Dimers or Solid-State Solvation? Intermolecular Effects of Multiple Donor–Acceptor Thermally Activated Delayed Fluorescence Emitter Determining Organic Light-Emitting Diode Performance

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Dedicated to Professor Karl Leo on the occasion of his 60th birthday

Organic light-emitting materials exhibiting thermally activated delayed fluorescence (TADF) show great promise for improving display applications. Recently, intermolecular effects between emitting molecules have been given more attention, revealing strong solid-state solvation or aggregation induced changes of sample performance. Implications of this on device performance are not yet fully covered. In this work, a thorough investigation of a novel TADF emitter, methyl 2,3,4,5,6-penta(carbazol-9-yl)benzoate (5CzCO2Me), is provided. Steady-state emission spectra reveal a luminescence redshift with increasing emitter concentration in a small molecule host. In all investigated concentrations, the emission profile remains the same; thus, the redshift is attributed to the solid-state solvation effect. The highest photoluminescence quantum yield (PLQY) is achieved in the 20 wt% sample, reaching 66%. The best organic light-emitting diode (OLED) in terms of current–voltage–luminance and external quantum efficiency (EQE) parameters is the device with 60 wt% emitter concentration, reaching maximal EQE values of 7.5%. It is shown that the emitter transports holes and that charge-carrier recombination does not take place on the bandgap of the host, but rather, a mixed host–guest concentration-dependent recombination is seen. The hole-transporting properties of 5CzCO2Me allow for a new dimension in tuning the device performance by controlling the emitter concentration.

1. Introduction

Organic materials exhibiting thermally activated delayed fluorescence (TADF) have been extensively investigated in the past decade.[1–3] Because of their molecular design, wherein charge donating and accepting moieties are spatially separated, their lowest excited singlet and triplet states lie very close in energy, allowing for a thermally activated upconversion from the latter to the former, called reverse intersystem crossing (rISC).[4,5] Typically, triplet states are nonemissive in purely organic emitters, limiting their quantum efficiency. This is especially relevant in OLEDs, due to fundamentally occurring initial singlet fraction of ¼ upon charge-carrier recombination.[6] TADF materials overcome this limitation by harvesting the triplet states, giving rise to a delayed fluorescence with an emission spectrum of the singlet state and an excited state lifetime of the triplet state. Therefore, utilizing

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TADF in OLEDs can greatly increase their efficiency and reduce power consumption compared to conventional fluorescence-based OLEDs. Most TADF emitters in literature consist of multiple donors (D) or acceptors (A) with a certain spatial or angular separation between them. Because of the D–A nature, the lowest emissive state in these materials is an intramolecular charge-transfer (iCT) state. CT states are sensitive not only to conformational changes, but also to changes in the polarity of their surroundings even in the solid state.\(^{[7]}\)

Recently, there have been investigations of concentration-induced effects of TADF emitters.\(^{[8–13]}\) Observed effects include changes in photophysical and electrical properties when increasing the emitter concentration in a matrix, leading to a shift in emission spectrum, photoluminescence quantum yield (PLQY), excited state lifetime, turn-on voltages, and external quantum efficiency (EQE) values in devices. A new pathway for device optimization should be considered, as a change in the host/guest ratio can influence the CT state energy in different ways. Solvation effect due to change in the environment of the exciton in the solid state, known as the solid-state solvation effect (SSSE),\(^{[14–16]}\) and intermolecular interactions or formation of new emissive species like dimers or aggregates\(^{[8,12,17]}\) have both been shown to have tremendous impact on the emissive properties of materials.

In this work, we investigate a novel TADF emitter, methyl 2,3,4,5,6-penta(carbazol-9-yl)benzoate (5CzCO\(_2\)Me), at various impact on the emissive properties of materials. With the concentration-dependent changes taken into account, and additional measurements on single-carrier devices are conducted, uncovering new TADF OLED design considerations with the concentration-dependent changes taken into account.

### 2. Density Functional Theory Calculations

The model compound is analyzed with density functional theory (DFT) at the B3LYP/6-31G(d) level,\(^{[19]}\) and transition energies in the optimized \(S_0\) geometry are calculated with time-dependent density functional theory (TD-DFT) using the same hybrid functional and basis set (Table 1).

In each carbazole, the highest occupied molecular orbital (HOMO) and HOMO–1 levels are rather close in energy, so that five carbazole ligands result in altogether ten highest valence states within an energy window of only about 0.44 eV for their Kohn–Sham energy eigenvalues, where the five highest lying orbitals are dominated by combinations of the carbazole HOMOs cover an energy range half as wide. Lowest unoccupied molecular orbital (LUMO) and LUMO+1 are localized on the methyl benzoate group, with patterns on the phenyl resembling the two degenerate LUMOs of benzene. The LUMO extends somewhat toward the methyl benzoate functionalization (Scheme 1d), so that it lowers its energy by about 0.16 eV with respect to the LUMO+1 with a node plane along the bond toward the methyl benzoate, avoiding an energetic influence of this ligand. Instead, the LUMO+1 contains antibonding contributions involving the nitrogen atoms of four carbazole ligands (Scheme 1e).

In TD-DFT, singlet excitations from 1 to 20 correspond to transitions between ten highest valence states given by superpositions of HOMO or HOMO–1 orbitals on each carbazole group toward the two lowest virtual states on the acceptor group, covering a range from 3.10 to 3.77 eV. The strongest among these CT transitions is \(S_5\) at 3.29 eV, with an oscillator strength as low as 0.073. Twenty five excitations dominated by transitions among carbazole HOMO and LUMO states cover an energy range from 4.06 to 4.54 eV, the strongest among these transitions being \(S_{24}\) at 4.12 eV, with an oscillator strength of 0.071, i.e., quite close to the HOMO–LUMO transition energy on free carbazole, with a calculated TD-DFT value of 4.15 eV.

At the B3LYP/6-31G(d) level, the lowest triplet transition \(S_0 \rightarrow T_1\) turns out to be a mixture of CT and local excitations (LE) on the acceptor group. As the energy alignment of CT and local excitations is problematic in TD-DFT based on classical hybrid functionals without range separation, this transition will not be discussed any further. Concerning the obvious pairs of singlets and triplets dominated by transitions between the same pair of Kohn–Sham orbitals, the singlet–triplet splitting scales roughly with the oscillator strength of the respective singlet transition, as expected

\[
S_0 \rightarrow S_2\text{ and } S_0 \rightarrow T_2 \text{ show a splitting of } \Delta E_{ST} = 0.05 \text{ eV} \tag{1}
\]

\[
S_0 \rightarrow S_3\text{ and } S_0 \rightarrow T_3 \text{ are split by } \Delta E_{ST} = 0.12 \text{ eV} \tag{2}
\]

\[
S_0 \rightarrow S_4\text{ and } S_0 \rightarrow T_4 \text{ by } \Delta E_{ST} = 0.07 \text{ eV} \tag{3}
\]

### 3. Photophysical Properties

#### 3.1. Steady-State Spectra and PLQY

To investigate the photophysical properties of the emitter 5CzCO\(_2\)Me, thin films with varying concentrations of the emitter in the host DPEPO were prepared. A total of eight different samples were produced by thermal co-evaporation on quartz substrates, using different evaporation rates to ensure

| Transition   | Energy [eV] | Oscillator strength | Largest contribution |
|--------------|-------------|---------------------|----------------------|
| \(S_0 \rightarrow S_1\) | 3.10 | 0.025 | CT, HOMO → LUMO |
| \(S_0 \rightarrow S_2\) | 3.12 | 0.047 | CT, HOMO → LUMO+1 |
| \(S_0 \rightarrow S_3\) | 3.17 | 0.014 | CT, HOMO → LUMO+2 |
| \(S_0 \rightarrow T_1\) | 2.82 | Mixed: CT and acceptor LE |
| \(S_0 \rightarrow T_2\) | 3.00 | CT, HOMO → LUMO+1 |
| \(S_0 \rightarrow T_3\) | 3.05 | CT, HOMO → LUMO |
| \(S_0 \rightarrow T_4\) | 3.09 | CT, HOMO–2 → LUMO |
different concentrations: 1, 5, 20, 30, 40, 60, 80, and 100 wt% (neat film of emitter), with the film thickness always being 50 nm. No solutions of the emitter could be prepared as the material showed very little solubility in typical organic solvents.

The fluorescence spectra (Figure 1a,c) appear broad and structureless throughout the concentration range investigated. The emission of the 1 wt% sample is sky blue, with the emission peak at 2.6 eV, and the 100 wt% sample appears yellow–green, with emission at 2.3 eV. Thus, the emitter can be tuned in a wide range of the visible spectra just by changing its concentration in the film.[20] In recent TADF literature on novel materials, a common motif is observed at higher emitter concentrations, the emission spectrum redshifts.[13] Contrasting explanations have been offered for the archetypical TADF emitter 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN),[1] which shows a similar redshift feature. Kim et al. suggested that the observed effect is due to SSSE, [15] while Etherington et al. followed up the study and revealed that dimer formations are the more likely reason.[8] In the context of photophysical properties, dimers are considered as a new emissive species, with distinct spectral and temporal characteristics.

Emission spectra of fluorescence (Figure 1a) and phosphorescence (Figure 1b) are displayed in energy and normalized by a factor of $E^1$ related to the density of states of photons. Hence, these rescaled emission spectra reveal a line shape arising directly from the molecular deformation in the relaxed excited geometry. Due to very low signal, no reliable phosphorescence spectrum could be recorded for the 1 wt% sample. A line shape fitting, where each spectrum is fitted to a single vibronic progression, as described in ref. [21], is carried out, allowing for an average energy ($E_{\text{vertical}}$) estimation for both fluorescence (Figure S1, Supporting Information) and phosphorescence (Figure S2, Supporting Information). The summary of this line shape analysis is given in Table S1 (Supporting Information).

The energy average $E_{\text{vertical}}$ represents the vertical energy difference between the potential minimum of an electronic excited state and the ground state in the same relaxed excited geometry. The range of the redshift between 1 and 100 wt% samples is around 0.3 eV, when comparing emission peaks. However, if each spectrum is shifted downward by its average energy $E_{\text{vertical}}$, it becomes clear that the shapes of the fluorescence and phosphorescence emission spectra do not depend on concentration (Figure 1c,d). This suggests that at high concentrations, the emitter does not form dimers or aggregates, which would result in a new emissive species with a different emission spectrum.[8,10] Rather, intermolecular interactions like SSSE change...
the CT energy,\textsuperscript{[16]} which implies that the polarizability of the emitter is larger than that of the host DPEPO. We know from DFT calculations shown in the previous section that the lowest excited states in our emitter are of CT character, so this behavior can be expected. In this case, higher emitter concentration in the film means a more polarizable environment overall, leading to the self-tuning of emitter to lower energies, while maintaining the same emission shape. To confirm these findings, thin films with the emitter embedded into 1,3-di(9H-carbazol-9-yl)benzene (mCP) were produced. mCP in this case acts as a less polar host, wherein the SSSE effect should also be present to a larger extent. Indeed, this is what is observed from fluorescence spectra (Figure S3a, Supporting Information). Shifting the emission spectra in mCP yields the same result with perfectly overlapping emission shapes (Figure S3b, Supporting Information). The only difference is low concentration samples (1, 5, and 20 wt% to some extent). The emission spectra of 1 and 5 wt% samples in mCP have the same shape, which displays a clear vibronic structure, indicating that the environment at low concentrations is not polar enough to stabilize a CT state. Increasing the emitter concentration in the films yields the same redshift as in DPEPO, with monotonically decreasing $E_{\text{vertical}}$ values (Table S2, Supporting Information), confirming that the emitter is responsible for SSSE in our samples.

Molecular packing plays a major role in our samples, and quenching is present in the film at higher concentrations, as seen in the reduced PLQY and time-resolved data (Tables 2 and 3). In addition, the packing of the emitter molecules has a large impact on OLED performance, as will be discussed later.

Fluorescence emission spectra as a function of wavelength are displayed in Figure S4 (Supporting Information). Since phosphorescence spectra (Figure 1b,d), recorded at 77 K, shift with emitter concentration in the same fashion as discussed above, it should be concluded that the emissive triplet state in this case is also influenced by its surroundings, indicating a $^{3}\text{CT}$ state.\textsuperscript{[22]} This assumption is supported by literature, where carbazole and methyl benzoate triplet energies can be found,\textsuperscript{[23,24]} with peaks corresponding to around 3.05 and

![Figure 1. a,b) Fluorescence spectra and phosphorescence spectra, c,d) fluorescence and phosphorescence spectra shifted according to $E_{\text{vertical}}$, and e) absorption spectra of all eight samples. f) The $E_{\text{vertical}}$ energy values for fluorescence and phosphorescence spectra for each sample and their resulting difference.](image-url)
3.37 eV, respectively. No emission is recorded in that range in our samples, indicating that phosphorescence arises not from a locally excited unit of carbazole or methyl benzoate, but from a larger excited state, likely spanning both or more units. Notably, in Figure 1b, there is a shoulder peak at around 2.75 eV, which is especially visible at lower concentrations (see 5 wt%), which seems to be decreasing monotonically with increasing concentration after shifting the spectra (Figure 1d); however, at higher than 5 wt% concentrations, the change is more minor. The reduction in intensity of this shoulder peak could arise due to self-absorption in the samples. Nevertheless, this could serve as an indication that residual 3LE state contributes to the phosphorescence spectra, indicating that the lowest excited triplet state has mixed 3LE and 3CT characters.

Table 2. Photophysical properties of the samples of 5, 20, 60, and 100 wt%.

| Concentration | 5 wt% | 20 wt% | 60 wt% | 100 wt% |
|---------------|-------|--------|--------|---------|
| \( E_{\text{vertical}}^{\text{sto}} \) [eV] | 2.46304 | 2.36957 | 2.27265 | 2.2334 |
| \( E_{\text{vertical}}^{\text{phos}} \) [eV] | 2.45231 | 2.40899 | 2.3635 | 2.2943 |
| \( E_{\text{vertical}}^{\text{sto}} - E_{\text{vertical}}^{\text{phos}} \) [eV] | 0.01073 | -0.04132 | -0.09805 | -0.06143 |
| \( E_0^{\text{phos}} \) [eV] | 2.70531 | 2.64428 | 2.56622 | 2.4659 |
| \( E_0^{\text{phos}} \) [eV] | 2.76837 | 2.72054 | 2.66538 | 2.65666 |
| \( \Delta E_{ST} \) [eV] | -0.06306 | -0.07626 | -0.09916 | -0.19076 |
| PLQY_{ambient} [%] | 28 | 38.8 | 26.7 | 14.4 |
| PLQY_{degassed} [%] | 50 | 66 | 47 | 32 |

Table 3. The averaged lifetimes of prompt (\( \tau_p^{\text{sto}} \)) and delayed (\( \tau_p^{\text{phos}} \)) fluorescence of the four PL samples with different SCzCO2Me concentrations, contributions of prompt and delayed components to the total PLQY (PLQY\(_p\), PLQY\(_d\), respectively), obtained from comparing areas under the prompt and delayed decay curves and the ratio of delayed and prompt areas A\(_d\)/A\(_p\).

| Concentration | 5 wt% | 20 wt% | 60 wt% | 100 wt% |
|---------------|-------|--------|--------|---------|
| \( \tau_p^{\text{sto}} \) [ns] | 6.34 | 8.34 | 7.60 | 6.35 |
| \( \tau_p^{\text{phos}} \) [ns] | 6.70 | 4.94 | 1.07 | 0.50 |
| A\(_d\)/A\(_p\) | 7.82 | 9.18 | 2.04 | 0.76 |
| PLQY\(_p\) [%] | 5.6 | 6.4 | 15.4 | 18.1 |
| PLQY\(_d\) [%] | 44.4 | 59.6 | 31.6 | 13.9 |
| \( k_p \) [s\(^{-1}\)] | 8.9 \times 10\(^6\) | 7.7 \times 10\(^6\) | 2 \times 10\(^7\) | 2.8 \times 10\(^7\) |
| \( k_{\text{davg}} \) [s\(^{-1}\)] | 1.5 \times 10\(^8\) | 1.1 \times 10\(^8\) | 1.11 \times 10\(^8\) | 1.3 \times 10\(^8\) |

To understand the influence of varying emitter concentration on exciton dynamics, photoluminescence transients were

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The TADF emitter 5CzCO2Me shows typical transients of well-resolved prompt and delayed components. The prompt component appears to be almost independent of emitter concentration in the sample, while the delayed component changes strongly. The decay transients are displayed in Figure 2, measured at 480 nm (2.58 eV).

The prompt transients were fitted to a bi-exponential decay model and the delayed transients were fitted to a tri-exponential model for best-fitting results, accounting for different possible conformations of the emitter in the thin film. The resulting fitting values ($\tau_p$, $\tau_d$) are summarized in Table 3, in form of averaged lifetime values (see Experimental Section), and the fits are displayed in Figure S7 (Supporting Information).

As discussed previously, each sample investigated has a distinct emission spectrum, which is shifted according to the emitter concentration in the guest-host blend. Since the shape of the emission does not change and arises from the same emissive species in the sample, the spectrum should not shift drastically in time, apart from spectral diffusion. Wavelength-dependent TCSPC experiments were performed on the two most extreme cases—1 and 100 wt% samples (Figures S5 and S6, Supporting Information, respectively). Our findings go in line with the results discussed in ref. [29], where no dynamic red-shift of TADF emission is observed due to SSSE. Nevertheless, SSSE plays a major role in the TADF performance of our samples. Notably, the delayed emission component goes in line with the PLQY values reported in Table 1, where the area of the delayed emission follows the same trend as the PLQY values, 20 wt% being the highest and 100 wt% the lowest in both cases. 20 wt% emitter concentration in the film leads to a more favorable lowest excited singlet and triplet energy level splittings, which can have an effect on the rISC rate in the sample, leading to higher PLQY values as well as higher intensities of the delayed components in time-resolved data. This is indicated by comparing the areas under the decay curves of prompt and delayed components as well as contributions to total PLQY for each sample (Table 3). The ratio of these areas $A_d/A_p$ reveals that at low emitter concentrations TADF is dominating, with values of 782 and 9.18 for 5 and 20 wt% samples, respectively. At higher concentrations, this ratio drops dramatically to 2.04 and 0.76 for 60 and 100 wt% samples, respectively. From this it can be concluded that at higher concentrations, the TADF process is less efficient, either due to increasing $\Delta E_{ST}$ or due to quenching. Table 3 also includes radiative and nonradiative rates of the prompt components ($k_{p,r}$ and $k_{p,nr}$ respectively), determined according to ref. [30]. We observe that the radiative rate increases at high emitter concentrations, while the nonradiative component does not change strongly between samples. Thus, the quenching in the samples arises from excited triplet states; otherwise, an increase in nonradiative rate would be observed in the prompt rates as well. A reduced radiative rate of the prompt fluorescence is often found as a result of strong solid-state solvation effects. [8,16] However, here the opposite is observed. At higher emitter concentrations (>20 wt% in the present concentration series), the radiative rate of prompt fluorescence increases and the decay lifetime decreases from 20 to 60 and 100 wt%. This indicates that the change of the prompt emission component with increasing emitter concentration is likely governed by a more complex combination of processes, where the data at hand do not allow further interpretation and require additional future investigations.

Exciton quenching cannot be excluded in our samples, since it is a typical effect in films with high emitter concentrations. [15] The long tail of the transients slower than 100 ns observed in samples with higher emitter concentration (60 and 100 wt%) could be a result of emission from bimolecular quenching events like triplet–triplet annihilation (TTA). This is likely part of the reason behind a reduced $A_d/A_p$ ratio in these samples. A higher number of emitters in the sample at higher concentrations make it likely that longer-living triplet states could interact. This effect is sometimes observed in TADF materials but the tails are not included in the transient fitting.

4. Film Morphology and Electrical Properties

4.1. Grazing-Incidence Wide-Angle X-Ray Scattering Measurements

The film morphology and structure of the thin-film samples have been studied with grazing-incidence wide-angle X-ray scattering (GIWAXS) experiments. These were performed on films with different emitter concentrations in the DPEPO matrix. Figure S8 (Supporting Information) shows the resulting 2D images with the quartz being background-subtracted. The prominent ring at $Q \approx 0.75$ Å$^{-1}$ is attributed to disordered lamellar stacking of the small molecules in the film. A second ring at 1.4 Å$^{-1}$ can be observed for the pure DPEPO film and the low emitter concentration films. In order to further analyze the molecular orientation in the films, line cuts in the in-plane direction close to the horizon have been performed and are shown in Figure 3.

For the DPEPO sample, two peaks can be seen: one at small $Q_{xy}$ values, which originates from the lamellar stacking, and one at larger $Q_{xy}$ values, which has a large contribution from the quartz substrate background. The lamellar peak at 0.75 Å$^{-1}$ in the pure DPEPO film shifts gradually with increasing emitter concentration. For the neat film, the peak is located at 0.54 Å$^{-1}$. 

![Figure 2. Photoluminescence transients of four samples with different concentrations of 5CzCO2Me. Areas under the prompt and delayed components are compared in Table 3, and the fits are displayed in Figure S7 (Supporting Information).](image-url)
This corresponds to a real-space distance of 8.3 Å for DPEPO and 11.5 Å for the emitter, which can be explained by the larger size of the emitter compared to DPEPO. The second peak at ≈1.5 Å is dominated by the background signal from the quartz substrate. Background-subtracted line cuts are shown in Figure S9 (Supporting Information), which have shown that beneath the background radiation, a second peak is located at 1.4 Å, which diminishes with increasing concentration and completely vanishes at 60 wt% emitter concentration. At 40 wt% emitter concentration, another peak starts to emerge at 1.0 Å, which is clearly visible in the neat emitter sample. The peak at 1.5 Å for the neat emitter sample only consists of a background signal. Most importantly, no peak or ring can be seen at around 1.8 Å for the high-concentration samples, which would indicate the presence of π–π stacking in the film. Instead, the peak emerging at 1.0 Å indicates that the emitters are loosely packed. Because of the loose packing in the neat emitter film, we assume that no dimers are formed.

4.2. Emitter Orientation

In the previous section, we show that the emitter 5CzCO2Me exhibits molecular stacking without forming dimers. Thus, in order to get more insight into the film morphology, the orientation of the transition dipole moment of the emitter molecules is investigated by angle-resolved photoluminescence spectroscopy.[32] This method is sensitive to even small fractions of emitter molecules in case of low doping concentrations.

The angular spectra at the maximum emission wavelength of 460 nm are depicted in the inset of Figure 4 and show a clear decline of the second emission peak around 55° with increasing doping concentration. Since the emission to large angles mainly originates from vertical dipoles, this indicates a trend to a more horizontal transition dipole alignment. A quantification of this observation is given by the anisotropy coefficient. It corresponds to the relative number of vertical dipoles and takes values between zero (pure horizontal emission) and one (pure vertical emission). It is determined by a numerical approximation of the measured angular emission spectra assuming a constant layer thickness of 50 nm and refractive indices in the range from n = 1.6 to n = 1.8. The resulting dependency is shown in Figure 4, indicating an approximately linear decrease between a = 0.18 (5 wt%) and a = 0.06 (100 wt%).

Such a concentration dependence has been observed for phosphorescent emitters[33] and is described as takeover of the host orientation in case of low doping. The measured pronounced horizontal orientation is remarkably strong for such a rather spherical molecule. For instance, similarly shaped TADF emitters like 4CzIPN (a = 0.27)[33] and 1,3,5-tris(4-(diphenylamino) phenyl)-2,4,6-tricyanobenzene (3DPA3CN) (a = 0.25)[34] show only slight deviations from a random distribution (a = 0.33). Especially, the value of a = 0.06 obtained for the neat layer is in the range of the most horizontally aligned TADF molecules.[35–38]

4.3. UPS Measurements

To investigate the influence of the structural changes on the energetics, ultraviolet photoelectron spectroscopy (UPS) measurements have been carried out on the pure materials as well as on blends with emitter concentrations of 5, 20, and 60 wt%. The resulting spectra can be found in Figure S10 (Supporting Information), and Figure 5 shows the estimated ionization energy (IE) as a function of the emitter content. Within the limits of accuracy of the measurements (~70 meV, see the “Experimental Section”), the IE displays no dependency on the emitter content and is more or less constant. Additionally, a pure DPEPO film is investigated, revealing IE of around 7.2 eV, which is significantly larger than the values reported in literature.[39] Hence, it can be concluded that the observed structural changes have no effect on the energy levels.

5. Current–Voltage–Luminance, EQE, and Spectral Characteristics

In order to evaluate the TADF dynamics and the influence of different concentrations of 5CzCO2Me under electrical excitation, thermally evaporated OLEDs were prepared.
The devices consist of indium tin oxide (ITO)/molybdenum trioxide (MoO$_3$) (0.6 nm)/N,N’-di(1-naphthyl)-N,N’-diphenyl-(1,1’-biphenyl)-4,4’-diamine (NPB) (30 nm)/mCP (5 nm)/DPEPO:5CzCO2Me (x wt%) (15 nm)/2,2’-2″-(1,3,5-benzinetriyl)-tris[1-phenyl-1H-benzoimidazole (TPBi) (65 nm)/lithium fluoride (LiF) (0.8 nm)/Al (100 nm), where MoO$_3$, NPB, and mCP are used as hole injection, hole transport, and exciton-blocking layers, respectively. TPBi () and LiF () are used as electron transport and electron injection layers, respectively. The emitting layer (EML) consists of DPEPO as the host material and 5CzCO2Me as the emitter, doped with varying concentrations into the host by co-evaporation.

DPEPO was selected as the host material because of its high singlet (3.92 eV) and triplet (2.98 eV) energies, because of the observed redshift, are also a reason for extended device lifetime. However, it is commonly used in OLED research and thus serves as a model host for this study.

The $j$–$V$–$L$ curves of OLEDs with the four selected concentrations of the emitter are plotted in Figure 6a. The emitter concentration plays an important role in charge transport in the emitting layer of these devices, leading to different charge-carrier recombination at different concentrations, which is evident from the strong shift of turn-on voltages and steepness of the $j$–$V$ curves.

The recombination current, appearing as an exponential current increase, shifts according to the emitter concentration in our OLEDs. At 5 wt%, the $j$–$V$ curve is shifted to higher voltages and shows a leakage current up to around 4 V. The amount of emitter molecules at 5 wt% is minimal, and a higher voltage is required to fill the EML with holes to balance out the injected electrons by charge-carrier recombination. Therefore, we see a shift from electron leakage to recombination current at around 4 V. At higher emitter concentrations, less voltage is required to inject and transfer holes in the EML, which is evident from a shift in turn-on voltages. The electron injection current in the devices with DPEPO is constant. In all four OLEDs we see a different slope of the exponential regime (Figure 6a,b), corresponding to different hole injection voltages. This is shown in the zoomed-in $j$–$V$ plot in Figure 6b. The lowest hole injection current is seen in the 5 wt% device and the highest—in the 100 wt% device. This increase of hole injection current with increasing emitter concentration is the main factor, governing the performance of our devices. The steepest $j$–$V$ curve is observed for the 60 wt% OLED. Since the emitter has five carbazoles as its side moieties, the hole-transport properties are enhanced by introducing more emitter into the EML, because high exciton energies under electrical excitation.

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OLED lifetime increases with increasing emitter concentration (Figure 6d). As shown in ref. [49], the dominating degradation mechanism in TADF OLEDs with emitters based on multiple carbazole donors and a single acceptor is triplet-polaron quenching (TPQ). Since we improve the charge balance in our devices at higher emitter concentrations, such TPQ events occur less often, leading to less degradation. Lower emission energies, because of the observed redshift, are also a reason for extended device lifetime, as the initial fast degradation of the devices occurs mostly due to bond cleavage on the emitter itself because of high exciton energies under electrical excitation. In electroluminescence (EL) spectra (Figure 6e,f) we observe the same kind of redshift of emission peak with increasing emitter concentration as in thin films. Using the same principle as discussed in Section 3.1, we can show that the emission profile of EL largely remains the same. Therefore, the emission properties influenced by SSSE are valid in OLEDs. The emission spectrum is slightly narrower in the 100 wt% OLED. The emitter concentration affects the emission color, electrical device properties, and efficiency. OLED improvement by charge balance control has been investigated in fluorescent OLEDs by selecting appropriate blocking layers. Here, we show that a
similar improvement can be seen by adjusting the emitter concentration. Key OLED parameters are summarized in Table 4.

The results discussed in this section point to a novel pathway for TADF OLED optimization. In TADF emitters with multiple donors or acceptors, it becomes likely that the emitter itself becomes responsible for charge-carrier transport and balance, given favorable HOMO and LUMO alignments with adjacent layers in the device. Thus, by controlling the emitter concentration in the emitting layer of the OLED, charge balance can be optimized leading to improved electrical characteristics, especially if no strong detrimental concentration-induced effects like bimolecular quenching are observed.

6. Summary and Conclusions

In conclusion, we have demonstrated a novel TADF emitter 5CzCO2Me, and thoroughly investigated its morphological and luminescent properties. The emitter shows a redshift in the emission spectra with increasing concentration in DPEPO, which is assigned to the solid-state solvation effect. Morphological analysis indicates lamellar stacking, but no new emissive species like dimers or aggregates are observed, leading to a highly angle-dependent emission of the molecules at high concentrations. The emitter maintains the same spectral shape

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**Table 4.** Key OLED parameters: turn-on voltage ($V_{on}$), peak EQE (EQEmax), peak emission wavelength ($\lambda_{max}$) and time until 10% of initial luminance is reached ($LT_{10}$).

| Concentration | 5 wt% | 20 wt% | 60 wt% | 100 wt% |
|---------------|-------|--------|--------|---------|
| $V_{on}$ [V]  | 4.6   | 3.6    | 3.3    | 3.9     |
| EQEmax [%]    | 3.4   | 6.8    | 7.6    | 5.6     |
| $\lambda_{max}$ [nm] | 508   | 521    | 536    | 545     |
| $LT_{10}$ [h] | 0.16  | 1.16   | 3.02   | 5.4     |
at all concentrations investigated. The highest PLQY is seen in the 20 wt% sample, but the best-performing OLED is the one with 60 wt% emitter concentration. The mismatch of PL and EL performance arises from improved charge balance in the devices at higher emitter concentrations. It is shown that the emitter transports holes in our devices, leading to turn-on voltages smaller than the bandgap of DPEPO. Our results offer new considerations for TADF emitters with multiple donors and a single acceptor, indicating that without inert moieties that prevent stacking, intermolecular effects play a major role in OLED performance. This work acts as a case study for such emitters; it is shown that aggregation is not the reason for varying emitter performance at different concentrations. Electrical properties of OLEDs based on this emitter are analyzed in detail, leading to a new perspective on OLED stack design, wherein the emitter plays a double role of recombination and hole transport.

7. Experimental Section

Photophysical Measurements: The host–guest films were prepared by thermal co-evaporation with respective evaporation rates to ensure desired emitter concentrations. The steady-state photoluminescence of the materials was measured using a mounted UV-LED (Thorlabs M340L4), with excitation at 340 nm (3.65 eV) in an integrating sphere in inert atmosphere. The phosphorescence measurements were recorded in liquid nitrogen with an internal delay of 10 ns, integrated over 500 ms. A CAS 140 CT Compact Array Spectrometer (Instrument Systems) was triggered using a Hewlett Packard 8114A Pulse Generator. For transient measurements, a picosecond time-correlated single photon counting technique was used. After exciting the sample with a laser diode head (PicoQuant LDH-D-C-375) at 375 nm with a pulse width of 44 ps, the emission was collected from a photomultiplier tube (PicoQuant PMA Hybrid), and data acquisition was handled by a TCSPC module (PicoQuant TimeHarp 260). The photoluminescence quantum yields of the materials were measured using an integrating sphere flooded with nitrogen. The bi- and tri-exponential decays were fitted with

\[ I(t) = \sum A_n e^{-t/\tau_n} \]

with \( n = 1 \) and 2 in the bi-exponential case and \( n = 1, 2, 3 \) in the tri-exponential case. The resulting average lifetime was calculated using the following equation

\[ \tau_{\text{avg}} = \frac{\sum A_n \tau_n^2}{\sum A_n \tau_n} \]

Line Shape Analysis: The distinct sub-bands of the emission spectra were assigned to a progression over an effective internal vibration with an energy of \( \hbar \omega \). For a single molecule, the Franck–Condon coefficients, which are the normalized transition probabilities \( P_n \) from the lowest vibrational level in the electronic excited state toward the \( n \)th vibronic level in the ground-state potential, are given by a Poisson progression determined by the effective Huang–Rhys factor \( S(2,51) \)

\[ P_n = e^{-S} \frac{S^n}{n!} \]

The contribution of each sub-band to the resulting emission spectrum was modeled by a normalized Gaussian. The emission spectrum \( I(E)/E^2 \) can then be fitted by a sum of such Gaussian curves

\[ I(E)/E^2 = \sum P_n (S) \frac{1}{\sqrt{2\pi}\sigma_n} \exp \left( -\frac{(E - E_0)^2}{2\sigma_n^2} \right) \]

The factor of \( E^2 \) arises due to the density of states of photons.\(^{(2)}\) On this basis, the average emitted PL energy corresponds to \( E_{\text{emitted}} = E_0 - \hbar \omega \), where \( E_0 \) is the energy of the 0–0 transition. This represents the average vertical energy difference between the potential minimum of the excited electronic configuration and the electronic ground state in relaxed excited geometry.

GIWAXS: GIWAXS measurements were carried out at the XRD1 beamline at the ELETTRA synchrotron in Trieste, Italy. The incidence angle of the beam was 0.13° and the beam energy was 12.4 keV. The Dectris Pilatus 2M area detector was placed at ~35 cm behind the sample. The sample exposure time was 120 s. The obtained data were analyzed with the WxDiff software (c S.C.B.M.).

UPS: The ultraviolet photoelectron spectroscopy spectra were obtained by a PHOIBOS 100 analyzer system (Specs, Berlin, Germany) at a base pressure of 10⁻¹³ mbar using He I excitation lines (21.22 eV). The spectra were calibrated to the Fermi edge of silver substrates. The energy resolution of the setup obtained from the broadening of the Fermi edge was of around 150 meV, but repeating the sample production under the same experimental conditions gave an experimental resolution of 70 meV. All samples were produced by thermal (co-)evaporation in ultrahigh vacuum at a base pressure of 10⁻¹³ mbar using individual quartz crystal monitors for each material to control the emitter concentration. Rates of 0.1–0.2 Å s⁻¹ were used, and sputter-cleaned silver foils covered with 5 nm of mCP were used as substrates. The layers investigated had a thickness of 15 nm.

Angle-Dependent Emission: The orientation of the transition dipole moment with respect to the surface normal was determined by angle-resolved photoluminescence spectroscopy. Single layers with a thickness of 50 nm and doping concentrations between 5 and 100 wt% were excited by a 405 nm laser. The glass substrates were attached to a glass half-cylinder which was placed on a rotary stage. The emission spectra for each rotation angle were recorded in steps of 5° in a range from −70° to +70°. Two additional lenses were inserted between the half cylinder and detector to enhance the signal-to-noise ratio.

OLED and Single-Carrier Device Preparation and Characterization: Prior to device fabrication, 1” × 1” glass substrates coated with 90 nm thick ITO contacts were cleaned in an ultrasonic bath with N-methyl-2-pyrrolidone, distilled water, and ethanol. Oxygen plasma treatment was applied to the substrates after drying. An ultrahigh-vacuum tool (Kurt J. Lesker, Co., Jefferson Hills, PA, USA) was used for device manufacturing. The evaporation tool has a chamber size, which allows simultaneous evaporation on a 4” × 4” substrate wafer. The wafer was rotated at a constant rate of 10 rpm during evaporation of all layers. Organic and metal layers were thermally evaporated at a rate of 0.5 Å s⁻¹ in a vacuum with a pressure of 10⁻⁷–10⁻⁸ mbar. Thicknesses and evaporation rates of all layers were monitored in situ via a quartz crystal microbalance (QCM). Layer doping was achieved by co-evaporating two materials at the same time with corresponding rates. The devices were encapsulated immediately after thermal evaporation in an inert atmosphere.

The measurements of the encapsulated devices were done under ambient conditions. Electrical and optical characteristics of the devices were measured using a source measuring unit (Keithley SMU 2400) and a calibrated photodiode. Spectral radiance in the forward direction was acquired using a calibrated spectrometer (Instrument Systems GmbH CAST140).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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OLED, organic light-emitting diode, solid-state solvation effect, SSSE, TADF, thermally activated delayed fluorescence

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