its own characteristic kinetics.

Our observations also contribute to understanding the photoinduced absorption measurements of Hosokai et al., who reported TADF from “local” and “delocalized” CT triplet states. Their observations of the photoinduced absorption of these states in toluene solution of 4CzIPN would be consistent with excited-state-induced absorption from monomer and dimer states, respectively. Moreover, we find that the 1CTD−LE_D gap is very small, giving efficient TADF in nonpolar hosts, consistent with the observations of Hosokai et al. that the best design of a TADF emitter comes from the delocalized component (or in our interpretation, the dimer). However, the low PLQY of the dimer state means that it is more likely to act as a triplet-trap state in applications.

This work highlights the ubiquity and importance of dimerization in carbazole-based materials and the effects this
can have on TADF behavior and color purity. Without this knowledge, spurious interpretations may be made. We suggest that the unpredictable behavior of many well-known carbazole-based TADF emitters may arise from similar dimer formation in films. As a result, observations in the literature should be reinterpreted within this model and future molecular design should be directed to the choice of bulkier sterically hindered units, which will minimize intermolecular interactions and ensure the predictable properties of the emitters in OLEDs.

**EXPERIMENTAL SECTION**

**Sample Preparation.** Zeonex films were prepared via drop-casting using a mixture of dopant and host (zeonex) at the weight percentage specified. The initial solution concentrations were 1 mg/mL for the dopant and 100 mg/mL for zeonex. The films were dropcast onto a quartz substrate at room temperature to avoid any thermal annealing. The crystal samples were prepared using either the sublimed or solvent-grown crystals fixed with vacuum grease on a quartz substrate. The 4CzIPN-doped mCBP films were evaporated at 100 nm thickness onto a sapphire substrate using a Kurt J. Lesker deposition chamber at a vacuum below 10⁻⁶ mbar.

**Sublimation.** The materials were sublimed using a Creaphys DSU05 organic sublimation system.

**Optical Characterization.** Optical measurements in solution used concentrations in the 10⁻⁵–10⁻² M range. Degassed solutions were prepared via the freeze–thaw method (5 repeats). Absorption and emission spectra were collected using a UV-3600 double beam spectrophotometer (Shimadzu) and a Fluoromax fluorimeter (Jobin Yvon). The MCL measurements were performed using an Ocean Optics spectrometer and a 395 nm UV torch. The PLQY measurements were performed with 365 nm excitation from an Ocean Optics QePro Spectrometer.

**Time-Resolved Photoluminescence.** Time-resolved photoluminescence spectra and decays were recorded using a nanosecond gated spectrograph-coupled iCCD (Stanford) using either an Nd:YAG laser emitting at 355 nm (EKSPLA) or an N₂ laser (Lasertechnik Berlin) emitting at 337 nm. Values of ᵦₑ were calculated according to “approach b” reported by dos Santos et al. using the natural lifetime and the integrals of the prompt and delayed fluorescence.

**Device Fabrication.** OLED devices were fabricated using precleaned indium tin oxide (ITO)-coated glass substrates with an ITO thickness of 50 nm. A 20 nm thick PEDOT:PSS layer was spin-coated to the precleaned ITO substrates and the substrates were heated afterward for 10 min at 180 °C. The small-molecule and cathode layers were thermally evaporated using a Kurt J. Lesker deposition chamber below 10⁻⁶ mbar.

**Single Crystal X-ray Diffraction.** Experimental details and a detailed description of the 4CzIPN crystal dihedral angles can be found in Figures S39–S42 and Tables S16–S18.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b01458.

General methods; synthetic methods; Photographs of 4CzTPN in powder form and DMSO solution under room light and UV light conditions; Photoluminescence (PL) spectroscopy of zeonex films and methylcyclohexane solution of 4CzIPN; PL spectroscopy of sublimed crystals of 4CzIPN; molecular packing and interactions in the solids; mechanochromic luminescence; X-ray crystallography (PDF).

Breakup of dimer species in pristine films of 4CzIPN and 4CzIPN:Bu₈ (AVI) (AVI)

CCDC 1873416–1873427 contains the supplementary crystallographic data for this paper (ZIP).

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**Notes**

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**NOTE ADDED AFTER ASAP PUBLICATION**

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